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मनोज सिंह MANOJ SINGH



अध्यक्ष, वैज्ञानिक सूचना संसाधन प्रभाग भाभा परमाणु अनुसंधान केंद्र Head, Scientific Information Resource Division Bhabha Atomic Research Centre

PREFACE

The evolution of scholarly communication has been driven by the global academic community's collective yearning for greater transparency, equity, and accessibility in disseminating information. Central to this transformation is the movement towards **Open Access (OA) publishing**, which seeks to remove financial barriers to scientific knowledge, enabling researchers, institutions, and the public to access, use, and build upon scholarly works freely.

In May 2024, the Department of Atomic Energy (DAE) signed a Transformative Agreement (READ and PUBLISH) with two publishers, namely M/s. Springer Nature Group and M/s. Wiley India Private Limited, under a new buzzword "One DAE One Subscription (ODOS)".

This agreement is a first-of-its-kind agreement between DAE and publishers, which allows DAE researchers to publish their articles in 2,686 Springer Nature Hybrid journals and 1353Wiley journals as open access without any Article Processing Charges (APC) till 31 December 2024.

This compilation, named "*OpenGRID - Exploring Beyond Boundaries*", is the first series of publications under the OpenGRID banner. This series captures 58 published articles in Springer Nature and 10 in Wiley during May-December 2024, by BARC researchers, which is a significant milestone in the transformative journey of **Open Access (OA) publishing at Bhabha Atomic Research Centre (BARC)**, Trombay, Mumbai.

One of the most notable highlights of this publication is that it provides hyperlinking and QR codes to full-text access to all 68 article collections. As we move forward, it is essential to recognise that Open Access is not an end but a means to a larger goal of an inclusive, transparent, and collaborative scientific temperament that serves the public interest.

I commend all my SIRD colleagues involved in this pioneering effort and hope this compilation will inspire other research organisations in DAE units and across India for Open Access (OA) publishing.

(Manoj Singh)



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A Facile Synthesis of 3-Substituted Coumarins and Investigation of Their 3CLpro Inhibition Activity Against SARS-CoV-2

Manoj K. Choudhary,^[a, b] Khalid Ansari,^[c] Vivek Junghare,^[d] Sandip K. Nayak,^[a] Saugata Hazra,^{*[d]} and Soumyaditya Mula^{*[a, b]}

The major threat to public health due to the outbreak of severe acute respiratory syndrome coronavirus-2 (SARS-CoV-2) infection has been recognised as a global issue. The increase in morbidity is primarily due to the lack of SARS-CoV-2 specific drugs. One of the major strategies to combat this threat is to deactivate the enzymes responsible for the replication of corona virus. To this end, 3-arylidene/3-hydroxycoumarin induced deactivation of 3-chymotrypsin like protease (3CLpro) enzyme, which takes the pivotal role in the replication and maturation, was investigated. For ready availability of the compounds for the above investigation, we have developed a user-friendly protocol for the synthesis 3-hydroxycoumarin in two steps; i) Bronsted acid catalysed Friedel-Crafts alkylation of phenols with Morita-Baylis-Hillman adducts followed by

Introduction

The emerging pandemic outbreak in the present century due to severe acute respiratory syndrome coronavirus-2 (SARS-CoV-2) has become a global threat to public health because of its high rate of infection leading to mortality. The primary cause of morbidity is due to lack of SARS-CoV-2 specific drugs or vaccines. The 3-chymotrypsin like protease (3CLpro) plays a pivotal role in the replication and maturation of coronavirus-2, including the severe acute respiratory syndrome coronavirus-2

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intramolecular lactonization to trans-3-arylidenechroman-2ones in one-pot and ii) ozonolysis in reasonably good yields. Pharmacokinetic assessments of coumarin derivatives revealed drug-like characteristics with moderate or low toxicity values. Notably, these hydroxycoumarins exhibited enhanced binding affinity against the 3CL protease of SARS-CoV-2, fitting well into the binding pocket akin to the previously studied inhibitor N3. Furthermore, a molecular dynamics study elucidated the dynamic behaviour of these small molecules when bound to the protein, showcasing intriguing complexities within the active site. Despite backbone variations and residual fluctuations, compounds 3d-f and 6a exhibited a consistent behaviour, instilling confidence in the therapeutic potential of these coumarins for combating SARS-CoV-2.

(SARS-CoV-2) responsible for the COVID-19 pandemic.¹¹¹ To address this issue, development of potential drugs that target the 3-chymotrypsin like protease (3CLpro), was chossen as main strategy for antiviral drug development. Although synthetic pharmaceuticals have traditionally been explored as 3CLpro inhibitors, there is a growing interest in using naturally derived small organic molecules for their potential inhibitory effects. Natural compounds isolated from plants, herbs, and various origins boast a rich history of medicinal use and present a diverse array of bioactive molecules capable of interacting with the 3CLpro enzyme. Numerous studies have underscored the potential of naturally derived drugs in inhibiting 3CLpro activity and disrupting viral replication. For instance, polyphenols such as quercetin, epigallocatechin gallate (EGCG), and curcumin have exhibited inhibitory effects on 3CLpro activity in vitro.^[2,3] These compounds, present in various plant sources, possess antioxidant and anti-inflammatory properties that contribute to their potential antiviral activity.

Dietary polyphenols, isolated from plants/plant-derived foods, are known to display several biological properties, including anti-oxidative and anti-inflammatory activities. Naturally occurring flavonoids, have also shown inhibitory effects against 3CLpro. Recent study have shown that the polyhydroxy flavones such as baicalin, luteolin, and apigenin can effectively inhibit the proteolytic activity of the enzyme through binding to the enzyme's active site.^(4,5) Also, medicinal plant derived alkaloids, such as berberine and tetrahydroprotoberberine derivatives, have shown great promise as 3CLpro inhibitors,

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exhibiting antiviral activity that disrupts viral replication by targeting the enzymatic activity of 3CLpro.¹⁶¹ Additionally, terpenoids, including essential oils derived from plants, have displayed inhibitory effects against 3CLpro. Compounds such as thymol, carvacrol, and eugenol have been shown to interfere with the enzyme's activity, potentially hindering viral replication.[7]

The in-depth study on the mechanism of interactions of naturally derived drugs with the 3CLpro enzyme remains a challenging task in the development of antiviral therapies. Researchers are now aiming to understand the structural characteristics of 3CLpro and the specific mechanisms by which these compounds engage with the enzyme. This pursuit seeks to develop effective inhibitors capable of disrupting viral replication, thereby mitigating the impact of coronavirus infections. In essence, the investigation on naturally derived drugs as 3CLpro inhibitors provides a hopeful avenue for antiviral therapy development against coronaviruses. The rich array of bioactive compounds found in nature serves as a valuable resource for discovering and optimizing potent inhibitors. Continuous research and optimization of these compounds present substantial potential in the ongoing battle against viral infections.

Natural products are consistently used as lead material in drug development programme due to their biological compatibility.^[8] Several natural products show promise as candidates for developing 3CLpro inhibitors of SARS-CoV-2.191 Previously, we have also shown that dihydrobenzofuro[3,2b]chromenes exhibit favorable binding interactions with 3CLpro.^[10] Among the naturally occurring oxygen heterocycles, coumarin and its derivatives are crucial core units in various bioactive natural products and pharmaceutical compounds, as well as essential building blocks in organic and medicinal chemistry.^[11] They demonstrate diverse bioactivities, including antioxidant, anti-cancer, anti-inflammatory, cardioprotective, and MAO inhibitory activity.^[12,13] While their activities against 3CLpro have been studied, there is limited information on the structure-activity relationship concerning their inhibitory activity.

Recent advances in synthetic methodologies that allow rapid access to a wide variety of functionalized heterocyclic compounds are of critical importance to the medicinal chemist as it provides the ability to carry out in depth study in drug discovery programs. Furthermore, the development of efficient synthetic protocols to generate bulk guantities of a desired heterocyclic compounds will certainly help to accelerate the drug development process.

A large number of coumarin derivatives including 4hydroxycoumarins are known to possess various important biological activities. Hydroxycoumarins, particularly 4- and 7hydroxycoumarins, have been extensively studied for their diverse bioactivities, such as anticoagulant, antioxidant, cytostatic, antibacterial, antiviral, xanthine oxidase inhibition, antihypoglycemic, and casein kinase 2 inhibitory activity with low side-effects and minor toxicity.¹¹⁴⁾ Many of them also act as metal chelators and free radical scavengers.[15] Although the 3hydroxycoumarin scaffold is present in medicinally active

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natural products,^[16] there are limited reports on their synthesis.[17] This has become a major hurdle on the investigation of their biological activities in drug discovery program.[16]

Accordingly, a facile protocol has been developed for the synthesis of 3-hydroxycoumarins using cheap and readily available starting materials. To this end, (±)-camphor-10sulfonic acid catalyzed Friedel-Crafts alkylation-lactonization of 4-substituted phenols with Morita-Baylis-Hillman (MBH) adducts (derived from aromatic aldehydes and methyl acrylate) proceeded in one-pot under solvent-free conditions to afford 3methylene/3-arylidenechroman-2-ones (S_N2' product) in good yields. The present method offers several advantages such as low catalyst loading and a solvent-free green approach, a distinct advantage over existing synthetic methods. The synthesized 3-methylene/3-arylidenechroman-2-ones in turn converted into corresponding 3-hydroxycoumarins in good yield via ozonolysis.

In-silico structure construction of small molecules was performed using ChemDraw Ultra in 2D, followed by energy minimization using the built-in tool of the Chem3D tool to obtain three-dimensional structures. The SARS-CoV-2 3CLpro enzyme was obtained from RCSB using PDB ID 6LU7. Molecular docking with Autodock Vina software was conducted to study the interactions of fifteen synthesized compounds with 3CLpro. Molecular dynamics simulations were performed for selected compounds for a total of 100 ns each (total computational time700 ns duration). Analysis techniques, including root mean square deviation (RMSD), root mean square fluctuation (RMSF), hydrogen bonds, radius of gyration, and solvent accessible surface area (sasa), were employed to study conformational and structural stability. A brief analysis of the compounds' compatibility with the protein was also conducted. Lastly, in-silico ADMET screening of the fused flavonoids examined various physicochemical characteristics such as cell permeability, lipophilicity, water solubility, and various pharmacokinetics.

Results and Discussion

Synthesis

Morita-Baylis-Hillman (MBH) reaction is now considered as a standard synthetic method for the preparation of a new class of densly-functionalized allylic alcohol via the reaction of electrondeficient alkene with an aldehyde in the presence of a tertiary amine as catalyst.^(18a,b) Thus, MBH reaction using aromatic aldehyde and methyl acylate afforded a highly reactive alcohol (both an allylic as well as benzylic alcohol). MBH adducts are being recognized as one of the most important precursor in organic synthesis as it possess three important functional groups viz. a hydroxyl group, a double bond and an electron withdrawing group.^[18c-e] The potential of MBH adduct has been demonstrated in the synthesis of wide range of heterocycles including chromenes, chromones, furanones, furo-pyrans, spiroγ-butyrolactones, spiro-isoxazolines, piperdines, pyrazolines, indoloazocines, quinolones, indolones, y-lactams.^(18,19) Previ-

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RESEARCH ARTICLE

A thiourea-bridged ^{99m}Tc(CO)₃-dipicolylamine-2-nitroimidazole complex for targeting tumor hypoxia: Utilizing metabolizable thiourea-bridge to improve pharmacokinetics

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Abstract

The 2-nitroimidazole based 99mTc-radiopharmaceuticals are widely explored for imaging tumor hypoxia. Radiopharmaceuticals for targeting hypoxia are often lipophilic and therefore, show significant uptake in liver and other vital organs. In this context, lipophilic radiopharmaceuticals with design features enabling faster clearance from liver may be more desirable. A dipicolylamine-NCS bifunctional chelator that could generate a thiourea-bridge up on conjugation to primary amine bearing molecule was used to synthesize a 2-nitroimidazole-dipicolyl amine ligand for radiolabeling with 99mTc(CO)3 core. Corresponding Re(CO)3-analogue was prepared to establish the structure of 2-nitroimidazole-99mTc(CO)3 complex prepared in trace level. The 2-nitroimidazole-99mTc(CO)3 complex showed a hypoxic to normoxic ratio of ~2.5 in CHO cells at 3 h. In vivo, the complex showed accumulation and retention in tumor with high tumor to blood and tumor to muscle ratio. The study demonstrated the utility of metabolizable thiourea-bridge in 2-nitroimidazole-99mTc(CO)3 complex in inducing faster clearance of the radiotracer from liver. The dipicolylamine-NCS bifunctional chelator reported herein can also be used for radiolabeling other class of target specific molecules with ^{99m}Tc(CO)₃ core.

KEYWORDS

bifunctional chelator, hypoxia, nitroimidazole, technetium tricarbonyl complex, technetium-99m, thiourea-bridge

1 | INTRODUCTION

The negative role of hypoxia in determining the success of cancer therapy is well documented. (Gray et al., 1953) Establishing the presence or absence of hypoxia in cancer tissue, therefore, assumes significance in the clinical management of cancer. Fluorine-18 based radiopharmaceuticals, primarily [¹⁸F]FMISO (FMISO – fluoromisonidazole), is the radiopharmaceutical of choice for routine clinical imaging of tumor hypoxia. (Lee & Scott, 2007) Other fluorine-18 based radiopharmaceuticals include [¹⁸F]FAZA (FAZA-Fluoroazomycin arabinoside), [¹⁸F]HX4 (HX-flortanidazole), [¹⁸F]FET5 (EF5-2-(2-Nitro-1Himidazol-1-yl)-N-(2,2,3,3-pentafluoropropyl)acetamide), [¹⁸F]FETNIM

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(FETNIM-fluoroerythronitroimidazole), etc. (Huang et al., 2021; Wuest & Wuest, 2013) However, nuclear characteristics of technetium-99m $[t_{1/2} = 6 h, E_{\gamma} = 140 \text{ keV}]$, its availability from a molybdenum-99/ technetium-99m generator system, possibility of developing a freeze-dried kit for radiopharmaceutical preparation, wider availability of SPECT machines compared to PET machines, etc. provides an impetus to develop a technetium-99m alternative to the existing positron emitting radiopharmaceuticals for imaging hypoxia. The efforts made so far to develop a hypoxia imaging agent based on technetium-99m is reported elsewhere. (Giglio et al., 2012; Mittal & Mallia, 2023; Nguyen & Kim, 2023b; Saxena et al., 2023).

Among different approaches for radiolabeling bioactive molecules with technetium-99m, (Banerjee, Maresca, et al., 2005; Jürgens et al., 2014; S. Liu & Edwards, 1999; Meszaros et al., 2010; Sidorenko et al., 2023) the method using [99mTc(CO)3(H2O)3]* precursor complex, introduced by Alberto et al., is particularly attractive. The [99mTc (CO)₃(H₂O)₃]⁺ precursor complex can be prepared using a freezedried kit and its versatile coordination chemistry permits formation of inert 99mTc(CO)3-complexes with a broad spectrum of ligands that can be conjugated to target specific biomolecules. (Alberto et al., 2001) The [99mTc(CO)3(H2O)3]⁺ precursor complex can be used to radiolabel a mono-dentate, bidentate or a tridentate chelator. However, enhanced chemical stability of the complex makes the use of tridentate chelator more attractive. The most common tridentate chelators for radiolabeling with [99mTc(CO)3(H2O)3]+ precursor complex are histidine, iminodiacetic acid, diethylene triamine, aminoethyl glycine, dipicolylamine (DPA) and picolylamine monoacetic acid. (Mallia et al., 2014; Müller et al., 2004, 2007; Schibli et al., 2000) Among them, DPA is particularly attractive due to the presence of two aromatic amine groups which forms a 99mTc(CO)3-complex with high thermodynamic and kinetic stability. (Alberto et al., 1999) Initially, Liu et al. had proposed a DPA-based bifunctional chelator (BFCA), BPABA (N,N-bis(2-pyridylmethyl)-4-aminobutyric acid), for radiolabeling biologically active small molecules and peptides with ^{99m}Tc(CO)₃-core. (G. Liu et al., 2004) Subsequently, several DPA-BFCAs were explored which used different strategies like acid-amine coupling, click-reaction, thiol-malemide coupling, etc for conjugating with suitable biomolecules. (Banerjee, Schaffer, et al., 2005; Kasten et al., 2014; G. Liu et al., 2004; Maresca et al., 2009; Moore et al., 2010) We had envisaged and synthesized a DPA-NCS BFCA for modifying biologically active molecules to radiolabel with 99mTc (CO)3-core in our laboratory. Later, Kasten et al. reported a similar isothiocyanate DPA based chelator with a longer linker. (Kasten et al., 2016) The presence of isothiocyanate functionality in BFCA ensured facile conjugation with a variety of biomolecules with primary amine group such as antibodies, peptides, and small organic molecules, with high conjugation yield, under mild reaction conditions without using coupling agents. Herein, we used this strategy to synthesize a nitroimidazole-DPA ligand for radiolabeling with 99mTc (CO)3-core for use as a hypoxia imaging agent.

Nitroimidazoles undergo oxygen dependent enzymatic reduction leading to their preferential accumulation in hypoxic cells, but not in normoxic cells. Therefore, nitroimidazole derivatives tagged with a gamma/positron emitting radioisotope are used as a non-invasive probes for in vivo imaging of tumor hypoxia. (Allott et al., 2021; Mittal & Mallia, 2023; Nguyen & Kim, 2023a, 2023b; Wang et al., 2021) The underlying mechanism of hypoxia selectivity of nitroimidazoles has been reviewed elsewhere. (Krohn et al., 2008; Tocher, 1997) Several nitroimidazole 99mTc(CO)3-complexes are reported for targeting hypoxia (Mallia et al., 2008, 2012, 2014, 2015, 2016, 2018) and some of the lipophilic complexes had shown significant uptake in tumor. However, significant accumulation and slow clearance of the radiotracer from nontarget organs such as liver and blood pool were undesirable observations. (Mallia et al., 2014, 2016) Designing a hydrophilic nitroimidazole complex to minimize liver uptake and induce rapid clearance from the blood pool was not helpful either since the radiotracer require time to distribute and undergo oxygen dependent accumulation in tumor. (Mallia et al., 2014) Envisaging a lipophilic complex that could metabolize in liver to enhance clearance, we synthesized a 99mTc(CO)3-complex with an ether linkage between the nitroimidazole and a 99mTc(CO)3 moiety. (Mallia et al., 2012) This strategy was adopted from clinically established myocardial perfusion imaging agents' 99mTc-Sestamibi, (Savi et al., 1989) 99mTc-tetrofosmin (Kelly et al., 1993) and other similar agents (S. Liu et al., 2006) containing ether groups which are believed to enhance the clearance from liver. (Kim et al., 2010) However, this approach met with limited success. (Mallia et al., 2012)

Like ether linkage, thiourea linkage is known to undergo metabolism in liver. Paulsen et al. had shown that thiourea can be metabolized using isolated hepatic enzymes from porcine liver. (Poulsen et al., 1979) Recently, Kumar J et al. demonstrated the metabolism of thiourea derivatives in liver and subsequent clearance from the body, primarily through kidneys. (Kumar et al., 2023) A report by Hoigebazar et al. compared two ⁶⁸Ga-NOTA-2-nitroimidazole complexes; one with amide linkage and other with thiourea linkage. Analysis of their biodistribution results showed higher initial uptake of the complex with thiourea linkage in liver with rapid clearance of activity between 10 min p.i. to 2 h p.i. This observation is also supported by corresponding increase of activity in intestine. The complex with amide linkage, however, had lower initial uptake but cleared slowly from the liver. (Hoigebazar et al., 2010) Similarly, Mohsin et al. studied ¹¹¹In, ⁹⁰Y and ¹⁷⁷Lu-labeled DOTA analogues prepared by conjugating a variety of DOTA-BFCAs [N-hydroxysuccinimdyl ester of DOTA ("NHS-DOTA"), p-NCSbenzyl-DOTA ("Back-DOTA") and p-NCS-O-methoxy-benzyl-DOTA ("Arm-DOTA")] to monoclonal antibody B72.3. An analysis of the biodistribution patterns of these complexes also revealed faster clearance of radiotracer from liver with thiourea linkage compared to the complex with amide linkage, agreeing with the earlier observations. (Mohsin et al., 2007) The isothiocyanate type BFCAs, therefore, combines the advantage of easy conjugation to potential target specific biomolecules and rapid clearance from liver due to its susceptibility to metabolism by liver enzymes.

Though NCS-functionalized BFCAs are frequently used for convenient conjugation of suitable chelators to target specific biomolecules for radiolabeling with a variety of diagnostic and therapeutic radioisotopes, a NCS-bifunctional chelator for radiolabeling with $[M(CO)_3]^+$ core [M = Tc, Re] is less explored. Additionally, the NCS- group of the



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RESEARCH ARTICLE

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Beyond traditional methods: Exploring strippable gel based on deep eutectic solvent for efficient radioactive surface decontamination

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Abstract

This study introduces a technique for decontaminating radioactive surfaces by employing a gel, herein termed as radiation decontamination gel with eutectic liquids (RADGEL), composed of a deep eutectic solvent and polyvinyl alcohol, with the goal of enabling reuse of the surface post-decontamination. The decontamination effectiveness of RADGEL underwent thorough evaluation through trials conducted on different simulated surfaces, achieving decontamination efficiency up to 99.9% for alpha as well as gamma radionuclides. The various parameters influencing decontamination factors such as amount of complexing agent used, polymer film thickness, nature, and magnitude of radioactivity, as well as surface characteristics of substrates to be decontaminated were optimized. Additionally excellent mechanical strength of RADGEL, affirms its potential as practically efficient, cost-effective, and safe option for surface decontamination. The Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analysis suggest RADGELs capability for both physical and chemical interactions with contaminants, thus highlighting its comprehensive decontamination efficacy. The outcomes of this study carry substantial implications for the decontamination of surfaces contaminated with various types of radionuclides.

KEYWORDS

applications, decontamination, deep eutectic solvent, gels, separation techniques

1 | INTRODUCTION

Throughout the evolution and utilization of nuclear energy, the persistent threat of nuclear pollution has cast a shadow over humanity.^{1,2} Radioactive contamination, posing a significant hazard to both human health and environmental well-being, arises from the advancement of nuclear energy and radiological incidents.^{3–6} Addressing

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radioactive pollution effectively and facilitating decontamination requires an active exploration of materials and technologies.^{7,8} Radioactive contamination, which can manifest in various processes including nuclear accidents, nuclear fuel mining, fuel cycle operations, operation and decommissioning of outdated nuclear facilities, and so forth⁹⁻¹¹ that demands efficient decontamination before any further handling. The International Atomic Energy Agency (IAEA) offers technical reports and guidelines for radiological decontamination during the operation, outage, and decommissioning of such facilities.¹²⁻¹⁴ The use of surface decontamination technologies, aiming to reduce waste volume while efficiently removing radioactivity, is crucial for cost reduction and enhanced safety during waste treatment and disposal. Various surface decontamination methods namely chemical, physical, biological, and microbiological approaches are practiced.15-20 Among these, the physical method is commonly employed for swift responses and large-scale decontamination, allowing the rapid removal of radioactive pollutants to help safe disposal. Numerous physical techniques, including mechanical, wet, and dry approaches are utilized for surface decontamination.21-23 In practice, high-pressure water jet-based washing, a prevalent method primarily used in nuclear accident sites like Chernobyl and Fukushima,²⁴⁻²⁶ resulted in considerable radioactive wastewater production, while limited contamination removal, making it less favorable.26 Alternatively, techniques such as detergent scrubbing, steam cleaning, vacuums, and the use of strippable coatings are reported in the literature.23-28 Of late, the use of a strippable coating, which involves using a polymeric solution sprayed to form a strippable film that absorbs and lock surface contamination in solid film.²⁹⁻³¹ Strippable coatings have garnered attention due to its notable advantages, such as generating only a single solid waste without secondary liquid waste, additional radioactive aerosols, or suspended matter. Numerous experimental studies and applications of commercial products utilizing strippable coatings for radioactive decontamination have been documented, for examples DeconGel, foams, and Argonne supergel are commercially available, proving effective in surface decontamination during facility operation or decommissioning.23,27,28 Although these coatings have been reported to be highly successful in decontaminating surfaces, development of a versatile gel for universal decontamination across various surfaces is still awaited.

Recently, deep eutectic solvents (DESs), composed of a quaternary ammonium, phosphonium, or sulphonium salt and a hydrogen bond donor (HBD) with a melting point below 100°C,³² have been reported to possess good biocompatibility, low production cost, tunability, and good metal oxide solubility, rendering them as potential candidates for economical, efficient, and environmentally friendly decontamination processes.32-35 Our recent study also demonstrated that, a DES, developed using heptyltriphenylphosphonium bromide (hydrogen bond acceptor) and decanoic acid (hydrogen bond donor) maintaining a molar composition of 1:2,34,36,37 showed promising capabilities in effectively forming complexes with highly toxic radionuclides.36 We envisaged that incorporation of this DES in a strippable gel, may lead to development of an efficient decontaminating agent. Herein, polyvinyl alcohol (PVA) has been used as a gel-forming agent due to its superior film-forming ability, easy availability, nontoxicity, and biocompatibility, 29,38,39 and a gel was developed by combining DES as a complexing agent with effective decontamination properties against common radionuclides like Cs(I) and Pu(IV). The thin film fabricated using developed gel was further characterized to evaluate various physical properties such as tensile strength (TS), elongation break strength (to ensure smooth peeling), and thermal stability. To assess the impact of HBDs in DESs on film fabrication and decontamination efficiency, various hydrophobic DESs were synthesized, including C7-3LA, C7-2TBABr, and DEHPA-4Betaine. Unfortunately, only the C7-3LA DES yielded a stable and peelable film, achieving successful fabrication at up to 20% DES content. The resulting 20% DES-PVA film exhibited optimal pliability and strength. Subsequent evaluations focused on its decontamination efficiency across common substrates. In contrast to the >99% decontamination efficiency observed for C7-DA DES, the C7-LA film demonstrated relatively lower decontamination efficiency, ranging from 80%-90% across all studied substrates. Additionally, the C7-LA film required an extended curing/drying time of 3-4 days compared with the 10 h needed for a film of the same thickness based on C7-DA, with relatively lower strength and flexibility. Consequently, C7-DA DES-based films emerge as more favor-

2 | EXPERIMENTAL

ceramic surfaces.

2.1 | Materials and methods

Triphenylphosphine (PPh₃) (99% purity, CAS number 603-35-0) 1-bromo heptane (99% purity, CAS Number 629-04-

able, given their shorter fabrication time, excellent

decontamination efficiency, and convenient film recovery

from surfaces. This study led to the development of a

strippable gel named RADGEL, representing "radioactive

decontamination gel with eutectic liquids." RADGEL was

evaluated as a potential candidate for surface decontami-

nation applications, through extensive trials on simulated

surfaces such as stainless-steel trays, stainless steel fume

hoods, Polyvinyl chloride (PVC) floors, granite, glass, and



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BODIPY-Helicene Based Heavy-Atom-Free Photocatalyst for Oxidative Coupling of Amines and Photooxidation of Sulfides

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To develop heavy-atom-free triplet photosensitizers (PSs) based photocatalysts, we designed and synthesized two BODIPY-helicene dyes by fusing the BODIPY core and modified [5]helicene structures. These BODIPY-helicenes structures are twisted and their twisting angles are increased by the developed synthetic method. The BODIPY-helicenes have broad absorption bands over UV-visible region with high triplet conversions and long triplet lifetimes as compared to planar BODIPY dye, PM567. Consequently, these dyes are also highly efficient in generating $^{1}O_{2}$ by transferring their triplet energy to $^{3}O_{2}$. All these are confirmed by dye-sensitised photooxidation reaction, nanosecond transient absorption spectroscopy study,

Introduction

Photocatalysis is a process where catalysts upon photoexcitation transfer energy/electrons/holes to the substrates which ultimately allow breaking/forming of bonds in the substrates for their synthetic transformations. During the past few decades, photocatalytic organic reactions are getting much attention from synthetic organic chemists due to simple and mild reaction conditions, easy separation, reusability of the catalyst etc. Triplet photosensitizers (PSs) which on photo-

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phosphorescence measurement and DFT calculations. Finally, photocatalytic activity of the highest ${}^{1}O_{2}$ generating BODIPYhelicene (**4b**) was checked. **4b** is highly efficient in photocatalytic oxidative coupling of differently substituted amines through aerobatic oxidation using ${}^{1}O_{2}$ generated by its photosensitization. It is also highly efficient photocatalyst for aerobatic oxidation of sulfides to sulfoxides. Importantly, the photocatalyst could be quantitatively recovered and reused for several cycles. All these results confirmed the potential use of the BODIPY-helicenes as PSs for photocatalytic organic reactions and the design strategy will be useful for the future development of heavy-atom-free photocatalyst.

excitation efficiently convert into their triplet states are well explored photocatalysts. PSs are highly useful for photoredox organic reactions like photolysis of water for hydrogen (H₂) production, cross dehydrogenative coupling (CDC) reactions, oxidative coupling of amines, aza-Henry reaction etc.^[11] The ideal PSs useful as photocatalysts should possess the following properties: (1) broad absorption spectrum in visible region, (2) high molar absorptivity for strong light absorption, (3) high triplet conversion yield, (4) long triplet lifetime important for efficient energy/electron/hole transfer, (5) easy modification of the molecular structure to tune its photophysical and electrochemical properties and (6) heavy-atom-free.

So far iridium and ruthenium polypyridyl complexes based PSs are mostly studied as they showed efficient photocatalytic properties due to their efficient electron/hole/energy transfer processes.^[1a,2] But these inorganic PSs have several limitations like absorption below 450 nm with low absorption coefficients and structural modifications are also not possible to tune their absorption properties. Additionally, heavy metal atoms increase their cost, impart high environmental pollutions and decrease triplet state lifetime. In this respect, organic photocatalysts are very good replacement for these heavy atom containing photocatalysts. In fact, various classes of organic compounds like porphyrinoids, xanthene dyes, pyriliums, phenalenones, thiazines etc were successfully applied in many photocatalytic reactions.[3] But low to moderate molar absorptivity, narrow absorption profile, synthetic difficulties to tune their photophysical and electrochemical properties by structural modifications restrict their wide applications in photocatalysis. Thus, search for ideal heavy-atom-free organo-photocatalysts is still on.

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During the last few decades, boron-dipyrromethene (BODI-PY) class of compounds have emerged as one of the most versatile dyes for numerous applications.^[4] Strong absorption and fluorescence properties, reversible electrochemical properties along with easy structural modifications to tune these properties made them so attractive for new era of modern chemistry.⁽⁵⁾ Unfortunately, their narrow absorption profile and low triplet quantum yields made them unsuitable as triplet photosensitizers as well as efficient photocatalysts.^[6] Efforts are being made to enhance their triplet conversions by attaching with heavy metals or halogens (Br/I) which were successfully applied to photocatalyse various organic reactions.[1,6b] But attachment of heavy atoms decrease triplet lifetimes as well as enhance production cost and environmental toxicity which make them unsuitable for practical applications. PSs based on heavy-atom-free BODIPYs are also developed by twisting dye structures, making conjugates with fullerenes, thionation etc.^[7] In all the cases, synthesis and functionalization are relatively difficult. Also, designing new PSs with desirable excited state properties are extremely difficult with these methods. Thus, development of heavy-atom-free BODIPYs with necessary properties required for efficient photocatalyst remains a challenge and require utmost attention.^[8]

The rate constant (k_{ISC}) for the intersystem crossing (ISC) of singlet excited state (S_m) to the triplet excited state (T_n) can be written as⁽⁹⁾

$$k_{ISC} \propto \frac{\langle T_n | \mathcal{H}_{SO} | S_m \rangle^2}{\left(\varDelta E_{S_m - T_n} \right)^2} \tag{1}$$

where H_{so} is the spin-orbit coupling (SOC) Hamiltonian *i.e.* k_{ISC} is proportional to square of SOC matrix element. Heavy atom attachment is very effective to increase the SOC which is being followed routinely for development of PSs.^(9b) On the other hand, $k_{\rm ISC}$ is inversely proportional to the square of the S_m to T_n energy gap (ΔE_{sm-Tn}). Thus, design of low ΔE_{sm-Tn} molecules is also very effective for development of efficient PSs without attaching any heavy metal atoms.[10] It is observed that the $\Delta E_{\rm Sm-Tn}$ of planar conjugated aromatic molecules are high due to very strong spatial overlaps of the molecular orbitals. Thus, ISC process is very slow in these molecules. BODIPY being a planar conjugated aromatic structure, its $\Delta E_{\rm Sm.Tn}$ is very high which restricts ISC leading to very low triplet quantum yield. Interestingly, molecular twisting helps to reduce $\Delta E_{\text{sm-Tn}}$ which enhances ISC rate i.e. the triplet quantum yield.^[11] Helicenes are the best examples for this type of PSs. Twisting of their molecular structures reduces ΔE_{Sm-Tn} enhancing their triplet conversions. Importantly, their triplet quantum yields are proportional to their twisting angles as predicted from Equation (1).^[11,12] But, helicenes are not good candidates for photocatalysis due to their very low absorption in the UV region and difficulties in synthesis and functionalization.[13] Twisting of the BODIPY core is also expected to enhance its triplet conversion rate. Using this concept, helical BODIPYs are also being explored very recently as heavy-atom-free PSs but very few reports are only available so far.^[14] In majority of these cases, synthesis of the helical BODIPYs are not easy and

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systematic investigation is rare to show how the ISC efficiency changes with the twisting angle. Recently, we developed a new class of BODIPY-hetero[5]helicene which showed enhanced triplet conversion as compared to planar BODIPY dye and their ISC efficiencies increase proportionally with increase in their twisting angles. This 1st generation of BODIPY-helicene (A, Chart 1) has relatively low singlet oxygen generation capability and lower absorption maximum. Here, we designed second generation BODIPY-helicenes (4a, b) fusing the BODIPY core with the hetero-[5]helicene moiety (Chart 1). In the BODIPYhetero[5]helicene (A), thiazole unit was used to construct the BODIPY core whereas in newly designed BODIPY-helicenes (4a, b), benzothiazole unit is used to enhance thionated chromophore-induced ISC.^[7a,15] Also, substitution of benzothiazole in 4a, b was anticipated to show bathochromic shift in the absorption profile as well as to increase the triplet conversion. Boron substitutions were also done to increase twisting angles as well as to shift the absorption maxima bathochromically. Both the dyes showed superior photophysical properties with broad absorption spectra expand over whole UV-visible region. Also, they are efficient triple photosensitizers with high ISC. These observations are explained by nanosecond transient absorption spectroscopic studies, phosphorescence measurement and DFT calculations. Finally, application of dye 4b as efficient photocatalyst in oxidative coupling of amines and photooxidation of sulfides were investigated. All these are described below.



Chart 1. Chemical structure of 1st generation BODIPY-helicene (A) and 2nd Generation BODIPY-helicenes (4a, b).

Results and Discussion

Synthesis. First, 6-pentyl-5,11-dihydroindolo[3,2-b]carbazole was selectively brominated using FeBr₃ to synthesize 6-bromo-12-pentyl-5,11-dihydroindolo[3,2-b]carbazole (1).^[16] Then, compound 1 was subjected to Pd-catalysed borylation reaction using pinacolborane to get 6-boryl-12-pentyl-5,11dihydroindolo[3,2-b]carbazole (2).^[17] Pd-catalysed Suzuki-Miyaura reaction was used to couple this borylated compound 2 with 2-bromobenzthiazole to synthesize ligand 3. Finally, reaction of ligand 3 with BF₃·OEt₂ furnished the BF₂-dye 4a (Scheme 1). In another attempt, ligand 3 was reacted with B(Ph)₃ to get BPh₂-dye 4b (Scheme 1). Benzothiazole moiety

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Combining Thermogravimetry-Mass Spectrometry and Target Factor Analysis for Rapid Characterization of Volatiles from Degradation of Epoxy Paint

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Keywords: epoxy paint | mass spectrometry | paint degradation | target factor analysis | thermogravimetric analysis | volatiles

ABSTRACT

Thermogravimetry coupled with simultaneous evolved gas analysis by mass spectrometry was used for discerning organic compounds released during the thermal degradation of paint whose chemical compositions are not readily accessible. Thermogravimetric analyses up to 600° C revealed distinct degradation patterns under inert and oxidative conditions. Significant degradation of paint initiates at around 360° C and concludes at 500° C in a nitrogen atmosphere. However, under oxidative conditions, degradation began at 100° C, with notable mass loss extending from 300 to 600° C, with a distinct event at 500° C. Moreover, the overall mass loss in air has been observed to be 3% higher than that in nitrogen. The rapid characterization of the volatiles was made possible by model-free target factor analyses of evolved gas mass spectra. The temperature-correlated mass analyses revealed potential volatile sources, including structural breakdown and oxidative conversion. Comparative analyses revealed predominantly oxidative conversion of organics to CO_2 during degradation in air. The evolution of several classes of organics during the thermal degradation of paint is a matter of great concern for postulated accident scenarios in nuclear power plants. The low molecular weight organic volatiles may be taken up by iodine aerosols released into the containment during an accident, potentially forming organic iodides, which are biological hazards. Thus, identifying these volatile organics is crucial for accurately estimating the source term of volatile organic iodine.

1 | Introduction

Epoxy paints have found widespread use due to their high adhesion, corrosion resistance and thermal stability [1, 2]. These properties make them excellent choices for coatings on metallic surfaces in harsh environments particularly in space and nuclear facilities. Epoxy paints are mostly based on diglycidyl ether of Bisphenol A and are cured with various hardeners, such as amines, amides, and alcohols [3]. Additionally, they may include mineral whiteners, pigments, solvents, plasticizers and other additives for adhesion, preservation and stability. Due to the strong proprietary interest in the complex formulation of individual varieties of paints, only limited information on their formulations is available. With particular reference to containments of nuclear plants, under normal operations, paint undergoes natural ageing, during which it is exposed to substantially elevated temperatures (~80°C), high humidity and low radiation doses for prolonged periods (12-18 months) [4]. However, during reactor accidents, the painted surfaces inside nuclear containments may undergo accelerated ageing due to the very high temperature and radiation doses (10⁴ Gy/h) [5]. The volatiles released during the degradation of paint may provide the

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Analytical Science Advances, 2024; 0:e202400047 https://doi.org/10.1002/ansa.202400047 organics necessary for the formation of volatile organic iodides inside the containment [6-8]. The various chemical compounds present in the paint and their degradation products will therefore determine the speciation of the organic iodides thus formed which is vital for accurate estimation of iodine source term [4]. Therefore, it is necessary to have tentative information on the various classes of compounds that may be released under such conditions. Traditional analytical methods, such as pyrolysis gas chromatography-mass spectrometry (GC-MS), provide valuable information on volatile components [9]. However, they often fail to capture crucial details about temperature-resolved evolution. Alternatively, thermogravimetry (TG) coupled with MS, that is, TG-MS enables real-time detection of evolved gases. This combined TG-MS method enables the correlation of changes in mass with heat effects and identifies the types of volatiles released during thermal degradation [10-12].

In this work, we have investigated the thermal degradation of paint by TG-MS. To correlate the evolved chemical species with the associated thermal events, the degradation of paint under an oxidising atmosphere (air) was compared with an inert (nitrogen) atmosphere. Simultaneous identification and determination of the evolution profile of each individual component from the accumulated mass spectra of the evolved gas containing several co-eluting chemical compounds is cumbersome and challenging. To this end, a model-free analytical method based on multivariate target factor analysis (TFA) has been employed to identify the individual chemical compounds as well as to predict their evolution profiles over the entire temperature range. The combined TG-MS-TFA method presented in this work provides a deeper understanding of the thermal degradation behaviour of complex polymers, such as paints whose chemical compositions are not readily available.

2 | Material and Methods

2.1 | Paint Sample Preparation

The paint sample was obtained in the form of its individual liquid components, "hardener" and "resin". The "hardener" and "resin" were mixed in equal volumes; the mixture was applied on the surface of glass slides. The painted glass slides were left to cure in a dust-free atmosphere at room temperature. Dried paint samples were collected by scraping the glass slides and analysed by TG-MS. Details on spectroscopic characterisations on resin, hardener and paint can be found in Supporting Information.

2.2 | Experimental: TG-MS

Thermogravimetric analysis (TGA) was performed using Linesis STA PT1600. The evolved gas was analysed by Pfeiffer Vacuum Thermostar GSD 320 single quadrupole mass spectrometer coupled to TGA. Paint samples weighing 20 2 mg were placed in an alumina crucible (inner diameter 4 mm, volume 180 μ L) and heated under the following temperature programme: isothermal hold for 2 min at 30°C; heat from 30 to 600°C at a rate of 10°C/min; isothermal hold for 1 min at 600°C. The atmosphere surrounding the samples was controlled using a continuous purge gas flow of 50 mL/min. The gaseous products were introduced

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into the mass spectrometer using a Thermostar, quartz, 1 m long, 2 mm internal diameter gas sampling line maintained at 150°C to prevent the condensation of the evolved gas vapours during analysis. The mass spectrometer was set to scan between 2 and 251 amu and was operated in electron impact (EI) mode at 70 eV. The resolution was 1 amu. Each scan lasted 50 ms. This gave a total of 68,400 scans in 57 min of the MS data collection period. Repeatability was determined by performing three repeats of the TGA-MS analysis on each sample. The data gathered by the mass spectrometer were processed off-line with in-house developed multivariate TFA coded in MATLAB [13].

2.3 | Target Factor Analysis

The real-time mass spectra of the gas released during the thermal degradation of paint can be represented as a data matrix **D** with dimensions $t \times m$. Here, each row is a mass spectrum at a different temperature, and each column is the profile of a specific mass-to-charge ratio (m/z) over the temperature range. In the present work, t ranges from 30 to 600°C and m ranges from 41 to 251 amu. A compound is likely to be present in the evolved gas if its mass spectrum (or target vector r_{target}) is present in the spectral vector sub-space of **D** constituted only by the significant factors. The information deeply embedded within such complex data matrices can be extracted using factor analysis-based methods.

In factor analysis, the data matrix **D** is decomposed into a product of two matrices, **R** and **C**, where the columns of **R** and rows of **C** respectively represent the evolution profiles and corresponding mass spectra of the significant factors. This can be expressed by Equation (1)

$$\boldsymbol{D}_{t\times m} = \boldsymbol{R}_{t\times sf} \, \boldsymbol{C}_{sf\times m} + \boldsymbol{E}_{t\times m} \tag{1}$$

where *sf* denotes the number of significant factors involved in the process and E represents the associated experimental noise. The decomposition of D was performed by the popular and robust singular value decomposition (SVD) algorithm which yielded three matrices, U, S, V for

$$\boldsymbol{D}_{t\times m} = \boldsymbol{U}_{t\times m} \, \boldsymbol{S}_{m\times m} \, \boldsymbol{V}_{m\times m}^{t} \tag{2}$$

the case m < t and is shown in Equation (2). The column matrices U and V corresponds to eigenvectors spanned over concentration and mass spectral vector space, respectively. The diagonal singular values matrix S contains the square root of the corresponding eigenvalues, also known as singular values (s_u) . The large eigenvalues indicate significant components whereas, the experimental error corresponds to lower s... During SVD, the singular values (s_v) are arranged in decreasing order. This arrangement ensures that the eigenvectors in U and V correspond to the most significant factors first, with their significance decreasing afterwards. Due to the presence of experimental noise, there was no clear demarcation between high and low s_v values, making the determination of sf from such experimental dataset having a very large number of co-eluting species, challenging. The estimation of sf were carried out using three different plots of (a) s_v, (b) indicator values (IND) and (c) % significance level (%SL) versus number of factors [14-16].

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ORIGINAL ARTICLE



6

Developing a peripheral blood RNA-seq based NETseq ensemble classifier: A potential novel tool for non-invasive detection and treatment response assessment in neuroendocrine tumor patients receiving ¹⁷⁷Lu-DOTATATE PRRT

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Abstract

Neuroendocrine tumors (NETs) are presented with metastases due to delayed diagnosis. We aimed to identify NET-related biomarkers from peripheral blood. The development and validation of a multi-gene NETseg ensemble classifier using peripheral blood RNA-Seq is reported. RNA-Seq was performed on peripheral blood samples from 178 NET patients and 73 healthy donors. Distinguishing gene features were identified from a learning cohort (59 PRRT-naïve GEP-NET patients and 38 healthy donors). Ensemble classifier combining the output of five machine learning algorithms viz. Random Forest (RF), Extreme Gradient Boosting (XGBOOST), Gradient Boosting Machine (GBM), Support Vector Machine (SVM), and Logistic Regression (LR) were trained and independently validated in the evaluation cohort (n = 106). The response to PRRT was evaluated in the PRRT cohort (n = 46) and the PRRT response monitoring cohort (n = 16). The response to ¹⁷⁷Lu-DOTATATE PRRT was assessed using RECIST 1.1 criteria. The Ensemble classifier trained on 61 gene features, distinguished NET from healthy samples with 100% accuracy in the learning cohort. In an evaluation cohort, the classifier achieved 93% sensitivity (95% Cl: 87.8%-98.03%) and 91.4% specificity (95% CI: 82.1%-100%) for PRRT-naïve GEP-NETs (AUROC = 95.4%). The classifier returned >87.5% sensitivity across different tumor characteristics and outperformed serum Chromogranin A sensitivity ($\chi^2 = 21.89$, p = 4.161e-6). In the PRRT cohort, RECIST 1.1 responders showed significantly lower NETseq prediction scores after ¹⁷⁷Lu-DOTATATE PRRT, in comparison to the non-responders. In an independent response monitoring cohort, paired samples

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(before PRRT and after 2nd or 3rd cycle of PRRT) were analyzed. The NETseq prediction score significantly decreased in partial responders (p = .002) and marginally reduced in stable disease (p = .068). The NETseq ensemble classifier identified PRRTnaïve GEP-NETs with high accuracy ($\ge 92\%$) and demonstrated a potential role in early treatment response monitoring in the PRRT setting. This blood-based, non-invasive, multi-analyte molecular method could be developed as a valuable adjunct to conventional methods in the detection and treatment response assessment in NET patients.

KEYWORDS

¹⁷⁷Lu-DOTATATE PRRT, liquid biopsy, NETseq ensemble classifier, neuroendocrine tumors, treatment response monitoring

1 | INTRODUCTION

NETs are well-differentiated neoplasms accounting for 80%-90% of neuroendocrine neoplasms (NENs).¹ The incidence and prevalence of NETs demonstrate a rising trend globally,2-5 being presently the 2nd most prevalent gastrointestinal cancer and the 10th most prevalent cancer in England.⁶ NETs represent a diverse group of solid tumors that develop in the hormone-secreting cells of the neuroendocrine system. The tumors are heterogeneous for the primary site, histological features, cell-specific hormone secretion, spatial (within the tumor) or temporal (between tumors) diversity in the molecular constitution, clinical aggressiveness, type- and site-specific prognosis, and response to treatment.⁷ Thus, NETs are clinically challenging as the disease course varies with regard to the site of primary, tumor grade, hormonal syndrome, somatostatin receptor expression, ¹⁸F-FDG avidity, and bone metastasis, 5.8.9 and about 50% of the patients present with metastases due to delayed diagnosis on account of indolent disease biology and none or non-specific symptoms, 2,10

The diagnosis, staging, and work-up of NETs largely rely on the assessment of clinical presentation, biochemical tests, tumor histopathology, and anatomical and metabolic imaging.¹¹ The last decade has witnessed rapid progress in the development of liquid biopsy molecular diagnostics for various cancers.^{12,13} In 2013, Modlin et al. reported the development of the first multi-transcript qPCR assay-the NETest-that evaluates the expression of 51 tumor-derived NEN-transcripts in the blood.¹⁴ The utility of the NETest for differentiating various NETs from controls, and stable disease from progressive disease has been extensively analyzed.^{15,16}

Emerging evidence suggests that tumorigenesis is a function of spatial/temporal tumor heterogeneity, paracrine interactions in the tumor microenvironment, and systemic changes in the tumor macroenvironment.¹⁷⁻¹⁹ Circulating tumor-originated molecules and tumor-educated immune cells in the peripheral blood have been successfully employed in the development of molecular assays. For example, circulating tumor-derived cell-free nucleic acid (ctDNA or cfRNA) biomarkers have been exploited for cancer diagnosis, genotyping, and detecting minimal residual disease.^{20,21} Rapid advances in next-generation sequencing have improved the detection of subtle but definitive changes in transcript expression or sequence variations, and

have enabled the development of multi-analyte classifiers using machine learning (ML) approaches.²² A gene panel selected from RNA-Seq profiles of tumor-educated platelets (TEPs) has been used for the detection of early- and late-stage non-small-cell lung cancer.²³ Distinct changes in the transcriptomes of tumor-associated macro-phages (TAMs) and circulating monocytes in endometrial or breast cancer patients have been associated with cancer sub-types and disease-specific outcomes.²⁴ Similarly, tumor-educated B cells have been implicated in the formation of the lymph node premetastatic niche in breast cancer.²⁵ Thus, tumor-regulated local and systemic changes in peripheral blood have been successfully employed to develop molecular methods for the detection and prognostication of cancers with high accuracy. Nevertheless, systemic changes in the peripheral blood of NET patients and the diagnostic or predictive potential of differential signatures remain unexplored.

In this study, we report the development and validation of a multigene NETseq ensemble classifier from peripheral blood RNA-seq for non-invasive identification of NETs and assess its potential for early treatment response monitoring following ¹⁷⁷Lu-DOTATATE PRRT.

2 | MATERIALS AND METHODS

2.1 | Diagnosis and treatment of NETs

In this study, NET patients undergoing ¹⁷⁷Lu-DOTA-D-Phe-Tyr3-octreotate (¹⁷⁷Lu-DOTATATE) Peptide Receptor Radionuclide Therapy (PRRT), and asymptomatic healthy donors (HD) were included. In a standard workup, NET patients underwent radiological investigations, and histopathological examinations. The values of pre-PRRT serum chromogranin A (CgA) levels were taken from the patients' clinical records. CgA levels were measured using the solid phase sandwich ELISA method at the National Accreditation Board for Testing and Calibration Laboratories (NABL) and/or The College of American Pathologists (CAP) accredited commercial pathological laboratories in India. The value of 95 ng/mL of CgA was used as a unified cut-off.²⁶ The dual-tracer diagnostic imaging with [⁶⁸Ga]-DOTA-D-Phe-Tyr3-octreotate (⁶⁸Ga-DOTATATE) and [¹⁸F]-fluorodeoxyglucose (¹⁸F-FDG) positron emission tomography-computed tomography



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RESEARCH ARTICLE



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Formation of Bainite in a Low-Carbon Steel at Slow Cooling Rate – Experimental Observations and Thermodynamic Validation

Poulami Chakraborty,* Suman Neogy, Nilabja Kanti Sarkar, Harish Donthula, Subir Kumar Ghosh, Hillol Kumar Nandi, Bandarupalli Gopalakrishna, Ilangovan Balasundar, and Raghvendra Tewari

Bainitic microstructures in high-strength steels are obtained either by continuous cooling or isothermal holding. Both scenarios necessitate faster cooling to keep the parent austenite phase untransformed till the bainite-start temperature. The present study reports the development of bainitic microstructure in a low-carbon steel with minimal alloying additions, under continuous cooling at very slow rates, similar to furnace cooling. For understanding the related transformation pathways, samples from the forged-steel ingot are austenitized and cooled at different rates, viz. water quenching, air cooling, and furnace cooling. Microstructural characterization reveals development of acicular microstructures in all samples including the forged one, with gross absence of carbides. X-ray diffraction confirms the ferritic nature of acicular plates and also indicated retained austenite present in some samples, the content of which could be correlated to the extent of bainitic transformation. Thermodynamic calculations together with microstructural observations (e.g., ferrite plate size) and hardness data established the development of fully martensitic microstructure on water quenching, while that of a mixed microstructure comprising predominantly of bainite in the forged, air cooled, and furnace-cooled condition. The aforementioned findings could have wider implications in developing fully bainitic microstructures in large components, where uniform rapid cooling is not practically feasible.

material. In this regard, ferrous alloys, especially steels, are beneficial due to their lower cost and tailorable mechanical properties.^[1] One of the primary objectives of steel designers at present is to enhance the strength of steels without compromising on its toughness.^[2] Commercially available high-strength multi-phase steels such as transformation induced plasticity (TRIP) steels, TRIP-assisted steels, high-strength low-alloy (HSLA) steels and dual-phase steels provide a maximum strength of around ≈1 GPa and ductility up to 40%.^[1–5] These values are, however, not sufficient to meet the desired requirements of modern day applications in nuclear, transportation, and construction sectors. Such applications demand sufficiently high strength exceeding 1.1 GPa along with satisfactory fracture toughness of around 125 MPa-m^{1/2}.^[6] Moreover, fabrication of large components mandates the achievement of uniformity of microstructure and properties across thick sections. This poses challenges to those fabrication routes which rely on rapid heating and cooling cycles to generate specific

1. Introduction

Higher strength, ease of fabrication, good weldability, and low cost are the essential attributes for selecting a desirable structural

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microstructural features. One such scenario is the fabrication of nuclear reactor pressure vessels where through-thickness micro-

structure and mechanical properties vary significantly owing to the large thickness of the vessels (${\approx}400{-}800$ mm). $^{[7,8]}$ Thus, there

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is a continuous quest for developing economically viable newer materials processed at slower cooling rates exhibiting better microstructural uniformity, high strength and toughness, lower residual stresses in bulk, together with better fabricability, and good weldability.

Bainitic steels exhibiting good strength (≈1 GPa) and creep resistance have been traditionally used over the years in transportation and power-generation industries.^[9] Limited alloying additions in these steels (generally less than 5%) make them cost effective as well.^[10] It is well known that bainite is an aggregate of ferrite and carbide phases which forms in steels at temperatures above martensite formation but below that of pearlite nucleation.^[11] In bainite, the fine ferrite platelets form in clusters appearing in the form of wedge-shaped plates on a macroscopic scale known as "sheaves".^[11,12] A lot of investigations have been carried out to decipher the nature of bainitic transformation, that is, to establish whether austenite transforms to bainite in a diffusional or displacive manner. However, experimental evidences favour the displacive theory given by Bhadeshia and co-workers who have shown that the bainite transformation is accompanied by a shape deformation which is related to an invariant-plane strain having a large shear component.[11,12] Thus, the transformation of austenite to bainitic ferrite is essentially diffusionless, although carbon atoms partition into the untransformed austenite (or precipitate as carbides) shortly after the growth of the ferrite plate is stifled.^[12] The precipitation of a thick layer of carbide at the platelet boundaries in case of upper bainite vis-a-vis fine intra-platelet and inter-platelet precipitation in lower bainite compromises the toughness of the microstructure, especially in the case of upper bainite.[12,13]

To circumvent such loss of toughness arising out of the precipitation of carbides, recently carbide-free nanostructured bainitic steels consisting of a fine network of bainitic ferrite platelets interspersed by thin retained austenite films have emerged as a viable solution. Such carbide-free nano-structured bainitic steels have also turned out to be a material of choice for high strength applications, like in railways, defence, aerospace, and automotive sectors.^[14,15] These steels provide an optimum combination of ultra-high tensile strength exceeding 2.5 GPa and elongation up to 20%.^[14,15] The basis of this high strength lies in the nanoscale thickness of bainitic ferrite platelets.^[16,17] It has been reported that the addition of silicon and/or aluminium in such steels suppresses the precipitation of detrimental carbides (M₃C, M₆C, etc.).^[18-20] In the absence of carbides, the metastable retained austenite present in between the fine bainitic ferrite platelets can contribute to an increased ductility via the TRIP effect.^[18–20] Several research groups across the world have tried or been trying to develop novel ultra-high strength and tough carbide-free bulk nanostructured bainitic steels either by transforming the parent austenite phase isothermally or by continuously cooling it.^[17,21] The high carbon content usually present in such steels (≥1 wt%) allows isothermal bainite transformation (austempering) at much lower temperatures due to significant lowering of the martensite-start (Ms) temperature, thus enabling formation of finer bainitic ferrite platelets.^[22-24] However, on the negative side, the high carbon content results in a poor weldability of these steels.^[25] This issue can be mitigated either through a modification of the welding process^[26] or through the development of nano-bainitic microstructures in medium or low carbon steels.^[14,21,27]

In this context, on-going global research has identified several medium and low-carbon steel compositions that produce nanobainitic microstructures. In general, the carbon content in these steels ranges between 0.24% and 0.41% by weight, while other alloying elements put together are present in quantities between 5.4% and 9.5% by weight.^[18,27–32] On one hand, these alloying elements (like Mn, Ni, Si, Mo, Cr, Al, and V) are essential for obtaining the desired properties, while on the other hand these are relatively expensive. Thus, the need of the hour is to lower the carbon content of steel so as to avoid challenges associated with welding together with minimizing addition of expensive alloying elements to make the steel cost effective. This approach is particularly important for sectors involving large-scale consumption of steel.

Against the above backdrop, a program has been initiated at Bhabha Atomic Research Centre (BARC) to develop a low-carbon carbide-free bulk nanostructured bainitic steel with reduced alloying content. The overall scope of the program encompasses designing a low-carbon low-alloy steel composition followed by delineation of its thermomechanical processing regime which would enable the development of a nanobainitic microstructure without resorting to faster heating/cooling cycles. This would certainly improve the microstructural uniformity, weldability, and cost competitiveness besides exhibiting high strength and toughness usual of carbide-free nanostructured bainitic steels.

In this regard, the initial step involved 1) designing of the steel composition followed by its melting and forging and 2) investigation on the possibility of evolution of carbide-free bainitic microstructure through both isothermal holding^[33] as well as via continuous cooling. The outcome of these investigations will serve as an input to optimize the processing parameters so as to obtain a carbide-free nanobainitic microstructure, which is the ultimate goal of the program. The study reported herein puts forth a detailed account of the alloy design philosophy and the continuous cooling experiments conducted on the forged ingot. In this context, one of the prime focus has been to explore the possibility of obtaining bainitic microstructures at relatively slower cooling rates, as low as furnace cooling, keeping in mind the wider section thicknesses of large size industrial components. To the best of our knowledge, obtaining fully bainitic microstructure in a low-carbon low-alloy steel at such slower cooling rate has not been attempted before.

2. Experimental Section

2.1. Designing of Steel Composition

Development of uniform nanobainitic microstructure across thick sections of low-carbon steels necessitates a careful selection of alloying additions so as to satisfy the following three basic requirements: 1) transformation at lower temperatures, 2) enhanced driving force for the transformation, and 3) transformation under slower cooling rates.

In view of this, the targeted steel composition listed in **Table 1** was designed taking help of the mucg.83 program.^[34] The mucg.83 is an open source software suite developed at the University of Cambridge, UK for modeling the thermodynamics

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RESEARCH ARTICLE

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Theoretical studies on the kinetics and mechanism of hydroxyl radical reaction with quinclorac and quinmerac herbicides in aqueous media

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Abstract

The kinetic and mechanistic studies for the reaction of hydroxyl radical with two quinoline based herbicides, namely, quinclorac and quinmerac has been performed using various computational methods in aqueous media. Geometry optimizations were performed using Density Functional Theory (DFT) methods including water as the solvent. Local reactivity parameters of these herbicides towards the "OH radical are predicted using condensed Fukui function. Single point energies of various species were calculated using double hybrid method, namely, B2PLYP-D for better accuracy. The pKa values for these acid based herbicides allow them to exist in deprotonated form in aqueous condition. Hence, the calculations are also performed for the deprotonated or the anionic form apart from the neutral species. Individual rate coefficients for *OH radical addition reaction with each carbon atoms were evaluated using conventional transition state theory using one-dimensional tunneling corrections. The solvent effect on reaction is implemented through Collins-Kimball formulations. Both the approaches, namely, the Fukui index and individual rate constant determination confirms that the most reactive site for the *OH radical addition in these two herbicide is the carbon atom attached to the -COOH group. The total rate constant for the 'OH radical reaction with both neutral and anionic forms of these two herbicides are relatively high and equal to its diffusion-limit value. Evaluation of the ecotoxicities of the parent herbicides and their OH adducts is estimated using the structure-activity relationship concept.

KEYWORDS

auxin mimics, density functional theory (DFT), OH radical reaction, oxidative degradation pathways, quinclorac and quinmerac, quinoline based herbicides

1 | INTRODUCTION

Herbicides can be defined as a class of chemicals which is mostly used to kill or control unwanted vegetation, that is, weeds. The usage of herbicide is widespread starting from crop farming, lawns, parks to golf courses and other areas. Herbicides can be also applied to water bodies to control aquatic weeds [1]. Various mechanisms have been reported in the literature by which these herbicides kill weeds [2]. One of these

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mechanisms involves the uncontrolled and disorganized growth of the weeds. These types of the herbicides fall under the category of auxin mimics, which mimic the plant growth hormone auxin. These herbicides cause uncontrolled and disorganized growth in the weeds and eventually kill the unwanted plants [3]. Generally, these auxin mimics herbicides are mostly aromatic acid based compounds which are highly soluble in water [4]. In this context, the present study revolves around two synthetic auxin mimic quinoline carboxylic acid based herbicides, namely, quinclorac (3,7-dichloroquinoline-8-carboxylic acid) and quinmerac (7-chloro-3-methylquinoline-8-carboxylic acid).

All over the world, the major usage of these quinoline based herbicides is in the agricultural productions which not only improves the quality but also the quantity of the crops. However, the excessive application of these herbicides poses enormous potential risks ranging from contamination of groundwater, loss of soil fertility, nitrate leaching and finally the loss of biodiversity [5, 6]. These herbicides are also chemically stable molecules which poses considerable risks on the ecosystem and human health [7]. Hence, it is desirable to study their environmental impacts and different effective removal strategies [8].

Due to their low pK_a values, the quinoline acid based herbicides gets deprotonated forming anionic species and become extremely soluble in water which increases their mobility [9]. This augments their availability for its degradation processes. Various types of degradation processes are applied for these herbicides which are mainly based on biological degradation methods [10–16], chemical methods [17, 18] and photodecomposition methods [19–23]. In many instances, it has been observed that a combination of chemical method with photocatalysis is also used widely and considered as the most effective oxidative degradation process [24]. This is often known as advanced oxidation process (AOP) [25–28]. The AOP involves the generation of highly reactive oxidizing species, such as, hydroxyl radical (*OH) which finally degrades the organic substances. Hence, it is desirable to know the complete knowledge of the initial mode of attack, the rate constant and the nature of final product in the reaction of *OH radical with these herbicides. This type of study will lead us to understand their degradation mechanism and lifetime in the environment. In this context, the present study is carried out to understand the kinetics, mechanism and the degradation pathways for two quinoline based carboxylic acid herbicides, namely, quinclorac and quinmerac, with *OH radical reaction, theoretically.

Quinclorac is considered to be a potential groundwater contaminant due to its water solubility (0.065 mg kg⁻¹ at pH 7). It is also stable towards hydrolysis enabling it to bind with soils (K_{oc} : 50 mL g⁻¹) with an aerobic soil half-life of 211 d [23]. In literature one can find few studies on degradation process of quinclorac [23, 29–31]. Utilizing a biotransformation strategy with Burkholderia cepacia WZ1, Li et al. studied its biodegradation process [32]. Similarly, Rohers et al. studied the bioremediation of quinclorac in water using a combination of aquatic plants and bacteria [33]. Few other studies are also available in the literature in the area of bioremediation of quinclorac using various bacteria and bionanocomposite [31, 34–36]. Various studies are also available in the literature regarding the AOP process using different technique. Pareja et al, studied the photolytic and photocatalytic degradation of quinclorac in ultrapure and paddy field water using AOP [23]. Similarly, in one of study, carbon coated nitrogen doped TiO₂ was used for the photocatalytic degradation [29, 37]. Similarly, permanganate and nano-Fe⁰/peroxymonosulfate system has been used in some of the degradation process of quinclorac [37, 38]. In the theoretical side, chemical reactivity of quinclorac was studied employing the hard-soft acid-base (HSAB) local principle by computing Fukui function [39]. Apart from this lone theoretical study, the literature devoid of any such theoretical study on the degradation of quinclorac.

Similar to quinclorac, quinmerac has similar chemical structure in which one of the Cl atoms is replaced by the methyl group. The only experimental study available in the literature is by Despotović et al. where they have studied the photocatalytic degradation of quinmerac in various types of natural water utilizing TiO₂ suspensions [40]. On the theoretical side, very recently Ngo et al. studied the oxidation process of *OH radical with quinmerac in aqueous phase [41]. The study elaborates namely adduct formation, hydrogen transfer and single electron transfer mechanism for the oxidation process. Apart from these two studies, the literature is devoid of any more studies.

In this context, the present endeavor is a sincere effort to throw some light on the reaction mechanism, specially the initial mode of attack of *OH radical, the formation of *OH radical complex, the *OH radical total rate constant in liquid phase and the ecotoxicity of the final products through computational approach. Branching ratio has been also calculated and discussed in light of the local reactivity parameters calculated using the concept of Fukui indices.

2 | COMPUTATIONAL DETAILS

2.1 | Electronic structure calculations

Potential energy surfaces (PESs) for the various channels in the 'OH radical reaction with quinclorac and quinmerac were generated using ab initio molecular orbital (MO) calculations. Mainly, three types of reaction channels are involved in the reaction of 'OH radical with these herbicides. First, the addition reaction channel, second, it is the H-atom abstraction channel and finally the third one is the electron transfer reaction channel. It is well known that the 'OH addition reaction which forms the OH-adduct is the major reaction channel in case of unsaturated hydrocarbons [42, 43]. Hence, only addition reaction channel has been considered in the present study. The geometry optimization process of the these herbicides in the ground electronic state including all the intermediates and transition states were performed using Coulomb attenuating method



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RESEARCH ARTICLE OPEN ACCESS

Theoretical Study on the Dissociation Mechanism of Thiophene in the UV Photoabsorption, Ionization, and Electron Attachment Processes

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Keywords: G4 method | intramolecular hydrogen transfer | reaction mechanism | thiophene | thiophene ring-fragmentation

ABSTRACT

A computational study on the intricate mechanism of thiophene ring-fragmentation (TRF) in the UV photodissociation, dissociative ionization, and dissociative electron attachment process has been performed. The complete fragmentation process is studied using high level G4 composite method for neutral, cationic, and anionic species by elucidating a detailed mechanism for various reaction channels. The study shows that for neutral thiophene, the major pathway is the migration of H atom and subsequent fragmentation through a transition state yielding acetylene (HC \equiv CH) and H₂C=C=S. However, for the thiophene cation, the acetylene (HC \equiv CH)+H₂C=C=S⁺ channel is a two-step and barrier less process. The onset of CH₃+HC=C=C=S channel has been observed in both the thiophene cation and anion which was absent in the neutral analogue. Similarly, the onset of H₂S+HC \equiv C—C \equiv CH channel has been found to operate only in the thiophene cation. Others, such as HCS and HS elimination channels have been found in all the species showing similar dissociation mechanism. For the thiophene anion, the TRF process is very much similar to that of thiophene cation. However, the reaction enthalpies of the various elimination channels in the anionic species are lower as compared to that of cationic species. During the study, the ionization energies and electron affinities of various molecules/radicals produced during the fragmentation process of thiophene were also computed.

1 | Introduction

The fragmentation process of aromatic hydrocarbons has attracted a great deal of interest in fundamental chemistry and astrophysics due to its importance in the chemistry of interstellar medium (ISM) [1-3]. One of the key areas in this type of process is to study the competition between the ionization and the fragmentation process of these molecules caused by electromagnetic radiation in the ISM [4, 5]. Another area where the knowledge of various fragmentation processes is very crucial is the fate of ions in the mass spectrometer. It is very important to have the knowledge of the mechanisms by which ions decompose in the mass spectrometer [6, 7]. One of the biggest challenges in the discussion of mass spectral mechanisms is our lack of knowledge of the structures of various decomposing product ions [8, 9]. A detailed study including the structures of these ions is crucial to a realistic discussion of mass spectrometric mechanisms. Various experimental techniques using laser pulses, synchrotron radiation, ion/electron beams, and plasmas are generally employed to study the ionization and fragmentation process of these polyatomic molecules and sometimes these results are often supplemented with theoretical

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International Journal of Quantum Chemistry, 2024; 124:e27503 https://doi.org/10.1002/qua.27503 studies. The theoretical studies generally optimize the structures; compute the energetics and arrive at the kinetics of the various fragmentation pathways by creating the entire potential energy surfaces (PES) including transition states, stationary points and the final products. Additionally, the kinetic rates of the various fragmentation pathways and the branching ratio can also be estimated using Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Among various molecular species, the fragmentation chemistry of aromatics compounds has drawn a lot of interest due to its rich fragmentation pattern. The mass spectral behavior of aromatic compound suggests an extensive hydrogen randomization followed by the ring cleavage giving rise to various fragments [10-12]. One of such aromatic compound is thiophene, where massive hydrogen randomization process was first shown by Williams et al. and later supported by Meyerson and Fields [13-15]. The process of hydrogen randomization is also active in other systems like benzene, furan, tetrahydrofuran, tetrahydropyran, isoxazole, thiadiazole, and pyridine [12, 16-22].

Thiophene is a five-membered heterocyclic compound, containing four carbon atoms and one sulfur atom in the ring. The delocalization of electron lone pairs on sulfur, in the conjugated π system, makes thiophene behave like an aromatic compound [23]. In literature, one can find many investigations, both experimentally and theoretically, in context with the photochemistry of thiophene, especially in the UV region [24]. Few experimental works include the studies related to its UV absorption spectrum in the gas phase, and the electron-energy loss spectrum [25]. Using femtosecond pump-probe photoelectron spectroscopy and resonance Raman spectroscopy, excited-state dynamics of thiophene has been also investigated [26, 27]. Theoretical studies such as the electronic structure calculations in the Franck-Condon region with complete active space self-consistent field (CASSCF) and density functional theory and multi-reference configuration interaction (MRCI) calculations were also performed, to understand its UV spectrum [28]. Various other phenomena such as ultrafast internal conversion, and photodissociation dynamics were also studied. Very recently, ultrafast deactivation processes of photoexcited thiophene were studied theoretically [29, 30].

The gas phase UV absorption spectrum of thiophene shows an A-band located at 225 nm (5.5 eV), in the lowest valence state, which has been attributed a $\pi \rightarrow \pi^*$ transition. The fragmentation of thiophene at 213.9, 228.8, and 253.7 nm, in the gas phase has been studied using end-product analysis [31]. Similarly, infrared laser multiphoton dissociation (IRMPD) studies were carried out in gas phase and a mechanism involving breakage of the C-S bond in thiophene has been postulated to form an unstable 1,5-diradical, which further decomposes via different channels [32]. In another study involving the flash photolysis of thiophene, a transient absorption spectrum in the region 377-417 nm was observed, which was tentatively assigned to the absorption due to the transient C4H3 radical [33]. The photodissociation process of thiophene at 193 nm was studied using photoionization detection of the various hydrocarbon products and sulfur atom and it was concluded that only two dissociative channels, namely, C2H2S+C2H2 and C4H4+S are important channels [34]. Later on, similar photodissociation studies at 193 nm were performed using synchrotron radiation as a universal product probe, where

five primary channels have been observed and it was concluded that all the dissociation processes occur on the ground-state surface, following fast internal conversion [35].

Pyrolysis studies of thiophene have been a key area of research owing to its presence in petroleum and its allied products. Recently, a comparative ab initio study on the mechanism of unimolecular pyrolysis of thiophene and furan has been performed [36, 37]. Similarly, thermal decomposition mechanism of thiophene has been investigated both experimentally and theoretically. Whereas, thermal decomposition experiments were done using pulsed silicon carbide microtubular reactor, theoretical investigations were performed at CBS-OB3 level of theory [38]. Both, experimental and theoretical findings indicate a massive H atom rearrangements leading to the formation of acetylene as a major product. In another work, high temperature pyrolysis of thiophene has been investigated using Born-Oppenheimer direct dynamics simulations to establish the atomic level mechanisms of the initial decomposition steps of thiophene [39].

The photoabsorption and ion fragmentation studies of thiophene were studied using double ion chamber and synchrotron radiation source and valence shell spectroscopic and thermodynamic properties were evaluated [40]. In another similar study, threshold photoelectron photoion coincidence spectroscopy was employed to examine the loss of neutral acetylene from ionized thiophene near the dissociation thresholds [41]. The threshold photoelectron spectrum of thiophene and photoionization efficiency curves for thiophene and its various product ions such as, C4H3S+, C3HS+, C2H2S+, CHS+, and C3H3+ were measured in the 8-14 eV photon energy range [42]. Recently, positive and negative photoion spectroscopy studies on monochlorothiophenes were conducted, using synchrotron vacuum ultraviolet radiation [43]. Very recently in our group, the fragmentation pattern of 2-chlorothiophene has been studied using laser-based multiphoton ionization and time-of-flight detection of various product ions and results are supported with computational studies [44]. In another study, a detailed experimental and theoretical investigation on the fragmentation dynamics of doubly ionized molecular thiophene is presented [45]. Electron collision processes with thiophene have been previously studied using experimental and theoretical methods. The dissociative electron attachment (DEA) study for thiophene was performed in the energy range of 0-12 eV by recording the mass spectra in the gas phase [46]. Similarly, a study involving the theoretical calculations and experiments involving electron energy loss spectra (EELS) for electron scattering from thiophene has been performed in order to identify and characterize its core-excited resonances [47]. The electron transmission spectra (ETS) for thiophene was recorded below 4.5 eV with two intense resonances at 1.15 and 2.63 eV, associated with electron capture into the two lowest empty π^* molecular orbitals (MOs) [48].

In this context, the present theoretical study on the fate of thiophene initiated by UV photon absorption, ionization and electron attachment process has been carried out by monitoring the fragmentation mechanism of neutral, cationic, and anionic species of thiophene. All the theoretical calculations are performed using a high-level composite method, namely, G4 method. During the

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Unveiling the Ultrafast Excitation Energy Transfer in Tetraarylpyrrolo[3,2-b]pyrrole-BODIPY Dyads

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We have synthesized two dyads (dyad 1 and 2) comprising of tetraarylpyrrolo[3,2-b]pyrrole (TAPP) and BODIPY. In dyad 1, two BODIPYs are directly connected with TAPP moiety whereas in dyad 2, BODIPYs are connected through phenylethynyl linkers. TAPP is a blue energy donor which is easy to synthesize and functionalize as compared to other well-known blue energy donors like pyrene, perylene etc. This is the first report of using TAPP as an energy donor in BODIPY based dyad molecules. Complete quenching of TAPP fluorescence in the dyads suggests fast energy transfer from TAPP to BODIPY unit (ETE~99.9%). Ultrafast fluorescence and transient absorption

Introduction

Electronic excitation energy transfer (EET) or resonance energy transfer (RET) is a photophysical phenomenon generally observed in electronically decoupled multichromophoric systems.⁽¹⁾ In such systems, a donor chromophore (absorbs at lower wavelengths) and an acceptor molecule (absorbs at higher wavelengths) are either tethered by covalent bond or remain supramolecularly bound while maintaining spatial vicinity. When the donor chromophore is photoexcited, it transfers its excitation energy to nearby acceptor chromophore which fluoresce at a longer wavelength than what is expected otherwise resulting a virtual enhancement of Stokes shift. Such types of energy transfer systems are immensely useful in clean energy production to advanced bio-technological applications. For example, multichromophoric arrays act as an artificial lightharvesting antenna for conversion of solar energy to electricity in dye based solar cells^[2] or solar fuel production by artificial photosynthesis.^[3] On the other side, this kind of RET based

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spectroscopic studies of dyad 1 showed TAPP to BODIPY energy transfer in 125 fs (k^{ET} = 8.0×10¹² s⁻¹) which is one of the fastest energy transfer events in BODIPY based dyad reported so far. Whereas, in dyad 2, energy transfer is almost four times slower (480 fs, k^{ET} = 2.1×10¹² s⁻¹). These results were rationalized by theoretical Förster formulations. This study shows that suitably matched optical properties of TAPP and BODIPY dyes along with their easy syntheses will be the key to develop highly efficient energy transfer systems in future for multiple applications.

systems are advantageous for energy transfer mediated improved chemical sensing⁻¹⁴ as well as advanced bio-imaging¹⁵ applications owing to the increased virtual or pseudo-Stokes shift. RET based multichromophoric systems are also instrumental in developing broadband triplet photosensitizers for next generation photoredox catalysis, photodynamic therapy to triplet-triplet annihilation up-conversion applications.¹⁶ Efficacy of the RET systems in all these applications mainly depends on their energy transfer efficiency (ETE) and rate of energy transfer (k^{ET}). Thus, over the years, scientists have tried various combination of donor and acceptor systems to enhance the ETE and k^{ET} of RET systems.

BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) class of dyes are quite versatile considering their wide spread applicability⁽⁷⁾ including energy transfer applications. In the past, it has been extensively used both as energy donors as well as energy acceptors.⁽⁸⁾ BODIPY dyes work nicely as energy acceptors by offering an astonishingly high molar absorptivity, sharp absorption profile, tunable emission at longer wavelength with simple functionalization.[7a] However, they suffer inherent limitations in their full-fledged applicability as an energy donor simply because its core absorption lies in green region (around 500 nm) and it is hardly tunable to blue region.⁽⁹⁾ To address this problem, synthetic chemists developed a number of RET based systems conjugating different polycyclic aromatic hydrocarbons (PAHs) like pyrene, perylene, anthracene, triptycene, fluorene etc as energy donors with functionalized BODIPYs as energy acceptors.^[5e,10] These PAHs generally absorb in ultraviolet region (200-400 nm) and are useful for excitation energy transfer from blue to green or even to red region. Such systems also help in enhancing virtual Stokes shift of BODIPY dyes which is a major drawback of the BODIPY class of dyes. But these polyaromatics are difficult to synthesize as well as to functionalize which are the main bottleneck of their synthetic applications. Polyaromatics are traditionally synthesized using

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Scholl reaction which only works effectively on electron rich substrates under acidic conditions.^[11a] The main difficulty lies in preparation of selective precursors which involves multiple steps and complex procedures. Further, selective post functionalization on PAH cores is also challenging due to presence of active sites of similar reactivity. Thus, a new fluorophore which is easy to synthesize and functionalize with absorption and emission in blue region will be real boost for the development of the multichromophoric systems for diversified applications.

Tetraarylpyrrolo[3,2-*b*]pyrrole (TAPP) (Figure 1), a new class of fluorescent dye, has got considerable attention since its serendipitous discovery by Gryko *et. al.* back in 2013.^[11b] It triggers a dramatical research interest yielding back to back synthetic reports in recent times.^[12] In general, these dyes are relatively easy to synthesize and there is ample scope for post functionalization of the pyrrolo[3,2-*b*]pyrrole core.^[13] These dyes generally absorb around 400 nm having high molar absorptivity and emit at around 450 nm with good fluorescence quantum yield making them potential candidate as blue emitting fluorophore.^[12b] In turn, it opens up opportunities for their wide range of applications like two-photon absorption,^[13c,14] solidstate emitters based on aggregation induced emission (AIE).^[15] organic light emitting diodes (OLEDs) and organic optoelectronics.^[12a]

Earlier, donor-acceptor type system was synthesized by connecting the TAPP scaffolds with electron deficient aromatic systems for two-photon absorption application.^[13a] Realizing the potential of TAPPs as a blue light emitting donor, we were interested to construct TAPP-BODIPY based bi-chromophoric donor-acceptor molecules to delve into the photoinduced electronic energy transfer processes in such systems which is not known so far. Herein, we present first ever synthesis of TAPP-BODIPY dyads, dyad 1 and dyad 2 (Figure 1). In the dyad 1, BODIPY moiety (acceptor BODIPY 8) is directly linked with the pyrrolo[3,2-b]pyrrole (donor TAPP 3) core through a common phenyl ring whereas in dyad 2, two chromophores (donor TAPP 14 and acceptor BODIPY 8) are linked through an alkyne spacer (Figure 1). Detailed photophysical and electrochemical characterization of these dyads were done. Both the dyads are having high virtual Stokes shift and the underlying EET processes were explored using steady state and time-resolved spectrophotometric techniques that subsequently unraveled one of the fastest excitation energy transfer process ever reported.^[16a] All of these are systematically unfolded in the following sections.

Experimental Section

Detailed synthetic procedure of all the compounds along with their characterization data and NMR spectra are included in the supporting information. Steady state absorption spectra were recorded in a guartz cuvette (path length: 1 cm) using JASCO make UV-vis spectrophotometer (Model: V 670). Steady state emission studies were done using a JASCO make spectrofluorometer (Model: FP 6500). Femtosecond resolved transient fluorescence and absorption experiments were carried out using fluorescence upconversion (FOG100, CDP corporation, Russia). The up-conversion spectrometer was coupled to a femotosecond Ti-Sapphire oscillator which delivers ~80 fs 800 nm laser pulse at a repetition rate of 80 MHz. Laser wavelength was converted to 400 nm by second harmonic generation in a thin BBO crystal and is used to excite (pump) the sample kept in a 1 mm rotating cell. Transient fluorescence from the sample was gated with the residual 800 nm beam and the up-converted signal generated in the UV wavelength was selected by a monochromator and detected by a photomultiplier tube. The transient change in emission signal was recorded by scanning the delay of the gate pulse. Relative polarization of pump and the gate pulse was kept at magic angle to eliminate any effect of rotational depolarization on the transient emission data. The temporal resolution of fluorescence upconversion set-up was determined to be ~150 fs from the time response of the Raman signal of ethanol.



Figure 1. Chemical structures of tetraarylpyrrolo[3,2-b]pyrrole (donor TAPP 3, donor TAPP 14), acceptor BODIPY 8, Dyad 1 and Dyad 2.

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A comparative study of long-term measurements of natural gamma absorbed dose rate in outdoor air by TLD and GM detectors

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Abstract

This paper investigates and compares two widely employed techniques for measuring natural gamma absorbed dose rate in outdoor air: the thermoluminescent dosimeter (TLD) and the Geiger-Mueller (GM) detector-based environmental radiation monitor (ERM). Over two decades (2003–2023), measurements were conducted at eighteen investigation sites having a wide variation of local dose rate values. The TLDs accumulated quarterly doses, while the ERMs recorded hourly dose rates. The comparison of mean dose rates obtained by the two methods agreed within 30% for all sites. A strong positive correlation was obtained between the two methods.

Keywords Outdoor natural gamma dose rate · Geiger-Mueller detectors · Thermoluminescence detectors

Introduction

Evaluating the natural gamma absorbed dose rate in outdoor air holds significant importance for gauging external radiation exposure and potential risks to public health [1]. Three major techniques can be employed for this purpose: integrated dose measurements by thermoluminescent dosimeters (TLDs), instantaneous or long-term direct dose rate measurements by portable survey meters (PSMs) or permanently field-installed environmental radiation monitors (ERMs), respectively, and gamma spectrometric (GS) analysis of collected soil samples in the laboratory to find the activity concentrations of terrestrial radionuclides. These methods have been extensively utilized in prior studies [2–6].

TLDs find extensive application in measuring environmental gamma doses, as well as in personnel and medical dosimetry. They are characterized by high sensitivity, good dose linearity and flat energy response [7–9]. Some commonly employed TLDs are LiF:Mg,Cu,P, CaF₂:Dy, and CaSO₄:Dy [10]. These TLDs have the capability to accumulate gamma radiation doses over specified time intervals.

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The average gamma dose rate (D) can be estimated by simply dividing the accumulated dose by the measurement time. This approach provides statistically more significant values compared to instant dose rate values measured by a PSM [7].

The PSM method commonly utilizes high-pressure ionization chambers (HPICs), plastic scintillators (PSs), or Geiger-Mueller (GM) counters for measurement [7-11]. The PSM method is known for its cost-effectiveness, ease of use, and ability to provide rapid results, making it particularly suitable for large-scale surveys [12]. This method allows for the observation of time variations in gamma dose rates, including those occurring under different weather conditions [5]. On the other hand, long-term continuous monitoring of gamma absorbed dose rate in outdoor air can be carried out by permanently field-installed GM detector-based ERMs [13, 14]. If data logging is done in short intervals, the near real time dose rate values can be obtained. Also, as these instantaneous dose rate values are available over long periods of time, the same can be time-averaged to give statistically more significant results. However, this method requires a lot more resources compared to the PSM method and as a result large-scale surveys become much more expensive.

The third method, involving the use of gamma spectrometry (GS) technique with either high purity germanium (HPGe) or scintillator detectors, is widely employed by sampling soil and analysing the activity concentrations of the U-series, Th-series and ⁴⁰K radioisotopes. The well-known Beck formula [15, 16] is then used to estimate the terrestrial

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dose rate in air at 1 m above ground. The cosmic dose rate is then added in order to obtain the total absorbed dose rate (D) in outdoor air.

All the three methods are widely utilized for environmental gamma dose rate surveys, each offering distinct advantages and disadvantages. However, there is a notable absence of reported methodology comparisons, barring a few [2, 3, 6, 7, 15].

In India, the Department of Atomic Energy (DAE) carries out radiation surveys around its nuclear and other facilities for routine monitoring as well as for monitoring and assessment of potential radiological impacts from discharges. Typically, TLDs are employed for quarterly collection and averaging of dose rates, while ERMs are installed for online gamma dose rate monitoring in near real time. This study aims to present, for the first time, a comparative analysis of the two fundamentally different methodologies for long-term (2003–2023) measurement of natural gamma absorbed dose rate in outdoor air: the TLD-based (passive) methodology and the ERM-based (active) methodology.

Materials and methods

Measurement sites

The measurements were carried out at 18 sites spread across different parts of India. These sites were characterized by a wide variation of dose rate values among themselves. The locations of the sites are shown in Fig. 1.



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ORIGINAL PAPER





A Probe in to Site Occupancy of Uranium in Barium Aluminium Borate (BaAl₂B₂O₇) Matrix by EXAFS and its Photoluminescence Studies

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Abstract: A host matrix with a potential of incorporating heavy element like uranium, that have several forms of stabilization is the key interest. Uranium-doped $BaAl_2B_2O_7$ is synthesized through solution combustion synthesis method. The luminescence studies indicate suitability of this alumino borate matrix to stabilize uranium as uranate (UO_6^{6-}). The uranium life-time values suggest uranium to be surrounded by two different environments with varied defect concentration. The site occupancy of uranium in $BaAl_2B_2O_7$ is probed through EXAFS studies. It is observed that the preferred sites for uranium incorporation is the Al^{3+} regular lattice sites.

Keywords: Uranium; Uranate; Lattice sites; Photoluminescence; Decay time; Site occupancy

Introduction

Alkaline-earth aluminium borates are known to be potential phosphors in designing efficient luminescent materials [1, 2]. Emergence of this material is associated with its low synthesis temperature, high UV transparency, high luminescence brightness, good thermal stability and also nonlinear optical properties that make the material useful for application in plasma display panels (PDPs), UV devices and nonlinear optical materials [3-5]. This matrix is well known as an ideal host to several rare earths and contributes towards developing WLED (white light emitting diodes) materials [6-9]. Among the alkaline-earth aluminium borates, BaAl₂B₂O₇ has evolved as a potential phosphor material. The most fascinating about Alkalineearth aluminium borate (BaAl2B2O7) being a host is its crystal structure that was first described by Hubner and latter it was discussed by Ye et al. [10, 11]. The BaAl2B2O7 lattice follows rhombohedral structure, here the prominent units are AlO₄ tetrahedra and BO₃ triangles and in between these two units the Ba ion gets sandwiched. The Ba ion gets stabilized in a large cavity surrounded by six oxygen atoms at its vertices forming an octahedron like structure

and similarly another six more distant oxygen atoms form an octahedral arrangement. The well-occupied Ba ion sites seem to be ideal host sites for many guest ions. Pekgözlü et al. [12] have reported blue emission from Pb²⁺ doped BaAl₂B₂O₇. Camardello et al. [13] have studied optical spectroscopy, thermal quenching and electron- vibrational interaction of BaAl2B2O7: Eu2+. Recently, an abnormal reduction in Eu³⁺ to Eu²⁺ in oxidizing environment under UV excitation is also observed in BaAl₂B₂O₇ matrix [5]. However, incorporation of actinides in alkaline-earth aluminium borate lacks literature support. At present, solid host matrices doped with uranium are being investigated with an approach of storage matrices for radioactive waste [14-19]. Although many works have been carried out on uranium doped borates but uranium doped alkaline-earth aluminium borate is still an untouched one [20-22]. In the present investigation, luminescence of uranium in BaAl₂B₂O₇ host matrix has been carried out. As it is known that solubility and site occupancy of uranium in solid matrices, being a heavy metal ion is always challenging so it is interesting to study BaAl₂B₂O₇. U system. Uranium shows various oxidation states i.e. from trivalent to hexavalent and interestingly each of these state shows their characteristic optical spectroscopic properties [23-29]. The uranium in hexavalent state appears in different forms such as UO_4^{2-} , UO_6^{6-} or UO_2^{2+} . So, the form of stabilization

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Fig. 1 XRD patterns of un-doped and uranium doped BaAl₂B₂O₇ with a reference of standard ICDD 86–2168 pattern

or speciation is also an important factor for investigation and towards this end luminescence technique is very useful. The present study is intended to probe $BaAl_2B_2O_7$. U system and extract information regarding speciation of uranium, its photophysical properties as well as its site occupancy in $BaAl_2B_2O_7$ host matrix.

Experimental

The uranium doped and undoped samples were prepared via solution combustion technique. Analytical reagent (AR) grade chemicals were used. In order to synthesize, stoichiometric weight proportions of Ba (NO₃)₂, Al (NO₃)₃ 9H2O, H3BO3 (5 mol % excess), and UO2(NO3)2 6H2O were taken. These salts were ground together in an Agate Mortar with little mixing of distilled water and an aqueous homogeneous solution was obtained. Excess water was made to evaporate by heating at low temperature, and precursor solution was obtained. Then the precursor solution was heated at 600 °C inside a muffle furnace. The solution attended boiling and foams were appeared and suddenly it got ignited and flame was observed. After the flame disappeared a voluminous, foamy precursor powder was obtained. The entire combustion process was for 5 min only. The well-mixed precursor powders were made into pellets. The pellets were annealed in a muffle furnace at a temperature of 900 °C for 3 h and quenched to room temperature.

The physical characterization was carried out by powder X-ray diffraction technique. The used instrument is a Philips diffractometer (model PW 1071) operated with monochromatic CuK_{α} (λ = 1.5418 Å) radiation. The Shimadzu RF 5301pc spectrofluorometer with 150W CW (continuous wave) xenon lamp as the excitation source was used for Photo luminescence (PL) studies. In this instrument, the emission monochromator is protected by a longwavelength-pass filter (UV-35, Shimadzu) that reduces incident beam scattering. Similarly, the Xe lamp output is also get auto corrected by a monitoring photomultiplier that dynamically correct the gain of the photomultiplier tube. The room temperature PL decay time studies were done by Edinburgh FLS-900 time resolved fluorescence spectrometer.

The investigation on site occupancy of dopant was carried out by doing X-ray absorption (XAS) measurements at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. Here the facility of





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ORIGINAL PAPER



Ambient Radiological Condition around an Operating Uranium Mill Tailings Disposal Facility at Turamdih, India

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Abstract: Large quantity of the feed forms part of the solid waste (tailings) slurry in the low grade uranium ore processing plant at Turamdih in Singhbhum region of Jharkhand, India. Coarser size fraction of this waste is used for backfilling of the underground uranium mines and fine fraction is discharged into an engineered impoundment system or tailings pond. Since inception of the discharges, field expeditions have been performed as part of the comprehensive radiological monitoring program for the facility. The monitoring program broadly consists of ambient gamma dose rate, atmospheric ²²²Rn and long lived alpha activity measurement around the facility and the estimation of radionuclide in diverse environmental matrices collected from the adjoining sites. Findings reflect that the radiological conditions are comparable to the pre-existing background level adjoining the tailings pond impoundment. Further, measurements for more than a decade confirm that the atmospheric radon concentration profile just a few meters beyond the embankment is indistinguishable from the background.

Keywords: Tailings pond; Radon; Alpha activity

Introduction

Processed fine solid waste (tailings) slurry contains the entire spectrum of uranium series radionuclides. The disposal is normally carried out within a stable natural impoundment with site specific engineered control measures and surveillance systems. Due to the presence of moderate amount of activity from uranium series radionuclides, the site can be considered as potential source of exposure for the population residing around the facility [1]. A comprehensive radiological monitoring plan is worked out for evaluating the radiological impact of such discharges. The monitoring plans are part of the regulatory appraisal program of the facility consisting of radiological surveys in the surrounding area and the estimation of radionuclides of concern in the environmental samples. Environmental radiological surveillance around the tailings impoundment facility includes ambient gamma radiation, atmospheric radon activity concentration and long-lived alpha activity in respirable dust particles. Radiation dose to

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members of the public is assessed using these radiological parameters. Radon is a daughter product of ²²⁶Ra which is present in uranium mill tailings responsible for higher concentration of radon over and around the tailings disposal facility. Therefore, monitoring and assessment programs are undertaken to ensure that the radiological conditions are markedly deviating from the background or the public exposure surrounding the facility is not exceeding beyond the approved regulatory levels. The findings are quite helpful in reviewing the integrity of the waste management system vis a vis required interventions for the long term protection. The uranium mineralized region has a tropical climate with extended summer from April to June and a relatively short winter from December to February. Maximum temperature may exceed 40 °C during day time and 18 °C during the night. Maximum temperature during the winter is normally lower than 30 °C during the day and 10 °C during the night. The area witness more than 1400 mm annual average rainfall mostly due to the South-west monsoon extending from mid-June to mid-September [2]. The region hosts two underground uranium mines at Turamdih and Mohuldih and an opencast uranium mines at Banduhurang. The centralized ore

processing unit at Turamdih receives the ore feed from all the three mines for the recovery of uranium ore concentrate or yellow cake [3]. The hydrometallurgy of ore is carried out in sulphuric acid medium using pyrolusite oxidant, followed by ion exchange separation and product recovery. The solid waste produced is separated in coarse and fine fractions, later discharged into an engineered impoundment system with natural hill barriers on two sides [4]. Typically the fine fraction discharged at tailings pond has a size distribution of < 75 micron. The area (Fig. 1) is hosting large quantity of process fine tailings stored during the past decade which can be a potential source of exposure for public residing around. Periodic radiological monitoring has been carried out around adjacent to and around the facility since inception of the discharges during previous decade.

Present paper is an overview of the radiological monitoring program for tailings disposal site of the low grade uranium ore processing plant at Turamdih Jharkhand. The findings in this paper consist of results of gamma level, atmospheric radon and estimated long lived alpha activity in the respirable dust.

Tailings Pond at Turamdih

The design feature of tailings pond at Turamdih is based on the latest state of art technology, situated in a geologically stable area with a number of additional control measures in place such as embankment, linings, covers and water control structures like spill way and drainage systems. Two parallel hills act as natural barrier for long term storage. Tailings pond is constructed using downstream method in a sloping valley with dams at eastern side and western side of the impoundment. A compacted impervious clayey material of very low permeability $\sim 1 \times 10^{-9}$ m s⁻¹ has been used as a random fill for prohibiting the contaminant migration. Runoff water channels and garland drains are constructed around the impoundment to avoid the collection of excess water inside. The design features duly



Fig. 1 Map of the study area

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RESEARCH ARTICLE



Ammonium transporter genes in millets: insights into structure, function, evolutionary conservation, divergence, and phylogenetic analysis

Tanushree Sarkar · Suman Bakshi

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Abstract Millets, resilient and nutritionally rich crops, are increasingly recognized for their potential in sustainable agriculture. Ammonium transporter (AMTs) gene family significantly contribute to the absorption and transport of NH₄⁺ form of nitrogen in plants. The information about the structure and function of ammonium transporter genes in millet species is lacking. The millet crops such as pearl millet, proso millet, finger millet, sorghum, foxtail millet and green foxtail millet exhibit genetic variation in AMTs, which can be harnessed to improve NUE. Thus, genomic sequences of the six millet species were used and a total of 53 AMT genes were identified. Further, comprehensive analysis of chromosomal distribution, transmembrane structure prediction, presence of exons and introns, domain and motif organization, phylogeny, and synteny analysis were carried out. The phylogenetic analysis illustrated that millet AMTs belong to two subfamilies AMT1 and AMT2 (AMT2/AMT3/AMT4). Ka/Ks analysis showed that segmental duplications have contributed considerably in the evolution of millet AMTs. Phylogenetic classification of members of Poaceae

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10722-024-02092-2.

T. Sarkar - S. Bakshi (🖾) Nuclear Agriculture and Biotechnology Division, Bhabha Atomic Research Centre, Mumbai 400085, India e-mail: sumansud@barc.gov.in using the amino acid sequences of *AMT1.1* genes confirms the speciation patterns shown by *matK* gene sequence. Promoter analysis of millet AMTs showed presence of cis-elements related to light response, anaerobic induction, growth hormones, drought stress, biotic stress and several endogenous signals related to plant growth and development. This research provides insights into the structural and functional aspects of ammonium transporter genes in millets, and will serve as a foundation for utilizing AMTs for devising NUE strategies.

Keywords AMT · Millet · NUE · Evolution · Transmembrane domain · Cis-elements

Introduction

Nitrogen (N) is the most commonly required macronutrient for plant growth and development. It is an essential element for the synthesis of biomolecules such as nucleotides, amino acids, proteins, chlorophyll, and several others (Marcos de Leão et al. 2020). Nitrogen in the soil exists in three forms, which include organic nitrogen compounds, ammonium (NH_4^+), and nitrate (NO_3^-) ions (Williams and Miller 2001). Plants absorb nitrogen primarily in the ammonium and nitrate forms, and the organic nitrogen compounds need to be converted to these two forms before being taken by the plants. The use of nitrogen by plants involves absorption,

assimilation, and remobilization during plant growth and development. In addition to N absorption from the soil, nitrogen use efficiency (NUE) depends on the assimilation of inorganic nitrogen from the soil, and the utilization of nitrogen during the life cycle of a crop plant (Masclaux-Daubresse et al. 2010; Xu et al. 2012). Plants have a preference for ammonium N form over nitrate nitrogen for uptake from the soil due to the direct assimilation of NH4+ into amino acids in plant cells, whereas, NO37 nitrogen has to be reduced to NH4⁺ before assimilation (Bloom et al. 1992; Jiang et al. 2019; Boschiero et al. 2019). The biological assimilation of nitrogen occurs either through the glutamine synthetase/glutamate synthase pathway (GS/GOGAT) or through glutamate dehydrogenase (GDH), resulting in the synthesis of glutamine which is the substrate for the synthesis of other amino acids via transamination reactions. Ammonium transport is tightly regulated during plant growth and development by the activities of high- and lowaffinity ammonium transporters (Loque et al. 2006; Yuan et al. 2007; Kiba and Krapp 2016). Generally, high-affinity ammonium transport is preferred for NH4⁺ acquisition by plants due to the low ammonium concentration (<1 mm) in the soil (Hao et al. 2020).

Ammonium transporters (AMTs) involved in the uptake of NH_4^+ have been identified in varied plant species (Couturier et al. 2007; Yuan et al. 2007; Tang et al. 2020). These AMTs are distributed in the plasma membranes of plant cells and form homo-or heterotrimers complexes for facilitating the passing of NH_4^+ ions or NH_3 through the pore (Shelden et al. 2001; Ludewig et al. 2003). The transport mechanism of plant AMTs could be an NH_4^+ uniporter, $NH_4^{+/}$ H⁺ symporter, or NH_3/H^+ co-transporter. Plant AMTs can be divided into the following two subfamilies: the AMT1 subfamily (AMT1 cluster) and the AMT2 subfamily (AMT2/3/4 cluster) (Huang et al. 2022).

The AMT genes were identified both in prokaryotic and eukaryotic organisms (Mcdonald and Ward 2016). The first ammonium transporter genes were identified in Saccharomyces cerevisiae and Arabadopsis thaliana (Marini et al. 1997; Ninnemann et al. 1994). Further, AMT family genes were characterized in several crop species namely; Zea mays (Gu et al. 2013), Glycine max (Kobae et al. 2010), Arabidopsis thaliana (Loqué et al. 2006; Yuan et al. 2007, 2009, 2013; Lanquar et al. 2009; Huang et al. 2015), Lotus japonicas (Guether et al.

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2009; Wang et al. 2022), Oryza sativa (Ferreira et al. 2015; Li et al. 2016), Medicago truncatula (Breuillin-Sessoms et al. 2015), Populus trichocarpa (Wu et al. 2015), Triticum aestivum (Duan et al. 2016; Li et al. 2017), Coffea canephora (Santos et al. 2017), Medicago truncatula (Breuillin-Sessoms et al. 2015), Pinus (Castro-Rodriguez et al. 2016), Solanum lycopersicum (Filiz and Akbudak 2020), and Malus domestica (Huang et al. 2022).

Millets, a group of small-seeded grains, have gained recognition as a pivotal component in achieving global food security and contribute to agricultural sustainability. Millet species include pearl millet (Pennisetum glaucum), finger millet (Eleusine coracana), green foxtail millet (Setaria viridis), foxtail millet (Setaria italica), great millet (Sorghum bicolor), proso millet (Panicum miliaceum), kodo millet (Paspalum scrobiculatum), Japanese barnyard millet (Echinocloa esculenta), Indian barnyard millet (Echinocloa frumentacea), and little millet (Panicum sumatrense), among others (Goron and Raizada 2015). Millets are hardy, resilient crops that thrive in diverse agro-climatic conditions, making them an essential resource for enhancing agricultural sustainability. Their exceptional nutritional profile, including high levels of protein, fiber, and essential micronutrients, placed millets as key contributors to improving food security, especially in regions grappling with malnutrition and food scarcity (Ceasar 2023). Improving the NUE of the cereals is essential to enhance yields under low-nutrient soils and conserve the fertility of the soils (Baligar et al. 2001; Bariya and Ahish 2014; Naeem et al. 2017; Nieves-Cordones et al. 2020). Several investigations have been conducted during the last decade by the wider scientific community, employing various molecular genetic tools to study and improve the NUE of crop plants. These include the utilization of genome-wide association study (GWAS) approach, molecular marker-assisted breeding (MAB), nutrient transporter characterization and functional genomics approaches. These investigations have been reported for model crop plants to improve NUE (Hawkesford 2012; Avin-Wittenberg et al. 2018). However, genome-based and forward genetic research may not be easy for millets with limited genomic resources.

Complete annotated genome sequence information is lacking for many millet species, which limits the understanding of gene sequences involved







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ORIGINAL PAPER



Atmospheric Pressure Portable Catalytic Thermal Plasma System for Fast Synthesis of Aqueous NO₃ and NO₂ Fertilizer from Air and Water

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Abstract

Meaningful deployment of plasma water-based nitrogen fixation in agricultural application is hindered primarily due to its poor synthesis rate in compact systems. The study reports a directly deployable thermal plasma based portable catalytic compact system, offering typical synthesis rate as high as 1035 mg/min for nitrate and 635 mg/min for nitrite directly from naturally abundant atmospheric air and water. Developed technology is clean, sustainable, easily decentralizable, and completely free from fossil fuels and harmful intermediates like ammonia. The system avoids safety hazards and costs related to the requirements of continuous energy resources, pressurized environment for synthesis, regulated storage, refrigeration need, transportation of raw materials and distribution of fertilizer, as may be required by other competing technologies. Described system, consisting of air plasma torch, reaction chamber, water injection manifold and catalytic bed creates a unique nascent reactive plasma environment at ambient pressure that auto activates the catalyst in the field of thermal plasma for highly efficient fixation of nitrogen. Presented results indicate that use of combination catalysts with mechanically enhanced surface area allows drastic enhancement in the nitrogen fixation. Possible reaction chemistries, results of trials with different catalysts, time evolution of concentration, auto-conversion from nitrite to nitrate in aqueous media, time stability of concentration of the synthesized nitrate and observed remarkable effectiveness in the actual field trials are presented. Achieved synthesis rates are compared with those reported in literature in the area of thermal and nonthermal plasma.

Keywords PWBNF · PAW · Nitrogen fixation · Plasma fertilizer · Thermal plasma · Plasma catalysis · Nitrate · Nitrite

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Introduction

Nitrogen is an essential part of every living organism. Vital organic compounds for life like amino acids, proteins, nucleic acids associate nitrogen. Nucleoside triphosphates, the molecular precursors to DNA and RNA also contain nitrogen bases. Interestingly, in spite of nitrogen being highly abundant in atmosphere, it cannot be directly used by most of the living organisms due to existing strong triple covalent bond between the atoms in the molecule. This makes nitrogen to behave almost like an inert gas. It must combine with some other elements to form more functional compounds like ammonia, nitrate or nitrite which can be directly used by living organisms. The process is called nitrogen fixation [1]. The study presents atmospheric pressure portable catalytic air plasma system for fast fixation of nitrogen in the form of aqueous NO_2^- and NO_3^- fertilizer in high concentration.

In nature, nitrogen gets fixed by bacteria like azotobacter, archaea etc. through special catalytic process driven by enzymes. It also gets fixed through natural lightning, and also via symbiotic relationship between termites and fungi [2]. However, these natural processes are awfully insufficient to meet the demand of growing population of the world [3–6]. At present, drastically increasing global population heavily depends on the industrially fixed nitrogen.

Over a century, numbers of efforts have been made to industrially fix nitrogen into reactive nitrogen compounds through number of distinct processes to increase agricultural yields. Most successful industrial attempts in nitrogen fixation include the Birkeland–Eyde (B–E) process [7–11], the Frank–Caro (F–C) [12] process and the Haber–Bosch (H–B) process [12–14]. B-E process produces NOx, F–C process produces calcium cyanamide and H-B process produces ammonia as the form of reactive nitrogen. While B-E process was industrially used for quite some time, it is gradually phased out due to the invention of the more efficient Haber–Bosch process. In B-E process, while the plasma reactor takes the major part of the investment, the absorption towers contribute significantly towards the capital and operational expenditure. Such systems are not decentralizable and cannot be run with intermittent renewable energy sources. In F–C process calcium carbide reacts with nitrogen gas at about 1000 °C to produce calcium cyanamide (nitrolime). The process stands as the first industrial technique to fix atmospheric nitrogen.

At present, nitrogen is almost exclusively fixed through H-B process. Although, it is the most matured and the most efficient industrial process of nitrogen fixation till date, it associates some major operational and environmental issues [15–17]. The process uses fossil-derived hydrogen, results in enormous carbon footprint, requires very high temperature (>400 °C), very high pressure (>200 bars), too much of energy (~2% of global energy requirement) for the synthesis, generates millions of tons of greenhouse gas (CO₂) per year and cannot accommodate the intermittency of renewable energy sources [3]. It uses fossil fuels and hence not sustainable in the long run. It involves transportation and distribution cost as the process is not decentralizable due to requirement of heavy installations related to high temperature and high pressure. Nevertheless, H-B process still continues to be the primary means to support the ever-growing population on earth [16, 17].

Presently, plasma catalysis based nonthermal plasma processes form an active field of research in the area of decomposition of volatile organic compounds, removal of tar component, NOx conversion, CO₂ splitting, H₂S removal, NH₃ synthesis, NH₃ decomposition etc. [18–29]. Related studies are mostly confined within the domain of cold non-thermal DBD kind of plasma. Possibility that plasma and catalyst are mutually influencing each other is a major conclusion of these studies. While similar studies are

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RESEARCH



Bis(glycinium) oxalate: effect of deuteration, single crystal neutron diffraction and Raman spectroscopic studies

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Abstract

The crystal structure of bis(glycinium) oxalate (BGO) is stabilized by a very strong O–H..O hydrogen bond apart from N–H...O and C-H...O hydrogen bonds. To probe the effect of deuteration on these hydrogen bonds, fully deuterated (FDBGO), C-deuterated(CDBGO), and N-deuterated bis(glycinium) oxalate (NDBGO) crystals were grown. Single crystal neutron diffraction and Raman spectroscopic studies were carried out. It was found from neutron diffraction studies that the O...O distance of the O–H...O hydrogen bond reduced on deuteration showing an inverse Ubbelohde effect. The neutron diffraction and Raman spectroscopic studies also revealed partial deuteration. The DSC studies showed no phase transition. Variation of the melting point amongst the four crystals was in a very small range from 151 to 158 °C.

Keywords Glycine · Oxalic acid · Deuteration single crystal neutron diffraction · Raman spectroscopy

Introduction

The approval of the first deuterated drugs in 2017 by FDA in treating Huntington's disease has generated renewed interest in studying deuteration effect in small molecules. Deuteration in a molecule replaces H with D leads to minimum modification in a molecule. But it can bring in significant changes in the chemical and physical properties like kinetics and equilibrium constants [1–3] because of the difference in atomic mass, volume, and spin as compared to that of hydrogen. In general, isotopic substitution does not bring about a structural change, but effects the molecular spectroscopy via the geometric effect [4–6]. The perturbation resulting due to deuteration in molecular rearrangement has been extensively enumerated in the study by Merz and Kupka [7]. The term isotopic polymorphism was coined to structures which exhibited structural

R. Chitra rchitra@barc.gov.in changes on deuteration [8]. Many studies have been carried out to study the effect of deuteration on the structures and properties of the crystal [9, 10]. Glycine is the only achiral amino acid. Being the simplest amino acid, complexes of glycine have been studied from biological and as well from point of ferroelectricity. There exists a large number of complexes of amino acids which have shown ferroelectricity, like triglycine sulfate family of crystals [11], diglycine nitrate [12], glycine phosphite [13], and glycine silver nitrate [14]. The deuteration effect in partially deuterated and fully deuterated triglycine sulfate increases the curies point by 12 K and 10 K respectively and doesn't bring about any change in the crystal structure [15, 16]. Similarly in glycine phosphite, there is no structural change due to deuteration but the transition temperature is raised by 100 K [17]. The first organometallic crystal of glycine with silver and nitrate, which showed ferroelectricity was GSN [18] and undergoes displacive phase transition. Our earlier study on fully deuterated GSN(FDGSN) [19] and partially deuterated CDGSN and NDGSN showed that the crystal structure changes on full and C deuteration [20] showing isotopic polymorphism. Bis(glycinium) oxalate (BGO) crystallizes in P21/n space group and the interaction of glycinium ion with oxalate moiety is through very strong and short O-H ... O hydrogen bond apart from the N-H ... O and C-H .. O hydrogen bonds [21, 22]. The high pressure Raman and X-ray diffraction

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[23] and IR studies [24] on BGO showed a phase transition around 1.7 GPa. The new phase was interpreted in terms of loss of center of inversion and breaking and reforming of N-H...O hydrogen bonds [23]. It is interesting to see how the deuteration is going to perturb the structure, hence FDBGO, CDBGO, and NDBGO were grown. Single crystal neutron diffraction is a unique technique to distinguish the hydrogen and its isotope the deuterium; hence, the single crystal neutron diffraction of FDBGO, NDBGO, and CDBGO was undertaken. Raman scattering experiments of the above crystals were also performed to identify the various modes. DSC measurements were undertaken to understand the effect of deuteration in the melting points of each of the crystal.

Table 1Crystallographic andrefinement details of FDBGO,CDBGO, and NDBGO

Crystallization

Colorless single crystals of FDBGO were grown as threedimensional crystals by mixing fully deuterated α glycine and oxalic acid in 2:1 ratio respectively in D₂O. Colorless single crystals of CDBGO were grown as three-dimensional crystals by mixing deuterated α glycine and oxalic acid in 2:1 ratio respectively in H₂O. Colorless single crystals NDBGO were grown as three-dimensional crystals by mixing α glycine and oxalic acid in 2:1 ratio respectively in D₂O. For further improving the deuteration level of FDBGO and NDBGO, the crystal obtained during the first crystallization were again dissolved in D₂O to obtain fresh crystals of FDBGO and NDBGO.

CCDC	FDBGO	CDBGÖ	NDBGO
Deposition number	2,383,589	2,383,588	2,383,587
Source	Neutron	Neutron	Neutron
Empirical formula	C2H0.45D11.56NO2.0.5(C2O4)	C2H8D4NO2.0.5(C2O4)	C2H8.84D3.17NO2.0.5(C2O4)
Formula weight	251.80	244.20	243.36
Temperature (K)	300 K	300 K	300 K
Wavelength (Å)	0.995	0.995	0.995
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2 ₁ /n	P 21/n	P 2 ₁ /n
Unit cell dimensions			
a (Å)	4.939 (9)	4.910 (3)	4.9101 (7)
b (Å)	9.932 (3)	9.957 (3)	9.859 (5)
c (Å)	10.942 (8)	10.826 (4)	10.8638 (14)
B(°)	99.430 (3)°	97.52 (2)	97.670 (10)°
Volume (Å ³)	529.6 (11)	524.7 (4)	521.2 (3) Å ³
Z	2	2	2
Calculated density (Mg m ⁻³)	1.579	1.546	1.551
Orange for data collection (°)	41.8°	42.6	42.3°
Limiting indices	$0 \le h \le 6$	$-6 \le h \le 6$	$-6 \le h \le 6$
	$-12 \le k \le 13$	$-13 \leq k \leq 9$	$-12 \le k \le 8$
	$-14 \le 1 \le 13$	$-9 \le 1 \le 14$	$-11 \le 1 \le 14$
Unique reflections collected/	1316	1351	1317
Data/restraints/parameters	1316/0/132	1351/0/127	1317/0/129
Goodness-of-fit on F2	1.09	1.17	1.07
Final R indices $R[F^2 > 2\sigma(F^2)]$	R1 = 0.109 wR $(F^2) = 0.38$	$R_1 = 0.086$ wR (E^2) = 0.334	R1 = 0.109 wR $(F^2) = 0.389$



Fig. 1 Ortep [26] picture of Asymmetric unit of CDBGO, FDBGO, and NDBGO, symmetry code -2-x, 1-y,-z

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Chemical characterization of lithium based ceramics utilizing charged particle activation and ion beam techniques

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Abstract

Non-destructive methodologies using activation analysis and ion beam analysis techniques were optimized for the chemical characterization of ceramic materials, lithium titanate and lithium niobate, which have application in tritium breeding blanket. The analyses were carried out as a part of chemical quality control exercise. The atomic ratios of Li/Ti, Li/Nb were quantified by charged particle activation analysis using 13 MeV proton beam from variable energy cyclotron facility and particle induced gamma ray emission/Rutherford backscattering spectrometry using 3 MeV/2 MeV proton beam from 3MV tandem accelerator facility. The results of these different analytical methods are in good agreement, which established the applicability of these activation analysis and ion beam techniques for the chemical characterization of these ceramic materials.

Keywords Lithium titanate · Lithium niobate · CPAA · PIGE · RBS

Introduction

Necessity and problems of tritium production

The fast exhausting stock of energy resources and environmental concerns across the world has seen the attention in energy research shift its direction to alternative and green energy sources in recent years. The possibility of utilizing Nuclear Fusion reaction as a long serving energy source has seen encouraging technological and scientific developments in the past few years. With the continuous research in the fields of sustenance of the plasma core of a fusion reactor and controlling the fusion reaction—the International Thermo-nuclear experimental reactor (ITER) is nearing the reality. The deuterium–tritium (D-T) fusion is the most

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feasible (from energy requirement point of view) [1] reaction and is to be used to fuel the ITER. It has the added advantages of its minimal environmental impact and absence of radioactive products, thereby eliminating the allied radioactive waste management processes involved and radiation exposure as well. Deuterium is present in sufficient amount in nature and can be easily extracted. Owing to the extremely low amount of Tritium present in the environment; its production becomes a vital issue for fuelling the fusion reactor. lithium (Li) undergoes a nuclear reaction with neutrons (Eq. 1) to produce Tritium [2]. As a result, fusion reactors having tritium breeding ratio, (TBR)>1, using of lithium containing blankets with neutrons multipliers are subjected to extensive study. Lithium containing materials have been subjected to a lot of studies for their properties. High melting lithium containing ceramic materials have attracted much attention in this regard. In addition to this, TBR have been improved using neutron multiplier such as beryllium and lead, in lithium blanket materials [3, 4]. A series of Li containing blanket materials were synthesized and tested for the principle breeding requirements in fusion reactor as tritium breeder.

 ${}^{6}\text{Li} + {}^{1}\text{n} \rightarrow \text{He}(2.1 \text{ MeV}) + \text{T}(2.7 \text{ MeV})$ (1)

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Possible target materials for tritium production

The probable Li-based (also enriched in ⁶Li) ceramics candidates for application as tritium breeder, are lithium titanate (Li2TiO3) [5], lithium-zirconate (Li2TrO3) [6, 7], lithium silicate (Li2SiO3) [8], lithium niobate (LiNbO3) etc. In addition, the lithium titanate-zirconate (Li2+x(Ti,Zr) O3+z) has been reported recently as a super advanced (SA) tritium breeder material [9]. Some of these tritium breeder materials have also been tested in ITER test blanket module (TBM) and for DEMO reactor [10, 11]. As a result the analytical study of the detailed composition and nature of the probable fuel materials to be used is of major importance. In the proposed fusion reactor, a mixture of (80% Ar and 20% H2) sweep gas will be used to extract the generated tritium from the breeder blankets. In the sweep gas atmosphere lithium titanate has been found to show mass loss due to Li vaporization and reduction of Ti⁺⁴ to Ti⁺³ associated with oxygen (O) loss [12, 13]. Such processes render the fuel pellets brittle and also change the thermal diffusivity properties. To prevent the mass loss and conserve the physical and chemical properties of the fuel at elevated temperatures, excess Li addition to the fuel has been suggested [12, 14, 15].

Analytical methods to characterize the breeding blankets

Several methodologies for the synthesis of ceramic breeder materials were developed such as Sol-gel synthesis [16, 17], solid state synthesis [18], solution based methods [8, 18, 19] etc. The ratio of Li/M (M-metal) may vary depending on the use of above methods and this in turn affects the TBR and other properties of the breeding material [20]. Therefore the chemical analysis of the above synthetic ceramic materials for ensuring chemical quality control, is of utmost importance. Unfortunately, the compositional analysis of ceramic materials is quite difficult, especially by employing conventional solution based methods as these materials are difficult to dissolve due to their refractory nature. The conventional analysis methods of chemical constituents for ceramics are long, tedious and sometimes do not enable for both the elements as reported here [21-27]. Analysis using laser ablation ICP-MS [28], LIBS (laser induced breakdown spectroscopy) can be utilized for the solid state analysis, although matrix interference can cause major problems. Though quantification of titanium (Ti) and niobium (Nb) are possible with instrumental neutron activation analysis (INAA), particle induced X-ray emission (PIXE), X-ray fluorescence technique (XRF), they are unsuitable to

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be used to quantify Li. In recent times there have been reports of non-destructive and simultaneous analysis of chemical compositions of ceramic samples by NAA, PIGE [29-32]. Non-destructive nuclear techniques such as particle induced gamma ray emission (PIGE) and charged particle activation analysis (CPAA) can however quantify lithium with high precision. PIGE [32] and Proton Rutherford backscattering spectrometry (p-RBS) has been reported to have been successfully employed for simultaneous determination of lithium and titanium in lithium titanate. Charged particle activation analysis (CPAA) is a simultaneous multi-elemental determination technique, similar to NAA. CPAA has widely been used for the determination of several elements in trace and ultra trace levels [33-36]. There are very few reports for the determination of elements in ceramic samples using CPAA [37]. During the present work, lithium titanate and lithium niobate samples were analyzed by CPAA techniques using 13 MeV proton beam from K-130 cyclotron at Variable Energy Cyclotron Centre (VECC), Kolkata, India. The proficiency of CPAA in compositional analysis of technologically important ceramic compounds is presented. The same samples were also analyzed by particle induced gamma ray emission (PIGE) and Proton Rutherford backscattering spectrometry (p-RBS) [38, 39] using 3 MV tandem accelerator machine from National Centre for Compositional Characterisation of Materials (NCCCM), Hyderabad, India for validation purposes.

Experimental

In CPAA, the selection of proton energy depends upon the type of nuclear reaction to be used to produce the desired isotope from the target element. The (p, n) reaction channel is widely used for determination of trace elements by instrumental approach in CPAA due to high cross section, less nuclear interference and low matrix activation. The nuclear reactions used to quantify the elements of interest in this CPAA work were-nat.Li(p, n)7Be; nat.Ti(p, n)48 V and nat.Nb(p, n)93mMo. Available literature shows that the ^{nat.}Li(p, n)⁷Be reaction is having cross section 0.03-0.5 b in the 2.2–13 MeV energy range of proton with $\sigma_{max} = 0.5$ b at 2.3 MeV [40]. The reaction cross sections for natTi(p, n)^{48} V and $^{nat}Nb(p,\,n)^{93}Mo$ reactions have σ_{max} of 63 mb [40-42] and 30 mb [40, 43-45] at ~11 MeV respectively. There was a significant interference of nitrogen (N) on the determination of Li using proton beam of energy 14 MeV and above [37]. Moreover, the higher reaction channels, e.g., (p, 2n), (p, pn) will start competing with (p, n) reaction channel at 15.6, 11.9 MeV and 9.4, 9.0 MeV respectively for the afore-mentioned 48Ti and 93Nb isotopes [46]. Thus, considering the interferences as mentioned above, a proton





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RESEARCH



Competition-driven phenotypic plasticity in Iron acquisition and aromatic utilization confers a fitness advantage to *Pseudomonas putida* in an Iron-limited rhizospheric environment

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Abstract

Iron scarcity poses a critical challenge for rhizospheric bacteria like *Pseudomonas putida* in the competitive rhizosphere. Despite its dependence on iron for essential functions such as root colonization, motility, and aromatic compound utilization, *P. putida* exhibits limited capability for heterologous siderophore utilization and primarily relies on the secretion of a single siderophore, pyoverdine. This study investigates the mechanisms by which *P. putida* acquires iron in an iron-limited, aromatic-rich, rhizosphere-like environment. Our findings demonstrate that *P. putida* exhibits significant phenotypic plasticity, dynamically modulating pyoverdine secretion in response to competitive pressures and substrate availability. This adaptive strategy optimizes energy expenditure and iron acquisition, providing a competitive advantage. Comparative gene expression analysis supports these observations, revealing the molecular underpinnings of this plasticity. Enhanced pyoverdine production driven by competition compensates for the bacterium's limited siderophore repertoire and facilitates rapid aromatic compound utilization, conferring a distinct fitness advantage in iron-deprived conditions. This study elucidates the complex interplay between competition, iron uptake, and aromatic compound utilization that underpins the rhizospheric success of *P. putida*.

Keywords Aromatic substrate · Competition · Siderophore · Pseudomonas putida · Rhizosphere

Introduction

In competitive ecological niches, microorganisms are constantly engaged in life-or-death battles within diverse communities (Hibbing et al. 2010). These interactions are typically classified as (1) exploitative, involving the deprivation of essential substrates from competitors and (2) interference, where toxins and antibiotics are employed to hinder competitor growth (Cornforth and Foster 2013). Both exploitative and interference competition are closely linked to the energy status of organisms. The expenditure of energy for toxin and antibiotic secretion (interference) and the up-regulation of

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auxiliary pathways for quicker assimilation of available resources (exploitative) are critical determinants of competitive fitness (Cornforth and Foster 2013; Sexton et al. 2017; Maan et al. 2022; O'Brien et al. 2023). Thus, an accurate assessment of competition is essential for organisms to respond appropriately; otherwise, the metabolic efforts invested in competitor response mechanisms become futile (Maan et al. 2022). However, any delay in deploying effective strategies may result in an organism becoming outcompeted. Therefore, organisms must promptly sense competition and initiate the necessary responses (Joshi et al. 2014).

Despite its abundance, iron exhibits limited solubility at physiological pH, severely restricting its bioavailability and intensifying competition among microbes for this essential resource (Lamont et al. 2002; Hibbing et al. 2010). Siderophore secretion is a primary strategy employed by bacteria to capture environmental iron. However, this capability is widespread, with many bacteria producing siderophores, resulting in complex competitive interactions for the scarce iron supply (Niehus et al. 2017). Traits such as the ability to utilize heterologous siderophores or produce diverse

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siderophores confer competitive advantages, but these are largely dependent on genomic composition present in given organism (Arif et al. 2012). Interestingly, numerous organisms lacking diverse iron uptake capabilities not only survive but thrive in iron-limited environments. A comprehensive investigation into the competitive strategies employed by organisms by these organisms expected to reveal alternative iron acquisition mechanisms, thereby helping us to understand the intricate ecological dynamics within these environments.

Despite its well-documented reliance on iron for both aromatic degradation (Ramos et al. 1997) and environmental adaptation (Dinkla et al. 2001; Molina et al. 2005; Matilla et al. 2007), Pseudomonas putida KT2440 possesses a surprisingly limited iron acquisition repertoire. This paradox is particularly intriguing considering its competitive advantage in iron-deficient environments (Nancharaiah et al. 2008; Venkata Mohan et al. 2009; Yu et al. 2010). Notably, P.putida produces only a single siderophore (pyoverdine) (Matilla et al. 2007) and exhibits limited capacity to utilize heterologous ones (Matthijs et al. 2009). This apparent contradiction begs the question: how does P. putida, a highly competitive bacterium in aromatic-rich, iron-deficient settings, thrive with such restricted iron acquisition capabilities? This apparent contradiction fuels our current investigation into the strategies employed by P.putida to augment its iron supply, a critical facet we aim to unravel in this study.

This study investigates the mechanism(s) employed by P.putida KT2440 to achieve competitive success in ironlimited, aromatic-rich environments, particularly within the dynamic rhizosphere. Iron availability is critical for the root colonization and proliferation of P.putida, but securing this vital nutrient presents a crucial bottleneck amidst numerous competitors. This competitive landscape is further intensified by the plant's iron-deficiency response, characterized by elevated phenolic secretion, which potentially selects for bacteria capable of both iron acquisition and aromatic degradation (Shafer and Blum 1991; Jin et al. 2007, 2010). We hypothesize that P. putida, despite possessing only one type of siderophore (pyoverdine) and limited capability to utilize heterologous siderophore, achieves competitive success through dynamic modulation of pyoverdine secretion in response to both competition and the availability of aromatic substrates. To test this hypothesis, we evaluated siderophore secretion profiles of P.putida under competitive pressure in two contrasting environments: an aromatic-rich environment and environment containing an alternative substrate requiring iron-independent metabolic pathways. Our results reveal that P.putida dynamically modulates pyoverdine secretion in response to competition and carbon sources. This enables it to strike a crucial balance between energy conservation and effective iron acquisition, ultimately outcompeting competitors. These findings offer valuable insights into adaptive

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strategies adopted by *P.putida* in iron-limited environments, further supported by comparative gene expression profiling under competitive and comparative environments.

Material and methods

Strain and growth condition

The experiments utilized Pseudomonas putida KT2440 (P. putida), chromosomally marked with DsRed and carrying the gfpmut3b-modified KanR plasmid pWWO, as previously described (Joshi et al. 2009). Additionally, a gfpmut3b-modified Kan^R plasmid pWWO harboring a siderophore-negative mutant of P.putida KT2440 (APpsD), with a mutation in the ppsD gene (PP 4219), was employed to investigate the role of siderophores in aromatics utilization. Benzyl alcohol degrading, gentamycin-resistant Pseudomonas aeruginosa, and E.coli JM101 (Non-degrader) were used for competition experiments. All the experiments were carried out in Tris minimal media { composition per liter of H2O: (A) Tris 6.05 g, Sodium chloride 4.67 g, Potassium chloride 1.5 g, Ammonium chloride 1.06 g, Sodium sulfate 0.42 g, Magnesium chloride 0.233 g, Calcium chloride 0.03 g, and Sodium dihydrogen phosphate (dehydrate) 0.004 g. (B). A trace elements stock solution: Zinc sulfate (heptahydrate) 143.77 mg/l, Magnesium chloride (Tetrahydrate) 98.96 mg/l, Boric acid 61.83 mg/l, Cobalt chloride 190.34 mg/l, Copper chloride 17.05 mg/l, Nickel chloride 23.77 mg/l, and sodium molybdate 26.29 mg/l. From this solution, 100 µl/liter was added to the Tris solution. All chemicals used were of analytical reagent (A.R.) grade and obtained from Merck, Germany) seeded with either 5 mM of Benzyl alcohol (BA) as an aromatic substrate or with 1% Glucose as the sole source of carbon and energy.

Simulated competition experiment (for determination of absolute and relative fitness)

To demined the fitness of *P.putida*, $1X10^6$ cfu/ml of the overnight grown culture of *P.putida* (WT)/*P.putida* (Δ PpsD) and *P.aeruginosa/E.coli* was inoculated in Tris- minimal media having Benzyl alcohol (5 mM) or glucose (1%) as the sole source of carbon. To determine absolute fitness, $1X10^6$ cfu/ ml (equal number) of overnight grown cultures were inoculated in separate flasks. The growth of each organism was monitored by plating the appropriate dilution on selective L.B. plates (i.e., *P.putida* (WT) on Tetracycline, *P.putida* (Δ PpsD) on kanamycin, and *P. aeruginosa* on gentamicin.

For determination of relative fitness, *P.putida* (WT) or *P.putida* (Δ PpsD) were co-cultured (dual species competition in single flask) with either *P.aeruginosa* or *E.coli* in





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ENVIRONMENTAL ISSUES FOR THE PLANET: SOLUTIONS FROM SCIENCE AND TECHNOLOGY



Comprehensive assessment of groundwater quality in the Prayagraj District, Ganga Basin

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Abstract

Urbanization has severely impacted the world water resources especially the shallow groundwater systems. There is a need of a robust method for quantifying the water quality degradation, which is still a challenge for most of the urban centers across the world. In this study, a highly urbanized region of Ganga basin is selected to critically evaluate commonly used WQIs and compare with fuzzy modeling. A total of 28 water samples were collected from diverse sources (surface and groundwaters) in the vicinity of urban region covering an area of 216 km² during the premonsoon period. TDS, TH, NO₃⁻, and F⁻ values were found to be above the permissible limits in 57%, 89%, 4%, and 7% samples, respectively. The WQIs (entropy and integrated) outputs were found to be similar with 89% of the samples falling under moderate category. Fuzzy modeling was carried out allowing user-defined weighting factors for the most influential ions, and the output suggested 96% of the samples falling under moderate to excellent categories. Based on the chemical results and considering the lithology of the study area, the geochemical reactions controlling the water quality were deduced. This study outlines a systematic approach of evaluating the overall water quality of an urban region highlighting the merits and limitations of WQIs. It also justifies the immediate need to generate more robust data to achieve the sustainable development goals 6 (clean water and sanitation) and 11 (sustainability of cities and human settlement).

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Highlights

- Water quality is mainly impacted by the presence of high amounts of secondary contaminants.
- Spatial variability in water quality can be attributed to anthropogenic contributions.
- Irrigation parameters suggest marginal suitability of groundwater.
- Most influential ions impacting drinking water suitability are SO₄²⁻, Cl⁻, and K⁺.
- The WQIs and fuzzy modeling output were found to be consistent.

Extended author information available on the last page of the article

Environmental Science and Pollution Research

Graphical Abstract



Keywords Fuzzy logic · Entropy water quality modeling · Pollution Index · Urban center · Ganga Plains · Prayagraj

Introduction

Urban regions have been contributing to the rapid population growth in Ganga Plains, and the data suggest that approximately 42% of the total population in India are supported by this basin. Due to poor quality of river water and increase in population, dependence on groundwater resources for freshwater supplies has been raising continuously (Sharma et al. 2016; Mishra 2023). The groundwater resources in Ganga basin are considered essential source of good quality drinking water. However, studies reported that shallow aquifers of Middle and Deltaic Plains of Ganga basin are highly susceptible to contamination from sewage effluents; elevated levels of inorganic contaminants (F⁻, NO₃⁻, and As), volatile organic carbons, and several kinds of pharmaceuticals pose a great risk to public health (Central pollution Control Board (CPCB) 2013; Krishan et al. 2023). Studies also indicated that prolonged intensive pumping has potential to alter natural flow regimes in Gangetic Plains and might lead to vertical migration of contaminants to greater depths > 150 m (Lapworth et al. 2018). Clearly, these factors constrain the usability of available water resources in the Gangetic Plains. Therefore, proper assessment of water quality becomes imperative for sustainable management of water resources.

An urban region belonging to Middle Ganga Plains (MGP), viz., Prayagraj district of Uttar Pradesh, India, was selected for detailed evaluation for the water quality. Previous studies have indicated that the groundwater pollution is mainly derived from anthropogenic sources like municipal wastes and industrial effluents (Central pollution Control Board (CPCB) 2013; Ghirardelli et al. 2021; Krishan et al. 2023; Richards et al. 2023). It was also observed that heavy metal residues in sediments as

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well as in river water are higher than the permissible limits (Pandey and Singh 2017). Microbial contamination and presence of inorganic carcinogenic elements like Cr, Cd, As, and Pb were also reported in the Ganga Plains (Maurya et al. 2019). Studies have revealed that synthetic fertilizer and industrial effluents are the main sources of nitrate in the Ganga River (Sharma et al. 2023; Balkrishna et al. 2024) and also groundwater (Madhav et al. 2018). The key indicators of water quality degradation are typically nitrate, fluoride, chloride, sodium, potassium, and dissolved oxygen (Al-Ani et al. 2019). Despite amplified anthropogenic activities and rapid industrialization, a comprehensive understanding on water quality and contamination levels in groundwater is still missing in the study area, which is partly due to compounded complexity through urbanization and continuous changes in land use and land cover.

Several Water Quality Indices (WQIs) are available in the literature with their own merits and limitations (Amiri et al. 2014; Mukate et al. 2019; Agbasi et al. 2023; Kumari et al. 2023). In this research, we have specifically used Entropy Water Quality Index (EWQI), Integrated Water Quality Index (IWQI), and Integrated Water Pollution Index (IWPI), which are well-established for obtaining overall water quality of a given area. In addition, Fuzzy Water Quality Index (FWQI) was attempted in this article, and the output is compared with the other water quality indices (WQIs). EWQI is one of the water quality probing indices, in which all the measured parameters playing a pivotal role in water are aggregated into single index (Amiri et al 2014). IWQI follows the same principle of aggregation for all the parametric concentrations into single one, but steps applied for calculation are different from other indices (Agbasi et al. 2023). Thus, in this method,





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Continuous monitoring of outdoor natural gamma absorbed dose rate in air: a long-term study in Kolkata, West Bengal, India

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Abstract

This study contributes to the overarching Indian Environmental Radiation Monitoring Network initiative, concentrating on the continual assessment of the gamma absorbed dose rate in outdoor air attributable to natural gamma radiation in Kolkata, West Bengal, India. Over a span of fourteen years (2011–2024), data were gathered from 32 monitoring sites within the city utilizing permanently installed Geiger-Mueller detector-based environmental radiation monitors. This paper offers an analysis of extensive findings from long-term monitoring efforts. The absorbed gamma dose rate in outdoor air varied among the monitoring sites, ranging from 78 5 to 137 4 nGy h⁻¹, with a mean value of 107 12 nGy h⁻¹. The estimated mean annual effective dose due to outdoor natural gamma radiation ranged from 0.10 0.01 to 0.17 0.01 mSv y⁻¹, with an overall mean of 0.13 0.01 mSv y⁻¹.

Keywords Outdoor natural gamma dose rate · Geiger-Mueller detectors · Annual effective dose

Introduction

Estimating the natural radiation dose to members of the public holds significant importance, constituting approximately 80% of the total radiation dose received by the global population on average [1]. This exposure primarily occurs through various pathways, including inhalation of ²²²Rn, ²²⁰Rn, and their progenies, ingestion of natural radionuclides found in food and beverages, and direct exposure to terrestrial and cosmic radiation. The outdoor natural background gamma radiation level at any location is predominantly influenced by the presence of natural radionuclides such as ²³⁸U, ²³²Th, and ⁴⁰K in the terrestrial environment, along with cosmic ray particles and their secondary radiation reaching the Earth's surface.

The correlation between soil radionuclide (²³⁸U, ²³²Th, and ⁴⁰K) concentrations, which can be measured in collected and suitably processed soil samples by using high resolution high purity germanium (HPGe) or medium resolution

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scintillator based spectrometers [2–7], and the outdoor gamma absorbed dose rate in air (D), which can be measured directly through various measurement techniques such as thermoluminescent dosimeters (TLDs), scintillator-based devices or Geiger-Mueller (GM) detector-based radiation survey meters [8–12], has been well established. Conversely, continuous monitoring of D using field-installed environmental radiation monitors (ERMs) demands substantial resources but yields results with greater statistical accuracy due to long-term averaging [13–15].

The principal objective of this article is to consolidate the results obtained from the long-term measurements of Din Kolkata, West Bengal, India. These results should serve as the baseline data for the study area, providing a reference point against which any increase in this quantity due to radiological or nuclear events can be compared. This extensive, long-term measurement initiative spanning numerous locations within the city is unprecedented and has not been previously documented. Additionally, the article assesses the annual effective dose (*AED*) resulting from outdoor natural gamma radiation. The measurement findings from Kolkata are also juxtaposed with regions globally recognized for their elevated natural background radiation levels.

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Materials and methods

Study area and site selection for the installation of ERMs

Kolkata, situated in the eastern Indian state of West Bengal, serves as its capital. Positioned in the southern part of the state, Kolkata is situated within the Bengal basin of the Ganges Delta, a component of the expansive Indo-Gangetic Plain. The city's elevation hovers near mean sea level (MSL), ranging from 1.5 to 9 m, with an average of approximately 5 m. Once a marshy wetland, Kolkata's current landscape has evolved over time. The predominant soil composition in the area is alluvial, with a Quaternary sedimentary formation comprising clay, silt, and various grades of sand and gravel.

As a component of a comprehensive environmental radiation monitoring initiative, 32 environmental radiation monitors (ERMs) were installed across Kolkata city, covering the geographical coordinates ranging from 22.465° to 22.622°N latitude and 88.282° to 88.484°E longitude. The ERMs were installed at government-owned premises, away from buildings. The detector centers were positioned at an approximate height of 1 m above ground level.

Measurement period

The deployment of the ERMs commenced in 2011 and then progressed gradually. The data presented in this paper were collected from all 32 ERMs, specifically during their operational periods (see Table 1), with brief intermittent maintenance periods excluded. For currently operational ERMs, the data included was up to January 31, 2024. As a result, different ERMs were considered over distinct timeframes. However, the shortest measurement period for any ERM spanned a minimum of two years, guaranteeing that statistical fluctuations in the data, even during the shortest measurement periods, are nearly imperceptible.

Description of the ERMs

The ERMs deployed were standalone, solar-powered, and battery-operated units equipped with three energy-compensated, halogen-quenched, Ne-filled GM detectors. Two detectors (GM1 and GM2) were high-sensitivity detectors used for measuring low absorbed dose rates (0.05— 870μ Gy h⁻¹), while one detector (GM3) had low sensitivity and was employed for high absorbed dose rate measurements (150— $1 \times 10^7 \mu$ Gy h⁻¹). The combined measurement range spanned from 50 (minimum detection limit, MDL) to 1×10^{10} nGy h⁻¹. All the data presented in this paper originated from GM1 and GM2, as the operating range of

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GM3 started well above typical background radiation values, resulting in a zero reading in such scenarios [14, 15].

The testing of the ERMs prior to installation involved gamma absorbed dose rate response assessments at the calibration facility of the Radiation Standards Section (RSS), Radiation Safety Systems Division (RSSD), Bhabha Atomic Research Centre (BARC), Mumbai, India. The BARC serves as the designated institute in India for ionizing radiation measurements. The conversion factors obtained from these tests were utilized to convert the count rates into absorbed dose rate (D) values. The gamma absorbed dose rate response plots for the individual GM detectors have been previously published [16].

It is important to mention here that although some countries report the ambient dose equivalent rate ($H^*(10)$, nSv h⁻¹), we report D (nGy h⁻¹). The latter, however, may be converted to the former using the conversion coefficient of 1.21 Sv Gy⁻¹, as suggested in [17].

Data processing

The GM detectors were set with a counting time of 5 min, generating a reading every 5 min. To compute the hourly average dose rate (in nGy h^{-1}) for each detector, 12 consecutive readings were collected within an hour and subsequently averaged. These hourly averages were wirelessly transmitted via the Global System for Mobile Communication (GSM) from each ERM positioned in the field to three redundant, geographically separated data receiving central stations. This transmission process occurs twice daily [14, 15].

Estimation of annual effective dose (AED)

To estimate the annual effective dose (*AED*, mSv y⁻¹) resulting from outdoor natural gamma radiation, the following conversion formula [1] was utilized, employing the measured outdoor gamma absorbed dose rate in air (*D*, nGy h⁻¹):

 $AED(mSvy^{-1}) = D(nGyh^{-1}) \times 8760(hy^{-1}) \times 0.2 \times 0.7(SvGy^{-1}) \times 10^{-6}$ (1)

In Eq. (1), the value 0.2 represents the outdoor occupancy factor, and the value 0.7 Sv Gy^{-1} serves as the conversion coefficient from absorbed dose in air to effective dose.

Results and discussion

Data reproducibility

During the data analysis phase, any hourly data points where the variation between GM1 and GM2 measurements in any ERM exceeded 20% were disregarded. This step





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RESEARCH ARTICLE



Delving into the time dependent properties of thorium laser induced plasma by optical emission spectroscopy

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Abstract

Laser-induced breakdown spectroscopy (LIBS) presents a promising avenue for both qualitative and quantitative analysis. This technique utilizes emission spectral study from laser-induced plasma (LIP) generated due to ablation of samples from surfaces. From the point of view of understanding plasma physics, this study delves into the parametric analysis of Laser-induced plasma of Thorium, which is a key element in India's pioneering three stage power program. Following optimization of experimental parameters like acquisition delay and number of laser shots, key plasma parameters such as Temperature and Electron density of the plasma were computed. For description of LIP, 'Local Thermodynamic Equilibrium' (LTE) model is widely used. The model's validity was meticulously scrutinized in entire temporal region of analysis. Furthermore, investigations into the impact of laser parameters like irradiance, revealed changes in magnitude of plasma parameters along with their evolution pattern and it was concluded that the temporal holding region of LTE strongly depends upon the laser parameters. Next, temporal evolution study of the peak broadening within the plasma revealed the importance of optimization of the experimental parameters, and differences between the decay trends of ionic and atomic lines were clarified. In addition, experiments were carried out exploring the influence of different ambient atmospheres (Air, He, and Ar) on spectral intensity and plasma lifetime, both of which were found to have the order Ar>Air>He. This provided crucial insights into the plasma-atmosphere interaction, which was also manifested by the different rates of decay trend of plasma parameters. In summary, this complete study offers a valuable tool for diagnosing the plasma properties of complex sample matrices like Thorium, thereby advancing our understanding of LIBS applications a step forward.

Keywords LIBS · Plasma · Thorium · LTE · Ambient atmosphere

Introduction

Multifarious applications in various fields like Archeology [1], Nuclear industry [2, 3], Semiconductor industry [4] and Bio-medical uses [5], have already proven the capability of Laser induced breakdown spectroscopy (LIBS) as a promising technique for qualitative as well as quantitative analysis. In this methodology, owing to the breakdown of the sample by laser, a plasma is created depending upon the irradiance threshold, which is in turn dependent upon both laser and

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India sample characteristics. The characteristics of both ablation and hydrodynamics of plasma depend upon complex lasermatter interaction [6], for which many times numerical methods are employed for modeling [7]. The formed plasma is not static, instead, it expands at a super-sonic speed, and after a persistence time of microseconds, it quenches. Along with the temporal evolution of the plasma, the associated plasma parameters like plasma electron temperature (T_e), and plasma electron density (N_e) exhibit a characteristic trend. To use LIBS for analytical purposes, it is therefore very important to understand the physics of associated plasma parameters.

In India's three-stage power program, utilization of Thorium (Th) stands as the ultimate objective within the nuclear industry. This is primarily attributed to Th's vast abundance within the country [8]. In Indian Molten Salt Reactor (MSR), the proposed fuel consists of UF₄ and ThF₄ in the matrix of LiF [9]. There is a scarcity of studies in the field

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of LIBS application specifically focused on Th. Sarkar et al. has demonstrated that with the application of partial least square regression (PLSR) in the analysis of Th based waste glass, Th determination can be done with ~5% precision [10]. Judge et al. have shown the comparison of actinides like U and Th detection capability using both powders and pressed pellets by LIBS [11]. However, being a high Z element, the emission spectra of Th is highly complicated. According to a report made by Redman et al. in 2014, the region of 350 nm to 1175 nm, contains 19,874 Th lines [12]. Due to the inherent complexity, it is very important to optimize experimental conditions to minimize the effect of spectral broadening and continuum reduction among other conditions, which may affect the analytical outcome of a Th analysis by LIBS. Hence having a proper understanding of the evolution of the plasma parameters is of prime importance. For theoretical modeling of plasma and checking the applicability of different associated theories, the presence of Local Thermodynamic Equilibrium (LTE) is an important assumption, the assertion of which needs to be focused upon.

In this study, along with the study of the temporal evolution of plasma parameters already mentioned, the criteria for holding LTE was checked temporally. For ascertaining the effect of laser properties on LTE, experiments were carried out in different irradiance conditions after optimization of the experimental conditions. The line broadening and shifting in laser-induced plasma (LIP) due to Stark broadening was also studied with both atomic and ionic lines and the difference in their behavior was rationalized. Also, to ascertain the effect of atmospheric conditions on the LIP parameters, Th LIP's emission spectra were recorded in three different ambient air conditions, namely, Air, Argon (Ar), and Helium(He) and the corresponding changes in intensity pattern and lifetime were studied. In summary, this paper extensively explores the parametric study of Th LIP. The forthcoming MSR power program will employ Th based complex fuel systems. For analytical quantification and related studies by LIBS, a proper understanding of associated plasma physics is necessary. Specially, selection of emission lines, optimal experimental conditions, and the identifying holding region of LTE is of prime interest. Also, for proper quantification, understanding the temporal variation of line broadening is crucial. Therefore, this study of complete understanding of Th - LIP, paves a footstone for a better analytical comprehension of Th plasma characteristics by LIBS.

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Experimental

LIBS system and measurements

The LIBS study employed a Q-switched Nd: YAG laser (Brilliant B, Quantel) with a pulse width of ~7 ns and a repetition rate of 10 Hz. The laser was operated in 2nd harmonics of 532 nm and focused utilizing a plano-convex lens with broadband AR coating (Thorlabs, LA4380, f=100 mm), while light collection from plasma involved a biconvex lens with a focal length of 35 mm. The gathered light was directed to the Czerny-Turner spectrometer (SR750 Shamrock, Andor) via an optical fiber bundle (D=200 µm, SR-OPT-8024, ANDOR) through an f-matching setup. For the analysis, 2400 groves/mm grating was used. The spectral recording was performed using an ICCD detector (1024×1024 pixels, iStar DH334T-18 F-03, Andor). Wavelength calibration relied on a Hg-Ar lamp certified by NIST (HG-1, Ocean Optics, USA). For intensity calibration, a Deuterium-Halogen lamp (DH-2000-BAL, Ocean Optics) was used. To measure the laser pulse energy, a handheld pyroelectric meter (Ophire Photonics, Israel) was employed. Sample holder integrated with computercontrolled XYZ-translational stage facilitated changing the surface position for each measurement. The LIBS setup's schematic diagram is presented in Fig. 1. Spectral analysis algorithm 'ANUSAP', was developed in-house, using Lab-VIEW 2013 (National Instruments).

For this study, certified reference material (CRM) ThO_2 prepared by Radiochemistry Division, BARC in association with Nuclear Fuel Complex, India was used [13]. The CRM-ThO₂-B was chosen as this had the lowest impurity concentrations. For preparation of the pellet, 30 bar of pressure was applied on the sample for 10 min, and a 10 mm diameter pellet was obtained. Afterward, the pellet was sintered at 800°C in an inert atmosphere for 4 h.

Emission lines selection for analysis

As already mentioned, being a high Z element, Th possesses numerous numbers of energy levels, making the emission spectra highly complex. Therefore, before choosing the region of analysis, careful observation must be done to ensure fulfillment of factors like abundant line intensity, spectral purity, and good signal-to-background ratio among others [14, 15]. Considering all the factors, the region of 405–411 nm was determined to be suitable for analysis as it encompasses both Th(I) and Th(II) lines, crucial for this analysis. Moreover, to ensure accurate identification of the Th peaks, Fe emission lines from a NIST-certified SRM sample of stainless steel (SRM-1295) were recorded in the region of 406.359 nm to 410.980 nm. Subsequently,





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RESEARCH



Design and Development of Arduino-Based Four-Channel Data Acquisition System with Digital Temperature Control for Chemiresistive Sensors

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Abstract

We report the design and development of simple and economical Arduino-based four-channel data acquisition system with digital temperature control that is suitable for sensor parameter optimization involved in the search of appropriate chemiresistive gas sensing material for a particular gas. The developed system is capable of simultaneously capturing the data as well as controlling the desired operating temperature (up to 300 °C) of four sensing elements. This is achieved by employing sixteen analog and digital channels of the Arduino nano microcontroller. The sensing circuit is capable of recording the resistance changes from 20 k Ω to 5 M Ω at a rate of 15 kHz. The developed system has been tested rigorously, validated and demonstrated for its effectiveness towards investigating the gas sensing properties of chemiresistive NO₂ sensors realized using ZnO nanowires. The present simple and low-cost alternative finds its application for developing the target specific chemiresistive sensors in particular for investigating the gas sensing properties of metal oxide semiconductors.

Keywords Data acquisition \cdot Microcontroller \cdot Control circuit \cdot Chemiresistive sensors \cdot ZnO \cdot NO₂

Deepak Goyal and Soumyabrata Patra have contributed equally to this work.

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Sensing and Imaging

1 Introduction

Rapid industrialization and urbanization have resulted in the increase of environmental pollution due to toxic gases such as NO2, NO, CO, CO2, NH3, H2S, and volatile organic compounds (VOC). This has caused hazardous health diseases, acid rain, depletion of ozone layer, and global warming [1]. Due to concerns about health safety, food safety, public security, and air quality monitoring, a miniature, highly sensitive portable gas sensor for real-time monitoring is needed. The market for gas sensors is envisaged to reach ~ 2.3 billion USD by 2027 [2]. The good-quality gas sensor is required to follow the Ramgir '4S' criteria, which means it should be highly sensitive, selective, stable and suitable. Nanotechnology has played a vital role in the development of small and portable gas sensors. The nanomaterials have the potential to compensate for all '4S' parameters required for a good sensor [3]. This has been attributed to the high surface area-to-volume ratio along with dimensions comparable to Debye length. For example, 1-D ZnO nanowires have demonstrated excellent sensing properties with quick reaction kinetics at lower temperatures [4]. It is important to note that use of single nanowires could possibly help to detect different gas molecules, simultaneously. Further, the control over growth position, location, aspect ratio could lead to the integration of several devices in a miniaturized size. However, their use is restricted owing to non-availability of the miniaturized multiplex data acquisition systems (DAS) and the complexity involved when using large number of sensors. Such smaller systems are envisaged to play the important role in concepts like Smart-cities, Smart sensors, point of care devices. For example; internet of things (IOT)-enabled miniaturized sensors possibly as electronic nose (e-nose) for monitoring human health or indoor as well as outdoor air quality [5].

Basically, the DAS system comprises of a sensor, signal conditioning circuit, analog to digital converter, and a recording unit [6–8]. The sensor converts the physical parameter into the output value in the form of electrical signal. The noise in the electrical signal is resolved with the help of signal conditioning. Herein, the filter and amplification circuits are used to separate noise from the real signal and sometimes to strengthen the weak signals. The microchip is then used to convert a physical analog signal into a digital signal i.e., data that can be recorded. Data sampling refers to the process of sampling data at a rate in terms of frequency (F). The collected data can be recorded using the serial plotter software and saved as a file on the computer system. The microcontroller and computer system can be connected to different types of systems to acquire and transfer data, including USB ports, and Ethernet ports [7]. There are different configurations of the DAS systems such as simple embedded system-based DAS [8], web-based DAS [9], image-based DAS [10], and inexpensive Arduino-based DAS [11, 12].

Arduino-based single-board microcontrollers, which are commercially available, have gained tremendous popularity in the scientific community owing to their user friendliness and simplistic performance [11]. In general, Arduino is an open-source software and hardware company that designs and manufactures microcontroller-based kits for various digital devices. In particular, the Arduino board comprises of numerous microprocessors and controllers and is equipped with sets of digital and/ or analog input or output pins along with a serial communication interface, namely

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Determination of rare earth elements in ferrocarbonatite using ICP-AES and ICP-MS

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Abstract

A method has been developed for the determination of Rare Earth Elements (REEs) in ferrocarbonatite using Inductively Coupled Plasma—Atomic Emission Spectrometer (ICP-AES) and Inductively Coupled Plasma—Mass Spectrometer (ICP-MS). The conventional dissolution procedures are tedious, with large measurement uncertainty and are thus not suitable for certified reference material (CRM) production and exploration of REEs. The described method involves leaching of sample using 3 M HCl followed by dissolution of residue (silica and REEs) by HF then determined REEs using ICP-AES and ICP-MS. The leaching step prevents formation of fluoride precipitates of matrix (Ca, Mg, Ba and Al). The method has been validated using CRMs.

Keywords Ferrocarbonatite · Rare earth elements · Carbonatite · Carbonate mineral · Igneous rocks

Introduction

Rare Earth Elements (REEs) are Lanthanide group of elements along with scandium (Sc) and yttrium (Y). REEs have unique fluorescent, conductive and magnetic properties, and hence their alloys are being used in various important industrial applications. REEs play vital role for the development of energy technologies such as rechargeable batteries, solarpanels, super conductors etc. [1, 2]. Due to their strategic application, their requirements are increasing every year in the world. Carbonatites are major sources of REEs [3, 4]. They are igneous rocks derived from the mantle containing more than 50% carbonate mineral and <20% silica [5]. Ca, Fe, Mg and Mn are the major carbonate minerals present in

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carbonatite. Based on the concentration of theses elements carbonatites are sub-classified as calciocarbonatite, magnesiocarbonatite and ferrocarbonatite (FC). FC contains high concentration of REEs, in particular it contains Neodymium is in the order of 10³ mg/kg [6]. It is an important element for the production of super magnet due to its special magnetic properties.

Individual and total concentration of REEs present in FC decides economical extraction procedure. Therefore, it is very much essential for accurate and precise determination of REEs. In-house Reference Material (RM) or Certified Reference Material is required for the determination of these important elements in such complex nature of matrix. Matrix dissolution procedures are preferred analytical method for the precise determination in geological matrices [7]. Analytical method for the exploration of REEs need to be simple and fast for routine analysis of large number of samples. Only few methods are available in the literature for the determination of REEs in ferrocarbonatite. Conventional sample dissolution methods use mixture of acids containing HCl-HNO3-HF and HClO4 [8, 9]. These procedures are tedious, lengthy and taken even upto 2 days for complete dissolution of sample. After the dissolution of sample followed by analyte separation often results in significant loss of REEs [10]. Determination of REEs in FC is carried out by NaOH dissolution followed by measurement using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [7].

It cannot be applied for the determination of some H-REEs using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) due to the requirement of large sample dilution and poor detection limit compared to ICP-MS. Instrumental Neutron activation analysis (INAA) [11] and ICP-AES [12] are being widely used for the determination REEs in variety of matrices. ICP-AES suffer interference among REEs due to complexed, close spectral emission lines of REEs. In ICP-MS, isobaric interferences due to the formation of oxides and hydroxides of L-REEs gives false positive result on H-REEs. In this paper, a simple, fast and accurate two steps dissolution procedure is demonstrated for the analysis of REEs in FC. An accuracy of the proposed method was assessed using internationally available two reference materials. The sample solutions are analysed by both ICP-AES and ICP-MS techniques, results were statistically evaluated.

Experimental

Materials

All chemicals used were of analytical grade. REE mixed element standard solution of iNORGANIC VENTURES was used. Individual Rare Earth Element of Merck standard

Table 1 ICP-AES instrumental setting parameters

Table 2 ICP-MS Instrumental

setting parameters

solutions were used for peak search in ICP-AES and LaO⁺/ La⁺ ratio measurement using ICP-MS.

Instrument

A Horiba scientific model of ULTIMA-2 Inductively Coupled Plasma—Atomic Emission Spectrometer (ICP-AES) was used. The instrumental operating conditions are given in Table 1. ThermoFisher scientific model of Thermo Scientific[™] iCAP RQ[™] Inductively Coupled Plasma—Mass Spectrometer (ICP-MS) was used. The instrumental operating conditions are given in Table 2.

Method

Around 0.2 g of accurately weighed ferrocarbonatite (FC) sample is taken in a 100 mL glass beaker, to which 15 mL of 3 M HCl was added, covered with watch glass, and heated on a hot plate at surface temperature of ~ 100 °C for 30 min. Additional 15 mL of 3 M HCl was added and the process was repeated for 30 min. After cooling, the volume was adjusted to approx. 30 mL using 3 M HCl and the solution was filtered through filter paper (No. 40). The beaker was rinsed well using DI water and the filtrates were collected. Total volume of the filtrate was kept at less than 70 mL (solution A). The filter paper with residues was taken in

Parameter	Setting condition	
Power, kW	1.0	
Plasma gas flow rate, L/min	12	
Nebuliser type	Concentric	
Spray chamber	Cyclonic	
Nebulizer gas flow rate, L/min	1.7	
Auxiliary gas flow rate, L/min	0.52	
Elements wave length (nm)	Ce-418.660; La-333.749, Nd-430.357; Pr-422.293; Yb-328.937; Y-371.030; Sm-371.030; Eu-381.965; Gd-381.965; Dy-353.170; Er-261.542	

Parameter	Setting condition
Power, kW	1,5
Plasma gas flow rate, L/min	14.1
Dwell time (s)	0,01
CRC conditions	7.9 mL/minute of He
Auxiliary gas flow rate, L/min	0,78
oxide levels; LaO ⁺ /La ⁺	<1%
Sampler and skimmer cone	platinum
Mass number (amu)	Ce-140; La-139, Nd-145; Pr-141, Yb-174; Y-89; Sm-152; Eu-151; Gd-160; Dy-154; Er-167

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Development of analytical method for zirconium determination in U–Pu–Zr alloy samples

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Abstract

The study focuses on developing a robust method for determining zirconium in U–Pu–Zr alloy samples, crucial for assessing fuel composition and ensuring uniformity. Using mandelic acid precipitation and spectrophotometric quantification with Arsenazo-III, the method achieves high sensitivity and reproducibility, crucial for handling microgram-levels of Pu. By optimizing conditions to maintain Pu in its + 3 oxidation state, interference during Zr precipitation is minimized. Comparative analyses with ICP-AES validate the accuracy and reliability of the results. This approach not only enhances analytical precision but also reduces radioactive waste, making it suitable for nuclear fuel characterization.

Keywords Zr determination · U-Pu-Zr alloy · Mandellic acid precipitation · Spectrophotometric determination

Introduction

The Fast Breeder Test Reactor (FBTR) represents the first step in the second stage of the Indian Nuclear Programme [1]. (U,Pu)C is used as fuel in the FBTR due to its superior thermal conductivity and high heavy metal density compared to oxide fuels [2]. For future fast reactors, metallic fuels are preferred due to their enhanced breeding capabilities, better thermal conductivity, ease of fabrication, and improved compatibility with cladding. Furthermore, metallic fuel with pyrochemical reprocessing is being investigated as a cost-effective alternative to the PUREX process. Alloys of Zr, such as U–Zr alloy and U–Pu–Zr alloy, are planned for use in fast research and power reactors, respectively [3].

Determining the composition of these alloy fuel samples is essential for assessing the fissile content of the fuel and ensuring the homogeneity of its constituent elements. The

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gravimetric determination of Zr in a U–Zr matrix using mandelic acid ($C_8H_8O_3$) precipitation is sensitive but requires a large amount of starting material [4]. For the U–Pu–Zr matrix, applying the gravimetric method necessitates handling large sample quantities in a glove box, which requires glove box based systems for dissolution, digestion, and combustion. Operation and set up of these systems in a fume hood is easier, but due to the low permissible limits of Pu in a fume hood, the gravimetric method is unsuitable. Instead, an analytical method using dissolved samples containing microgram-level Pu is needed.

Although many methods exist for the precise determination of U and Pu [5, 6], Zr can also be determined spectrophotometrically at the µg level with the required sensitivity. S. Ganesh et al. [7] demonstrated the selectivity of Chrome Azurol S, a chromogenic reagent, for Zr over UO2(II), Gd(III), Sr(II), and Rb(I). Nagarkar et al. [8] used 4-(2-pyridylazo)resorcinol as a spectrophotometric reagent and established the upper tolerance limits for several ions. Recently, Uysal et al. [9] synthesized a chromatographic reagent, Tetrahydroxyazon SC, and applied it for Zr determination in aluminium, zinc, and copper-based certified standard alloys without any separation procedure. However, a selective chromogenic reagent for Zr(IV) in the presence of Pu has not been reported, indicating the need to separate Zr from the matrix (i.e., U and Pu) before final determination. The separation of Zr can be achieved by extraction, precipitation, or ion exchange, which can then be coupled with suitable spectrophotometric analysis.

Bauchanan et al. separated Pu(IV) using an anion exchange process followed by spectrophotometric determination [10]. The spectrophotometric method reduces the required sample size, facilitating sample processing in a fume hood and generation of low Pu-containing liquid waste. Additionally, the method's rapidity, simplicity, and low cost make UV–Vis spectrometry a preferred choice. Although ICP-AES and ICP-MS have been used for Zr determination at low levels, they require sophisticated and costly instruments that are difficult to adapt for radioactive samples [11, 12].

Among various separation procedures, precipitation is one of the rapid techniques. In this study, mandelic acid was used as a precipitating reagent. Mandelic acid forms Zr(C6H5CH(OH)COO)4 with Zr(IV) [13, 14] and is known to be a selective precipitating reagent for Zr(IV) in the presence of several cations, including U(VI) [15]. Kumins [16] first demonstrated the selectivity of mandelic acid for Zr. Hahn and Weber [17] further demonstrated quantitative precipitation of Zr-mandelate in hydrochloric acid medium. The separation of zirconium by precipitating it with mandelic acid, followed by dissolving the precipitate to enable spectrophotometric quantification, has been explored [18, 19]. The study reported in [18] have used ammonia dissolution which shows poor reproducibility due to the hydrolysis of Zr(IV) under basic pH conditions, whereas [19] utilized chloranilic acid which showed decrease in absorption at the concentration of acid required for dissolution. In the present work, Zr at the microgram level was separated by precipitation using mandelic acid, and the precipitate was dissolved in acid. The dissolved Zr was subsequently quantified by spectrophotometry using Arsenazo-III. To verify the spectrophotometric results, Zr in the dissolved precipitates was also determined by ICP-AES.

Experimental

Reagents

The standard zirconium solution was prepared by heating Alfa Aecer make zirconium oxychloride (>99% purity) to constant weight and then dissolving in HNO₃. High purity mandelic acid, hydroxyl amine hydrochloride and Arsinazo-III used were of Sigma-Aldrich make. All the solutions were prepared in Milli-Q water (18 M Ω cm⁻¹).

Procedure

Precipitation and determination of Zr in standard zirconium solutions

Aliquots of a Zr standard solution, containing 300 to 1500 µg of Zr in 1 mL of 1 M HCl, were heated in centrifuge tubes at 80–90 °C. Subsequently, 1 mL of a 16 wt% mandelic acid

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solution was added. After heating the solution for 1 h, zirconium mandelate precipitate formed. The mixture was then centrifuged to separate the supernatant from the precipitate. The precipitate was diluted with 1 M HCl and centrifuged again, with the supernatant subsequently removed. This process was repeated 4–5 times without losing any precipitate. The precipitate was then washed twice with water.

The Zr-mandelate $(C_{32}H_{32}O_{12}Zr)$ precipitate was dissolved in a mixture of 0.2 mL concentrated HNO₃ and 0.6 mL concentrated HClO₄. The resulting Zr solution was diluted to 10 mL with 1 M HNO₃ in a standard volumetric flask. A 0.5 mL aliquot of this diluted solution was added to a 10 mL standard flask containing an Arsenazo-III solution (0.1 mg/mL in 1 M HNO₃) for spectrophotometric determination. For samples with an optical density (O.D.) higher than 1, further dilution with 1 M HNO₃ was performed.

Precipitation in standard zirconium samples in presence of Pu

The separation and quantification of zirconium in standard samples containing plutonium in both + 3 and + 4 oxidation states were performed in 1 M HCl. Each sample, containing 200 mg of plutonium, was placed in centrifuge tubes. The oxidation state of plutonium was adjusted to either + 3 or + 4 by heating the solution (80-90 °C) with 0.01 M hydroxylamine hydrochloride for Pu(III) or 0.001 M sodium nitrite for Pu(IV) prior to the addition of mandelate, as described in references [20, 21]. To establish the Pu(IV) oxidation state, all Pu was initially converted to Pu(III) using 0.01 M hydroxylamine hydrochloride and subsequently oxidized to Pu(IV) using 0.001 M sodium nitrite. According to literature [22], complete reduction to Pu(III) with hydroxylamine occurs within 4 h, with the resultant Pu(III) remaining stable for several days. Similarly, the oxidation of Pu(III) to Pu(IV) is completed within a few hours, and the Pu(IV) oxidation state remains stable for over 10 days. To ensure complete conversion to Pu(III) and Pu(IV), the precipitation procedure with mandelic acid (outlined in the previous section) was conducted on the following day (24 h later).

Spectrophotometric measurement

A small aliquot (10–100 μ g) of standard Zr were added to arsenazo–III solution (0.1 mg/ml) in 1 M HNO₃ and spectra were measured in UV–Vis spectrophotometer JASCO 880. The absorbance of Zr-arsenazo(III) complex was monitored at a λ_{max} of 665 nm.

Zirconium determination in real alloy samples

Real samples of U–Pu–Zr alloy (wt % 74, 20, 6), were dissolved in 1 M HNO₃. The nitric acid medium was evaporated





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TECHNICAL ARTICLE





Development of Deterministic Reaction Triggering in UF₄ Magnesiothermic Reduction

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Uranium metal ingot is routinely produced by magnesiothermic reduction (MTR) at plant scale. In the conventional process, heating of the reaction vessel is continued till self-initiation or self-firing of the reaction occurs. A novel deterministic reaction triggering (DRT) method has been developed for the MTR process on a 5 kg uranium ingot scale, which makes the firing definite and decreases specific energy consumption and batch duration by about 33.8% and 30-50%, respectively, without affecting the process recovery. The pre-heat time and pre-heat temperature required for initiating the external trigger were estimated using COMSOL simulations and thermodynamic evaluation of the final product temperature, respectively. The process recovery with DRT (~93%) was comparable to that of the conventional self-firing process. A well-consolidated uranium ingot with a recovery of about 93% was obtained with 100 ppm Cr and 97 ppm Ni in the scaled up (50 kg) batch by employing deterministic triggering. This DRT method is applicable and useful for similar reaction processes for augmenting process capacity and energy utilization.

INTRODUCTION

The element uranium laid the foundation for nuclear energy, and uranium and its alloys and compounds fuel various power and research reactors worldwide. Apart from its use as fuel for nuclear energy, it is applied in shielding material for high-radiation fields, radiopharmaceutical man-ufacturing, irradiation targets for Mo-99 radioisotope production, and military armor applications and has been used in the past as a counterweight for aircrafts. Since its first isolation in 1841 by the reaction of chlorine gas with carbon and UO2, followed by the thermal treatment of the resulting chloride with potassium metal, uranium metal has been prepared by various methods, viz. high-temperature reduction, electrochemical reduction, radiochemical reduction, thermal decomposition, etc.¹⁻⁹ Among these, high-temperature reduction of uranium fluoride using calcium or magnesium is routinely employed for commercial production of uranium metal ingots.^{3,4,10} The reactions are represented below:^{9,11}

$${f UF_4+2Ca}\,=\,U+2{f CaF_{2-}}({f DH_{298}})\ =\,-128.5~{f kcal/mole})$$

$$\begin{array}{rl} {\rm UF_4}+\,2{\rm Mg}\ =\ U\,+\,2{\rm MgF_{2-}}({\rm DH_{298}}\\ &=\ -\,83.5\ {\rm kcal/mole}) \end{array} \tag{2}$$

Calciothermic reduction is more exothermic than magnesiothermic reduction and hence is expected to provide better slag-metal separation.⁹ The generated heat in reduction with calcium is sufficient to cause the temperature to rise beyond the melting point of both the products even without any preheating, i.e., even when the reaction is initiated at room temperature. However, this is not the case in reduction with magnesium. Thus, pre-heating the reaction mixture up to a certain temperature is necessary in case of magnesiothermic reduction of UF₄ to provide excess heat to allow a self-sustaining reaction and efficient slag-metal separation. For

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slag-metal separation, it is important that both products remain in liquid state for a sufficient duration to separate out because of the density difference. However, for plant-scale production, magnesiothermic reduction (MTR) is always preferred as it is more economical. Calcium due to its high cost and higher requirement per unit mass than magnesium, is not employed for plant-scale processes.⁹ For simplicity, magnesiothermic reduction of UF₄ is referred to as MTR in subsequent sections.

Ample literature exists on self-propagating hightemperature synthesis (SHS) reactions. The term describes a process in which the initial reactants, when ignited, spontaneously transform into products because of the exothermic heat of the reaction. A well-known example is the thermite reaction $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$, which is generally ignited generally using a magnesium ribbon, and the heat generated during the reaction generates temperatures above the melting point of Al₂O₃. However, this is not the case with magnesiothermic reaction of UF₄. When the MTR reaction is initiated at room temperature, the reaction heat is not sufficient to melt the reaction products (U and MgF₂) completely, and an additional heat of 6.8 kcal/mole is supplied to cause their complete melting.¹³ A method or mechanism for reactions that need to be triggered at higher temperatures for MTR of UF₄ has not been described in the literature. If the MTR reaction initiates at a lower temperature of < 175°C, most of the reaction-generated energy fails to provide sufficient heat to have a sustained reaction. In practice, to have a consolidated ingot well separated from the slag, the charge (UF₄ + Mg mixture) is added to a MgF_{2} lined vessel and heated in a resistive heating furnace. The furnace control is done as per a predefined heating schedule, i.e., an initial soaking at 500°C for 6 h and subsequently at 650°C till firing occurs (initiation of the exothermic reaction) for a 5 kg U metal batch. The soaking time varies depending upon the batch size. There is a significant decrease in the yield whenever the reactants are held at temperatures beyond 400°C for a long time.¹⁴ This decrease is attributed to the side reactions that occur at this temperature which do not contribute to the final product. The presence of H₂O and HF leads to evolution of hydrogen by prereaction during heating at lower temperatures of 380-600 °C.^{3,13} To achieve a higher reaction yield, such undesirable side reactions need to be controlled. This can be achieved to some extent by initiating the reaction close to 400°C.

The firing or self-initiation time of the reaction depends upon 12 parameters: (1) moisture content in UF₄, (2) free acid content in UF₄, (3) UO₂F₂ content in UF₄, (4) ammonium oxalate insoluble (AOI) in UF₄, (5) tap density of the UF₄, (6) moisture in the lining material (MgF₂), (7) uranium in the lining material, (8) iron content in the lining material, (9) loss of ignition (LOI) in the lining material, (10) tap density of the lining material, (11) Mg particle size, and (12) MgO content in Mg.¹⁵ Optimizing and estimating the firing time for every batch based on all these parameters is extremely complex and uncertain to some extent.

This calls for a method by which MTR can be triggered at a particular temperature to avoid undesirable side reactions, at the same time eliminating the need to wait for an indefinite period for the reaction to trigger and the consequent heat losses. Systematic studies on the approach and procedure for deterministic triggering for magnesiothermic reduction of UF4 have not been reported in the literature, and this forms the basis and motivation for the present study. The present study proposes a novel deterministic reaction triggering (DRT) method to initiate the reaction at a desired temperature to reduce the excess energy given to the system and to remove uncertainties in the estimation of the firing or self-initiation time. A correlation between the pre-heating temperature and the post-firing product temperature has been theoretically estimated and utilized to assess the pre-heat temperature required for efficient slagmetal separation and thus the yield. The variation of average temperature of the charge as a function of time has been understood using COMSOL simulations to be able to predict the pre-heating time required before externally triggering the reaction. Temperature profiles of the charge before and at the instant of initiation of the external trigger have been simulated in COMSOL. Experimental trials were carried out with the proposed DRT method and the conventional method for a 5 kg batch size at different average charge temperatures, and a comparative discussion on the outputs has been presented. The product quality is assessed based on consolidation, purity, and yield. Finally, the feasibility of scale-up of this process was successfully demonstrated for a 50 kg batch.

MATHEMATICAL FORMULATION

Simulation Model and Governing Equation

A 3D model of the system used for the computational simulation and meshing scheme of the charge used in the discretization of the computational domain is shown in Fig. 1a. The thermal diffusivities for both the UF4 + Mg charge and the MgF2 lining are quite low (as both have insulating properties), i.e., 0.207 mm²/s and 0.11 mm²/s, respectively (considering thermal properties at room temperature). Considering the boundary condition is given in terms of gradually increasing temperature and long duration of heating, initially a step size of 60 s was chosen to evaluate the problem. The domain was meshed using a three-noded (triangular) second-order element of size varying from 2 to 4 mm. Meshing was done using an inbuilt COMSOL mesh generator. The mesh consisted of 553,363



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ORIGINAL PAPER



Development of Flexible Rotor Balancing Procedure Using Response Matching Technique

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Abstract

Purpose The two main methods under use for balancing of flexible rotor know as Influence Coefficient Method (ICM) and Modal Balancing Method (MBM). It needs few trials to arrive at predicting the unbalance mass. In presence of initial bow along with unbalance these methods will fail to give accurate predictions. It becomes further complex when rotors are mounted on flexible supports. To overcome the limitations of these two methods, a new method called response matching method is disused here for flexible rotor balancing.

Method The objective of present work is to develop a balancing procedure for flexible rotor balancing, wherein unbalance response of Finite element model (FEM) is matched with experimental response using iterative technique. Unbalance masses, moments and shaft stiffness of FEM model was iterated to match experimental unbalance responses at three distinct speeds below its first flexural critical speed. Further, unbalances mass was estimated iteratively to cross the bending critical speed with lower residual amplitudes at critical speeds.

Results Experimental test setup was developed to validate the proposed method. Results show that present method predicts the unbalance masses and moments to compensate the bow more accurately.

Conclusion Results shows that with single run, rotor unbalance masses and movements are predicted accurately. Corrected masses are used in experimental test setup to check the rotor amplitudes during its bending critical speeds. It shows rotor passes first bending critical speed without excessive amplitudes.

K_{shaft}

Keywords Flexible rotor · Bending parameter · Response matching · Bow · Unbalance

List of symbols

- BP Bending parameter
- C Overall damping matrix
- $e_s = E_s = R_s r_s$, difference between target and model
- response
- f Overall force vector
- K Overall stiffness matrix

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- Overall mass matrix M Number of elements p Overall displacement vector q R. Target bending parameter for count s Model bending parameter for count s $\Gamma_{\rm S}$ Number of target response s S_{sym} Overall system matrix Time, seconds Ť Т Tolerable limit of vibration amplitude at critical speed. TBP Target Bending Parameter Node displacement in X-axis, at node p+1 $u_{x(p+1)}$ $u_{p+1} = u_{x(p+1)} + iu_{y(p+1)}$, Resultant node displace u_{p+1} ment at node p+1 XYZ Fixed coordinates axis Rotating coordinate axis xyz Greek letters Angular speed, rad/sec ω

Overall stiffness matrix of shaft

ω_c Critical speed

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 $\begin{array}{ll} \theta_{x(p+1)} & \text{Angular rotation in } x\text{- axis, at node } p+1 \\ \theta_{p+1} & \theta_{p+1} = \theta_{x(p+1)} + i\theta_{y(p+1)} \text{, Resultant angular rotations at node } p+1 \end{array}$

Introduction

All rotating machines experience mechanical vibration due to several factors which can produce synchronous and non- synchronous vibrations. Non-synchronous vibration cannot be corrected by improving the rotor balance alone. Causes for this type of vibration can be self-exited whirl motion caused by fluid film bearings, seals, aerodynamic effects, internal friction, shaft rubs, shaft asymmetry, or by external excitation through gear boxes, misaligned couplings, piping acoustics or transmitted foundation vibration. Were as synchronous vibrations can be corrected by identifying the unbalance mass and bow of the rotor. Successful balancing of rotating component results into minimum force transmission on supports and smooth running of rotating machines for the designed life time. Balancing of rigid rotors was quite straight forward as compared with flexible rotors, standard balancing machines can used to balance the rotors. ISO standards standard will guide the grade of balancing required. Whereas balancing of flexible rotors are not that straight forward, few techniques are discoursed in the literature as follows.

Balancing techniques used to balance the flexible rotors can be categorized into three sub-categories. Modal balancing method (MBM) [1–3], influence coefficient method (ICM) [4–6], and unified approach [7, 8]. MBM requires pre-existing knowledge of rotor modes shapes, modal mass, modal stiffness and damping properties. These quantities can be obtained experimentally or by theoretical analysis. ICM is comparatively easier than MBM and most balancing machines are equipped with ICM source code. One disadvantage of using ICM is that the method requires many trial runs which make the method very time consuming. Mixed methods combine basic principles of MBM and ICM to reduce balancing times.

Performance of these two methods reduces, in presence of bow in rotor. Nicholoas et al. [9, 10] provide valuable insights on the behavior of bowed rotors. A comparison of whirl produced by a rotating shaft subjected to bow and mass unbalance is described by Parkinson et al. [11]. Saldarriaga et al. [12] used an inverse problem approach to balance flexible rotating machines where response data is used to predict mass unbalance using artificial neural network.

From literature review it was observed that a sufficient work has been carried out in the field of flexible rotor balancing. Most of the methods discussed in the literature need more number of trails to balance the bending critical speeds. Whereas not much work was carried out to predict the unbalance of the flexible rotors in presence of bow and its validation with the experimental data. Response matching method was proposed here to find the unbalances of flexible rotors with one bare trail. Experimental rotor amplitudes are marched with theoretical Finite element model at three distinguished speeds to update the unbalance, bow and shaft stiffness. A new parameter called bending parameter (BP) is introduced to balance rotor at bending critical speeds and contributions of rigid modes can be neglected. An experimental test setup was developed to validate results.

Rotor Bearing System Model

Rotor bearing system consists of shaft, lumped mass discs and discrete bearings. Rotor is divided into smaller segments, which is modeled using Euler–Bernoulli beam elements. It is assumed here that rotor cross-section, dimensions and material constants are uniform for each segment. Figure 1 shows the coordinate





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Displacement chromatography of gadolinium isotopes with strong cation exchange resin using 1,2-cyclohexanedinitrilotetraacetic acid (CDTA)

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Abstract

Adsorptive separation of Gd^{3+} ions was evaluated using DOWEX-50×8 ion exchange resin. It has shown a maximum adsorption capacity of 228.50 mg/g at optimum pH 5 and room temperature. Separation of Gd isotopes was investigated using packed bed columns of the resin in displacement chromatographic techniques where 1,2-cyclohexanedinitrilotetraacetic acid was used as displacer in the mobile phase. Isotopic analysis data by using MC–ICP–MS confirmed that the front end of the Gd adsorption band exhibited enrichment of the heavier isotope (160 Gd), while the lighter isotopes (157 Gd and 155 Gd) were concentrated at the rear end of the stationary phase.

Keywords Gadolinium · Adsorptive separation · Isotope separation · Displacement chromatography · Cation exchange resin

Introduction

Natural Gd consists of seven stable isotopes: 152, 154, 155, 157, 158, and 160. The abundance ratios of the seven isotopes are 0.20, 2.18, 14.80, 20.47, 15.65, 24.84 and 21.86%, respectively [1]. Its exceptional ability to absorb thermal neutrons makes it a preferred choice as a burnable poison in nuclear reactors. This is due to the high neutron absorption cross sections of the 157 Gd (2.54×10⁶ barn) and 155 Gd (0.609×10⁶ barn) isotopes. Although natural Gd is presently used as a burnable poison in nuclear reactors, enriched 155 Gd or 157 Gd will be increasingly used as a viable neutron poison [2]. In addition, the 152 Gd isotope is used in producing radioactive 153 Gd isotopes. 153 Gd is used for research on osteoporosis and bone thickness estimations. Therefore, a process is needed for the enrichment of Gd isotopes. The standard methods for producing isotopes are electromagnetic

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enrichment [3–7] (calutron), distillation [8–10], and centrifuge enrichment [11, 12]. There are also many other methods, such as plasma separation, laser enrichment, and photochemical enrichment. However, every method has its own limitations in terms of cost and scale of production.

On the other hand, chemical exchange methods can be used for isotope separations. These processes are usually associated with smaller separation coefficient values and thus require more time to obtain enriched products than other physical processes; however, these chemical exchange reactions are naturally feasible equilibrium routes. Therefore, these methods are regarded as energy-efficient processes. Displacement chromatography employing ion exchange, which relies on the establishment of equilibrium between isotopic species across mobile and stationary phases, is a highly effective technique for isotopic separation. These methods have been successfully applied for the isotopic separation of different elements, such as Li [13], N [14], Ca [15], Zn [16-19], Ce [20], Cu [21, 22], Eu [23, 24], V [25], Nd [26, 27] and Gd [28-30]. We previously carried out isotope separation of Zn and Gd using chemical exchange methods along with computational methods [31-37]. However, to date, CDTA has not been utilized for displacement chromatography of gadolinium isotopes with strong cation exchange (DOWEX-50×8) resin. In the current study, we aimed to explore the use of CDTA as a displacement agent to separate Gd isotopes via DOWEX-50×8 resin. The following details are reported in the present paper.

- In batch-mode equilibrium studies, the effects of the initial concentration of Gd³⁺ ions and solution by DOWEX-50×8 resin pH by were reported. The adsorption data were fitted with different adsorption isotherm models.
- In kinetic studies, the effect of shaking time on the adsorption of Gd³⁺ ions from aqueous solution by resin at optimized pH and room temperaturewas reported. The data were fitted with kinetic models.
- In thermodynamics studies, the dependence of adsorption of Gd³⁺ ions from aqueous solution by the adsorbent resin on the temperature at optimized pH was reported. Thermodynamic parameters were calculated from the van't Hoff plot and Gibbs- Helmholtz equation.
- Furthermore, in the chromatographic experiments, the adsorption band of Gd was displaced using CDTA in the column loaded with DOWEX-50×8 resin to study the isotope separation of gadolinium.

Experimental

Chemicals

In this study, cation-exchange resin, DOWEX- 50×8 mesh size 20-50 was utilized. Gd(NO₃)₃ solutions were prepared using Gd₂O₃ (99.999%), sourced from Otto Chemical Industries. The other reagents were of analytical grade and used without additional purification in the present study.

Elemental analysis

For Gd concentration and isotopic analysis, samples were prepared using AR grade ~15.0 M HNO₃, > 18 MΩ-cm H₂O and ~30% hydrogen peroxide. The sample preparation was carried out in a manner similar to our earlier work [38]. Sample aliquots were diluted with 2% HNO₃ for Gd elemental analysis. The Gdcontent was measured using an inductively coupled plasma optical emission spectrometer (ICP–OES) model HORIBA ULTIMA.

Isotopic analysis

For Gd isotope analysis, the sample aliquots were diluted with 2% HNO3 to achieve concentrations ranging from 50 to 100 µg/L. Gd isotope measurements were conducted using a Thermo Fisher Scientific Neptune Plus multicollector inductively coupled plasma mass spectrometer (MC–ICP–MS) employing the standard sample introduction system at the Radiogenic Isotope Facility, Department of Geology and Geophysics, Indian Institute of Technology Kharagpur, India.

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Simultaneous detection of masses ¹⁵⁴Gd, ¹⁵⁵Gd, ¹⁵⁶Gd, ¹⁵⁷Gd, ¹⁵⁸Gd, and ¹⁶⁰Gd was achieved using Faraday cups. Instrumental mass bias and drift were corrected using the standard-sample-standard bracketing (SSB) technique. [38]. The mass bias factors were calculated assuming ¹⁵⁶Gd/¹⁶⁰Gd = 0.9400 and using the exponential law. The reproducibility of replicate measurements of the Fluka ICPMS solutions changed in the range of $0.11^{0}/_{00}$, $0.070/_{00}$, $0.02^{0}/_{00}$, and $0.07^{0}/_{00}$ for the ¹⁵⁵Gd/¹⁵⁸Gd, ¹⁵⁶Gd/¹⁵⁸Gd, ¹⁵⁷Gd/¹⁵⁸Gd and ¹⁶⁰Gd/¹⁵⁸Gd ratios, respectively.

Batch adsorption studies of Gd³⁺ by DOWEX-50×8

Batch adsorption experiments were conducted using DOWEX-50×8 to study Gd ion adsorption. Parameters like pH, contact time, Gd3+ ion concentration, and temperature were varied systematically. A 10000 ppm Gd3+ stock solution was prepared from Gd(NO₃)₃ in deionized water. A 200 mg of DOWEX-50×8 resin was mixed with Gd ion solution of desired concentration in a screw capped glass bottle at room temperature and the mixture was shaken for 60 min in an orbital incubator shaker (make: IKA, model: KS 4000). After settling down the resin phase on the bottom of the bottle, supernatant aliquot analyzed for Gd concentration using Inductively CoupledPlasma Optical Emission Spectroscopy ICP-OES (make: Horiba Scientific, model: JobinYvonUltima 2). pH studies were done with 5000 ppm Gd concentration, adjusting pH with HNO3 and NaOH solutions. Equilibrium studies covered Gd ion concentrations from 200 to 10,000 ppm. Kinetic studies were conducted at optimum pH and room temperature. Adsorption was tested at temperatures from 30 to 60 °C with constant adsorbent dosage. Adsorption equilibrium data were used for isotherm modeling, and kinetics were analyzed for the relationship between contact time and adsorption data. Thermodynamic properties were determined from temperaturedependent separation results. Adsorption capacity (Qe, mg/g) was calculated using Eq. 1.

$$Q_{\rm e} = (C_{\rm o} - C_{\rm f}) \times (V/m) \tag{1}$$

Here, C_o and C_f denote the initial and final equilibrium concentrations (mg/L) of Gd ions, respectively. V represents the volume of the solution (mL), and m indicates the weight of the adsorbent. Experiments were performed by duplicate and average values were considered for the calculation. The relative standard deviation of the repeat analysis was within 5%.

Chromatographic separation studies of Gd³⁺ ions by DOWEX-50 × 8 resin

Gadolinium isotope separation by displacement chromatography was carried out in a system for which a schematic of the experimental setup is displayed in Fig. 1. Three glass columns





ORIGINAL RESEARCH ARTICLE

Effect of Heat Treatments on the Microstructure and Mechanical Properties of SS317L/ASTM SA516 GR60 Steel Clad Plate Fabricated Through Hot Roll Bonding

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Triple-layer stainless-steel clad plate having 317L stainless steel (SS317L) as cladding layer and ASTM SA516 GR60 (GR60) as backing layer was successfully fabricated through vacuum hot roll bonding (VHRB) at 1373 K (1100 °C) temperature and strain rate regime of 1-5 s . which were identified through process efficiency maps of the base materials (SS317L and GR60). The process efficiency maps were constructed by conducting isothermal compression tests within the temperature range of 1173 K (900 °C)-1473 K (1200 °C) and 0.1-50 s⁻¹strain rate regime. Effect of post-rolling heat treatments on the mechanical properties of clad plate was studied after solutionization at 1173 K (900 °C) for 1 h followed by cooling at different rates, i.e., water quenching, air cooling, and furnace cooling. As compared to other post-rolling heat treatments, the ultimate tensile strength, uniform plastic elongation, and maximum shear strength showed a significant change from 524 MPa, 0.46 and 519 MPa to 652 MPa, 0.36 and 410 MPa, when the normalized clad plate was solutionized at 1173 K (900 °C) and water quenched. A drastic change in shear fracture mode from gradual failure in normalized condition to catastrophic failure was also noticed after water quenching. These changes are essentially manifestation of the microstructural change in GR60 layer which led to the change in mechanical properties.

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I. INTRODUCTION

CLAD steel plates are laminated composites having a corrosion-resistant cladding layer bonded on to a cheaper backing layer.^[1] These clad steel plates also possess excellent mechanical properties^[2] overcoming the shortcomings of individual base materials. Several industrial techniques are in practice to achieve bonding between cladding and backing layers such as explosive bonding,^[3] strip cladding or weld overlay,^[4] casting and molding,^[5] diffusion bonding,^[6] laser surface cladding,^[7] cold roll bonding,^[8] hot roll bonding,^[9,10] *etc.* Compared to the other industrial practices, hot roll bonding (HRB) is a high-efficiency, high-productivity, and green process, which can easily produce large, thick-clad

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plates having simple geometries with an almost defectfree joining interface. The hot roll bonding is usually carried out under a protective atmosphere such as argon,^[11] hydrogen,^[12] or vacuum^[10] to prevent oxidation at the interface. Among these, vacuum hot roll bonding (VHRB) is more commonly used for commercial production of large clad steel plates.^[13] VHRB is essentially a solid-state bonding process involving the breaking of the oxide layer under the influence of plastic deformation, exposure of fresh surfaces, bonding between contact surfaces through diffusional mass transport, and recrystallization involving atomic rearrangement.^[9] Clad steel plates with various combinations of cladding and backing layers such as Stainless Steel/Titanium,^[14] Carbon Steel/Stainless Steel,^[15] Carbon Steel/Alloy 625,^[16] *etc.* have been widely produced till date through VHRB process.

Large size stainless-steel clad plates with stainless steel as the cladding layer and carbon steel as the backing layer is one such combination usually produced through VHRB.^[9] The factors affecting the quality of bonding and mechanical properties of stainless-steel clad plates include hot rolling temperature,^[17] thickness reduction ratio,^[18] degree of vacuum,^[19] and final heat treatment.^[20] VHRB of stainless-steel clad plate has been



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mostly carried out in the temperature range 1173 K (900 °C)-1573 K (1300 °C) and higher rolling temperatures were found to be beneficial to achieve good metallurgical bonding and optimum mechanical prop-erties.^[11,17] An increase in thickness reduction ratio was also found to be beneficial in terms of mechanical properties by way of dispersing the oxide film at the interface,^[11] increasing the interface area fraction,^[15] and refinement of microstructure.^[18] A high degree of vacuum minimizes the chances of various metal oxides formation, which ultimately results in a sound metallurgical bonding and ensures higher interfacial strength.^[19] Post-rolling heat treatments such as solution annealing and water quenching have been shown to improve the mechanical properties of clad plates by promoting the diffusion of alloying elements^[20] and increasing the area fraction of the interfacial region.^[15] However, an application of post-rolling heat treatment can also affect the overall microstructure and mechanical properties of constituent material specially carbon steel, which could ultimately affect the mechanical properties of clad plate. This also provides a way to alter the mechanical properties of clad plate as stainless steel cannot be heat treated due to the stability of austenitic microstructure from room temperature to melting temperature. However, studies focusing on this direction are limited and the effect of microstructural changes in backing material on tensile and shear strength of clad plate has not been elucidated.

Furthermore, the rationale behind choosing the hot rolling parameters such as rolling temperature and strain rate has also not been clearly elucidated in the available published literature. In most of the cases, the backing and cladding materials possess widely different deformation behaviors. Therefore, finding a common domain for the co-deformation of these materials is vital for successful hot roll bonding as well as for achieving optimum mechanical properties. A process efficiency map^[21] showing the ideal regimes of temperature and strain rate to achieve an optimum microstructure can be a very useful tool in this regard.

Therefore, in the present study, an attempt was made to fabricate the stainless-steel clad plate through optimum processing parameters determined by process efficiency maps and explore the effect of post-rolling heat treatment on the mechanical properties of fabricated stainless-steel clad plate. The 317L grade of austenitic stainless steel (hereafter referred as SS317L) was chosen as a corrosion-resistant clad layer as it contains higher amount of Mo, and thus, provides better resistance to pitting corrosion with enhanced strength as compared to traditionally used SS316 grade.^[22] Lower carbon content in SS317L also makes it more resistant to sensitization due to lower precipi-tation of inter-granular Cr-carbide.^[23] On the other hand, ASTM SA516 Grade 60 (hereafter referred as GR60) of medium carbon steel that finds applications primarily in boilers and welded pressure vessels^[24] was chosen as backing layer. The SS317L/GR60 clad fabricated in present study has potential applications in various industries as material of construction for components operating in corrosive environment such as

pressure vessels, heat exchangers, *etc.* in power industry; pipe lines, storage vessels in petrochemical industry; and pipes and valves in pulp and paper industry. The use of clad plate instead of SS317L can lead to significantly reduce the material cost.

The overall objectives of the present study were to

- determine the suitable process parameters for successful hot roll bonding of SS317L stainless-steel and GR60 carbon steel using process efficiency maps
- analyze the effect of post-rolling heat treatments on the microstructural and mechanical properties of clad steel plate
- study the effect of heat treatments on the tensile and shear fracture behavior of clad steel plate.

II. MATERIALS AND METHODS

A. Materials

ASTM SA516 Grade 60 carbon steel and 317L austenitic stainless steel were used as backing and cladding materials, respectively. The nominal compositions and their room-temperature (RT) mechanical and thermophysical properties are given in Tables I and II, respectively. The phase transformation characteristics of both these base materials from RT till 1473 K (1200 °C) as depicted by their change in the lengths with temperature, measured through dilatometry, are shown in Figure 1(a). As observed from Figure 1(a), SS317L austenitic stainless steel remains in the austenite phase from RT till 1473 K (1200 °C). On the other hand, GR60 transforms from the ferrite phase to the austenite temperature range of 1008 K phase in the (735 °C)-1123 K (850 °C) making it amenable to different heat treatments.

B. Isothermal Compression Tests and Generation of Process Efficiency Maps

Isothermal compression tests were carried out on both the base materials GR60 and SS317L using a Gleeble® 3500 thermo-mechanical simulator to identify the optimized processing parameters for hot roll bonding. Compression tests were conducted at four different temperatures (1173 K (900 °C), 1273 K (1000 °C), 1373 K (1100 °C), and 1473 K (1200 °C)) and at four different strain rates (0.1, 1, 10, and 50 s⁻¹). Cylindrical specimens of 10 mm in diameter and 15 mm in height were extracted from the as-received plates of GR60 and SS317L along the direction perpendicular to the rolling plane. The specimens were resistance heated to the test temperature at a heating rate of 5 K s⁻¹ and held for 2 min at the test temperature and finally deformed to a compressive true strain of 0.7. A thermocouple was attached to the specimen to provide a feedback control of the temperature as well to record the rise in temperature due to adiabatic heating during deformation. Compressively deformed specimens were sectioned along the compressive loading direction to characterize

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ORIGINAL RESEARCH ARTICLE

Effect of Microstructure on Oxidation and Micro-mechanical Behavior of Arc Consolidated Mo-Ti-Si-(B) Alloys

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The present study deals with the development and characterization of Mo-35Ti-10Si and Mo-35Ti-10Si-2B (wt.%) alloy for ultra-high temperature applications beyond the temperature limit of existing super alloys. The microstructural characterization using scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), electron back scattered diffraction (EBSD), x-ray diffraction (XRD) revealed that the Mo-35Ti-10Si-2B alloy was consisted of three phases, namely, (Mo, Ti)_{ss}, (Mo, Ti)₅SiB₂ and (Ti, Mo)₅Si₃; whereas, Mo-35Ti-10Si alloy was found to be consisting of (Mo, Ti)ss, and (Mo,Ti)₃Si phases. Since quantification of boron is difficult by EDS, Particle Induced Gamma-ray Emission (PIGE), a nuclear reaction analysis technique was used for chemical composition analysis of boron. The oxidation behavior of the Mo-35Ti-10Si-2B alloy in the temperature regime of 825-1250 °C was studied in detail and compared with boron-free Mo-35Ti-10Si alloy. Mo-35Ti-10Si-2B alloy exhibited superior oxidation behavior at intermediate temperatures of 825 °C, and excellent oxidation resistance at higher temperatures between 1000 and 1250 °C due to the formation of the protective borosilica and double oxide layers (TiO2 and duplex borosilica-TiO2), respectively. High-temperature oxidation mechanisms were discussed using detailed microstructural cross section analysis of the oxidized alloy samples. The micro-mechanical behavior of constitutive phases of the Mo-35Ti-10Si-2B alloy were studied by microhardness, nano-indentation and micropillar compression testing. The micropillar compression of (Mo, Ti)_{ss} phase showed fairly ductile behavior with the evidence of activation of dislocation in the form of slip lines revealed through the postdeformation fractography. Deformation studies of (Mo, Ti)₅SiB₂ and (Ti, Mo)₅Si₃ phases were also carried out which showed large strain bursts indicating possibility of activation of dislocation activities even at room temperatures imparting low level of ductility.

Keywords borosilicate scale, micropillar compression, nano-indentation, oxidation behavior, refractory metals

1. Introduction

Substantial progress has been made in the development of multi-phase molybdenum-based alloys such as Mo-Si-B, Mo-Ti-Si which has shown progressive improvements with respect to high temperature properties and recommended to be among the potential candidates for ultra-high temperature applications (Ref 1-8). Typically, Mo-Si-B-based alloys comprise of Mo solid solution (Mo_{ss}) as the phase responsible of imparting room temperature toughness and Mo_5SiB_2 (T2) as the oxidation resistant phase (Ref 1, 2, 5). This has been shown and well

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documented that presence of boron in the T2 phase helps in the formation borosilicate passivating layer by decreasing its viscosity (Ref 2). Apart from Moss and MosSiB2 (T2) phases, either Mo₅Si₃ or Mo₃Si phases are also present in the Mo-Si-Bbased alloys depending on the Si concentration in the alloy. Mo₅Si₃ containing alloys are relatively more oxidation resistant as compared to the alloy containing Mo3Si because of the superior oxidation resistance of Mo₅Si₃ phase (Ref 2-4). Therefore, constituent phases of the alloy and their fractions are important which decides the ultimate mechanical and oxidation properties of a specific Mo-Si-B-based alloy. Optimization of mechanical properties and high temperature oxidation resistance of Mo-Si-B-based alloys relies on tailoring of microstructure with respect to phase fractions and to some extent by micro-alloying additions (Ref 1, 6-8). However, the optimization still faces many challenges because of the pesting phenomenon (catastrophic oxidation) in the intermediate temperatures range (Ref 9-13). Application of oxidation resistant coating over Moss rich, Mo-Si-B or Mo-Ti-Si is another approach for such applications, where mechanical property is important and trading off of mechanical properties is not recommended (Ref 14-17).

Yang et al. (Ref 6) reported that the macro-alloying of Mo-Si-B alloy with Ti was able to suppress the formation of comparatively oxidation prone Mo₃Si phase by replacing with Mo_5Si_3 (T1 phase). Attempts were made to enhance the oxidation resistance of Mo_5Si_3 , since, Mo_5Si_3 is not fully

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protective against oxidation below 1600 °C because of formation of a porous silica layer. The major breakthrough was achieved when researchers found Mo-37Si-40Ti alloy (close to single phase (Mo, Ti)5Si3) to be oxidation resistant in the intermediate temperature range 750-1300 °C (Ref 18-20). This approach has opened up a new dimension for study of quaternary Mo-Si-B-Ti alloys. Further studies also corroborated that Mo-Si-B alloys with addition of Ti exhibit superior oxidation resistance when compared to B-free Mo-Ti-Si or Tifree Mo-Si-B alloys by getting rid of pesting along with good creep resistance and lower density (Ref 21-31). In contrast to the previous approaches of designing Mo-Si-B alloys with maximizing the relatively brittle intermetallic phase, Mo₅SiB₂ for imparting oxidation resistance by trading off of mechanical properties, especially fracture toughness, the approach of macro-alloying relies on the addition of Ti as the passivating element for achieving optimum microstructure consisting of (Mo, Ti)_{ss}, (Mo, Ti)₅SiB₂ and (Ti, Mo)₅Si₃ phases. Although the beneficial effect of addition of Ti in Mo-Si-B system is reported but the mechanism is not well understood.

In the present investigation, the microstructure, micromechanical properties and oxidation resistance of Mo-35Ti-10Si and Mo-35Ti-10Si-2B (wt.%) alloys were investigated and discussed. We present experimental proof that Mo-35Ti-10Si-2B alloy can be made oxidation resistant by protective multi-layer oxide scales up to 1250 °C. Underlying oxidation mechanism and role of B in improving the oxidation resistance of the alloys is discussed by comparing the oxidation resistance of B free Mo-35Ti-10Si (wt.%) alloy. The micro-mechanical behaviors of three constitutive phases of the alloys were studied by nano-indentation and micropillar compression for investigating the microstructure–property correlation.

2. Experimental Procedures

Mo-35Ti-10Si (wt.%) and Mo-35Ti-10Si-2B (wt.%) alloys were prepared by arc melting of constituent elements Mo, Si, Ti and B, in a Zr-gettering high-purity Ar atmosphere. The alloys were melted multiple times for achieving homogeneity with controlled melting process by optimizing the parameters such as current and vacuum levels to avoid evaporation of alloying elements especially boron and silicon. The microstructure and compositional examinations were carried out using SEM (Model MV2300CT/100, Camscan, UK make) attached with EDS (Model: X-max 80, Oxford make). The microstructures were also observed after the annealing at 1250 °C for 100 h. The phase analysis was carried out by EBSD (Oxford Model: Nordlys Nano) and XRD (Inel-make unit, model MPD).

For generating samples for oxidation studies, multiple coupons of dimensions 5 mm \times 3 mm \times 3 mm were generated from the arc melted button using EDM wire cutting followed by metallographically polishing of all the sides. Non-isothermal oxidation studies were carried out in an in-house developed thermogravimetry analyzer (TGA) in static air condition with online weight change recording facility. During heating of the furnace, the samples were kept in the cold zone. The coupons were introduced into the hot zone of the furnace for isothermal oxidation tests, only when the temperature reached the desired temperature. The isothermal oxidation studies were carried out at 825, 1000 and 1250 °C for different

durations up to 100 h. The oxidized samples were characterized for phase analysis using XRD and the nature of oxide layers.

Since, boron analysis by EDS is not reliable because of low atomic number; therefore, Particle Induced Gamma-ray Emission (PIGE, FOTIA, BARC) (Ref 30) was used for boron analysis. Microhardness of the polished samples were measured using Vicker's hardness tester with a load of 100 g and a dwell time of 10 s. Hardness and elastic modulus mapping was carried out using a KLA Tencor make nano-indentation (Model: iMicro®)). The detailed methodology was discussed elsewhere (Ref 31, 32).

A number of micropillars were fabricated from three constituent phases [(Mo, Ti)ss, (Ti, Mo)5Si3, and (Mo, Ti)5SiB2] of Mo-35Ti-10Si-2B (wt.%) using a dual beam focused ion beam (FIB) in a SEM (Carl Zeiss FESEM). EDS and EBSD analysis were carried out to identify the phases before fabrication of the micropillars. Those grains with suitable orientations were selected for fabricating micropillar which possesses non-zero (preferably > 0.3) Schmid factor for at least one possible slip system. The sizes of micropillars were decided based on the size of the respective phases to avoid presence of other phases in a specific micropillar. Initial milling was done using Ga + ions beam with a current of 16 nA for fabricating a circular trench with the outer diameter of 40 μm and a coarse pillar of diameter of around 10 μ m at the center. Subsequently, the current was gradually lowered to 0.1 nA to fabricate polished micropillars with a final nominal top diameter of 1.5-5 μ m and aspect ratio (L/D) of ~ 2.5. Compression experiments using diamond flat punch were conducted using a nano-indenter in displacement-controlled mode at room temperature as described elsewhere (Ref 33). The compression tests on all the micropillars were carried out at a strain rate of 0.05/s. The deformed micropillars were observed under SEM for understanding their deformation behavior.

3. Results and Discussion

3.1 Microstructural Characterization

Figure 1(a) and (b) shows the representative back scattered electron (BSE) images of Mo-35Ti-10Si and Mo-35Ti-10Si-2B (wt.%) alloys, respectively. Mo-35Ti-10Si alloy was found to be consisting of two phases; while, Mo-35Ti-10Si-2B alloy was found to be comprised of three phases as seen in the BSE SEM images. EDS point analyses were carried out in different phases of the alloys and the results are summarized in Table 1.

From the EDS point analysis and XRD analysis, the Mo-35Ti-10Si alloy was found to be consisting of (Mo, Ti)₃Si phases. The detailed microstructural characterization was carried out for the Mo-Ti-Si alloys system in our previous study (Ref 30, 31). The EBSD band contrast image, phase map and inverse pole figures obtained from the Mo-35Ti-10Si-2B alloy is shown in Fig. 2. By comparing the EDS point analysis data, and EBSD analysis, constitutive phases were confirmed as (Mo, Ti)_{ss}, (Mo, Ti)₅SiB₂ and (Ti, Mo)₅Si₃. XRD patterns shown in Fig. 3 confirmed the presence of the identified phases.

External (in air) Particle Induced Gamma-ray Emission (PIGE) facility at FOTIA, BARC, was used for non-destructive quantification of Ti, Si and B in Mo-35Ti-10Si-2B alloy. Direct samples were placed outside the beam exit window in the

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ORIGINAL RESEARCH ARTICLE

Effect of Precipitation on Residual Stresses in Alloy 693

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Alloy 693 is a precipitation hardenable nickel base superalloy containing about 30% Cr, 4% Fe, 4% Al, 1.5% Nb and 0.3% Ti (in wt.%). At elevated temperatures, alloy precipitates out particles of an ordered γ' phase (L1₂ crystal structure) with Ni₃(Al,Ti,Nb) stoichiometry. These particles remain coherent and maintain a cube-to-cube orientation relationship with the face-centered cubic matrix. The alloy also has a tendency to form chromium-rich α phase (body-centered cubic crystal structure) particles at temperatures above 800 °C. The α phase particles maintain a Kurdjumov–Sachs orientation relationship with the matrix. This paper reports the effect of the precipitation of γ' and α phases on the residual stresses developed in the alloy, and correlates them with the misfit strains due to the precipitation of the two phases. Residual stresses have been measured using the blind hole drilling method, while the misfit strains have been calculated based on the lattice parameters of matrix, γ' and α phases determined using neutron diffraction. The precipitation of the γ' phase introduces tensile nature of stresses in the matrix, while that of the α phase introduces compressive stresses. The overall nature of the residual stresses in the alloy is governed by the volume fraction of the two precipitates.

Keywords α precipitates, γ' precipitates, Alloy 693, misfit strain, residual stresses

1. Introduction

Alloy 693 is a precipitation hardenable nickel base superalloy and is primarily strengthened by the precipitation of an ordered γ' phase (L1₂ crystal structure) particles of Ni₃(Al,-Ti,Nb) stoichiometry in the disordered γ phase (face-centered cubic crystal structure) nickel solid solution matrix. The alloy offers an excellent combination of mechanical properties and corrosion resistance especially in oxidizing and sulfurizing environments and to metal dusting for high temperature applications (Ref 1). The alloy finds applications in chemical and petrochemical processing industries, management of highlevel nuclear waste and high temperature fuel cells involved in synthesis gas production (Ref 2-4).

Table 1 gives the nominal composition of Alloy 693. The alloy is a solid solution at temperatures above 950 °C but

precipitates of y' phase particles form homogenously throughout the matrix even during water quenching after solution annealing (Ref 5). Singh et al. (Ref 5) have shown that the precipitation of the γ' phase can only be suppressed by employing a cooling rate of more than 4500 °C/min, which is practically impossible to achieve in any commercial heat treatment practice. The solution-treated and water-quenched alloy exhibits the presence of fine γ' precipitates of $\sim 10 \text{ nm}$ distributed homogeneously within the matrix (Ref 5). Precipitation of the γ' phase significantly improves the strength of Alloy 693. At elevated temperatures, their growth is driven by the extent of aluminum, titanium and niobium super saturation till the matrix saturates with respect to these solutes after which they coarsen, driven by the minimization of precipitate's total surface area. The coarsening of the γ' particles during aging of the alloy at 800, 875 and 900 °C starts approximately about 50, 10 and 5 h, respectively (Ref 6). During growth and coarsening of the γ' precipitates, their morphology evolves from spherical to cuboidal as they align themselves along < 100 > directions (Ref 6), which is consistent with their morphologies in most y' hardened superalloys. This change in the morphology is associated with the dominance of interfacial energy over elastic strain energy during later stages of transformation (Ref 7). Since the ordered L12 crystal structure is based on facecentered cubic crystal structure of the γ phase with almost similar lattice parameter (Ref 8), the γ' precipitates remain coherent with matrix and maintain a cube-to-cube orientation relationship (Ref 6). The alloy also exhibits a tendency to precipitate needle shape Cr-rich a phase (body-centered cubic crystal structure) particles, which forms in significant volume fraction at 900 °C. The (110), habit plane of the needle shape a phase particles maintain a Kurdjumov-Sachs type orientation relationship (i.e., $(110)_{\alpha} || \{111\}_{\gamma}$ and $[\overline{1}11]_{\alpha} || < \overline{1}10 >_{\gamma}$) with the γ matrix (Ref 9). The coherency strain due to the lattice mismatch between γ phase matrix, and the γ' and α phase particles gives rise to residual stresses in the matrix.

This invited article is part of a special topical issue of the Journal of Materials Engineering and Performance on Residual Stress Analysis: Measurement, Effects and Control. The issue was organized by Rajan Bhambroo, Tenneco, Inc.; Lesley Frame, University of Connecticut; Andrew Payzant, Oak Ridge National Laboratory; and James Pineault, Proto Manufacturing on behalf of the ASM Residual Stress Technical Committee.

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Table 1	Nominal composition of Alloy	693 and composition of Alloy 693 under study
A	A constraint to make a constraint of a constraint	the second second on the second

Nb Mn	Nb Mn	Al	Fe	Cr		Ni
	N 9		t.%)	n of Alloy 693 (wt.	inal Composition	Vominal
0.5-2.5 1.0 max 1.0	0.5-2.5 1.0 max	2.5-4.0	2.5-6.0	27-31	2	58 2
			(wt.%)	under study 693 (position of Alloy	Composi
1.53 0.20 0.3	1.53 0.20	3.94	3.98	31.26	2	58.42
1.53 0.20 0.3	1.53 0.20	3.94	3.98	31.26	2	58.42

Residual stresses are stresses that remain in a body that is stationary and is at equilibrium with its surroundings. The residual stresses may accelerate the onset of plastic deformation when the residual and applied stresses together become more than the yield strength in plastically deformable materials, which can be detrimental to their performance [see, e.g., (Ref 5)]. Residual stresses can be of different types depending upon the characteristic length scale over which they self-equilibrate. Long-range stresses that equilibrate over macroscopic dimensions are termed type-I residual stresses. These stresses result from long strain incompatibilities introduced by strain or temperature gradients during manufacturing or service. Ignoring polycrystalline discontinuities, such stresses vary continuously over large distances, and can be experimentally estimated by hole drilling. On the other hand, residual stresses that equilibrate over a few grains (microscopic scale) are termed type-II residual stresses. Type-II residual stresses represent the average stresses arising due to misfits between different crystalline phases formed during temperature or deformationinduced phase transformations in multiphase materials. Residual stresses that exist over atomic dimensions are termed type-III residual stresses. Type-III residual stresses are caused by dislocations and point defects and equilibrate within a grain. For multiphase materials, type-I stresses are continuous across phases but the type-II and type-III are not. As a result, even when the sampling area is greater than the characteristic lengths of type-II and type-III stresses, nonzero phase average microstresses exist. For this reason, phase-dependent residual effect over large distances may exist in multiphase materials even when the type-II and type-III stresses equilibrate over the appropriate small distances.

As Alloy 693 forms γ' and α phases with different kinetics, the effect of their precipitation on the build-up of type-I residual stresses is important to understand better the mechanical behavior of the aged alloy. In the present work, type-I residual stresses have been estimated in Alloy 693 with different microstructure states and correlated them with the misfit strain arising due to lattice mismatch (type-II residual stresses) between the matrix and the precipitates. The type-I residual stresses have been measured by the blind hole-drilling method, while the lattice parameters of individual phase (in constrained conditions) have been determined by Rietveld refinement of the neutron diffraction patterns.

2. Experimental Techniques

2.1 Material Under Study

Table 1 also gives composition of the Alloy 693 studied in the present work. The composition of the alloy was determined using inductively coupled plasma-optical emission spec-

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troscopy (ICP-OES) details of which are given elsewhere (Ref 6). This composition was within the range of alloy's nominal composition (Ref 1). The alloy was received as 10-mm-thick plate in mill annealed condition produced by M/s MIDHANI, Hyderabad. Specimens of $10 \times 10 \times 10 \text{ mm}^3$ size were cut from the plate subjected a solution treatment at 1100 °C for 2 h followed by water quenching (typical cooling rate > 1000 °C/min). Solution-treated (ST) specimens were isothermally aged at 800, 875 and 900 °C temperatures for 100 h followed by water quenching (WQ). Before subjecting the specimens to heat treatment, all specimens were sealed in quartz ampoules filled with high-purity He gas at a pressure of about 150 mm of Hg.

2.2 Microstructural Examination

Microstructural examination of heat-treated specimens was carried out in a field-emission scanning electron microscope (Carl Zeiss make SIGMA model) operated at 20 kV and a JEOL2000FX transmission electron microscope equipped with tungsten filament and operated at 160 kV. Specimen preparation procedures for microscopic studies are given elsewhere (Ref 6). Chemical compositions of phases were determined using energy-dispersive spectroscopy (EDS) analysis employing Oxford spectrometers attached to electron microscopes. Size of the γ' particles was measured using the free ware image analysis software ImageJ (Ref 10).

2.3 Phase Identification

Identification of phases was carried out using neutron diffraction employing multi-position sensitive detector (PSD) focusing crystal diffractometer (FCD) setup by UGC-DAE Consortium for Scientific Research Mumbai Center at the National Facility for Neutron Beam Research (NFNBR), Dhruva reactor, Mumbai (India), at a wavelength of 1.48 A (Ref 8). The samples were placed in a vanadium sample holder which were directly exposed to neutron beam for room temperature diffraction measurements. The diffracted neutrons from the sample were recorded by He³ filled liner PSDs by following charge division method. The neutron diffraction data was analyzed using the Rietveld refinement procedure employing Le-Bail fitting method in the Fullprof-Suite software package (Ref 11).

2.4 Residual Stress Measurement by Hole-Drilling Method

Residual stress analysis was carried out using hole-drilling method as per ASTM standard E837. This technique is a semidestructive technique and determines residual stresses in isotropic metallic materials within the elastic limit. The technique is suitable for measurements as long as the residual stress does not exceed $\sim 80\%$ of the material's yield strength for thick sections and $\sim 50\%$ for thin sections. Three resistance

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Effect of substituted cobalt-chromium-iron oxides' dissolution kinetics in oxidizing formulation on decontamination process

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Abstract

Removing radioactive corrosion products from Cr-containing iron oxides require a multi-step and multi-cycle decontamination process. The present article brings out the effect of divalent metal ion substitution on the release rate of chromium in the oxidative pre-treatment step. The non-stoichiometric cobalt chromium ferrites were synthesized, characterized and effect of Zn^{2+}/Ni^{2+} substitution on the dissolution behavior was probed. The dissolution rates decreased with increasing the degree of inclusion and showed minima at ~ 0.4–0.6 atom% which is explained on the basis of lattice structure. It is concluded that the dissolution kinetics of native nickel–chromium ferrites in reactors increases with metal ion inclusion.

Keywords Decontamination · Oxidizing formulation · Substituted ferrite · Dissolution kinetics · Activated corrosion products

Introduction

Water chemistry control in heat transport systems of nuclear reactors plays a vital role in the radiation dose rate checkin in nuclear power plants. The boiling water reactor's (BWR) heat transport system follows normal water chemistry (NWC) (pH=7.0, dissolved oxygen ~ 200 µg l⁻¹ conductivity ~ 0.005 µS cm⁻¹). This chemistry regime leads to the formation of a double-layered oxide film containing a mixture of various ferrites/chromites Fe₃O₄, NiFe_{2-x}Cr_xO₄, Cr₂O₃ and Fe₂O₃ on the surface of stainless-steel systems [1–4]. Some BWRs and pressurized water reactors (PWR)

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follow hydrogen water chemistry (HWC), where ~25 mg of H₂ per kg of light water coolant is maintained in the heat transport system to control dissolved oxygen concentration and minimize corrosion [5]. Maintenance of the HWC chemistry regime leads to modification in the double-layered oxides on the stainless steel surfaces compared to NWC [6, 7]. Under NWC conditions formation of α -Fe₂O₃ (having hexagonal close packed crystal structure) is favoured over spinel (MFe2O4) structure in the outer layers due to higher concentrations of oxidizing species (such as H2O2 and O2) from coolant water radiolysis. This hexagonal crystal structure has no preferred lattice sites for inclusion of cations (radioactive metal nuclides such as 60Co) resulting in lower cobalt pick-up [8]. Neutron activation of corrosion products and inclusion of fission products (from breached fuel) in the above corrosion films can generate a radiation field build-up in the out-of-core areas. Among the activated corrosion products (ACPs), ⁶⁰Co is the major contributor to the person-Sv budget because of its long half-life (5.27 y) and high y-energies (1.17 and 1.13 MeV).

To reduce the radiation field due to the cobalt, many of the BWR and PWR follow zinc injection (~10 μ g l⁻¹ of zinc). Zinc ion injection modifies the composition of both the layers of the double-layered oxide spinel in stainless steel compared to normal and hydrogen water chemistry [8–12]. According to Zhang et al., zinc injection mitigated stress corrosion in cold worked SS 316L and formation of ZnCr₂O₄ was detected on the crack walls and crack tips [12]. In a recent article it is reported that 40 μ g L⁻¹ zinc injection is sufficient in significantly inhibiting corrosion product deposition on the inner walls of the heat transfer tubes [13]. Many of these reactors follow a full system or component decontamination process to reduce the radiation field in the out-of-core area. These procedures are followed to help person-Sv-related problems. Variation in the oxide morphology with varying metal ions of mixed valency across the depth of the corrosion film makes it difficult to adopt a single decontamination procedure for the efficient removal of active metal nuclides. Understanding the dissolution mechanism and kinetics of these oxide films on stainless steel surfaces is essential to formulate the right strategy for obtaining effective decontamination factors with minimum active waste volume. The decontamination process choice with defined parameters becomes stringent, as the reactor circuits have a combination of different alloys exposed to different hydrothermal conditions. The permanganate-based CORD (chemical oxidation-reduction decontamination; developed by Siemens) process is used extensively for the decontamination of stainless steel and nickel-based alloy surfaces [14-16]. Alkaline oxidation gives higher decontamination factors (DFs) in high Ni alloys, whereas acidic oxidation is preferred (for higher DFs) for stainless steel surfaces [17]. Several alternatives to permanganate are under development, including ozone, permanganic acid (HMnO₄), potassium ferrate, and chromous LOMI (low oxidation state metal ion) reagents. From the experience it can be stated that the differences in decontaminating power of different decontaminating formulations used, is less significant compared to the differences between the oxide films of different power plants. The rate constant for the dissolution of CrxFe2-xO3 / NiCr_xFe_{2-x}O₄ in HMnO₄ was observed to be increased with Cr content in the oxide lattice [18]. Dependence of ozone solubility and stability on the pH and temperature of the decontaminating solution affects the dissolution rate of the chromium oxide [19]. However, the effect of zinc-substituted chromite commonly seen in the reactors following zinc water chemistry and its decontamination effectiveness was not extensively reported in the literature. In this manuscript, a series of synthesized oxides were used to discuss the mechanism and dissolution aspects of Zn/Ni substituted Co-Cr-Fe oxide in permanganate-based formulation.

Experimental section

Synthesis and of characterization of Ni/Zn/Co substituted Cr-Fe-O oxide by combustion route

Two sets of samples with composition $M_xCo_{1-x}CrFeO_4$ (M=Ni²⁺ and Zn²⁺ and x=0-1) oxides were prepared by

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combustion method. The method involves an exothermic and a self-sustaining redox reaction leading to oxide formation. The auto combustion synthesis route is one of the most preferred methods for the preparation of metal oxides (in nano range size) due to its low temperature of synthesis [20]. The process involves gel formation by mixing an aqueous solution containing organic complexant (fuel/reductant) and metal nitrate (oxidizer) [21]. The nitrate salts are favoured for the synthesis as they are water soluble low temperature oxidants serving as a nitrogen source [22]. This method generates pure oxide product because of in-situ generation of the high temperature which can remove the low boiling point impurities. Selection of appropriate complexant that act as fuel is important for phase formation in auto combustion method. Commonly used complexing agents or fuels are urea (CONH2)2, glycine (NH2CH2COOH) and citric acid (C6H8O6). Based on our earlier experience we have adopted urea (CO(NH₂)₂) as the fuel [18, 23, 24]. The fuel to nitrate molar ratio used was 1:1.

All the chemicals used in the dissolution studies were AR/ GR grade. For the preparation of oxides, a stoichiometric amount of salts, namely, chromium, ferric, cobalt, nickel and zinc nitrates ($Fe(NO_3)_3$,9 H_2O , $Cr(NO_3)_3$,9 H_2O , $Ni(NO_3)_2$,6 H_2O , $Co(NO_3)_2$,6 H_2O , and $Zn(NO_3)_2$,6 H_2O) were taken in DM water. To this salt solution, fuel was added with nitrate to fuel mole ratio of 1:1. The solution was heated slowly on a hot plate (~80 °C) until a dried mass was obtained, which was fired in the muffle furnace at 1000 °C for 4 h. Under complete combustion, the assumed chemical reaction can be written as follows:

$$M_{x}(NO_{3})_{2} + (1 - x)Co(NO_{3})_{2} + Fe(NO_{3})_{3} + Cr(NO_{3})_{3} + 8.5O_{2} + 3CH_{4}N_{2}O \xrightarrow{\Delta 1000^{\circ}C} M_{x}Co_{1-x}FeCrO_{4} + 14NO_{2} + 3CO_{2} + 6H_{2}O$$
(1)

The oxides synthesized by the combustion route were characterized by X-ray diffraction (XRD), Laser Raman Spectroscopy (LRS) and X-ray photoelectron spectroscopy (XPS). The XRD pattern was recorded covering a 20 range of 10°–80° using a Co K_a X-ray line (1.785 A°) with a Philips spectrometer. LRS Spectra were recorded on the samples using a Raman spectrometer "Model: LABRAM HR 800" with 532 nm laser. A grating 1800 groove/mm and 100X objective lens was used. XPS experiments were carried out at room temperature using an Al K_a X-ray source of energy 1486.74 eV, as the primary source of radiation. The anode was operated at 13 kV and the power level of the source was 300 W. Prior to the analysis, the grounded oxide samples were pressed onto sample stubs with carbon-based adhesive tape.





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Electronic nose based on Pd- and Pt-incorporated ZnO nanowires: a case study

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ABSTRACT

Effect of incorporation of sensitizers namely palladium (Pd) and platinum (Pt) on the gas-sensing behaviour of zinc oxide (ZnO) nanowires has been studied. The specificity achieved is further studied and demonstrated for its efficacy towards the simultaneous detection of multiple gases employing the developed sensors in an electronic nose configuration. Incorporation of salt solutions containing the desired sensitizer concentration in the starting reaction mixture of hydrothermal growth has been effectively used to achieve heterostructure ZnO nanowires. Pd and Pt gets incorporated as PdO and metallic Pt, in the host matrix resulting in the formation of random heterojunctions namely p-n junction and Schottky junctions. Consequently, an increase in the work function as studied using Kelvin probe studies is observed. Utilizing statistical implements namely principal component analysis (PCA) and hierarchical cluster analysis (HCA) the discrimination of three gases namely H₂, H₂S and NO₂ has been successfully accomplished. 3D PCA discriminates the three gases successfully with first three components exhibiting a percentage of variance of 42.32, 33.26 and 24.20%, respectively. A reasonable discrimination of H2, H2S and NO2, grouped into three clusters as evident from HCA dendrograms, was achieved using utilizing Ward's method and Euclidian distance metric approach.

1 Introduction

ZnO is a multifarious functional material, which has exhibited itself in the diversity of growth forms such as nanocombs, nanobelts, nanorings and nanowires (NWs) [1–3]. The associated high surface area-tovolume ratio coupled with the inherent oxygen nonstoichiometry has been effectively used to realize sensors with tailor response towards target gases. In pure form, ZnO often suffers from the drawback of cross selectivity i.e. nearly identical response characteristics is observed for all the gases. Accordingly, to improve the sensor response and selectivity towards the required gases, different approaches have been investigated. Surface modification with sensitizers like Au, CuO, NiO, PdO and Pt [4–7] is one of the most commonly employed method. Incorporation of sensitizers has been found to improve the response characteristics, which is attributed to the increase in the number of gas-specific selective sites for interaction with

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the target gas [8-10]. This has been predominantly explained using the chemical and electronic sensitization methods [11, 12]. In chemical sensitization, the sensitizers help to increase the oxygen coverage over the sensor surface thereby increasing the available sites for interaction. And in the electronic sensitization, the sensitizer itself takes part in the sensing mechanism. It provides the additional mid-gap states by forming a junction with the host material like p-n junction or Schottky junction. The resulting barriers have been found to have a strong dependence on the sensor environment and accordingly, the presence of target gases is expected to drastically alter the sensor properties. For example, we have demonstrated earlier an improvement in sensitivity and selectivity of ZnO NWs towards H2S and NO2 gases employing Au, CuO, TiO₂ and Al layer on top of the NWs [13–16]. Herein, the modulation in the response characteristics was governed by the creation and the breakdown of the p-n and Schottky barriers between sensitizer and ZnO [17, 18]. One of the crucial parameters to achieve the good sensor response characteristics is the control over sensitizer expanse and uniform dispersal on the sensor surface. If the amount is too low, it would not yield the improved sensor performances and if it is too high, the sensitizer itself dominants and consequently, the response characteristics achieved are those of pure samples which are often low. Hence, it is desired to find the way to achieve optimum concentration and distribution of the sensitizer over the sensor surface. The sensor is judged on its important sensor parameters, which includes sensitivity, specificity, faster response kinetics and life. Sensitivity is the ability of the sensor to produce maximum change in its properties for a small change in the gas concentration. It is defined as the sensor response per unit gas concentration. Selectivity is the ability of the sensor to produce maximum change when exposed to the target gas in the presence of other interfering gases. The sensor exhibiting highly repeatable and reproducible measurements with minimum drift in its response characteristics over a long-term measurement periods (>3 months) is considered to be highly stable.

To identify the sensor with potential for possible commercial viability, the sensor needs to satisfy the "4-S sensor selection or Ramgir criteria" [19, 20]. Herein, each S stands for high sensitivity, selectivity, stability and suitability. First three 'S's are related

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to the performance of the sensor, while the fourth 'S' takes into consideration of economic viability. It is desirable of the sensor to fulfil the criteria so as to stand a chance of commercial deployment and acceptance. In particular, the sensor with high sensitivity, selectivity towards a target gas, exhibiting a long-term stable performance under operating conditions and importantly having cost effective complete sensor fabrication process will find its place in the market. Accordingly, attempts are being directed towards finding the novel sensor configuration and methodologies to find sensors that could satisfy the above-mentioned criteria.

Now, in the similar context to surface modification, incorporation of sensitizers into the host material can also be looked upon as a potential way to achieve the improvement in sensing characteristics. Herein, again the amount and distribution of sensitizers in the host matrix is expected to play crucial role in determining the sensing characteristics. It is important to note that ZnO exhibits itself into hexagonal wurtzite structure that is characterized by the presence of alternate layers of Zn and O. ZnO NW structure in particular is characterized by the presence of polar Zn and O layers as top and basal planes with six non-polar side planes [21, 22]. It is noteworthy to mention that during growth, incorporation of impurities usually takes place along the side planes, thereby could be looked upon as a potential means to tailor the sensor response. Hence, Pd and Pt having ionic radii of 1.35 and 1.40 Å close to that of Zn (1.30 Å) are expected to easily get incorporated into the ZnO matrix and could help to achieve improved sensor response characteristics. Both Pd and Pt are known to act as a catalyst for H₂ oxidation and expected to improve the response characteristics. Besides, Pd could form PdO upon oxidation and help to increase the effective number of oxygen species on the sensor surface and being a p-type material might form a p-n junction. Contrary, Pt will get incorporated as Pt itself and may form Schottky barrier with ZnO. The formation and modulation or collapse of these properties may help to improve the response characteristics.

Accordingly, in the present work, incorporation of Pd and Pt into ZnO matrix has been investigated as a means to achieve improved response characteristics towards H₂, H₂S and NO₂. For this, incorporation of salt solution containing the desired sensitizer





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Enhancing the Sr uptake on resorcinol-formaldehyde polycondensates by modifying the structure and shape

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Abstract

Resorcinol-formaldehyde polycondensates—the well-established Cs-selective agents, along with their crown ether (18crown-6) composite discs, were synthesized, characterized (FT-IR, SEM–EDS, surface area, porosity) and applied for strontium uptake from aqueous solutions. Effects of crown ether amounts, Sr in feed, pH, equilibration time, temperature, competing ions, on the sorption, along with re-usability of synthesized sorbents, were evaluated. The fate of Sr was followed by EDXRF spectrometry on both solution and solid phases. Solution pH (3–12) and temperature (upto 100 °C) had negligible impact on the holding capacities. Sorption capacity was enhanced by ~33% upon modification, and followed pseudo-second order kinetics.

Keywords Resorcinol-formaldehyde-crown ether discs · Synthesis · Characterization · Strontium sorption

Introduction

Management of radioactive waste has utmost importance in nuclear fuel cycle, considering the recovery of wealth from waste. 90 Sr ($t_{y_2} \sim 29$ y), and 137 Cs ($t_{y_2} \sim 30$ y) are the two key radio-nuclides, holding the major share of radioactivity in spent fuel and associated containments in a nuclear reactor [1, 2]. Because of their high solubility, these radio-nuclides get easily transported in aqueous media, too. These radionuclides are invariably present in liquid waste, generated during the spent-fuel reprocessing in nuclear reactors [3]. According to IAEA guidelines, the maximum allowed concentrations of 90Sr and 137Cs, for safe discharge to the environment are 1 Bq g^{-1} (1.8×10⁻⁷ mg kg⁻¹) and 0.1 Bq g^{-1} (3.1×10⁻¹ mg kg⁻¹) respectively [4]. ⁹⁰Sr—being chemically similar to calcium, is a known "bone-seeker", and therefore, needs to be handled with utmost care [5]. On the other hand, $^{89}Sr\text{---a}$ pure β emitter (t_{1/2} ~ 50.5 days), is a very useful isotope in nuclear medicine, for bone pain palliative care for cancer patients [6]. Even though the separation of

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radioactive Sr from radioactive liquid waste is extremely necessary, it has got many practical challenges. Immobilization of trace levels of long-lived radioactive ⁹⁰Sr, from aqueous media, is one of the on-going activities in the Department of Atomic Energy (DAE), India.

The world-wide existing Sr-removal technologies are: evaporation [4, 7], ion exchange [8-10], membrane processes [11, 12], chemical immobilizations [13, 14], and sorption [15]. These methodologies are adopted singly or in tandem, for various utilities, depending on both the decontamination requirements and volume reduction factors [3]. Among all the existing procedures, ion exchange and sorption are the most efficient and economic routes [16]. In addition to their efficiencies, stability in radioactive environment is a vital criterion to be satisfied, for the present application. Resorcinol-formaldehyde polycondensate (RF) resins, with proven radiation stability, are well-reported in the literature for selective separation of Cs from radioactive wastes [17-21], via ion exchange mechanism. These resins may be one of the candidate sorbents for removal of radioactive Sr too. It could be congregated from a detailed literature survey that these condensates may necessarily be modified with appropriate functionality, to enhance selectivity towards the targeted metal ions. Crown ethers are quite known for their high selectivity for metal cations which exactly fit their macrocyclic cavities [22-24].

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In the present studies, bare as well as crown ether functionalized RF discs were synthesized and characterized using FT-IR, SEM, surface area, pore distribution analyses. Herein, 18-crown-6 (18C6) was selected for enhancing the Sr uptake and the RF poly-condensates were prepared in the disc shape, owing to the ease of handling, adaptability in batch modes of operation, and post-sorption separation, compared to the conventional bead shape. After stability assessment in various conditions like pH (1–14), temperature (30–100 °C), the synthesized discs were applied for the uptake of Sr^{2+} from aqueous solutions (0.5–10 mg mL⁻¹). All the laboratory scale studies were carried out using inactive Sr^{2+} solutions and the quantifications were carried out using energy dispersive X-ray fluorescence (EDXRF) spectrometry.

Experimental

Materials and methods

Resorcinol (Merck), formaldehyde (37–41% in methanol, AR grade, Thomas Baker), sodium hydroxide (NaOH, 99%, Thomas Baker), strontium carbonate (SrCO₃, 99.9%, Strem Chemicals, Inc., U.S.A.), 18-crown-6 (1, 4, 7, 10, 13, 16-hexaoxacyclo-octadecane, SIGMA Chemical company, U.S.A) were used for synthesis of native (alternatively named as bare) and composite discs. All the solvents and chemicals used were of analytical reagent grade. All dilutions were carried out in de-ionized water (conductivity = 5 μ S m⁻¹), drawn from Millipore water purification system.

Preparation of strontium standard solution

Strontium stock solution was prepared by dissolving 0.3880 g of strontium carbonate in 500 μ L supra-pure HNO₃ and diluted to 100 mL with de-ionized (DI) water, maintaining 0.5% acidity. The Sr concentration in the prepared standard solution was 2.3028 mg mL⁻¹.

Synthesis of resorcinol-formaldehyde and resorcinol-formaldehyde-crown ether composite discs with varying crown ether contents

The literature reported procedure for synthesis of RF resin beads [17–21] was followed, with a slight alteration in the last step. During the preparation of resin beads/fine powder materials, the final step involves dry-heating in an oven upto 100 °C for 72 h. This step was avoided during the present synthesis, as the discs started losing integrity beyond 60 °C, upon dry-heating in air. In a beaker (capacity ~ 5 mL), 135 mg resorcinol was dissolved in 1 mL of ~0.1 M NaOH

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solution and was divided into two parts. Further, 125 µL formaldehyde was added into above each part and was heated on temperature controlled hot plate (40 to 70 °C) (IKA® ETS-D5 / IKA® C-MAG HS7) till the solution became jellylike. In a similar fashion, around 50 preparations were done in separate, identical beakers (having capacity = 5 mL, base diameters ~1.5 cm each). These beakers were kept for a week for stabilisation to get the shape of uniform, stable discs. After the curing period, the resorcinol-formaldehyde (RF) discs got released from the bottom of each beaker. These were taken out from beakers and kept in closed container for further experiments. The composite discs with 18-crown-6 (RF-18C6) were prepared in similar fashion, by adding different amounts of 18-crown-6 (18C6), i.e., 0.4, 0.8, 1.5, 3.0, 5.0, 10.0, 30.0% by weight of the crown ether to the total volume of synthesis mixture, just prior to the addition of formaldehyde.

Characterization of the bare and composite discs

The average diameter and thickness of the formed discs were obtained from measurements on five representative discs, using a digital caliper (1,471,622, Pro'sKit).

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker TENSOR II FTIR spectrometer using an attenuated total reflection technique by measuring the transmittance from 400 to 4000 cm⁻¹ to analyze the functional groups of both RF and the composite, RF-18C6 discs.

Strontium sorption studies

Sorption experiments on both bare (RF) and composite (RF-18C6, having ~1.5% of 18C6) discs were carried out using aqueous solutions of Sr^{2+} , via batch mode of equilibration. The weights of sorbent discs were kept identical, i.e., ~0.2 g for each sorption study, for direct comparison of their performances.

Effect of pH

The Sr-stock solution was diluted to 50 mg L^{-1} , using deionized water, and divided into two sets (each containing three flasks) of 10 mL batches. In order to optimize the pH range for sorption of the Sr²⁺ by RF and RF-18C6 discs, both sets were adjusted to pH values of 3.0, 5.0 and 10.0 using 0.1 M NaOH and 0.1 M HNO₃. In another two sets (each containing five flasks) 0.2 mL of stock Sr standard solution was diluted to 10 mL with concentrated HNO₃, 1 M HNO₃, 0.1 M HNO₃, 1 M NaOH and 0.1 M NaOH, to get 50 mg mL⁻¹ Sr concentration. A Thermo scientific Orion STAR A111 pH Meter was used for all pH measurements and all the solutions were analysed for Sr, using energy dispersive X-ray fluorescence spectrometry (EDXRF). All EDXRF measurements were carried





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RESEARCH ARTICLE



Exploring genetic variability for morphological and yield contributing traits in sorghum (*Sorghum bicolor* (L.) Moench) germplasm from Southern India

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Abstract Sorghum is a major cereal crop grown worldwide for its grain, livestock feed and biofuel. In order to characterize the pattern of genetic diversity in the germplasm and advanced mutant lines, the present study was undertaken to evaluate 103 genotypes for 11 agro-morphological traits over two post rainy seasons in 2019 and 2020. Significant variation for quantitative traits was observed with a wide range of coefficients of variation (4.85-26.04%). A broad range of trait values was recorded for grain yield (13.0-152.6 g/plant), seed index (1.0-5.5 g/100 seeds), panicle length (9.2-31.4 cm) and panicle width (3.2-15.0 cm). The genotypic and phenotypic coefficient of variation were found high for panicle length, panicle weight, seed weight and grain yield. A broad sense heritability estimated in this population ranged from 0.79 to 0.99. Among the significant phenotypic correlations, grain yield was strongly correlated with leaf width, stem diameter, panicle width

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and weight. In addition, traits such as stem diameter, panicle weight, panicle width, number of leaves and leaf length showed significantly positive correlations with all other traits. Multivariate methods used in this study identified key traits associated with grain yield and grouped all the genotypes into six major clusters, clearly distinguishing germplasm and mutant derivatives. Among the genotypes studied, IC-288363 and EP-1 germplasm, and M-35–48 mutant exhibited high grain yield and more seed weight. Germplasm and mutant lines demonstrated wide variability for most of the quantitative traits and can be utilised for developing new cultivars or used as parents in the recombination breeding.

Keywords Correlation · Cluster analysis · Genetic diversity · Mutants · Sorghum germplasm

Introduction

Sorghum is the fifth-most important coarse cereal crop grown worldwide for food, fodder, and fuel. It is widely grown in countries across Asia, Africa and America and is known for its wide adaptability to a range of soil types, climatic conditions and environmental stresses such as cold, high temperatures, drought and salinity (Guitton, et al. 2018). It is cultivated on an area of 41.55 million ha, with a grain production of 64.36 million tonnes. The United States ranked first in production (11.37 million tonnes) followed by Nigeria (6.73 million tonnes) and India (United States Department of Agriculture (USDA), 2024). In India, it is the second most dry land crop after pearl millet with an area of 4.10 million ha and production of 4.40 million tonnes and a net productivity of 1100 kg/ha (USDA 2024). Increasing the productivity on marginal lands is a major objective of the breeders by improving the narrow genetic base of the genotypes, such that it can withstand against shootfly, charcoal rot incidence and terminal drought stress (Burow, et al. 2011). Under a changing climate scenario, there has been a drastic reduction in area and production due to the delayed onset of early rains, increased pests and diseases, and depleting residual soil moisture during maturity (Badigannavar et al. 2018). In addition, there is a need for the diversification of sorghum grain for feed and other industrial applications. Such challenges could be addressed by ensuring stable grain yields for both landraces and cultivars under diverse agroclimatic conditions. Such stable genotypes with wider adaptability would help in expanding their cultivation in non-traditional areas.

The cultivated sorghum is said to have originated in the north-east part of Africa, mostly around the region between Ethiopia and Sudan, where it was domesticated (Doggett 1988). The pattern of genetic diversity present in the sorghum genus can be characterized by a range of morphological, physiological, and biochemical adaptations developed by the plant to withstand against varied environmental aberrations (Borrell, et al. 2006). Such adaptations have led to evolutionary diversification into distinct racial groups such as bicolor, durra, kafir, caudatum, and guinea (Doggett 1988). Bicolor and durra types are predominantly grown in India, while guinea and caudatum are prevalent in Ethiopia and Sudan. Species belonging to the Kafir race are mostly grown in northern America (Harlan and deWet 1972). A diverse collection of sorghum germplasm (52,757) lines consisting of the entire gene pool species of all five races is being maintained at the "National Bureau of Plant Genetic Resources" (NBPGR), New Delhi, India (Elangovan and Venkatesh 2023). Looking at the spectrum of genetic diversity present in the germplasm and their inter-crossability, several populations have been developed as source of beneficial genetic stocks. Such populations have shown low to moderate diversity for biotic and abiotic stresses and yield-contributing traits (Teshome and Feyissa 2013). In addition, core

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and mini-core collections consisting of diverse germplasm lines have been evaluated for quantitative traits (Upadhyaya et al. 2009), which could be used as potential donors for genes related to resistance to pest and diseases, grain yield, and seed quality traits (Qualset et al. 1997).

In India, sorghum is cultivated in two seasons, and grains harvested in the rainy season are inferior in quality due to persistent rains and diseases during the seed filling stage. It is mainly utilized for livestock feed and industrial purposes. Whereas, grains harvested during the post-rainy season are used for human consumption due to their premium grain quality features. Wide genetic variability is observed for both pre and post rainy season grown sorghum landraces, which breeders can choose as the desired parents for developing heterotic hybrids (Adugna et al. 2002; Kalpande et al. 2021). In this direction, several national-level breeding programs were initiated on a pilot basis and developed high-yielding cultivars or hybrids by collaborating with state agriculture universities. Such crop improvement programs are valuable for integrating various breeding methods to develop elite genotypes by harnessing potential genes of commercial importance. In sorghum, selection of dwarf lines and exploitation of cytoplasmic-genic male sterile lines led to the development of high yielding hybrids (Dahlberg 2000). Further, hybridization and backcross programs involving well-adapted landraces, germplasm lines, and exotic genotypes resulted in the development of cultivars and inbred lines (Prasad Rao et al. 1995). Utilization of zera zera lines and USDA sorghum conversion programs has led to the development of agronomically important lines (Rosenow et al. 1995). Resistance to midge and downy mildew was achieved by introgression leading to stabilized sorghum genotypes in Australia and Argentina. For most of the sorghum improvement programs, zerazera lines from Ethiopia, Sudan and India have contributed to the development of multiple disease-resistant lines. Most of the improved cultivars were the result of pure line selection practiced in key local cultivars. Local x local hybridization followed by selection resulted in cultivars with a marginal increase in grain yield (Rao 1972). Notably, temperate x temperate and temperate×tropical crosses have increased the number of commercial hybrids since the 1960s. In this context, assessment of genetic variability has become important in identifying suitable parents





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ORIGINAL ARTICLE



Harvesting low grade waste heat through environment friendly n-Ag₂Se/p-MgAgSb based thermoelectric module

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Abstract

The majority of the primary energy in any process is wasted as low-grade heat (< 373 K). Thermoelectric power generators are ideally suited for conversion of such low-grade waste heat into electricity. So far Bi_2Te_3 -based alloys based thermoelectric generators are commercially ruling such energy conversion applications. From long term commercial sustainability point of view the scarcity of elemental Te in earth crest and the presence of heavy element Bi are issues of concern. Here we report environment friendly and Te free n-Ag₂Se and p-MgAgSb combination as an alternative to the Bi_2Te_3 -based alloys. The mechanically strong and low specific contact resistivity electrical contacts based on Ni and Ag were directly bonded on Ag₂Se and MgAgSb respectively using deformation bonding method. For a temperature difference (ΔT) of ~82 K, the unileg device displayed a conversion efficiency of ~1.9% that is comparable to the state-of-the-art Bi_2Te_3 -based thermoelectric module for a similar ΔT . Finally, a thermoelectric power generator module comprising of 18 p-n legs was coupled with a DC-DC boost converter for demonstration an application by harvesting low grade waste heat.

1 Introduction

World wide 72% of the primary energy is wasted as heat and among that 63% of the waste heat sources have temperatures below 373 K [1]. Such low temperature heat sources include vehicle exhaust, heat exchangers in a variety of industrial

Highlights

1. Environment friendly Te free economic thermoelectric

materials for sustainability are studied.

2. Low specific resistivity contacts were prepared on n-type Ag 2 Se and p-type MgAgSb.

T ~82 K was demonstrated.

 Low temperature operable thermoelectric module with DC-DC boost converter projected as a portable power source for IoT devices.

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processes, body of refrigerator, hot water springs, boilers, and human body, etc. Thermoelectric power generator (TEG) is a solid-state device comprising of p-n couples connected electrically in series and thermally in parallel, which can directly convert such waste heat into electrical energy (through Seebeck effect) [2-5]. Considering the large amount of low-grade waste heat emitted by the industrial sources (source temperature <373 K) the efficient TEG devices operating at low temperatures plays an important role. The development of an efficient TEG requires p- and n-type high figure-of-merit (ZT) thermoelectric materials having electrically and thermally transparent interfaces with the metallic interconnects [6]. So far, the Bi₂Te₃ based alloys are the conventional champion thermoelectric materials for harvesting low grade waste heat [7-9], however scarcity of Te in earth crest, poor ductility, toxicity of heavy element Bi, and high cost motivated the researchers to find alternative Te free materials. Recently, the high thermoelectric performance shown p-type MgAgSb based material suggest them as a promising alternative for the traditional Bi2Te3 alloys due to their compatible thermoelectric properties, excellent mechanical robustness, nontoxic nature, abundance of constituent elements [10]. The MgAgSb materials has a low temperature (≤600 K) semiconducting α -phase which exhibit high ZT due to intrinsic low lattice thermal conductivity. The mid-temperature range β-phase of MgAgSb is metallic and hence exhibits very poor thermoelectric properties [11]. In MgAgSb by substituting small size



^{3.} A uni-couple device exhibiting efficiency of ~1.9% at Δ

Mg with large Pb atoms, 40% improvement in ZT (~0.9 at 475 K) was witnessed [12]. Through Zn doping and long-term heat treatment a tremendous enhancement of average ZT up to 1.4 at 423 K is observed in the Mg_{0.97}Zn_{0.03}Ag_{0.9}Sb_{0.95} bulk [13]. Using Cu doped n-type Mg32Sb15Bi049Te001Cu001 and p-type Mg0.99Cu0.01Ag0.97Sb0.99 Liu et al. demonstrated a module having 8 p-n legs with a promising conversion efficiency of 7.3% at a temperature difference of 300 K [14]. A uni-leg device of p-MgAgSb with silver contact pads reported by Kraemer, et al. showed efficiency of ~8.5% for a temperature difference of 225 K [15]. In a very recent study by using AgMgMn_{0.1} as buffer layer between MgAgSb and metallic contact layer conversion efficiency of 9.1% was achieved at a temperature difference of 325 K [16]. It is important to mention that in all these studies the p-type MgAgSb is either studied individually or integrated with n-Mg3,2Sb1,5Bi0,5, which has Bi as a major constituent and Te added as a dopant. Recent studies suggest that Ag2Se is a low band gap n-type material exhibiting promising ZT near room temperature and show considerable application potential in wearable thermoelectrics [17-19]. The concept of phonon glass and electron crystal (PGEC) is very much relevant to Ag₂Se owing to it high electrical conductivity arising from intrinsic Se vacancies and low thermal conductivity due to phonon scattering through the disordered mobile Ag+ ions.20 The strategies employed to improve the ZT of Ag2Se-based bulk materials includes manipulation of the Ag/Se stoichiometry [21, 22], doping [23], introduction of secondary-phase in the matrix of Ag₂Se [24]. Recently Ahmed et al. showed a high ZT of 1.1 at 300 K in Al doped Ag2Se and a uni-leg device fabricated using Ag195Al005Se with electroplated Ni/Ag contacts showed a conversion efficiency of ~3.2% at a very small temperature difference of 93 K [25]. In a recent work by Jakhar et al. it has been demonstrated that with a simple scalable room temperature technqiue highly density Ag₂Se with reproducible thermoelectric properties can be realized [26]. The only issue with Ag₂Se is that it exhibits orthorhombic-cubic phase transition accompanied by onset of Ag⁺ ionic conduction at temperature ≥400 K that is detrimental for practical applications of Ag2Se at high temperature [27]. Considering the high ZT of Ag₂Se near room temperature, it is imperative to develop the TEG from earth abundant environment friendly materials (n- Ag,Se and p-MgAgSb) for harvesting low grade waste heat (temperature < 373 K). To the best of our knowledge so far there is no report on the development of TEG by combining environment friendly n-Ag₂Se and p-MgAgSb thermoelectric materials.

2 Material synthesis

In this work, we have synthesized n-type Ag₂Se and p-type MgAgSb materials using simple scalable process and fabricated a uni-couple as well as TEG module comprising of 18

چاممة قطر VATAR UNIVERSITY p-n couples. The reliable and mechanically strong and low specific contact resistivity Ni and Ag based electrical contacts were directly bonded on Ag₂Se and MgAgSb respectively using vacuum hot-press sintering.

The n-type Ag₂Se was prepared using vibration milling method. The constituent materials such as Ag (Purity: 99.9%) and and Se (Purity: 99.9%) metal powders (mesh size 100 micron) first loaded in a stoichiometric ratio (Ag: Se = 2:1.06) in a stainless-steel (SS) jar with SS balls. As per the reported literature, excess Se (0.06 mol) was taken to compensate for the loss of Se during vacuum hot pressing of the samples [21]. The Ag and Se filled in a SS jar was placed in a vibration mill and rocked for 6 h (5 min. hold after each hour) leading to formation of single phase Ag2Se [26]. The Ag₂Se powder was hot pressed with Ni powder (Purity: 99.9%) in a SS die set to form electrical contact at both ends of the hot-pressed pellet. Vacuum hot pressing is performed in a resistive heating furnace with a heating rate of 4°C/min at 350°C for 10 min with load of 33 MPa. During hot pressing the base pressure in chamber was 5×10^{-3} mbar. The cooling of furnace was 5°C/min. The density of hot-pressed pellet was found to be ~7.9 g/cc, which is 96% of theoretical density.

The MgAgSb was prepared by using vacuum melt technique. The constituent materials such as Ag (Purity: 99.9%), Sb (Purity: 99.8%), Mg (Purity: 99.8%), and Ni (Purity: 99.9%) were mixed in stoichiometric ratio of Mg: Ag: Sb: Ni as 1.23: 0.995: 1.02: 0.005 and packed in a lid tight Graphite crucible. To maintain the stoichiometry of Mg in MgAgSb sample an additional 23% of excess Mg (15gm MgAgSb) and 2% excess of Sb were taken to compensate for its loss during melting process. The excess Mg enhances the thermoelectric properties due to Ag vacancy along with the reduction in the content of secondary phases (Sb and Ag₃Sb) [28]. The Graphite crucible containing stoichiometric constituent materials (Mg, Ag, Sb, Ni) was vacuum sealed inside a quartz tube and this tube is loaded in a rocking furnace. The vacuum sealed crucible was heated up to 1000°C at a rate of 55°C/h. At 1000°C the material was rocked for 6 h and after that it is air quenched and rapidly cooled to 325°C and annealed for 120 h to form the desirable room temperature α -phase of the material. Finally, from 325°C it is cooled to room temperature at a rate of 50°C/h. Obtained ingot was grinded to make fine powder and checked for phase purity using XRD. The MgAgSb powder was hot pressed with Ag powder (Purity: 99.9%) to form electrical contact at both ends of the pellet. Hot pressing is done at 350°C for 3 h with a load of 120 MPa. The density of MgAgSb pellet was found to be 6.15 g/cc which is 98% of reported density of 6.28 g/cm-3 [15]. In the later part of manuscript, the samples Ag2Se1.06 and Mg1.23Ag0.995Sb1.02Ni0.005 prepared in







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High-entropy alloys for nuclear applications

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ABSTRACT

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High-entropy alloys (HEAs) because of their attractive properties, provide a unique opportunity to develop materials suitable for structural applications in the harsh environment (high-temperature and intense irradiation) prevailing in Gen IV nuclear power reactors. HEAs based on refractory elements (RHEAs) can display excellent stability at high temperatures and superior irradiation resistance due to the BCC-based structures obtained in most alloys. In this regard, the design and development of RHEAs based on the ZrNbVTiAl system have been actively pursued at BARC. Detailed characterization of microstructure and mechanical properties of these alloys having equiatomic and non-equiatomic compositions have been carried out. The study revealed the possibility of attaining significantly higher strengths up to 1.25 GPa and excellent fabricability as a result of dynamic recrystallization at high temperatures. In addition, the dissolution of AlZr-type intermetallics was observed after proton irradiation which helped in bringing the system towards a single-phase BCC structure.

Introduction

Nuclear energy has been crucial in supplying the world's energy needs, as it provides clean, dependable and sustainable power that has a potential to significantly meet the ever increasing energy demands for present and future generations [1]. Traditional nuclear power plants, like *Pressurized Heavy Water Reactor* (PHWR) or *Pressurized Light Water Reactors* (PWRs) have long met the aforementioned objectives, but they have a lower efficiency (<30%) and are bulky in dimension [1, 2]. With emphasis on reduction in carbon foot print, advanced nuclear reactors offering enhanced safety, efficiency and reduced environmental impact

https://doi.org/10.1007/s10853-024-10511-z Published online: 22 December 2024 have been proposed [3]. These reactors encompass a diverse range of designs, including liquid metal cooled fast reactors, molten salt reactors (MSRs), high-temperature gas cooled reactors (HTGRs) and small modular reactors (SMRs), each with unique demands on materials to ensure their functionality and longevity [4, 5].

However, full realization of their benefits hinges upon the meticulous selection and development of materials that can withstand extreme environments prevailing in these advanced nuclear reactors [6]. Materials utilized in such advanced reactors must endure high temperatures (500–800 °C), non-aqueous corrosive environments and intense radiation exposure (~ 100 dpa) [6, 7]. Conventional materials fall



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short in meeting these demands, necessitating development of advanced alloys, ceramics and composites with enhanced resilience and performance. Structural integrity and reliability of these materials are critical to ensure long-term viability and safety of advanced nuclear reactors [8].

In this context, high-entropy alloys (HEAs), which represent a revolutionary class of materials that deviate from conventional alloy compositions by incorporating multiple elements in nearly equal proportions, could provide a solution [9]. It may be noted that irradiation imparts defects in materials which induce a disorder into the system, thereby increasing its entropy. This is the one of the primary reasons why ordered alloys, though having attractive properties, have never been considered for reactor applications [10]. In this backdrop, HEAs provide a unique opportunity, as the alloys are already in the state of high entropy and thus cannot be subjected to further substantial increase in their entropy by irradiation [11]. Therefore, the entropy-driven stability contributes to the unique thermodynamic and phase stability of HEAs under extreme environments including irradiation [12]. In addition, HEAs characterized by the multiple principal element approach can present several advantages like significantly high melting points, enhanced high-temperature mechanical properties, and improved irradiation and corrosion resistance which make them a compelling alternative to Zircaloy in advanced reactor designs [11-14]. Furthermore, the ongoing worldwide research in the field of HEAs have uncovered several new compositions and processing techniques, expanding their potential applications in nuclear reactor technology [11-21].

In this regard, certain HEAs consisting predominantly of refractory elements such as Nb, V, Zr, Ta, Hf, Mo and W, commonly referred as refractory highentropy alloy (RHEA) has been recently emphasized as promising materials for the next-generation hightemperature reactors [14]. These RHEAs exhibit better high-temperature performance due to the high melting points of constituent elements and superior radiation resistance due to their BCC-type structures which are inherently resistant to irradiation swelling [15]. Recently, considering applications in high-energy neutron environment (e.g. in fusion reactor), a very recent separate class of low-activation HEAs (LAHEAs) have been proposed as an alternative to low-activation ferritic/martensitic steels [16]. Table 1 categorizes common alloying elements in structural materials according to

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their radioactive decay time limit when subjected to high-energy fusion neutrons [17]. As per the accepted criterion by fusion community, the radioactivity of materials used in the fusion blanket should reduce to an acceptable limit (safe for disposal in geological repository) within 100 years [18, 19].

It could be observed from Table 1 that only a few of the common alloying elements like W, V, Ta, Ti, Cr, V, Mn, Fe and Si satisfy this criterion and thus are known as low-activation elements which form the major constituents of LAHEAs. These HEAs not only possess high melting temperatures, superior mechanical properties and good oxidation resistance but also minimize the quantity of radioactive wastes. Their potential to function beyond the maximum operating temperature of current materials (e.g. ~ 550 °C in ferritic/martensitic steels restricted by its creep) makes them suitable for various components in fusion reactor-like plasma facing material, diverters, etc. [20].

In this aforementioned backdrop, a comprehensive programme has been initiated at Materials Group, BARC to develop HEAs based on refractory elements (i.e. RHEAs) for advanced nuclear reactor's applications, and the key activities and findings from this research work have been highlighted in this paper. It may be noted that HEAs belonging to the RHEA category are associated with specific challenges in their synthesis primarily due to the high melting point of refractory elements [15, 21]. Therefore, before examining the suitability of such alloys, challenges associated with the synthesis of this class of alloys need to be addressed. The present paper addresses some of these issues like selecting a right composition, introducing innovative processing routes like levitation melting

Table 1 Radio-active decay time of common alloying elements when subjected to high-energy neutrons as in fusion [19]

I-10 years	10– 50 years	50 100 years	100 300 years	\geq 300 years
Au	Ti	v	Co	Zr
	Та	Mn	Hf	Nb
	W	Fe	Al	Mo
	Cr	С	Cd	Ni
	Pb	Mg	Na	Cu
	Ge	Si	S	Zn
			Р	Sn
			В	Ag
				Te





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ORIGINAL ARTICLE



Improved thermoelectric performance of nanostructured tellurium thin films

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Abstract

We report nanostructured Te thin film exhibiting a high figure-of-merit (*ZT*) of ~0.34 at 493 K. The films exhibit temperature enhanced electrical conductivity~43 Scm⁻¹, very high Seebeck coefficient of ~385 μ V⁻¹K⁻¹ contributed by non-degenerate valence bands and low thermal conductivity~0.9⁻¹ Wm⁻¹K⁻¹ through suppression of bipolar effect. The *ZT* of nanostructured films is ~142% higher than the annealed films having larger grain size. The high Seebeck coefficient (~405 μ V⁻¹K⁻¹) of nanostructured Te films near room temperature prompted us to make a device, which was subjected to a very small temperature difference of ~4 K by touching with finger and produced an open circuit voltage of ~18 mV. The periodic generation of this open circuit voltage with fast response when repeatedly touched with finger, suggest the utility of these films in real time human touch applications and temperature sensing.

Keywords Thermoelectrics · Band convergence · Phonon scattering · Nanostructuring · X-ray photoelectron spectroscopy · Touch sensor

1 Introduction

The conversion efficiency of a thermoelectric material is expressed by the dimensionless figure-of-merit (*ZT*), which is defined as $ZT = \alpha^2 \sigma T/k$, where the thermoelectric parameters: Seebeck coefficient (α), electrical conductivity (σ) and thermal conductivity (κ) are functions of absolute temperature (*T*). Total thermal conductivity κ has electronic (κ_e) and lattice contriutions (κ_i) [1–6]. As thermoelectric parameters α , σ and κ are strongly coupled with each other, increase in one of these three parameters usually leads to a decrease in the other parameters. Considering these facts, minimizing the κ_i , has been proved to be one of the indpendent effective strategies for improving *ZT*, hence all well established

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thermoelectric matrials are alloy semiconductors (e.g. Bi₂Te₃, PbTe, GeTe etc.). Elemental Tellurium (Te) is an intrinsically p-type semiconductor with narrow band gap of ~0.34 eV in bulk state and with decreasing the thickness the band gap can enhanced from 0.34 eV to 0.92 eV [7]. The detailed band structure calculations for Te shows the presence of nested valence bands (similar to band convergence reported in SnTe, PbTe etc.) in Te that give rise to conduction channels for holes [8]. The presence of such degenerate valence bands in Te contributes in simultaneous enhancement of Seebeck coefficient (a) and electrical conductivity (σ) resulting in high power factor ($\alpha^2 \sigma$). The Te has tendency to grow in the one dimensional (1D) nanostructure (along c-axis) due to inherent structural anisotropy [9]. In a recent ab initio calculation based on density functional theory, it has been suggested that bulk Te has the potential to be a good p-type thermoelectric material with an optimum figure-of-merit (ZT) of ~ 0.31 (0.56) at room temperature (500 K) at an optimized hole concentration around $\sim 1 \times 10^{19}$ cm⁻³ when the transport is measured along c-axis [10]. For a similar carrier concentration the value of ZT perpendicular to c-axis is slightly lower~0.2 (0.42) at room tempearture (500 K). Lin et al. demonstrated $\kappa_1 \sim 1.5$ W K⁻¹m⁻¹ and ZT ~1 (at 600 K) in arsenic doped

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polycrystalline bulk Te [8]. In another study alloying bulk Te with a small amount of Sb resulted in a high ZT of ~ 0.9 at 600 K [11]. Undoped Te exhibits a deterimental bipolar effect on ZT which becomes weaker as the carrier concentration increases by doping. In a recent study, Decheng An et al, showed that the limited solubility of dopant As, Sb and Bi in Te results in formation of dopant induced metavalently bonded telluride precipitate in Te matrix [12]. The telluride/Te interfaces act like a charge reservoir for the Te matrix and due to favourable energy level alignment at these interfaces high electrical conductivity can be achieved.

Nanostructuring provides an opportunity to improve thermoeletric performnace by decoupling electrical and thermal transport properties [13, 14]. Inspite of such known adavntages of band converegence and nanostructuring the thermoelectric properties of Te as thin film (2D nanostructure) are less reported. However recently by vacancy engineering a high ZT~0.4 (at 400 K) is achived in 2D Te nanosheet [15]. In another work, the free standing flexible Te film exhibiting power factor of 3.2 Wcm⁻¹K⁻², $\kappa_1 \sim 4.38 \text{ W K}^{-1} \text{m}^{-1}$ resulting in ZT value of 0.02 near room tempearture was reported [16]. In a very recent work [17], using an aqueous solution synthesis approach, Te nanowires were synthesized and subsequently surface modified using sulfur moieties, demonstrating sulfur passivation not only safeguards the nanowires from environmental degradation but also enhancing their thermoelectric properties. For passivated tellurium nanowires, a Seebeck coefficient of 246 µV/K, electrical conductivity of 14.2 S/cm and power factors of 86.7 $\mu W/m\text{-}K^2$ were obtained at 560 K. In the arena of portable power source application, apart from traditional thermoelectric devices (bulk and flexible), another type of useful devices is Thermopower waves (TPWs) [18-20]. TPWs are relatively new concept of direct conversion of chemical energy into electrical energy by means of selfpropagating reaction waves guided along nanostructured thermal conduits. Interestingly Quantum confined materials such as CNT (carbon nanotubes) and graphene, due to the anisotropy in the transport properties, play ideal role in such kind of application. Te has natural nano structures and anisotropic TE properties such as thermal and electrical conductivity [10] and thus can be useful in future TPWs applications. Besides, by suspending TPW devices within an airgap flanked by parallel flexible or bulk TEGs can capture the radiative and convective energy losses very easily and thus can be beneficial in tapping additional waste heat [19].

Using Debye-Cahill model the minimal lattice thermal conductivity (κ_1^{\min}) for bulk Te is reported as $\sim 0.3^{-1}$ Wm⁻¹K^{-1.8} Comparing the experimentally achieved κ_l [15] with theoritically predicted κ_1^{\min} of $\sim 0.3^{-1}$ K⁻¹ suggest that there is huge scope of reduction in κ_1 of Te through

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nanostructuring strategy and grain boundary scattering and consequently an increase in ZT is expected. In another recent work [21], via. ab initio calculations, the effects of intervalley scattering on electron-phonon interaction and higher-order four-phonon interactions of α -Te and β -Te are investigated and it was shown that the strong intervalley scatterings suppress the lattice thermal conductivities of a-Te (1T-MoS₂-like structure) and β-Te (2H-MoS₂-like structures) by as much as 10.9% and 30.8%. The result further demonstrates that contributions of intervalley scattering to the electronic properties and thermal transport properties in band convergent thermoelectric materials such as Te, makes them potentially promising candidate for advanced thermoelectric applications. In the present work we report an enhnaced ZT of ~0.34 at 493 K in nanocrystalline Te thin films (thickness~120 nm) and the main contribution in such an improved ZT comes from high electrical conductivity~43 Scm⁻¹, high Seebeck coefficient~385 μ V⁻¹K⁻¹ and ultra low $\kappa \sim 0.9^{-1}$ K⁻¹ at 493 K through the supression of bipolar effect.

2 Experimental details

For preparation of Te thin films, elemental Te was deposited on Thin Film Analyzer chip (TFA chip shown in inset of Fig. 1(a), procurred from Linseis Germany) and flexible polyimide sheet by thermal evaporation technique keeping substrates at 300 K under high vacuum conditions (base pressure $\sim 2 \times 10^{-5}$ mbar). Another Te film sample was grown in identical experimental conditions except this time it was grown and in-situ anneald at 473 K (for 30 min) after deposition. In the later part of manuscript the room tempearture grown Te films will be termed as Te^{300} and 473 K grown and annealed film will be termed as Te473. The measurement of temperature dependent in-plane thermoelectric parameters α , σ and k were done using thin film analyzer (TFA, Linseis make) set-up. In the same setup, Hall coefficient, Hall carrier concentration (n), charge carrier mobility (μ)) etc. can also be measured simultaneously [22–24].

3 Results and discussion

The temperature dependent thermoelectric properties of both Te³⁰⁰ and Te⁴⁷³ films are shown in Fig. 1. It can be seen from Fig. 1(a) that both films shows nearly similar electrical conductivity (σ) at room temparture and it increases with tempearture. The enchnacement rate of σ with tempearture is higher for Te³⁰⁰ films. The α shows positive sign for both films suggesting holes are the majority carriers. For Te⁴⁷³ films the α increases with temperature and at around 425 K





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Isotope characterisation of groundwater resources in uranium impacted Fazilka, Punjab

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Abstract

Groundwater is the most reliable source for freshwater supplies in India and abroad. Population rise has affected the groundwater resources both in terms of quality and quantity. Punjab, being an agrarian state, is highly dependent on groundwater resources for both irrigation and drinking purposes. Recent studies have indicated presence of uranium in groundwater especially in southwestern parts of Punjab. In this research, water samples were collected from Fazilka district of Punjab for evaluating the water quality focussing uranium and identifying source and recharge processes of groundwater. Uranium concentration was found in both shallow and deep groundwater samples. Inter-ionic correlations signify that alkalinity and electrical conductivity of the water samples control the uranium mobilization from the aquifer matrix. Isotopic systematics demonstrate that groundwater recharge is mainly through rainwater infiltration.

Keywords WHO limit · AERB limit · Uranium · Stable isotope · Isotopic characterisation · Groundwater recharge

Introduction

Demand of fresh water is exponentially increasing due to population growth and associated water needs. Sustainable supply of fresh water is a major concern in many parts of the world especially in the developing countries. Groundwater is the most promising source of fresh water and heavy pumping coupled with improper management of these resources has led to quality and quantity issues. Declining water levels, increased salinity, contamination of nitrate, fluoride, arsenic, iron, and heavy metals are some of the major groundwater issues in India. Uranium is ominous in soils, water and rocks and its abundance is 2.8 ppm in earth crust. Uranium is mostly abundant in silicic igneous rocks such as rhyolites and granites, sedimentary rocks that are high in organic carbon and phosphorus such as black shale, lignite, and phosphorites.

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There are many other uranium deposits distributed all over the world. International Atomic Energy Agency (IAEA) has classified the uranium deposits in 15 categories [1]. Three naturally occurring radioactive isotopes of Uranium, namely 238U (99.27%), 235U (0.7%) and 234U (0.005%) have different radiological properties but similar chemical properties. 226Ra, and 222Rn, are the decay products of 238U with short half-lives, they are also known to causes cancer. Prolonged consumption of water with high uranium concentration can cause blood, lungs and kidney cancer [2]. Considering both chemical and radiotoxicity, there are two health-based limits for uranium in drinking water. World health organisation (WHO) has recommended maximum allowable drinking water limit of 30 µg/L based on chemotoxicity while Atomic energy regulatory board (AERB) has suggested uranium water levels up to 60 µg/L in drinking water based on radiotoxicity, signifying uranium is more harmful as a trace heavy metal altering the enzymatic functions at cellular levels than as a long-lived alpha emitting radioisotope [3, 4]. The most stable oxidation state of uranium in aqueous medium is U(VI), which normally exists as uranyl oxide (UO22+) and stabilised by counter anions such as bicarbonate, nitrate, fluoride in groundwater. Uranium in +4 oxidation state is immobile in the host rock. However, weathering process oxidize the uranium from +4 to +6 species and depending upon the

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availability of the counter ions, stable and soluble uranium complex form and move along with groundwater flows. Uranium mobilisation is highly dependent on pH and redox environment of water. In neutral to alkaline environment (pH = 7–9) and under oxidation environment uranium gets oxidised and comes to water. Under reducing environment (i.e. high Fe²⁺ and SO₄²⁻), uranium gets precipitated as UO₂ [5].

A recent report by Central Ground Water Board (CGWB) (2022) has indicated presence of uranium in groundwater samples of 12 states in India, including Punjab. Many studies have been conducted in Punjab with respect to groundwater quality and health risks associated with uranium toxicity [6, 7]. Uranium concentration of about 350 µg/L was reported in groundwater of Ferozpur and Moga districts of Punjab [6, 7]. Similar levels of uranium concentration were also reported in Bhatinda and Mansa districts [8]. The authors found that shallow aquifers are more affected with respect of uranium compared deep aquifers. Groundwater in Faridkot and Muktsar districts also indicated uranium concentration up to 190 µg/L [9]. In 2022, Sahoo et al. proposed that high total dissolved solid (TDS) and salinity are favouring factors for uranium mobilization in alluvial plains of Malwa region [10]. The hydrochemical studies performed in this area, suggest that source of contamination is mainly geogenic in nature [8, 9].

In addition to uranium, lead and arsenic contamination in groundwater is also reported in Fazilka district of Punjab [11]. Researchers have indicated that uranium concentration in groundwater of Fazilka show very high variation from 84 to 366 µg/L [12, 13], which could be due to discrepancy in, choice of different sampling sites or other hydrogeological factors. Therefore, it is important to identify the actual distribution of uranium concentration in groundwater and the factors governing its mobilization. In addition, the hydrogeological processes governing the distribution of groundwater within the aquifer system is also very crucial for planning sustainable water resources management.

In depth knowledge of aquifer recharge mechanism, origin of groundwater and its residence time can help in assessing the factors controlling groundwater quality and possible sources of contamination. Environmental stable isotopes are commonly employed to understand the hydrological processes and ²H and ¹⁸O of water act as most important tracers of hydrological cycle. The abundance of heavier isotopes in water is affected by processes involved in water cycle. During evaporation process the liquid phase gets enriched in heavier isotopes while lighter isotopes goes to vapour phase due to difference in their zero-point energies i.e. isotopic fractionation. However, in the event of precipitation, heavier isotopes tend to condense preferentially. Thus, rain water gets more and more depleted with respect to (w.r.t) heavier isotopes in water that is (i.e.) ¹⁸O and ²H. The depletion

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depends on temperature, latitude, altitude and extent of rainfall. The isotopic ratio is defined by δ values which is defined as Eq. (1).

$$\delta(\%c) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{sample}}} \times 1000 \tag{1}$$

Here, *R* is ratio of heavy to light isotopes, e.g. ¹⁸O/¹⁶O and ²H/¹H. Vienna Standard Mean Ocean Water (VSMOW) is an IAEA standard used for water samples. δ^2 H and δ^{18} O values in this standard are assigned to 0%*e*. In 1961, Craig measured precipitation samples throughout globe and plotted δ^2 H and δ^{18} O values. The data points were found to lie along a straight line indicating positive correlation. The best fit line drawn from this data is known as Global Meteoric Water Line (GMWL), %*e* which is represented by the following Eq. (2) [14]

$$\delta^2 H = 8 \times \delta^{18} O + 10\%$$
(2)

The data points falling close to GMWL in δ^2 H versus δ^{18} O plot suggest meteoric nature of water samples. Any deviation from GMWL suggests modification due to various physical and chemical changes before or after the water enters the subsurface. For example, if isotope data fall below GMWL with reduced slope then the water samples reflect their recharge from evaporated water source. On the other hand, Sample data falling above the GMWL suggest recharge from recycled moisture sources or higher altitude precipitation [15].

Study area

The district of Fazilka is located at south eastern part of Punjab and shares borders with Ferozpur in north, Muktsar and Faridkot in east, Rajasthan in south and Pakistan in the west. It covers an area of 3113 km² between 39° 39.6' N to 29° 57' N and 73° 52' E to 74° 27' E. The study area has a semi-arid type of climate with very hot summer and an average annual rainfall of 244 mm [16]. This area is a part of Indo-Gangetic Alluvial Plain and Flood Plain of Sutlej river with a flat region and a mild sloping towards southwest direction. The study area is covered by Quaternary sediments deposited by Sutlej river which flows through north west of this area. Aeolian alluvium and younger alluvium constitute the major aquifers in this area. The groundwater in unconfined condition up to 30 m and aquifer up to the depth of 175 m is found to be leaky. Water from aquifer below the depth of 200 m are confined with saline pockets [17].





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Regular Article - Experimental Physics

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Mass distributions in ${}^{12}C + {}^{232}Th$ fission: role of shell effects and excitation energy

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Abstract This article reports the measurement of cross sections of charge and mass identified fission products and the mass distributions in 232Th(12C,f) reaction at 62.5, 70.7 and 102.9 MeV beam energies to investigate the role of single particle effects. The study was carried out using the recoil catcher technique followed by off-line y-ray spectrometry. Cross sections of 32, 54 and 64 fission products were measured for 62.5, 70.7 and 102.9 MeV beam energies, respectively. The mass distributions obtained at 62.5 and 70.7 MeV show a flat-top nature indicating significant asymmetric fission contribution (heavy mass peak corresponding to Z range of 54-56), whereas, a nearly Gaussian behaviour was observed at 102.9 MeV indicating dominant contribution from symmetric fission. The experimental mass distributions were in gross agreement with the "GEF, 2021/1.1" calculations which predicted significant asymmetric fission contribution dominated by $Z \approx 55$ ('Standard 2' mode) at 62.5 and 70.7 MeV. The present study shows the significant role of charge polarization resulting in the deviation of the most probable charge (Z_P) values from those obtained using UCD hypothesis. "GEF, 2023/2.1" calculations were unable to explain the observed mass distributions with significant asymmetric fission contribution due to comparatively lower contribution from higher chance fission resulting from the lower saddle point energies. An attempt has been made to estimate the mass distributions arising from the complete fusion fission and a-transfer induced fission. The trend shows an increase in the α -transfer induced fission contribution with increasing beam energy which is in qualitative agreement with the sum-rule model calculations.

1 Introduction

Study of the mass yield distribution of charge and mass identified fission fragments/products plays an important role in understanding the mechanism of nuclear fission. The presence of the neutron and proton shells guides the formation of the fission fragments/products to a large extent at low to moderate excitation energies. Some of the important observations, like the formation of fission isomers and the new magic numbers in the exotic nuclei, are the results of the shell effects [1, 2]. Recent studies in nuclear fission have been mainly focused on investigating the role of neutron and proton shells in governing the fission process, and it has been proposed that the proton shells have a dominant role in guiding the nuclear fission process [3-5]. The effect of the proton and neutron shells has been found to exist up to several tens of MeV of excitation energy in the actinide and the pre-actinide region [4-7]. With increasing excitation energy of the fissioning system, the shell effect has been found to be gradually washed away along with the increase in the contribution of symmetric fission [8]. Thus, study of the nature of the mass yield distribution as a function of excitation energy can provide useful information regarding the role of shell effects. The mass yield distribution in heavy-ion induced fission of actinides is dominated by the Gaussian distribution which mainly arises from the complete fusion fission (CFF) process [9]. However, along with the CFF, there can also be transfer of nucleons from the projectile to the target, which may result in fission if the target like nucleus is sufficiently excited. Many studies reveal the presence of different transfer induced fission (TF) channels [10-18]. The mass distribution arising from the TF process is expected to be asymmetric due to the low excitation energy of the fissioning nucleus due to partial energy transfer to the target nucleus. In off-line measurements of the

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mass yields, the fission products having contribution from TF can be identified based on their A/Z ratio [16, 17]. Gubbi et al, reported the presence of TF in ¹⁹F + ²³²Th fission at beam energies of 95 and 112 MeV and showed that the contribution from TF relative to CFF decreases with increasing beam energy [17]. Gubbi et al. [17] and Sodaye et al. [18] obtained the contribution from TF by fitting a Gaussian curve to the mass yields corresponding to the products formed exclusively by CFF, and subtracting the CFF yields from the overall product yields to obtain the contribution from TF. Hogan et al. [19] and Todd et al. [20] used the measured ratio of the velocity of the compound nucleus to that of the fission fragment to fractionate the mass yields into CFF and TF components. The contribution of transfer induced fission in the fission fragment angular distribution for ${}^{13}C + {}^{232}Th$ and ${}^{12}C + {}^{232}Th$ system has been studied using the fission fragment folding angle measurement by Ajith Kumar et al. [21] and Mein et al. [22], respectively. At near and sub-barrier energies, the mass distribution may not show a Gaussian behaviour which may be due to the contribution from both CFF and TF having strong shell effects. However, the mass distribution shows a broad Gaussian behaviour at higher energies which can be attributed to the dominant contribution from the symmetric fission with the contribution from various transfer induced fission channels.

With the semi-empirical code GEF ("GEneral description of Fission observables") [23, 24], it is possible to obtain information about the pre-neutron as well as the post-neutron mass yields, fission fragment and product yields, prompt neutron emission, isomeric yields and other observables related to nuclear fission. GEF is a Monte-Carlo code based on the principles of quantum mechanics, nuclear dynamics and statistical mechanics, and computes the sequential decay of the fissioning system including the possibility of the multichance fission, production of the primary fission fragments, post-scission evaporation and y-ray emission [24]. As mentioned in ref [24], GEF code can be used to predict the fission observables for a wide range of isotopes from Z = 80to Z = 112 and beyond, up to excitation energies of about 100 MeV. The GEF code also provides a description of the processes leading to the formation of an excited compound nucleus in reactions induced by neutrons, y-rays and the charged particles including heavy ions. In the actinide region, GEF considers mainly the four fission channels (modelled as quantum oscillators in the fragment Z degree of freedom) to explain the mass distribution, which are the symmetric super-long (SL) channel, and three asymmetric channels ("standard" S1, S2, and "super-asymmetric" SA) [24]. As the excitation energy of the fissioning system increases, the asymmetric contribution to fission decreases with increasing contribution from the symmetric fission mode. Due to the contribution from multiple reaction channels along with the

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role of different fission modes, calculations with the GEF code can be very useful to investigate the role of different shells in governing the mass distribution, along with the estimation of the contribution from different fission channels.

In this work, the fission product mass distribution in the $^{12}C + ^{232}Th$ reaction system has been studied to investigate the role of the neutron and proton shell closure in governing the fission product mass distribution. Up till now there have been very few studies on the mass distribution of the $^{12}C + ^{232}Th$ reaction [25, 26]. A measurement of the fission product mass distribution in the ¹²C + ²³²Th reaction by Manohar et al. at a beam energy of 79 MeV shows a predominantly symmetric mass distribution [25]. However, a measurement of the fission product mass distribution in the ¹²C + ²³²Th reaction by Ramaswami et al. at a beam energy of 72 MeV shows a large deviation from the Gaussian distribution [26]. These observations suggest the requirement of a systematic study over a broad energy range to obtain a deeper insight of the role of the shell effects in governing the nature of the mass distributions. The experiment was carried out using the recoil catcher technique followed by off-line y-ray spectrometry with the identification of mass and charge of the measured fission products, which can be very useful for the comparison with future on-line measurements of the 12C + 232Th fissioning system using other facilities such as VAMOS++ [27] or gamma detector arrays [28]. Off-line measurements using the y-ray spectrometry have been extensively carried out to measure the fission product cross sections in the recent past [29-35]. In the present study, yields of 32, 54 and 64 fission products have been measured at the beam energies of 62.5, 70.7 and 102.9 MeV, respectively. The contribution from a-transfer induced fission was estimated from the experimentally measured overall yields of the fission products using the respective yield ratios of the fission products, obtained using the GEF code for the fission of ²⁴⁴Cm (formed by CFF) and ²³⁶U (formed by a transfer). The deviation of the most probable charge (Z_P) from that predicted using the Unchanged Charge Distribution (UCD) hypothesis 'ZUCD' [7], has been investigated. A detailed comparison has been carried out between the experimental mass distributions and the GEF calculations predicting contributions from various fission modes governed by the different nucleon shells.

2 Experimental method

The present experiments were performed at the BARC-TIFR Pelletron-LINAC facility at Tata Institute of Fundamental Research, Mumbai, India. Three self-supporting ²³²Th targets of thickness 2.02, 1.88 and 1.95 mg/cm² were used for the irradiation at three beam energies 62.5, 70.7







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Measurement of effective 98 Mo(n, γ) 99 Mo reaction cross-section in the epi-cadmium neutron flux produced by 10 MeV electron LINAC with Ta-BeO assembly

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Abstract

An experiment was carried out to study the feasibility of ⁹⁹Mo production using an electron accelerator based epi-cadmium neutron source. The neutrons were produced by the interaction of bremsstrahlung end-point energy of 10 MeV with BeO blocks and the neutrons thus produced were moderated using High Density Polyethylene blocks. Effective cross-section of ${}^{98}Mo(n,\gamma){}^{99}Mo$ reaction was measured using foil activation method. An enhancement in the effective cross-section due to resonances in the epi-cadmium region was observed. The photons and neutron production/transport in the experimental set-up were simulated using the FLUKA Monte Carlo code. The simulations were found to be in good agreement with the experimental findings.

Keywords ${}^{98}Mo(n,\gamma){}^{99}Mo$ reaction $\cdot {}^{99}Mo/{}^{99m}$ Tc Medical radioisotopes \cdot Electron accelerator \cdot Epi-cadmium neutrons \cdot Ta-BeO assembly

Introduction

Technetium-99 m Radiopharmaceuticals are the major diagnostic tool in the clinical practice of nuclear medicine worldwide. ^{99m}Tc is the daughter product of ⁹⁹Mo. The latter has a half-life of 65.94 h. Almost all supply of ⁹⁹Mo (nearly 90%) required for ^{99m}Tc generators is produced by the neutroninduced fission of ²³⁵U targets in nuclear research reactors [1]. A relatively lesser amount (~10%) is produced by low energy neutron capture in ⁹⁸Mo. In recent years, the ⁹⁹Mo supply crisis occurred as a result of various factors such as the extension of planned outages and the prolonged or

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unplanned shutdown of many reactors around the world [1–3]. With the aim of mitigating these supply-side disruptions, alternative routes for production of ⁹⁹Mo are being explored. These include photo-neutron reaction [¹⁰⁰Mo(γ , n)⁹⁹Mo] [4, 5], photo-fission reaction [²³⁸U(γ , f)] using high energy electron accelerators [6, 7], and fast neutron induced reactions [¹⁰⁰Mo(n, 2n)] [8–10]. Production of radioisotopes using particle accelerators has the advantages of negligible nuclear wastes in comparison to nuclear reactors, relatively lower cost, and higher availability. In view of higher availability and economical operation, electron accelerators are an attractive choice for the production of radioisotopes.

In the present work, an exploratory experiment was carried out to study the feasibility of ⁹⁹Mo production using (e- γ -n) cascade reaction. A high energy electron beam was made to fall on a high Z target (Ta). The bremsstrahlung photons thus produced were then made to strike BeO blocks. The photo-neutrons produced [11], were then utilised for neutron capture reaction in ⁹⁸Mo. Being a two-step process, the efficiency of this route is expected to be lower. However, the fast spectrum of neutrons produced can be shifted to the epi-cadmium energy region. Hence, there exists a possibility to increase the yield of ⁹⁹Mo. The reaction ⁹⁸Mo(n, γ)⁹⁹Mo has distinct resonances in the epi-cadmium region. Figure 1

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shows the cross-section of this reaction in the 260 energy group used by FLUKA [12, 13] Monte Carlo code for low energy neutron transport simulations. The cross-section curve shown in Fig. 1 has been extracted from the JENDL 4.0 library [14] using NJOY2016 [15] nuclear data processing code. The maximum group-averaged cross-section is nearly 10 b. The cross-section corresponding to thermal neutrons is nearly 0.13 b [16]. The resonance integral of the reaction is 6.9 b [17]. Clearly, there exists a possibility to increase the yield of 99Mo through the neutron capture (in ⁹⁸Mo) route by shifting the photo-neutron spectrum into the epi-cadmium energy region by controlled moderation. If a dominant fraction of neutrons stays in the epi-cadmium region of the spectrum (instead of complete thermalisation to thermal region), the effective cross-section of neutron capture in 98Mo can be more than the cross-section corresponding to thermal neutrons.

An increase in the effective cross-section of ${}^{98}Mo(n,\gamma){}^{99}Mo$ reaction due to shifting the neutron spectrum to the epi-cadmium region, has been demonstrated in the IRT-T research reactor, Russia. Here, light water was replaced by beryllium oxide at some irradiation locations inside the reactor core [17]. This resulted in under moderation of neutrons at those locations and consequently, the effective cross-section of ${}^{98}Mo(n,\gamma){}^{99}Mo$ reaction was reported to increase up to 0.70 b. Another similar work carried out in the Tehran research reactor (TRR) [18], reported

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that the effective cross-section of this reaction could be increased up to 0.52 b.

The present work aims to utilize the under-moderated neutron spectrum obtained from tantalum-beryllium oxidehigh density polyethylene (Ta-BeO-HDPE) set-up at an electron accelerator, for ⁹⁹Mo production. The energy distribution of photo neutrons was shifted from fast to epicadmium energy region by moderation (under moderation) using HDPE. The effective cross-section of the reaction was measured using the foil activation method. Thin metal foils of Mo, Au, and Cu were irradiated in the moderated neutron field emerging from the Ta-BeO-HDPE set-up. HØgdahl convention [19] was used for data analysis, to determine thermal and epi-cadmium neutron fluxes.

The following section of this article gives the details of the experiment carried out. The subsequent section describes the theory and the methods used. This is followed by a discussion regarding the data analysis for the experiment. In the subsequent section, results are compared with theoretical simulations and the last section gives the conclusions.

Experimental details

The experiment for the feasibility study of 99 Mo production through the (e- γ -n) reaction route was carried out at the 10 MeV electron accelerator at Electron Beam Centre





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Modeling the radon build-up in a closed environment using developed OpenFOAM solver

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Abstract

Modeling radon (²²²Rn) development in confined environments aids in predicting radon levels in dwellings and underground spaces, where radium ²²⁶Ra in building materials and soil emits radon gas via radioactive decay. Radon accumulates in poorly ventilated places, creating an inhalation hazard. In OpenFOAM, a C++-based computational tool, an existing heat conduction solver was adapted to simulate radon accumulation, considering radon's radioactive characteristics and material non-uniformity through which radon will permeate. The solver was validated against theoretical values in a one-dimensional system and then applied to study radon dispersion in containment, with potential for broader applications.

Keywords OpenFOAM · Solver development · Radon build-up · Indoor environment · 3D diffusion

Introduction

Radon (222Rn), a radioactive noble gas, the immediate decay product of radium (226Ra), is a major source of inhalation exposure along with its short-lived progeny [1, 2]. The gaseous radon can effectively migrate from the source and disperse in the surrounding environment. The association between radon (and progeny) exposure and lung anomalies at elevated levels has been widely investigated, and guidelines have been provided for action plans and mitigation strategies [3-5]. The radium content of a house's construction materials is typically considered a major source of radon [6-8]. The inbuilt radon inside the matrix finds its way toward the vacant space of a house through different mechanisms, such as emanation, diffusion, and exhalation [9-11]. Other mechanisms of radon removal in a closed system, except for radioactive decay, are practically ineffective, accumulating significant concentrations of radon within the enclosure. Under such circumstances, even with lower radium content in the construction component, a persistently

Dibyendu Rana dibyendu.rana12@gmail.com higher radon concentration above the reference level is not unlikely [12, 13].

Radon research has significantly advanced in recent decades, particularly in simulation techniques to model radon accumulation in closed indoor environments [14, 15]. Early research primarily relied on empirical measurements and simple statistical models to estimate radon levels [16]. However, modeling has become an increasingly important tool in environmental science, allowing researchers to study complex phenomena and predict future events. Despite the notable progress in modeling radon dispersion, the research community has largely relied on commercial packages like ANSYS Fluent and COMSOL, overlooking the potential of open-source software [17, 18]. The diffusion (radon diffusion) type of problem is the simplest CFD (computational fluid dynamics) study and is amenable to solutions in any simple language, such as FORTRAN, C, or C++ [19-21]. However, because meshing complex curved domains is difficult, their applications are limited, necessitating the use of CFD software. This has motivated the present work to develop a solver within an open-source CFD package to support researchers who lack access to expensive commercial software.

This paper investigates the radon buildup in a closed system using OpenFOAM. OpenFOAM, developed in 2004, is a C++-based finite volume-based open-source CFD tool that can run in parallel. Additionally, OpenFOAM provides free access to its source code, allows for customization according

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to user requirements, and benefits from robust support from the open-source community. While OpenFOAM includes a variety of solvers, none are specifically designed to model radon diffusion in heterogeneous media. To address this, an existing solver has been customized to develop a new one capable of accurately representing the required scenario (diffusion of radon in a heterogeneous medium). The validation test of the developed model has been carried out by comparing its results with available results in the literature for one-dimensional diffusion.

Along with theoretical predictions, the equilibrium radon concentration was measured with a continuous radon monitor (AlphaGUARD). AlphaGUARD uses an ionization chamber as a detector to measure radon concentrations using 3D alpha spectrometry. The measured radon concentration inside the closed system was compared to a theoretically predicted model.

Studied system

Fig. 1 Studied system with

soil-base

A radon build-up investigation has been conducted experimentally and numerically on an existing system constructed for future civil engineering projects. The system has an interior dimension of 9.8 m (L)×2.3 m (W)×2.35 m (H). The exterior side of the building had 1.5 cm of concrete plaster covering the 9 cm thick brick wall. The top side of the closed system was a concrete slab cover of 10 cm thickness, making the exterior dimensions 10.01 m (L), 2.51 m (W), and 2.45 m (H). Two narrow cylindrical air tunnels were available for ventilation in the enclosed component of the system. One of the ventilation pathways consisted of a 10-cm circular opening in the wall. The second pathway involved a horizontally extended cylindrical pipe, 3 m in length, which penetrated through the wall. The bottom side of the enclosure is a regular soil base without any specific treatment. Figure 1 shows the setup, along with the included extended soil base. The reason for the inclusion of the soil base is explained in Sect. 3.4.1. The origin of the coordinate system coincides with one end of the cubic structure, as represented in Fig. 1.

Computational fluid dynamic model

Mathematical background

Radon emitted from grains of construction materials (bricks, concrete, and soil) migrates into the indoor environment through diffusion. The diffusion of radon in a porous matrix is governed by the Eq. (1) [9].

$$\frac{\partial C_a}{\partial t} = D_r \frac{\partial^2 C_a}{\partial z^2} - \lambda C_a + \frac{\lambda R \rho_b E}{n_e}$$
(1)

In Eq. (1), C_a is radon concentration in air fraction of pore in Bq m⁻³, D_r is diffusion coefficient in m² s⁻¹, *R* is radium content in Bq kg⁻¹, ρ_b is bulk density in kg m⁻³, λ is the decay constant of radon in s⁻¹, *E* is emanation coefficient with $E = E_0(1 + 1.85(1 - e^{-18.8} \text{ m}))$, n_e is effective porosity with $n_e = n_T (1 - (1 - k)m))$. Here, *k* is the radon distribution fraction between air and water; m is the volumetric moisture fraction; and n_T is the matrix's total porosity. The radon flux from the matrix's surface follows Eq. (2).

$$f = -n_e D_r \frac{\partial C_a}{\partial z} \tag{2}$$

Equation (1) can be generalized into 3D, and the radon diffusion in the matrix can be represented as,

$$\frac{\partial (n_e C_a)}{\partial t} = \text{DT} \, \nabla^2 C_a - \text{decay } C_a + \text{source}T \tag{3}$$

In Eq. (3), $n_e D_r = DT$ is the effective diffusion coefficient [9], $decay = n_e \lambda$, and $sourceT = \lambda R\rho_b E$ is the source for radon generation. Unfortunately, no readily available solver in



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ORIGINAL ARTICLE



Molecular characterization and insilico expression analysis of ammonium transporter genes family in Sorghum bicolor

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Abstract

Nitrogen (N) is an essential macronutrient for plants, primarily absorbed from the soil as ammonium (NH4⁺) through Ammonium Transporters (AMTs), which are plasma membrane proteins. This study involved the genome-wide identification, characterization, and insilico expression analysis of sorghum (Sorghum bicolor L.) AMT genes (SbAMTs) in different tissues, including flowers, meristems, embryos, roots, and shoots, as well as under treatments with abscisic acid (ABA) and 20% polyethylene glycol (PEG). Structural analyses revealed conserved transmembrane domains, though SbAMT2.2 and SbAMT3.3 exhibited fewer domains due to their small protein size. Gene structure analysis showed significant intron variation between AMT1 and AMT2 families, while motif analysis suggested evolutionary divergence. Secondary and 3D structure analysis indicated that AMTs are predominantly composed of alpha-helices. Synteny analysis revealed strong gene conservation among Poaceae family members, especially with Zea mays. Gene ontology analysis (GO) and protein-protein interaction analysis highlighted roles in ammonium transport, nitrogen metabolism, and stress responses. Cis-element analysis of AMT promoter regions revealed regulatory elements responsive to light, hormones (eg. auxin, gibberellin, abscisic acid), and environmental stresses like drought and anaerobic conditions, suggesting AMTs' involvement in growth, development, and stress adaptation. Expression profiling revealed tissue-specific patterns, with SbAMT1.2 being highly expressed in roots, and SbAMT3.3 broadly expressed across tissues. Stress-induced upregulation of SbAMT genes under ABA and PEG treatments suggests their involvement in drought tolerance. These findings provide valuable insights into the structure, function, and evolution of AMTs in S. bicolor, with potential applications for improving nitrogen use efficiency and stress resilience in crops.

Keywords AMT · Sorghum bicolor · NUE · Millet

Introduction

Nitrogen is a vital nutrient for plant growth and development, playing a key role in the formation of amino acids and nucleic acids. In the soil, nitrogen occurs in three main forms: organic nitrogen compounds, ammonium (NH_4^+) , and nitrate (NO_3^-) ions. As sessile organisms, plants have developed various adaptive mechanisms to respond to both their internal nitrogen levels and the availability of nitrogen in their environment (Jahan et al. 2016). When both ammonium and nitrate are present, or in ammonium-rich conditions such

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¹ Nuclear Agriculture and Biotechnology Division, Bhabha Atomic Research Centre, Mumbai 400085, India as flooded or acidic soils, plants tend to prefer ammonium as their nitrogen source (Hao et al. 2020; Zhang et al. 2018). Upon sensing ammonium, plants initiate a signal transduction cascade that begins with the activation of ammonium transporters (AMTs) or specific sensors. These sensors trigger a series of intracellular signalling pathways, including phosphorylation events and secondary messengers, which modulate downstream gene expression related to nitrogen metabolism (Ludewig et al. 2007). This regulatory network coordinates cellular processes such as nitrogen assimilation, nutrient allocation, and metabolic adjustments, ensuring the plant responds appropriately to external ammonium availability by optimizing uptake, transport, and utilization (Giehl et al. 2017; Yuan et al. 2009).

The first ammonium transporter in plants was identified in *Arabidopsis thaliana* and demonstrated functional complementation of a yeast mutant impaired in ammonium uptake (Ninnemann et al. 1994). Plant ammonium transporters are

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categorized into two main subfamilies: AMT1 and AMT2. The AMT2 subfamily members exhibit lower sequence similarity to those in the AMT1 subfamily, indicating divergence in their evolutionary paths or functional specializations. However, AMT2 proteins share a high degree of homology with the AmtB transporter in Escherichia coli and Mep transporters in yeast, which belong to the MEP subfamily. This phylogenetic similarity suggests a conserved role in ammonium transport across different biological kingdoms, despite species-specific variations (Sohlenkamp et al. 2000; Howitt et al. 2000). Plant AMT proteins are primarily localized on the cell membrane and typically contain 11-12 transmembrane domains (Andrade and Einsle 2007). Based on kinetic studies, plant AMTs are classified into high-affinity and low-affinity ammonium transporters (Yuan et al. 2007; Loque et al. 2006; Kiba and Krapp 2016). These transporters play a critical role in regulating ammonium uptake, ensuring tight and dynamic control over ammonium availability during various stages of plant growth and development.

Ammonium concentrations in soils typically remain below 1 mM (Hao et al. 2020), necessitating the use of a high-affinity ammonium transport system for efficient absorption by plants. In A. thaliana, all six identified ammonium transporters (five from the AMT1 subfamily and one from the AMT2 subfamily) function as high-affinity transporters (Hao et al. 2020; Sohlenkamp et al. 2002). Notably, AtAMT1.1, AtAMT1.2, AtAMT1.3, and AtAMT1.5 are predominantly expressed in root tissues, including root hairs, where they facilitate NH4⁺ uptake. The expression of these transporters is upregulated in response to low nitrogen availability, highlighting their role in optimizing nutrient acquisition under limiting conditions (Yuan et al. 2007; Loque et al. 2006; Mayer and Ludewig 2006). Loss-of-function mutations in the AMT1.1, AMT1.2, and AMT1.3 genes resulted in a 90% reduction in ammonium uptake capacity in the roots of A. thaliana, indicating that these AMT1 transporters serve as the primary system for ammonium nitrogen acquisition from the environment (Hao et al. 2020). In contrast, the AMT2 subfamily does not play a significant role in the uptake of ammonium nitrogen from the soil. Instead, upon ammonium treatment, AMT2 is predominantly expressed in the stele sheath of the roots and facilitates the transport of ammonium from the roots to the shoots. This suggests that, while AMT1 transporters are critical for initial ammonium uptake, AMT2 contributes to the internal redistribution of ammonium within the plant (Giehl et al. 2017). AMT expression has been observed in various tissues, including roots, stems, leaves, petioles, and flowers across multiple plant species such as Coffea canephora (Santos et al. 2017), Glycine max (Yang et al. 2023), Lotus japonicus (Wang et al. 2022), Malus domestica (Huang et al. 2022), Medicago truncatula (Breuillin-Sessoms et al. 2015), Oryza sativa (Ferreira et al. 2015; Li et al. 2016), Populus trichocarpa (Wu et al. 2015),

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Pinus sp. (Castro-Rodríguez 2016), *Solanum lycopersicum* (Filiz and Akbudak 2020), *Triticum aestivum* (Duan et al. 2016; Li et al. 2017), and *Zea mays* (Gu et al. 2013). Loss-of-function mutations in some of these *AMT* genes have been associated with significant reductions in aboveground biomass, indicating their importance in plant growth and development (Gu et al. 2013; Ranathunge et al. 2014; Bao et al. 2015). These findings suggest that *AMTs* are differentially expressed in various plant tissues and play a crucial role in ammonium transport, highlighting their importance in overall nitrogen metabolism and plant health.

In addition to their specific patterns of expression and functional roles in nutrient uptake, several AMT genes are regulated by the circadian clock, demonstrating a link between internal biological rhythms and nutrient acquisition strategies. For instance, in A. thaliana, AtAMT1.3 exhibits a distinctive diurnal expression pattern, wherein its transcript levels increase significantly in anticipation of light, resulting in peak ammonium absorption at the end of the photoperiod. As light intensity declines, the rate of ammonium uptake correspondingly decreases (Hao et al. 2020). This rhythmic behaviour suggests a sophisticated regulatory mechanism that aligns nutrient acquisition with the plant's energy availability during the day. Similarly, rhythmic regulation has been documented for LeAMT1.2 and LeAMT1.3 in tomato plants (Von Wirén et al. 2000). This temporal regulation of AMT expression indicates that nutrient uptake and metabolism are intricately controlled by the biological clock, allowing plants to optimize resource utilization in accordance with diurnal cycles (Hsu and Harmer 2014). Such dynamics imply that the AMTs are critical for facilitating rhythmic changes in ammonium uptake, as well as its subsequent remobilization and assimilation, thereby ensuring efficient nitrogen utilization during both daytime and night-time periods. In addition to their primary function in ammonium uptake, ammonium transporters are also implicated in various biological processes, including plant-microbe interactions. For example, AMT1.1, AMT1.3, and AMT2.3 have been shown to play a role in the plant defense response to pathogens in crops such as rice and wheat (Wu et al. 2022a, b; Li et al. 2017; Jiang et al. 2019). This involvement suggests that AMTs may not only facilitate nutrient uptake but also contribute to the plant's ability to recognize and respond to biotic stressors. Moreover, growing evidence indicates that AMTs are integral to plant-microbe symbiosis. Specific AMTs, such as MtAMT2.3 in Medicago truncatula, as well as LjAMT2.1 and LjAMT2.2 in Lotus japonicus, are believed to be involved in the transport of ammonium from symbiotic host plants to nitrogen-fixing rhizobia and arbuscular mycorrhizae (Simon-Rosin et al. 2003; Guether et al. 2009; Breuillin-Sessoms et al. 2015). This transport mechanism is crucial for establishing effective symbiotic relationships, enabling the plant to obtain nitrogen in a form that





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MXene/rGO/sulfur loaded separator based current collector-free lithium sulfur batteries with high sulfur loading and cycle life

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ABSTRACT

Lithium-Sulfur batteries with high sulfur loading cathodes are highly desirable to achieve greater energy density. In this work, a high loading composite cathode is reported that is made by scalable vacuum filtration route, eliminating the need for a binder, conducting carbon, and metallic current collector. Moreover, capacity fade due to peeling off of coated active material from current collector is avoided, leading to excellent capacity retention. The coated separator affords a porous framework to (i) accommodate volume changes during cycling, (ii) allow higher sulfur loading, (iii) allow electrolyte wetting of active material in addition to (iv) functioning as a traditional separator and current collector by pressing against stainless steel casing. The MXene/reduced graphene oxide/S₈ composite with an areal loading of 2.52 mg/cm² exhibits a specific capacity of 495 mAh/g with a capacity retention of 97.5% after 200 cycles at a charge/discharge rate of 100 mA/g. At 500 mA/g discharge rate, an initial specific capacity of 378 mAh/g was obtained with 239 mAh/g retained after 750 cycles.

1 Introduction

The rapid miniaturization of consumer electronics has led to several technological marvels like compact cell phones and virtual reality headsets. The batteries that power these devices need to be compact, lightweight, affordable, and energy dense with a long cycle life. These requirements can be fulfilled by the next generation of lithium-based batteries, i.e., lithium sulfur batteries (LSBs). LSBs afford several benefits like (i) a high specific capacity (theoretical: 1675 mAh/g), (ii) high energy density (theoretical: 2600 Wh/kg), (iii) low cost, due to high earth abundance and environmental friendliness of sulfur, and (iv) better safety [1, 2].

One of the principal hindrances to their widespread adoption is due to the high resistivity of sulfur (~ 10^{-31} S cm⁻¹) and Li₂S (the species formed upon discharging the cell). This issue is generally overcome by utilizing nano-sulfur and incorporating it into some porous conductive matrix. The conducting matrices employed, thus, far include reduced graphene oxide (rGO) and graphene frameworks [3], carbon nanotubes [4], conducting polymers like polyaniline [5]

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and polypyrrole [6], as well as conducting inorganic compounds like MXenes [7].

The notorious "polysulfide shuttle" [1] in LSBs is addressed by various approaches such as incorporation of polar species in the cathode that can restrain the soluble polysulfides by absorption/adsorption. The chemical species may also be loaded on the separator that can then restrain the polysulfides in the catholyte region, thus, disrupting the shuttle and enhancing electrochemical utilization. The species used for this purpose are widely varying, ranging from carbon based (such as CNT, graphene oxide), inorganic compounds (MoS₂ [8], WP [9], TiO_x [10]), intermetallic catalysts (CoTe [11]), porous metal–organic frameworks [12, 13], as well as metal clusters on doped carbon hosts [14, 15].

The complete conversion of sulfur to Li_2S during discharge is accompanied by a very large (~ 80%) volume expansion which poses a huge roadblock for long-term cycling of the material. There have been several efforts to mitigate capacity fade due to the mechanical degradation and loss of conduction pathways during cycling by means of loading sulfur in porous conducting frameworks [16]. This approach ameliorates capacity fade at the cost of active mass dilution by the encapsulating porous framework.

Moreover, conventional electrode preparation involves making a slurry composed of active material, conductive carbon, and a binder which is then coated onto a metallic current collector. Due to large volume changes during cycling, the coated material peels off from current collector and there is loss of active mass and consequent capacity fade results. Typically, the active material is a composite of sulfur with another material which contributes conductivity and offers some form of physical/chemical hindrance to polysulfide migration. Since sulfur itself is a good binder [17] and there is a conducting component already present in our active composite, we propose to eliminate the metallic current collector, binder as well conducting carbon from an assembled cell. The active material is directly deposited by scalable vacuum filtration method onto one side of glass microfiber separator. This coated separator now takes on the role of (i) a porous framework holding the active material and accommodating volume changes during cycling, (ii) enable higher loading due to increased surface area compared to a metallic current collector, (iii) act as current collector by pressing intimately with stainless steel casing, and (iv) act as the separator itself. This

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approach leads to significantly higher active material (sulfur) loading on the final coated separator compared to conventional routes.

One of the approaches utilized to eliminate the Al current collector is to fabricate a free-standing cathode. Park et al. [18] have reported such an approach by fusing conductive carbon nanotubes (CNTs) with cellulose to make a free-standing 3D matrix for sulfur loading. These free-standing electrodes are then used alongside conventional glass microfiber separator for application in lithium sulfur batteries. They reported good initial specific capacity of 940 mAh/g at an areal current density of 1.57 mA/cm². N-doped carbon nano-fiber sheets impregnated with Mn₃O₄ nanoparticles were used as sulfur host by Chen et al. [19] to fabricate free-standing cathode. The synthesis protocol consisted of multiple steps, including electrospinning of template polymer with oxide precursor, carbonization under inert atmosphere and subsequent sulfur loading. They achieved a reversible areal capacity of over 8 mAh/cm². Bharti et al. [20] reported carbonized bacterial cellulose as a free-standing sulfur host that when coupled with bacterial cellulose as separator delivers a capacity of 740 mAh/g at 1C.

While this approach eliminates the need for aluminum current collector, the synthesis route for freestanding electrodes is generally cumbersome and a separator as well as binder are still needed. In this work, the performance and cycling characteristics of coin cell utilizing a coated separator with a high loading of S_8 , owing to the lack of binder, conducting carbon as well as aluminum current collector in the present design, have been assessed.

2 Experimental

2.1 Synthesis

The detailed synthesis of MXene ($Ti_3C_2T_x$), graphene oxide (GO), and reduced graphene oxide (rGO), and ternary composite MXene/rGO/5 (MGS) are discussed in our previous report [7]. Briefly, the synthesis of MGS involves addition of sodium thiosulfate and oxalic acid to an aqueous dispersion of MXene and rGO (refer Fig. 1, for a graphical schematic). The acid catalyzed disproportionation of thiosulfate leads to formation of nano-sulfur on the surface of rGO and MXene. The formed composite is collected by centrifugation, washed with distilled water, and then





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Natural hydrous sulphate minerals from Martian analogue area for sequestration of metal ions of nuclear significance

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Abstract

Naturally occurring hydrous sulphate minerals bearing rock, sampled from a Martian analogue area, Kachchh, India was investigated for sequestration of metal ions of nuclear significance in view of waste management applications. Structural analyses revealed the presence of alunite group minerals (such as hydronium jarosite, alunite, natroalunite) along with a phyllosilicate mineral—kaolinite in the sample. Sorption performance assessment in batch mode for cesium (Cs) demonstrated the influence of initial sorbate concentration and solution pH on the uptake of metal ions. Equilibrium sorption data upon correlation with the theoretical isotherms showed better agreement with Langmuir model with a monalayer sorption capacity of 26.4 mg g⁻¹ for Cs. Maximum uptake of metal ions in acidic pH is a signature of involvement of structural ions in the sorption process. EDXRF analysis demonstrated the loading of sorbate ions on the surface of sorbent after sorption. The studies highlight that the cation retention potential of naturally available hydrous sulphate minerals bearing rock could be instrumental for possible application of the material as barrier matrix to immobilize metal ions of nuclear importance in acidic conditions.

Keywords Hydrous sulphate minerals bearing rock · Martian analogue area · Alunite group minerals · Kaolinite · Cesium · Cation retention potential

Introduction

Hydrous sulphate minerals are prevalent in nature in acid rock drainage environments and sulphate rich soils [1, 2]. These minerals are generally formed under extreme conditions, typically due to alteration and hydrothermal intrusion of secondary mineral phases such as pyrite and forms in the oxidative weathering of sulphide-rich ore bodies at low

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temperatures and low pH (<3) levels [3–5]. The significance of these minerals is mainly due to their stability under highly oxidizing and acidic environments as well as their ability to retain potentially toxic ions [6, 7]. Therefore, these minerals are effective in restricting the migration of trace contaminants in the surroundings, and can be utilized to remediate various pollutants from the environment. Additionally, such materials can be used in the design of engineered barriers as immobilization matrices for waste management under acidic settings [8–11].

Recently Bhattacharya et al. has reported a Martian analogue terrestrial area hosting hydrous sulphate minerals and phyllosilicates of Paleocene age (~59 to 56 Ma) exposed at Mata no Madh Formation of Kachchh Basin, Gujarat [3]. After the detailed spectroscopic investigation of the host rock, the authors observed the occurrence of unusual jarosite mineral in coexistence with natroalunite and kaolinite- phyllosilicate mineral within the sedimentary formation overlying the altered basalt and thus mimicking the geological settings of reported jarosite localities on the Martian surface. The research related to the hydrous sulphate mineral jarosite has gained significance after its discovery on the

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Mars' surface. Jarosite acts as a mineralogical marker indicating aqueous activity on the surface of Mars. However, the occurrence of jarosite is restricted in terrestrial sites owing to the uncommon conditions (hydrous, acidic, and oxidizing sulphate bearing) under which the mineral is generally found [3].

The hydrous sulphate minerals being discussed herein are commonly classified under the alunite supergroup of minerals, which are represented by a general formula AB₃(TO₄)₂(OH)₆ [12]. 'A' site is generally occupied with ions (mono, di or trivalent) possessing coordination number \geq 9. 'B'site is filled up with trivalent ions like Fe³⁺, Cr³⁺ or Al^{3+} and the 'T' site is occupied by As^{5+} , P^{5+} or S^{6+} [13]. The alunite minerals comprises three-dimensional layered structure wherein the A⁺ ions placed in between the hexagonal sheets made up of interconnected BO6 octahedra (as corner-shared triangles), which are further connected with TO₄ tetrahedra located above and below the two-dimensional layers alternately. The cation retention ability of these minerals is mainly due to the possible ion exchange with 'A' and/ or 'B' site or surface complexation by utilizing the surface functional groups such as SO_4^{-2} .

This present study aims to characterize the hydrous sulphate mineral phases found alongside Palaeocene-aged (~59 to 56 Ma) outcrop in the Mata no Madh Formation of the Kachchh Basin in Gujarat and explore their metal retention behaviour. The structural characterization of the rock sample was performed using different instrumental techniques. The studies related to the retention of metal ions of nuclear importance like Cs on naturally occurring hydrous sulphate phases have not been reported till date. Herein, the Cs sorption performance assessment of hydrous sulphate minerals was carried out in batch mode under different experimental conditions. The experimental data is correlated with theoretical sorption isotherms for getting an insight to the sorption mechanism. The studies would generate a sorption database for naturally occurring hydrous sulphate minerals for probable waste management applications.

Geology of the Martian analogue area-Kachchh

Kachchh is a pericratonic rift basin with a nearly whole sequence ranging from the Triassic to the Recent period. Rifting started during the Mesozoic era as Gondwana land began to break apart and was succeeded by extensive volcanic eruption related to the Deccan Traps during the Late Cretaceous period [14, 15]. As the Deccan volcanic activity waned, clastic and volcanoclastics along with the reworked sediments that deposited on weathered deccan basalts within the fluvio-lacustrine environment, formed the Mata no Madh Formation [16]. The laterites at Mata no Madh belong to narrow laterite belt which runs parallel to the coastal boundary of Kachchh basin and covers the entire region from Anjar to Lakhpat (east to west) [17]. Within the lithological succession (Fig. 1a), hydrous sulphates appear as lenticular bodies associated with Paleocene sediments overlying the trap basalts identified as natroalunite in hillocks of Mata no Madh, capped



Fig. 1 a Field outcrop of the hydrous sulphate minerals bearing rock of Paleocene sequence at Mata no Madh area from Kachchh region, b Megascopic view of the rock specimen

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Regular Article - Experimental Physics

Neutron transfer in ⁷Li+²⁰⁵Tl system

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Abstract Neutron transfer cross sections for ⁷Li+²⁰⁵Tl system were measured near Coulomb barrier energies using online γ -ray detection technique. One neutron stripping, two neutron stripping, and one neutron pickup cross sections have been extracted and are compared with the Coupled Reaction Channel (CRC) calculations. The systematics of one and two neutron stripping and pickup cross sections with a ⁷Li projectile on several targets show an approximate universal behaviour. A comparison of integrated neutron transfer cross sections with complete and incomplete fusion cross sections available with ⁷Li projectile is presented to understand the systematic behaviour. The neutron transfer along with cumulative sum of complete and incomplete fusion was found to explain the estimated reaction cross section in ⁷Li+²⁰⁵Tl system.

1 Introduction

Over the past few decades, the study of heavy-ion induced reactions with stable weakly bound nuclei has gained importance for understanding the fundamental nuclear features related to structure and reaction dynamics [1–7]. These studies help in exploring reactions involving more exotic nuclei and radioactive ion beams. In this regard, reaction phenomenon particularly fusion, elastic scattering, inelastic excitation, breakup reactions etc., have been studied extensively for these nuclei. Additionally, measurement of direct nuclear transfer reactions involving the stable weakly bound nuclei ($^{6.7}$ Li, 9 Be) have been performed and the significance of nucleon transfer in the reaction dynamics has been inves-

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tigated in several studies [8–20]. In the subsequent studies, based on neutron transfer cross sections available with ^{6,7}Li and ⁹Be projectiles on various targets [15,21,22], it was concluded that there is no dependence on target structure. The projectile structure plays a major role in the transfer process; viz; the highest neutron stripping cross section is obtained with ⁹Be (S_n = 1.67 MeV) projectile followed by ⁶Li (S_n = 5.67 MeV) and ⁷Li (S_n = 7.25 MeV) projectile nuclei.

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The transfer of a single valence nucleon or a group of nucleons collectively at the periphery of the colliding partners are known to affect the fusion cross sections at energies near the Coulomb barrier due to presence of significant coupling effects of single particle and continuum of states. The enhancement in fusion cross sections at near barrier energies could also be explained considering the neutron flow model of Stelson [23,24]. This model is based on the neutron flow due to the exchange of neutrons between the interacting projectile and target nuclei and its usefulness has been demonstrated in various studies of fusion reactions with many projectiles [25–29].

Often, nucleon transfer is followed by various breakup modes of the projectile [30], with fragments potentially being absorbed by the target. There is a large probability that some of the breakup fragments may be subsequently absorbed in the field of the target leading to the process called as breakup fusion which makes contributions towards incomplete fusion (ICF). Some of other contributions to ICF can be ascribed to the transfer of the nucleons to the high-lying states in the continuum of the target. Separating the effects of transfer and breakup processes can be challenging, making it essential to understand them in a unified way. Further, knowledge about relative importance of the breakup and transfer processes and their contribution to the ICF, CF and reaction cross section is

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important for obtaining a better understanding of the reaction mechanism.

In recent times, various new theoretical models have been developed and employed for describing the data and obtaining the understanding of breakup-transfer processes for weakly bound nuclei. For the breakup reactions, the Continuum Discretized Coupled Channels (CDCC) has proved to be one of the most successful approaches for describing coupling effects due to breakup of nucleon(s) of the projectile nucleus. While the elastic part of the breakup is described very successfully through the CDCC method, the non-elastic breakup is not so easy to calculate. In recent times, the IAV and its extensions have been developed for modelling the inelastic breakup [31-34]. Extensions to CDCC have been also been made for calculating the ICF [12, 13, 35-40], where one of the fragments of the projectile is considered to be transferred to the target. Coupled Reaction Channel (CRC) calculations have been employed for studying the effect due to transfer channels and significant coupling effects due to one neutron transfer has been found in many systems [15-18,21,22].

With this motivation, neutron transfer in 7 Li+ 205 Tl system near Coulomb barrier energies have been studied, utilizing online γ -ray measurement and the results are compared with Coupled Channel (CC) calculations. Further, systematics of 7 Li induced reactions on several target systems along with the present data is studied. The paper is organised as follows. The experimental details are given in Sect. 2. The experimental results and the calculation details are given in Sect. 3 followed by the summary in Sect. 4.

2 Experimental details

The details of the experimental setup are given in our earlier work [41] and only a short summary is given here for completeness. The experiment was performed using 'Li beam from the BARC-TIFR Pelletron LINAC Facility, Mumbai, India at ten energy points in the energy range Ebeam = 25-40 MeV. The target ²⁰⁵Tl of 1 mg/cm², evaporated on 25 μ g/cm² carbon backing was placed inside a compact chamber made of aluminium alloy, surrounded by Indian National Gamma Array (INGA) setup [42]. The array was consisting of nine Compton suppressed High Purity Germanium (HPGe) Clover detectors for detection of y-rays from the residues populated in 7Li+205Tl reaction. Inside the chamber, three charged particle detector telescopes (AE $= 25 - 40 \ \mu m$, E = 1000 μm) were placed at 70°, 120° and 140°, respectively for detection of elastic and α particle events mainly. In addition, two Si surface barrier detectors with thicknesses 300 μ m, acting as monitor detectors were also placed at 25° for absolute normalisation purpose. The time stamped data were collected using a digital data acquisi-

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Fig. 1 γ -ray add-back spectrum from all the clover detectors obtained in ⁷Li+²⁰⁵Tl system at E_{beam} = 38 MeV. The γ lines following one neutron stripping (²⁰⁶Tl), two neutron stripping (²⁰⁷Tl) and one neutron pickup (²⁰⁴Tl) channels are marked

tion system with a sampling rate of 100 MHz [42]. Standard calibrated radioactive ¹⁵²Eu and ¹³³Ba sources were used for efficiency and energy calibration of the clover detectors. Figure 1 shows the typical γ -ray add-back spectrum from all the clover detectors measured at E_{beam} = 38 MeV for ⁷Li+²⁰⁵Tl system. The prompt γ -rays from one neutron stripping (²⁰⁶Tl), two neutron stripping (²⁰⁷Tl) and one neutron pickup (²⁰⁴Tl) channel are labeled.

3 Results and discussion

3.1 Data Reduction

The data reduction procedure for extraction of residue cross sections is similar as given in our previous work [41]. The cross sections for residues from one neutron stripping ²⁰⁶Tl,





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NO₂ and NH₃ detection using work function measurement of solvothermal synthesised ZnO–NiO nanocomposites: a case study

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ABSTRACT

Work function measurement using Kelvin probe method has been demonstrated as an effective and novel approach towards detection of NH3 and NO2 gases. using ZnO-NiO based nanocomposites. For this the nanocomposites were synthesised in different compositions using the solvothermal method. Formation of ZnO-NiO nanocomposites was confirmed using XRD and EDS studies. It is found that the nanoparticle morphology of NiO changes with different percentages of Zn addition. The work function of the sensing film was found to decrease and increase upon exposure to NH₃ (1.51) and NO₂ (1.18) gases owing to the reducing and oxidising nature of the test gases. Of the different composites, Zn075Ni025O exhibited highest sensor response towards the test gases. The increased response is attributed to the nanostructured morphology of the nanocomposite and the formation and collapse of the p-n heterojunction formed between p-type NiO and n-type ZnO. Besides, incorporation of NiO enhances the oxygen adsorption on the sensor surface assigned to the Ni²⁺ ions getting readily oxidised to Ni³⁺. Our results clearly suggest that the work function measurements could also be used as an effective way for NO2 and NH3 detection.

1 Introduction

Air pollution has recently emerged as the most serious environmental issue [1]. Of the various pollutants, ammonia (NH₃) and nitrogen dioxide (NO₂) are useful for numerous industries such as fertiliser, pesticides, petrochemical, chemical and medical [2–4]. NH₃ is a colourless, highly hazardous gas and the Occupational Safety and Health Administration (OSHA) has set an exposure limit of 50 ppm [5]. Above this, it leads to various health issues such as headaches, difficulty breathing, and vomiting. In the similar context, NO₂

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is highly toxic and responsible for acid rain and its exposure limit is set to 5 ppm [6]. For higher concentrations, it damages the human respiratory tract and could be fatal.

These gases have been monitored using several methods including optical [7], electrochemical [8], work function [9], chemiresistive [10], gas chromatography (GC), and mass spectroscopy [11]. Some of these techniques are sophisticated, expensive, and time-consuming. Among these, chemiresistive-based gas sensors are more popular in the current scenario. These sensors rely on the direct chemical interaction between the analyte species and sensing material. They are easy to use, durable, eco-friendly and cost effective. For this, several metal oxide semiconductor (MOS) nanomaterials such as ZnO, SnO2, NiO, and TiO₂ have been studied [12–15]. The sensing materials have been realized using different chemical methods, such as hydrothermal [16], wet chemical route [17] and solvothermal [18]. Among them, the solvothermal technique offers the advantage of being eco-friendly and accordingly, is commercially exploited for the synthesis of well-defined nano-morphologies [19]. Of the different MOS, ZnO, having a wide band gap of 3.3 eV and a large exciton binding energy of 60 meV [20], is considered to be a suitable candidate for gas sensing application.

ZnO is n-type in nature and has some unique properties like biocompatibility, good electron mobility, thermal and chemical stability. Another semiconductor material, NiO is p-type in nature, has wide band gap of 3.7 eV and exhibit good electrical, chemical, and

Table 1 Different ZnO/NiO nanocomposite based gas sensors

thermal stability. It also show good catalytic properties to oxidize metal oxides [21]. Thus, use of ZnO and NiO together is anticipated to form random nano heterojunction namely p-n junctions and thereby could show enhanced sensing responses. Table 1 compares responses of different ZnO/NiO-based nano-heterostructures towards different gases. The observed improved response kinetics have been attributed predominantly to the unique interaction with the test gases resulting in subsequent collapse and formation of p-n junctions resulting in a drastic change in electric properties thereby a higher sensor response [22]. The nanocomposites are investigated for their response towards different gases using chemiresistive principles. The chemical interaction on the sensor surface results in the large change in the resistance which is measured and calibrated with respect to gas concentration. As is evident from the Table 1, the ZnO/NiO heterostructure system has been explored for sensor towards gases like H2S, SO2, acetone and toluene. The heterostructure system has been rarely reported for the NOx detection. For example. Dong et al., investigated the litchi shell-like porous NiO/ZnO composite film realised using electrodeposition method for its response towards NOx at room temperature. The sensor film exhibited a response of 74.0% towards 100 ppm of NOx gas [23]. Similarly, NiO coated ZnO films realized using chemical bath deposition method has also been reported for the NO2 sensing by Mane et al. [24]. The sensor film exhibited a response of 76.5% towards 100 ppm of NO2 at moderate working temperature of 150 °C.

Material	Technique	Morphology	Analyte	Conc. (ppm)	SR/T (°C)	References
ZnO-Al	Hydrothermal	NW	NO ₂	4	6.2/230	[41]
NiO	Hydrothermal	NP	(CH ₃) ₂ CO	100	0.25/300	[47]
ZnO/NiO	Wet-chemical	Core shell	(CH ₃) ₂ CO	500	NA/300	[48]
ZnO/NiO	Co-sputtering	Thin film	C ₂ H ₆ O	100	5,4/300	[49]
ZnO/NiO	Electro-spinning	Multi-junction grains	(CH ₃) ₂ CO	100	6/25	[50]
ZnO/NiO	Hydrothermal	NW	H_2S	100	0.31/25	[51]
ZnO/NiO	Hydrothermal	Nano disk	SO ₂	50	28/240	[52]
ZnO/NiO	Chemical	Litchi shell	NOx	100	0.74/25	[23]
ZnO/NiO	Co-precipitation	Microspheres	Toluene	100	240/300	[53]
ZnO/NiO	Hydrothermal	Nanodisks	SO ₂	20	16.25/240	[54]
ZnO/NiO	Green method	Nanocubes	LPG	2.5 vol.%	7.72/32	[55]
ZnO/NiO	Hydrothermal	3D NW network	Ethylene glycol	100	58.87/175	[56]

SR sensor response, NW nanowires, NP nanoparticles, LPG liquified petroleum gas

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ORIGINAL RESEARCH



One pot gamma radiation mediated interfacial engineering of P-N synergistic flame retardant and antibacterial cellulose fabric: novel fabrics for future applications

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Abstract The work describes an ionizing radiation mediated, toxic solvent free interfacial engineering of a novel Phosphorus-Nitrogen functionalized bifunctional cotton cellulose fabric (*BCF*) endowed with flame retardant (FR) and antibacterial properties. Monomers bis[2-(methacryloyloxy)ethyl] phosphate (B2MEP) and [2-(methacryloyloxy)ethyl]trimethyl-ammonium chloride (MAETC) in different proportions were co-grafted onto cellulose fabric via ⁶⁰Co radiation mediated Simultaneous Irradiation Grafting Process (SIGP) to incorporate Phosphorus and Nitrogen functionalities. Effects of radiation dose, monomer concentration on the grafting yield (GY) were investigated and samples were characterized using TGA, ATR-FTIR, XRD, SEM–EDX, EDXRF,

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S. R. Kanatt · M. Tiwari Environmental Monitoring & Assessment Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India CHN Elemental Analysis and XPS analytical techniques. Limiting oxygen index (IS:13501/ASTM D 2863) and vertical flammability tests (IS11871-1986) were conducted to establish the halogen free, P-N synergistic FR properties of the fabric. All the cografted samples were observed to possess LOI values in excess of 30%, while BCF (1:2) (GY = $\sim 44\%$) demonstrated LOI of 32% with the least char length of 74 mm in the vertical flammability tests. Tear strength studies were carried out as per ASTMD 1424-09. Antibacterial assay revealed that the fabric possessed activity against both gram positive (S. aureus) and gram negative (E. coli) organisms, with BCF (1:4) (GY = $\sim 48\%$) demonstrating complete killing of ~5 log cycles for both microorganisms in 24 h. BCF retained its FR and antibacterial properties even after multiple washing cycles. With its bonafide green credentials, durability and unique properties, multifunctional BCF fabric prepared under optimized conditions of P/N ratio > 1.7 and GY ~ 45% can be a potential candidate for future applications.

Keywords Cellulose · Radiation grafting · Green synthesis · Synergism · Flame retardant · Antibacterial

Introduction

The diverse applications of cellulose and its multiple forms is well documented, with its primary application being in the form of fabric for apparel manufacture. Since ancient times, cotton fabric has been the preferred starting material for garments manufacture because of the comfort it provides, fabric softness, breathability, sustainability, low maintenance, non-toxicity, light weight and a number of other advantages (Ling et al. 2023). With modern requirements demanding modern innovations, significant amount of work has gone into imparting special properties onto the cotton fabric, such as hydrophobicity, antimicrobial properties, flame retardancy (FR), anti-creasing, enhanced durability, etc. Flame retardancy, in particular, is of critical importance for many niche applications where cotton fabric, despite its numerous other advantages, cannot be used owing to its high flammability (LOI of ~18%) and susceptibility to thermal degradation (He et al. 2018; Horrocks 2011; Mostashari and Mostashari 2008). Fire accidents caused by textiles account for~33% of all fires in the world. Therefore, incorporation of FR properties onto cotton fabric would benefit applications in areas such as the manufacture of curtains, carpets, car seats, sofas, firefighting clothes, etc. In fact, the global demand for flame retardants was estimated at over 2.904 million tons in the year 2020, with the market size of FR fabrics topping \$1,056 billion (Ling et al. 2023).

Most flame retardant treatments are categorized into four distinct groups, based on the use of halogenated organic, inorganic, organophosphorus, and nitrogen formulations (Kemmlein et al. 2009; Abou-Okeil et al. 2013; Liang et al. 2013; Ling and Guo 2020; Rosace et al. 2018). However, some of these products, especially those based on halogenated compounds, are notorious for the production of carcinogens, dioxins, corrosive compounds and toxic smoke during the burning process. Several countries have, therefore, already banned their use (Ling and Guo 2020). Consequently, polymeric intumescent coating based FRs containing phosphorus and nitrogen have become popular of late owing to their lower toxicity profiles, excellent durability and compact char formation during the burning process (Abou-Okeil et al. 2013). Interestingly enough, it has also been noted that the presence of N in P containing FR can yield some sort of synergistic effect resulting in enhanced performance and lower P content requirement than when P is employed alone (Nguyen et al. 2012). The synergism in P-N containing FRs probably arises

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due to the presence of electrophilic phosphorus, whose Lewis acidity promotes cellulose dehydration and char formation, and the nucleophilic attack of N on P that favours formation of polymeric species containing highly polar P-N bonds. This increases the electrophilicity of P facilitates phosphorylation of the C(6) primary hydroxyl groups of cellulose chains, thereby blocking levoglucosan formation. An anhydrous sugar, levoglucosan (1,6-anhydro- β -Dglucopyranose) is a major product formed during cellulose pyrolysis (Horrocks 1983, 2008).

With a view to further enhance the scope of cotton fabric application in the industry, numerous efforts have been made to endow cotton with some additional properties such as superhydrophobicity (Zhou et al. 2013; Liu et al. 2012), UV resistance (Duan et al. 2011), antistatic property (Zhang et al. 2014), anti-creasing property (Cong et al. 2021), antimicrobial properties (Goel et al. 2009), etc. Antimicrobial properties, in particular, are crucial from the health and safety aspect if cotton is to be used in applications where fabric would be in close contact with the human body or is prone to exposure to high humidity and contaminated environments. Cotton, due to its high hydrophilicity and porosity, is susceptible to microbial growth that can not only promote fibre degradation but also cause severe skin diseases (Fang et al. 2015). The focus has therefore shifted towards developing multifunctional cotton fabrics (Jianjun et al. 2023) with greater versatility in terms of applicability and durability. Working upon this concept, several methodologies have recently been reported for the development of multifunctional coatings on cotton fabrics, such as linear polysiloxanes (Jin et al. 2023), melamine tannic phosphate-polyvinyl alcohol (Makhlouf et al. 2021), flame retardancy-dopamine@ silver-polydimethylsiloxanes (Ling and Gu 2020), polyhexamethylene guanidine phosphate-ammonium polyphosphate assemblies, etc. (Fang et al. 2015).

Most of the reported work on multifunctional cotton fabrics rely on the conventional methods of finishing, such as the sol-gel process (Rosace et al. 2018) and the pad dry cure (PDC) process (Liu et al. 2021), involving a cross-linking agent/initiator. Conventional chemical grafting processes often necessitate the use of high temperature, solvents and chemical initiators that can adversely affect the environment as well as the strength of the fibre. To circumvent these shortcomings, radiation-based treatment methods have




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Radiological Facility

ORIGINAL PAPER



Optimization of Placement of Continuous Air Monitors in a

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Abstract

The airborne concentration of radioactive materials in radiological facilities is primarily influenced by the ventilation system, air purification system, and emission sources. Continuous Air Monitors (CAMs) are installed in these facilities to monitor the activity concentration of radioactive aerosols during both routine operations and any malfunctioning conditions. Typically, CAM placement is determined by the direction of maximum airflow. However, aerosols do not always adhere to the behaviour of airstreams, raising concerns about the suitability of CAM placement. To address this issue, this study employs software that integrates aerosol dynamics with computational fluid dynamics to calculate the CAM Placement Parameter. This parameter is derived from the peak aerosol concentration and the lag time to reach the specified CAM location, indicating the relative merit of positioning CAMs in a radiological facility under varying ventilation rates. The findings suggest that the coupled aerosol-fluid dynamics model accurately predicts the optimal placement of CAMs in workplace environments, thereby minimizing occupational exposure.

Keywords Airborne radioactivity · Continuous air monitor · Computational fluid dynamics · Aerosol dynamics · Occupational exposure

1 Introduction

Radioactive aerosols generated during normal operations of nuclear and radiological facilities can be released into the workplace environment due to breaches in protective barriers. Under such disruptions, aerosols may reach workers' breathing zones. Engineering safety features such as ventilation and filtration systems are designed to confine and remove these aerosols. Continuous Air Monitors (CAMs) detect and quantify airborne particulates, alerting workers if air concentrations exceed set limits. To minimize personal exposure, optimal CAM placement requires a detailed understanding of airflow patterns and aerosol distribution.

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This study focuses on determining the best locations for CAM placement using Computational Fluid Dynamics (CFD) simulations.

Previous studies, such as those by Zhang and Chen (2006a, b), have highlighted the necessity of CFD for enhancing worker safety in hazardous environments but did not include particle dynamics. Haim et al. (2000) and Konecni et al. (2000) demonstrated that numerical simulations of airflow in nuclear workplaces assist in determining appropriate air sampler locations. CFD simulations have been widely used to optimize ventilation design, worker safety, and facility costs (Chen et al. 2003; Konecni et al. 2002; Whicker et al. 1999).

In non-nuclear industries, CFD is extensively adopted to design indoor air conditioning systems, enhancing air quality and comfort (Yang et al., 2014). Hanafi et al. (2023) investigated airflow in swimming pools, finding that certain inlet configurations improved thermal comfort and air quality. Additionally, Devi & Chauhan (2022) and Adelikhah et al. (2023) used CFD to study thoron and radon concentrations, respectively, demonstrating its effectiveness in predicting and mitigating hazardous conditions.

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Studies incorporating aerosol dynamics into CFD, such as those by Mariam et al. (2021) and Salim et al. (2006), have further improved the understanding of aerosol behavior under various conditions. In nuclear environments, Dieguez-Elizondo et al. (2017) emphasized the importance of ventilation system positioning for managing aerosol dispersion and removal. However, few studies have specifically focused on CAM placement in nuclear facilities using coupled aerosol-CFD (A-CFD). Previous strategies (Whicker et al. 1997, 2002, 2003; Konecni et al. 2000; Geraldini 2016) employed metrics like lag time, peak concentration, and exposure fraction to optimize CAM locations.

The present study proposes a coupled A-CFD approach to examine spatial and temporal aerosol metrics, considering the dynamics affecting particle transport. We applied this model to a radiological facility, using lag time and peak aerosol concentration to evaluate the effectiveness of CAM placement. Additionally, this study introduces an examination of how varying ventilation rates influence the decisionmaking process for CAM placement.

2 Materials and Methods

2.1 Numerical Code

ANSWER is a finite volume-based CFD software (Patankar 1980; Versteeg & Malalasekera 2007) that solves the 3-D Navier-Stokes equations for incompressible and compressible fluid flows with arbitrary polyhedral grids. This code (ACRi, 2016) also incorporates various turbulence models, including Reynolds-Averaged Navier-Stokes (RANS)based models, Reynolds stress models, k-E, and LES (Large Eddy Simulation). The CFD framework of this code has been coupled with modules written for aerosol transport and dynamics, enabling it to handle aerosol dynamical processes such as coagulation and removal mechanisms as described in Eq. (1) (Rajagopal et al. 2021). Literature studies (Svenningsson et al. 1994; Eichler et al. 2008) indicate that the influence of water vapor condensation and hygroscopic growth is minimal (compared to growth due to coagulation) for RH levels below 50%, a condition typically maintained in laboratories to ensure comfort ventilation as part of standard operating procedures. Therefore, condensation process has not been included in the present study. Nucleation is ignored since we are interested in the release scenario involving direct emission of aerosol particles. Equation (1) represents an integro-differential equation, where the integral terms account for the coagulation process of particles, depicted on the right-hand side.

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$$\begin{aligned} \frac{\partial n (d_{p}, r, t)}{\partial t} + \nabla_{-} [Un (d_{p}, r, t)] \\ &= \nabla_{+} \{Dt (r, t) \nabla n (d_{p}, r, t)\} \\ &+ \frac{1}{2} \int_{-n}^{d_{p}} K (d_{p}^{\prime}, d_{p} - d_{p}^{\prime}) n (d_{p}^{\prime}, r, t) n (d_{p} - d_{p}^{\prime}, r, t) d (d_{p}^{\prime}) \\ &- n (d_{p}, r, t) \int_{-n}^{\infty} K (d_{p}, d_{p}^{\prime}) n (d_{p}^{\prime}, r, t) d (d_{p}^{\prime}) \\ &+ S (d_{p}, r, t) \\ &- \nabla_{-} [U_{d_{p} H} n (d_{p}, r, t)] \end{aligned}$$
(1)

where d_p and d'_p are particle diameters, $n(d_p, r, t)$ is the spatially (r) and temporally (t) varying number concentration distribution function for particle diameter d_p, U is the gas phase velocity, D' is the particle diffusivity, $K(d_p, d'_p)$ is the collision frequency between particles of different sizes, S is the source term and U_{drift} is the total drift velocity of the aerosol particles due to various mechanisms like gravitational settling, thermophoresis and turbophoresis. Second and third term on R.H.S. of the above equation describes the formation and loss of particle size d_p by coagulation. Since we are primarily interested in the earliest detection of the released aerosol and the evolution of its concentration distribution inside the facility, the phenomenon of resuspension, which occurs over a longer time, has been ignored.

The particle diffusivity used in Eq. (1) is also a function of particle size and is given by,

$$D' = \frac{K_b T C_e}{3\pi \,\mu_g d_p} \tag{2}$$

where K_b is the Boltzmann constant, T is the temperature, μ_g is the gas viscosity, and C_c is the Cunningham slip factor (Cunningham 1910; Davies, 1966)

$$C_c = 1 + K_n * (2.514 + 0.8 * \exp(-0.55/K_n))$$
(3)

where K_n (Knudsen number) is the ratio of the mean free path of the gas particles (λ) to the particle diameter (d_p) and is given as,

$$K_n = \frac{2\lambda}{d_p} \tag{4}$$

The aerosol general dynamic equation (Eq. 1) is solved for each aerosol particle diameter class d_p at every time step, with the particle diameter range divided into *m* classes in the discrete domain. This process is facilitated by the necessary inputs from flow field simulation results provided by the CFD part of the software. The master equation managing the aerosol dynamic equation comprises various sub-modules, each of which has been validated against analytical and/or experimental solutions by Rajagopal et al. (2018).



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Phosphorous determination in nuclear reactor materials: dysprosium titanate, titanium dioxide and uranium oxide

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Abstract

A reliable analytical methodology is developed to determine phosphorus as phosphate in nuclear matrices viz uranium oxide, TiO_2 and dysprosium titanate by spectrophotometric molybdenum blue method. Refractory matrices (TiO_2 and dysprosium titanate) are dissolved employing microwave technique. Calibration is linear in the concentration range from 0.1 to 1.0 ppm of phosphorous with r² better than 0.9989. LOD obtained is 0.03 ppm. Method and instrumental RSD is 1 and 0.3%, respectively at 0.33 ppm level. Recovery of P at 0.33 ppm level is better than 95%. The developed method is validated by comparing results obtained by ion chromatography.

Keywords Phosphorous determination · Spectrophotometry · Uranium · Titanium dioxide · Dysprosium titanate

Introduction

Materials having high neutron-absorption cross-section is used to control the reactivity of the nuclear reactors. Control rods based on boron are used in many reactors, however, there is large radiation induced damage with helium formation and swelling of clad material caused by (n,α) reaction of ¹⁰B [1, 2]. Among the materials explored for control rods having better radiation damage resistance, dysprosium titanate (Dy being a strong neutron absorber) is one of the promising materials for the thermal neutron reactors. There exist seven naturally occurring isotopes of dysprosium, ¹⁵⁶Dy, ¹⁵⁸Dy, ¹⁶⁰Dy, ¹⁶¹Dy, ¹⁶²Dy, ¹⁶³Dy and ¹⁶⁴Dy. Among these isotopes, 164Dy (28.18% natural isotopic abundance) has the largest absorption cross Sect. (2,650 barns) for thermal neutrons and thus used as burnable poison in nuclear reactors [3, 4]. Studies have shown that lanthanoid oxides (Ln₂O₃•MO₂) with the fluorite structure have the best radiation damage resistance [5, 6]. Dysprosium titanate (Dy2O3•TiO2) is used in control rods of thermal neutron reactors [7-9]. The main advantages of dysprosium titanate control rods in reactor

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conditions are low swelling, no gaseous formation and hence no bubbling, high melting point (~1870 °C), high neutron efficiency, non-interaction with cladding materials at temperatures above 1000 °C and easy fabrication. In addition, dysprosium titanate has good mechanical properties and thermal stability. Dysprosium titanate is produced either by high-temperature sintering of pelletized oxide mixtures or their induction melting followed by grinding and sieving into specific size fractions [5, 10] After fabrication, like other nuclear materials, its chemical quality control is crucial to ensure its desired performance in reactor. Analysis of nonmetallic phosphorus is a part of chemical quality control and specification limit is 100 ppm for raw material titanium dioxide of dysprosium titanate. To the best of our knowledge, no report is available in literature for phosphorus determination in dysprosium titanate. In uranium, the presence of phosphorous can cause complications during fuel fabrication and integrity of the cladding material during reactor operation. Phosphorous can be introduced into nuclear fuels during various steps in fuel processing and fabrication [11]. Specification of phosphorous in Nuclear-Grade, Sinterable Uranium Dioxide Powder is 250 µg/gU [12]. Therefore, studies were carried out to develop an analytical methodology for phosphorus determination in dysprosium titanate, titanium dioxide and uranium.

Dissolution of titanium dioxide and dysprosium titanate is very challenging as they are extremely refractory in nature. Microwave assisted dissolution is employed in case

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of extremely refractory materials. Thus in the present work, matrix dissolution using the microwave technique in pressurized closed vessels was studied and optimized [13, 14]. Uranium could be dissolved by heating on the hot plate in the acidic media. For phosphorus determination in different matrices, various analysis methods are reviewed [15-18]. Though, phosphorus determination can be done by electrochemical methods [19-24], fluorescence [25-30], LIBS [31, 32], ICP-AES [33], chromatography [34-36], ICPMS [37], NMR [38], XRF [39], Colorimetry [40, 41], Raman spectroscopy [42], ICPOES [43] and Capillary Electrophoresis [44], spectrophotometric molybdenum blue method reaction offers simple, cost effective and sensitive determination of phosphorus. In this method, phosphorus as phosphate reacts with Mo under acidic condition to form 12-molybdophosphoric acid which is then reduced to form intensely colored phosphomolybdenum blue (PMB) [45-53]. Spectrophotometric molybdenum blue method has been comprehensively reviewed [54, 55]. The molybdenum blue reaction occurs in two stages; the first stage involves the formation of a keggin ion around the analyte phosphate anion and the second stage involves the reduction of this yellow colored heteropoly acid to form mixed-valence species of blue-colored PMB. These stages can be described in the simplified forms as shown in Eqs. (1) and (2):

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \to H_3PO_4(MoO_3)_{12} + 12H_2O$$
(1)

$$H_{3}PMo(VI)_{12}O_{40} + red \rightarrow \left[H_{4}PMo(VI)_{8}Mo(V)_{4}O_{40}\right]^{3-} (2)$$

The blue color of the species formed is due to an intensely absorbing inter-valence charge transfer (IVCT) transition involving interconversion of Mo(V) and Mo(VI). Different kinds of reductants (e.g. ascorbic acid, SnCl2, hydrazine sulfate, hydroquinone) and acids have been used in this reaction. Depending on the type of reductant used, PMB has intense band in the range of 700-900 nm, and the typical molar extinction coefficients reported are between 10,000-34,000 L mol⁻¹ cm⁻¹ [54]. Among the reactants, ascorbic acid acts as a 2-electron reductant [56] and is less salt sensitive [57], however it has the disadvantage of slow color development [58]. To circumvent this problem, Murphy and Riley reported [45] that the addition of antimony as catalyst increases the rate of reduction of the complex and this became the most cited and adopted method for phosphorous determination. Though it was initially postulated that antimony acts as a catalyst, later it was shown that antimony is not a catalyst but is incorporated into the complex as PSb₂Mo₁₂O₄₀ and confirmed by Going and Eisenreich [59]. With reductant SnCl₂, the reaction kinetics and sensitivity is fast, however there is color instability, salt error and temperature dependence [60]. Final product formed from

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reductant SnCl₂ gives a twin peak spectrum ($\varepsilon \sim 19,000$ at λ 700 nm and $\varepsilon \sim 16,000$ at λ 620 nm) whereas with reductant ascorbic acid and Sb the twin peak spectrum has $\varepsilon \sim 34,000$ at λ 880 nm and $\varepsilon \sim 20,000$ at λ 710 nm.

The present work describes spectrophotometric molybdenum blue method adapted for nuclear matrices that is dysprosium titanate, titanium dioxide and uranium oxide subsequent to optimization of microwave assisted dissolution of nuclear matrices and matrix separation procedure employing cation exchange cartridge.

Experimental

Reagents/chemicals/materials

Unless otherwise stated, all reagents used were of analytical grade quality and were used without further purification. Hydrochloric acid, nitric acid, hydrofluoric acid and sulfuric acid were of supra-pure grade purchased from Merck India. Potassium antimonyl tartrate trihydrate ($C_8H_4K_2O_{12}Sb_2\bullet 3H_2O$) was purchased from Loba Chemie Pvt Ltd. Ascorbic acid was of S. D. Fine Chemicals and ammonium heptamolybdate tetrahydrate, ((NH_4)₆ $Mo_7O_24\bullet 4H_2O$ was of Merck. High purity deionized water (DI) of resistivity 18.2 M Ω cm from Millipore system was used throughout.

Preparation of stock solutions

0.274 g of potassium antimony tartrate trihydrate was dissolved in 100 mL of DI water. 2 g of ammonium heptamolybdate tetrahydrate was dissolved in 50 mL of DI water. 0.88 g of ascorbic acid was dissolved in 25 mL of DI water. A stock solution of phosphorous as phosphate (1 mg L⁻¹) was prepared by dissolving the 1.42 g of potassium dihydrogen phosphate in 1 L with DI water. Working solutions were prepared subsequently by appropriate dilutions.

All solutions were made in polypropylene flasks/polyethylene bottles and stored in refrigerator. Experiments were done in quartz apparatus.

Instrumentation

Jasco V670 from Hitachi (Japan) Double beam spectrophotometer was used for obtaining the normal and derivative spectrophotometric data. This instrument works in the wavelength range of 190–1100 nm and uses a photomultiplier tube as a detector. Microwave—3000 dissolution system from Anton Paar was used to dissolve the sample. Commercial cartridge (Onguard II H) of Dionex make was used to remove cations from the solution. A commercial Ion-Chromatography System (Dionex DX-500) ion chromatography





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Physicochemical and spatial distribution patterns of radon and its parent radionuclides in the uranium-mineralized Singhbhum Region, India

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Abstract

This study examined the distributions of radon and its parent radionuclides 226 Ra and 238 U in groundwater samples from the Singhbhum region, Jharkhand, India. Radon showed a heterogeneous spatial distribution pattern, with a lognormal distribution. A good correlation between radon bubbler-Lucas cells and liquid scintillation counting techniques was observed for radon monitoring. 222 Rn and 226 Ra were negatively correlated with pH, suggesting the mobilization of radionuclides at low pH. Uranium was positively correlated with common ions (e.g., Ca, Mg, and SO₄^{2–}). The activity ratios among the radionuclides indicated disequilibrium, with 222 Rn origin controlled by parent radionuclide activity in bedrock. The 226 Ra and 238 U concentrations in groundwater were lower than the limits recommended by the WHO.

Keywords Radon (222 Rn) · Uranium (238 U) · Radium (226 Ra) · Disequilibrium · Groundwater

Introduction

Groundwater contains radionuclides of natural origin in trace amounts depending on the geological (nature of rock and soil) and environmental conditions (temperature and rainfall) [1, 2]. Uranium is naturally present in soil and rock in different quantities and is released into groundwater by natural weathering and anthropogenic activities such as industrial mining, milling, and poor management of mining waste. The abundance of 238 U is greater (99.27%) than that of two other uranium isotopes: 234 U and 235 U [3]. Uranium mainly exist in two different oxidation states such as U⁴⁺ and UO₂²⁺ in aqueous environments. U(IV) produces polymeric mixed hydroxides under anoxic conditions which are insoluble, whereas carbonate complexes are formed in groundwater under natural conditions. In an oxidizing atmosphere, U(IV) oxidizes to U(VI), which can readily form many soluble species and become more vulnerable to migration during weathering [4]. pH, redox status, partial

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pressure of carbon dioxide, and the presence of complexing anions such as CO32-, PO43-, F-, and SO42- are the primary factors influencing the distribution pattern of uranium in groundwater [5]. Among the daughter products of ²³⁸U, the most important radionuclides are ²²⁶Ra and ²²²Rn because of their radiological significance. 226Ra is an alphaemitting radionuclide with a 1622-year half-life, possesses only Ra(II) as its oxidation state in the environment, and has chemical characteristics similar to those of other alkaline earth metals [6]. If radium is ingested, approximately 20% is absorbed and transported into the blood circulation, where it primarily builds up in the bones [7]. 222Rn is an immediate decay product of ²²⁶Ra, and its concentration is governed by the 226Ra content in different rocks, soils, and associated aquifers. Radon is a unique natural radionuclide in drinking water because it is a gas that does not have chemical affinities. Short-lived noble gas ²²²Rn (t_{1/2}=3.82 days) has the potential to either escape before decay or decay inside the matrix to create additional daughter products such as ²¹⁸Po, ²¹⁴Pb, ²¹⁴Bi, ²¹⁴Po, ²¹⁰Pb, ²¹⁰Bi, and ²¹⁰Po. ²²²Rn is not transported over long distances because of its short halflife, and its level in groundwater is regulated primarily by the rock lithology and soil around the borehole. In a mineralized region, higher ²²²Rn and ²²⁶Ra concentrations may be expected in groundwater, and sometimes higher concentrations of these radionuclides can help identify uranium

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mineralization in a particular zone and predict the nature of the rocks associated with the aquifers. ²²²Rn can enter the human body via the ingestion of water and/or inhalation of air. Fifty-two percent of the natural radiation dose to the worldwide population is contributed by 222Rn and its daughter products [8]. Indoor ²²²Rn is caused mainly by exhalation from adjoining soil and building materials. Drinking water contributes approximately 1-2% of the total exposure to radon through the inhalation of radon gas [9]. Dissolved ²²²Rn has also been highlighted as a public health concern when it is present in excessive quantities in potable water. A maximum contaminant level (MCL) of 11 Bql⁻¹ and an alternate maximum contaminant level (AMCL) of 148 Bql⁻¹ combined with requirements for multimedia mitigation (MMM) programs for community water systems serving up to 10,000 people have been recommended by the USEPA (United States Environmental Protection Agency) for dissolved radon in water [9]. Several studies have been carried out in other parts of the country and worldwide to assess radon levels in groundwater; however, few studies have explored the relationships of radon with its parent radionuclides and other physicochemical properties [10-13]. The current study area bears special significance because of the large deposit of uranium and other commercially significant minerals. A brief study on the distributions of ²²²Rn, 226Ra, and 238U activity and physicochemical parameters in groundwater was conducted around the mineralized Singhbhum region of Jharkhand, India. This study explores the influence of groundwater chemistry on the distribution of these radionuclides; the relationships among the occurrence of ²²²Rn, ²²⁶Ra, and ²³⁸U; and background databases for the assessment of alterations in radioactivity levels resulting from natural or anthropogenic activities in the future.

Materials & methods

The study area

Groundwater sampling was conducted in the southeastern part of Jharkhand state (Saraikela-Kharsawan and East Singbhum districts) in eastern India, which is a part of the highly mineralized Singhbhum shear zone (SSZ). The Singhbhum Shear Zone hosts a large quantity of established mineral deposits (copper, uranium, etc.) of significant commercial importance. The major copper deposits are located around Rakha, Surda, and Musaboni. The country's second-largest uranium deposits are located in the SSZ, where Jaduguda, Narwapahar, Turamdih, and Banduhurang are the major uranium mineralized deposits. Approximately 53% of the study area is occupied by residual mountains and hills composed of granite, quartzite, polymictic conglomerate, and various schists [14]. The main types of soil found in the research

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region include lateritic soil, red gravelly soil, red sandy soil, and red loamy soil [15]. The region's climate is described as extreme in nature, with scorching summers and chilly winters. The rainy season runs from June to September. In the studied region, rainfall is the key regulating factor for groundwater recharge, which ranged from 945 to 1498 mm and 1602 to 2147 mm, respectively, in Saraikela-Kharsawan and East Singhbhum in the last five years. Unconfined as well as semiconfined to confined aquifer conditions are found in the study areas. The unconfined state occurs in the weathered part of the mantle portion of the rock and generally ranges in depth from 15 to 34 m. Fractures occur at depths of 30–200 m below ground (mbgl) in hard rock terrains [16].

Sampling and processing

Groundwater samples (108 nos.) were collected from borewells and handpumps in precleaned plastic bottles for analysis of different radiochemical constituents during the postmonsoon season. Five liters of water from each location were collected, and the pH, temperature, oxidation reduction potential (ORP), total dissolved solids (TDS), and electrical conductivity (EC) of the samples were measured immediately after sampling. The groundwater sampling locations are presented in Fig. 1.

Assessment of ²²²Rn

²²²Rn in groundwater was estimated via a radon bubblerscintillation cell technique and liquid scintillation techniques. The water samples were sampled, handled, and stored as outlined in ISO 13164-4 [17].

Radon bubbler-scintillation cell technique

An approximately 80 ml water sample was taken into a radon bubbler, and immediately dissolved ²²²Rn gas was collected into a pre-evacuated Lucas scintillation cell with an internal volume of 150 ml. Three scintillation cells were used to ensure the quantitative transfer of ²²²Rn gas from the water samples. After attaining equilibrium between ²²²Rn and its short-lived daughter products (approximately 180 min), the cell was counted for alpha activity via an alpha counter (Make: M/s. Polltech Instruments, India, Model: PSI-PCS 2). The dissolved radon concentration in the water samples was estimated via Eq. 1 [18].

$$C_{Rn}(Bql^{-1}) = \frac{6.97 \times 10^{-5} \times C \times e^{\lambda t}}{EV(1 - e^{-\lambda T})}$$
(1)

where C is the net count at counting time T (10 min), λ is the ²²²Rn decay constant (min⁻¹), E is the efficiency of the





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RESEARCH



Promoter of COR2-like gene is a stress inducible regulatory region in banana

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Abstract A promoter is a crucial component in driving the expression of a transgene of interest for biotechnological applications in crop improvement and thus characterization of varied regulatory regions is essential. Here, we identified the promoter of COR2-like (codeinone reductase-like) from banana and characterized its tissue specific and stress inducible nature. MusaCOR2-like of banana is closely related to COR2 and CHR (chalcone reductase) sequences from different plant species and contains signature sequences including a catalytic tetrad typical of proteins with aldo-keto reductase activity. Transcript level of MusaCOR2-like was strongly induced in response to drought, salinity and exposure of signaling molecules such as abscisic acid, methyl-jasmonate and salicylic acid. Induction of MusaCOR2-like under stress strongly correlated with

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S. Bhakta · S. Singh · H. Tak Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400094, India the presence of multiple cis-elements associated with stress responses in the $P_{MusaCOR2-like}$ sequence isolated from Musa cultivar Rasthali. Transgenic tobacco lines harbouring P_{MusaCOR2-like}-GUS displayed visible GUS expression in vascular tissue of leaves and stem while its expression was undetectable in roots under control conditions. Exposure to drought, salinity and cold strongly induced GUS expression from P_{MusaCOR2-like}-GUS in transgenic tobacco shoots in a window period of 3H to 12H. Applications of salicylic acid, methyl-jasmonate, abscisic acid and ethephon also activate GUS in transgenic shoots at different period, with salicylic acid and abscisic acid being the stronger stimulants of P_{MusaCOR2-like}. Using P_{MusaCOR2-like}-GUS fusion and expression profiling, the current study sheds insights into a complex regulation of COR2-like, one of the least studied genes of secondary metabolite pathway in plants.

Keywords $Musa \cdot CO2$ -like \cdot Tobacco \cdot Promoter \cdot GUS \cdot Codeinone reductase

Abbreviations

ABA	Abscisic acid
AKR	Aldo-keto reductase
BAP	6-Benzylaminopurine
CHR	Chalcone reductase
COR	Codeinone reductase
DMAS	Deoxymugineic acid synthase
EF1α	Elongation factor 1-alpha
GUS	β-D-Glucuronidase

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hpt-II	Hygromycin phosphotransferase-II
MeJA	Methyl jasmonate
MGR	Methylecgonone reductase
NAA	Naphthaleneacetic acid
NOR	NAD(P)-linked oxidoreductase
NDCS	NADPH-dependent deoxychalcone synthase
SA	Salicylic acid
T-DNA	Transfer DNA
X-Gluc	5-Bromo-4-chloro-3-indolyl glucuronide

Introduction

Biotechnology has revolutionized the field of plant science resulting in immense progress in crop improvement. Development of a transgenic crop requires a considerable understanding of regulatory elements in a plant specific manner as the regulatory mechanisms generally differs in various species. Hence, efforts are required to identify and characterize promoters for their tissue specific and inducible nature. Banana is an economically important crop and is extremely sensitive to various stress conditions. The availability of stress inducible promoters will assist researchers in genetic engineering of banana for modulation of its biochemical and physiological aspects. Banana contains numerous secondary metabolites such as alkaloids, flavonoids, terpenoids, glycosides, phenolics and tannins among others (Onyema 2016; Zaini 2022). Codeinone reductases (COR), are important enzymes of aldo-keto reductase (AKR) superfamily and are involved in NADPH-dependent reduction of carbonyl groups in key intermediates (Mindnich and Penning 2009). COR plays a crucial role in biosynthesis of pharmacologically important narcotics such as codeine and morphine in the opium plant (Unterlinner et al. 1999). In opium, six alleles of COR were identified and four cDNAs were reported as isoforms of COR with similar substrate specificity (Unterlinner et al. 1999). Members of the AKR superfamily have been identified in all the organisms and are classified into 18 subfamilies with functions in metabolite synthesis, detoxification and carbon assimilation (Penning et al. 2015). AKRs are thus involved in synthesis of many metabolites such as tropanes, cardiac glycosides, important alkaloids, flavonoids and ascorbic acid (Agius et al. 2003).

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Many secondary metabolites are involved in stress responses and several of them including flavonoids, terpenoids, lignin and isoprenoids are induced in banana following infection of Xanthomonas campestris pv. musacearum (Tripathi et al. 2019). The antibacterial activity of banana leaf extract against methicillin-resistant Staphylococcus aureus had also been attributed to alkaloids and terpenoids (Sivasamugham et al. 2021). Jasmonic acid is a potent inducer of secondary metabolites including alkaloids in several plant species (Van der Fits and Memelink 2000). Further abiotic stresses such as salinity and drought have also been reported to positively influence the production of alkaloids in different plant species (Honório et al. 2021). However, cold stress has been documented to have a negative impact on production of alkaloids in Catharanthus roseus (Dutta et al. 2007). The regulation of different secondary metabolite genes especially those of alkaloid biosynthesis pathway under stress is poorly understood. Few reports on genome-wide identification of AKRs and their expression under stress have been documented in Medicago truncatula and Solanum lycopersicum indicating their importance in stress tolerance of plants (Yu et al. 2020; Guan et al. 2023). Reports on the beneficial effect of AKR overexpression on abiotic stress tolerance have also emerged confirming their diverse roles in various pathways of plant species such as peach, rice and Physcomitrella patens (Chen et al. 2019; Kanayama et al. 2014; Turoczy et al. 2011).

The regulation of CORs and their homologues under stress and inducible activity of their promoter regions in plants are largely unknown. Moreover, lack of adequate studies on promoter of secondary metabolism pathway genes have limited their applicability and hampered understanding of their compartmentalization in plants. Using promoter characterization, Dastmalchi and Dhaubhadel (2015) identified organs-specific expression of chalcone isomerase (CHI) genes in soybean. Bell-Lelong et al. (1997) characterized the tissue specific nature of cinnamate-4-hydroxylase (C4H) and correlated various cis-elements with its conditiondependent inducibility. However, only few studies on the promoter region of phenylpropanoid pathway genes such as CHI, F3'5'H and C4H have emerged providing clues on tissue specific and organ specific





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Regular Article - Theoretical Physics

Quantifying the jet energy loss in Pb+Pb collisions at LHC

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Abstract In this work, we give a method to study the energy loss of jets in the medium using a variety of jet energy loss observables such as nuclear modification factor and transverse momentum asymmetry in dijets and y-jets in heavy ion collisions. The energy loss of jets in the medium depends mainly on the size and the properties of medium viz. temperature and is a function of energy of the jets as predicted by various models. A Monte Carlo (MC) method is employed to generate the transverse momentum and path-lengths of the initial jets that undergo energy loss. Using different scenarios of energy loss, the transverse momentum and system size dependence of nuclear modification factors and different measures of dijet momentum imbalance at energies $\sqrt{s_{NN}}$ = 2.76 TeV and 5.02 TeV and γ -jet asymmetry at $\sqrt{s_{\rm NN}} = 2.76$ TeV in Pb+Pb collisions are simulated. The results are compared with the measurements by ATLAS and CMS experiments as a function of transverse momentum and centrality. The study demonstrates how the system size and energy dependence of jet energy loss can be quantified using various experimental observables.

1 Introduction

The PbPb collisions at Large Hadron Collider (LHC) are performed to produce and study the properties of bulk strongly interacting matter at high temperatures where the quarks and gluons provide the basic degrees of freedom [1]. The matter in this phase is called quark gluon plasma (QGP) which is short-lived but leaves its imprints on many observables which are captured by gigantic multi particle detectors. The experimental probes are categorised in terms of soft probes which determine the global properties of the system and hard probes which give tomography of the system; jets are in the later category. When two hadrons collide at high energies, the hard scattering of partons produces two virtual back-to-back

partons. These partons subsequently evolve as parton showers, hadronize and are observed as two back-to-back hadronic jets. In heavy ion collisions, the quarks and gluons produced in the hard scattering interact strongly with the hot QCD medium due to their color charges, and lose energy, either through the collisions with medium partons or through gluon bremsstrahlung [2,3]. The jet properties are thus modified in heavy ion collisions, a phenomenon which is termed as jetquenching [4]. Since the hard partonic scattering occurs early in the collisions, the produced jets probe the medium properties such as stopping power and transport coefficients. The jet-quenching can be quantified in many ways. The most conventional way is the nuclear modification factor R_{AA} which is defined as the ratio of number of jets in heavy ion collisions to the suitably scaled number of jets in pp collisions. The nuclear modification factor for light hadrons at high p_T is also a measure of jet-quenching at RHIC [5] and at LHC [6-8]. The R_{AA} values for hadrons at RHIC and the LHC are very similar although one would expect the energy loss to increase with increased collision energy. QCD-motivated models are generally able to describe inclusive single particle R_{AA} qualitatively.

The fully reconstructed jets have allowed to measure the momentum imbalance between the leading and sub-leading jet in each event which are quantified using dijet asymmetry variables. Due to kinematic and detector effects, the observed energy of dijets is not perfectly balanced, even in pp collisions. Thus to obtain a quantitative measure of the dijet imbalance, systematic comparison of results from heavy ion collisions with pp collisions are done. The dijet measurements from the ATLAS [9] and CMS [10,11] show that, the distributions of dijet asymmetry for peripheral PbPb collisions are similar to those from pp collisions but are broader for central PbPb collisions. Recently, ATLAS measured jet imbalance after background subtraction and applied unfolding procedure to account for experimental effects [12, 13] with similar conclusions. A recent measurement from ATLAS gives



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substructure-dependent jet suppression in Pb+Pb collisions at 5.02 TeV [14]. There have also been results from RHIC; The measurements from STAR experiment [15] using a high momentum component selection ($p_T \ge 2 \text{ GeV/c}$) observed the similar energy imbalance seen by ATLAS and CMS. With the large statistics data collected during the PbPb runs of the LHC at 5.02 TeV, the measurements of γ -jet and Z⁰-jet pairs have become accessible. Both the photon and Z⁰ do not participate in strong interactions and hence escape the medium unattenuated and thus the energy of the paired jet can be determined precisely. The CMS measurement [16] of isolated photons with $p_T \ge 60$ GeV/c and associated jets with $p_T \ge 30$ GeV/c in PbPb collisions at $\sqrt{s_{\rm NN}} = 2.76$ TeV demonstrates that jet loses energy increasingly with increasing centrality. Recent measurements of Z boson-tagged jets in PbPb collisions at $\sqrt{s_{\rm NN}} = 5.02$ TeV [17], although with limited statistics, show that the transverse momentum of the jet shifts to lower values.

There are many approaches to describe the jet-medium interactions. In Gyulassy-Levai-Vitev (GLV) formalism [21,22], a systematic expansion in opacity is used to extract the radiative energy loss of partons inside QGP which has logarithmic dependence on jet energy. In the Baier-Dokshitzer-Peigne-Schiff (BDPS) approach, a fast parton radiates gluon by multiple coherent scatterings in the thick medium [2]. The finite medium effect was discussed in BDMPS work [23,24]. Phenomenological models of parton energy loss [25] in QGP tend to define simple dependence of the radiative energy loss of the parton on the energy of the parton inside the medium. The energy loss can be characterized in terms of coherence length lcoh, which is associated with the formation time of gluon radiation by a group of scattering centres, the mean free path (λ) of the parton and the medium size L [26,27]. If $l_{\rm coh} < \lambda$, the energy loss per unit length is proportional to the energy of the parton which is known as Bethe-Heitler regime. The regime $l_{\rm coh} > \lambda$ corresponds to Landau-Pomeranchuk-Migdal (LPM) regime where the energy loss per unit length is proportional to the square-root of the incoming parton energy. If $L \gg l_{\rm coh}$, the energy loss per unit length is proportional to the square root of the energy of the parton (BDPS result). For $L \ll l_{coh}$, the energy loss per unit length is independent of energy but proportional to the parton path length. These simple dependencies have been used to explain the charged particle spectra at RHIC and LHC in heavy ion collisions [28,29].

Recently the fragmentation of partons propagating in a dense quark gluon plasma is studied using leading double logarithmic approximation in perturbative QCD [30]. The effects of the medium on multiple vacuum like emissions is found to modify the in medium parton showers in comparison to the vacuum showers [30]. These modified parton showers are then used to study the jet nuclear modification factor R_{AA} and the distributions of jet splitting function Z_g at LHC

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energies using Monte Carlo methods [31]. It is found that the energy loss by the jet is increasing with the jet transverse momentum, due to a rise in the number of partonic sources via vacuum like emissions [31]. Another consequence of the jet substructure modification inside QGP will demonstrate itself through the cone size dependence of jet energy loss. An analytical description has been obtained for the cone size dependent jet spectrum in heavy ion collisions at the LHC energies implemented in a event by event setup including hydrodynamic expansion of the quark gluon plasma and accounting for multiple scattering effects [32]. The calculation yields a good description of the centrality and p_T dependence of jet suppression for R = 0.4 together with a mild cone size dependence, which is in agreement with recent experimental results [32].

The measured R_{AA} of jets is used to obtain energy loss of jets in many phenomenological studies [33-35]. Such studies assume that the energy loss is given by a power law in terms of p_T and the value of power index is obtained by fitting the R_{AA} as a function of p_T and centrality. In Ref. [36], the power law function is applied to describe the transverse momentum distributions of charged particles and jets in heavy ion collisions which includes the transverse flow in low p_T region and the in-medium energy loss (also in terms of power law) in high pT region. The jet-quenching is quantified using jet nuclear modification factors in various kinematic regions in terms of parameters of a power law function assumed for energy loss [37]. Although there are simulation packages like JETSCAPE [38] which deal with the system more elaborately but simple models provide easy alternatives to characterize the essential features of energy loss using different variables in different collisions systems.

In this work, we have proposed a method which calculates experimental energy loss probes namely dijet asymmetry as well as RAA taking different energy loss prescriptions as inputs. The aim is to obtain the energy loss dependence on variables like transverse momentum and centrality. We obtain the parameters of these energy loss formulas from experiments hence quantifying the energy loss. Once the parameters are obtained by fitting over large datasets it has excellent predictive power in other kinematics regions. The aim of comparing the measurements at different collision energy and by different experimental group is to bring out the underlying difference due to physics or due to different method of analysis affecting the energy loss probes. We assume that the energy loss of jets in the hot medium is a function of jet energy in the form of power law where the power index is extracted using the R_{AA} and dijet asymmetry data from the LHC. In addition, we use (GLV) form of energy loss which is logarithmic in energy [21,22]. Determining the pathlenth of the jets in the medium is equally important to know the energy loss suffered by jets. Guided by these considerations, Monte Carlo method is employed to generate the





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ORIGINAL ARTICLE

RCM based optimization of maintenance strategies for marine diesel engine using genetic algorithms

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Abstract In the modern world the availability of the machinery for any industry is of utmost importance. It is the right maintenance at right time which keeps these machineries available for their jobs. The primary goal of maintenance is to avoid or mitigate consequences of failure of equipment. There are various types of maintenance schemes available such as breakdown maintenance, preventive maintenance, condition based maintenance etc. Out of all these schemes Reliability Centred Maintenance (RCM) is most recent one and the application of which will enhance the productivity and availability. RCM ensures better system uptime along with understanding of risk involved. RCM has been used in various industries, however, it is very less explored and utilized in marine operations. Hence in the present study maintenance schemes of a marine diesel engine has been considered for optimization using RCM.Failure Modes and Effects Analysis and Fault Tree Analysis (FTA)are some of the basic steps involved in RCM. Due to the scarcity of reliability data particularly in the marine environment some of the components data had to be estimated based on the operating experience. As FTA is based on binary state perspective, assuming the system exist in either functioning or failed state, some of the components (whose performance varies with time and degrades) cannot be modeled using FTA. Hence, in this paper reliability modeling of performance degraded components is dealt with Markov models and the required data is evaluated from condition monitoring

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Keywords Maintenance · Optimization · RCM · Genetic algorithms · Marine diesel engine

1 Introduction

Maintenance is the essential part of production process in today's industry. The primary goal of maintenance is to avoid or mitigate consequences of failure of equipment. There are different types of maintenance strategies applied in industry such as corrective maintenance, preventive maintenance, predictive maintenance etc. These techniques have been evolved over a period of time and are grouped under various generations (Moubray 1997) (Arunraj and Maiti 2007). The 1st generation (1940-1955) is based on breakdown maintenance, the 2nd generation (1955-1975) is based on time based maintenance and the 3rd generation (1975-2000) is based on condition based maintenance. The current generation (yr 2000+) is called 4th generation and here the prime focus will be on elimination of failures. Each one has its own advantages and disadvantages. Challenge here is to choose the proper ones for the specific operation conditions and equipment.

Reliability Centred Maintenance (RCM) is a process to ensure that systems continue to perform their intended function in the present operating environment and is attributed as third generation technique. Successful implementation of RCM will lead to increase in cost effectiveness, reliability,





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machine uptime, and a greater understanding of the level of risk that the organization is managing. RCM is widely being used in airline industry (MIL-STD-2173 (AS) 1986; Ahmadi et al. 2009; Guo et al. 2016), nuclear industry (Durga et al. 2007; Kadak and Matsuo 2007), transportation (Carretero et al. 2003), defense sectors (MoD 2006), medical industries (Shamayleh et al. 2020; Mahfoud et al. 2018, 2016), railway sector (Singh et al. 2020) etc. Bae et al. (2009) applied RCM technique to a standard electric motor unit subsystem and optimized the maintenance time using evolutionary algorithm. Ilya and Tore (2012) have worked on a methodology for development of condition based maintenance program for surface drilling machine. Seyed and Uday (2016) applied RCM technique to fully automated underground mining machineries. Lazakis et al. (2009) utilized a methodology combining risk and criticality approach to develop effective maintenance strategies for a ship.

Grall et al. (2001) applied condition-based maintenance policy for stochastically deterioration systems. Hiroyasu (2003) utilized Genetic Algorithms for optimization of diesel engine emissions and fuel efficiency. Abdul-Kader (2009) designed a prototype fuzzy knowledge base system to improve the capabilities of fault tracing for a ship diesel engine. Girtler Jerzy (2015) presented semi-Markov models of technical state transitions for diesel engines, useful for determining the reliability of engines. Awang et al. (2020) presented a study of 2-stroke main propulsion marine diesel engine characteristic using ultrasound signal monitoring condition based maintenance. Shi et al. (2023) proposed an integrated decision-making approach that uses the 2-tuple linguistic term to prioritize key practices for marine diesel engine maintenance.

Based on the literature review the following gap areas have been identified such as, RCM is being applied in various industries however it is very less explored and utilized in marine operations. Failure rate models for components under specified environmental conditions are not available. Traditionally, system reliability has been analyzed as a binary perspective, assuming the system and its components exist in two states that is either completely functioning or failed state. However, performance of some of the components varies with time and one needs to capture this behavior precisely to represent the component reliability correctly. Hence, in this manuscript reliability modeling of performance degradation of the components is dealt with Markov models and the required data is evaluated from condition monitoring techniques. The marine diesel engine considered for the study mainly maintained by the Planned Preventive Maintenance schemes and is not cost effective due to the lack of optimal maintenance strategies. Hence, the primary objective of the current study is development of new maintenance schemes by using RCM technique for conventional marine diesel engine.

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To achieve the above mentioned objectives the work was divided into two parts, in the first part reliability of the marine diesel engine was analysed by carrying out Failure Modes and Effects Analysis (FMEA) (Banks et al. 2001; Peters et al. 2018; Muzakkir et al. 2015) to identify various failure modes of the components and performed Fault Trees Analysis (FTA) (Peters et al. 2018). Markov analysis has been used for modelling performance degraded components and utilised in FTA. Post completing the FTA, based on the importance ranking, critical components have been obtained for optimizing the maintenance schedules. In this paper genetic algorithm approach has been used to optimize the maintenance schedules.

2 Reliability centered maintenance

The different maintenance strategies developed over the decades as discussed previously are briefly explained as follows:

- a) Breakdown Maintenance (First Generation): This maintenance strategy is also known as corrective maintenance. This strategy focuses on corrective actions which are mainly on the objective "NO FIX UNLESS BROKE" (Moubray 1997). This strategy has no downtime of assets between failures. But this has few disadvantages as well. This strategy requires large spare part inventories. It leads to unscheduled work outages and longer restoration time with high cost. This strategy ultimately leads to collateral damage with low manageability of budget and safety of personnel.
- b) Time based maintenance (Second Generation): This maintenance strategy is based on fixed cycle repair. It focuses on reducing risk of catastrophic failure, prevents equipment failure and overcomes disadvantages of Runto-Failure strategy. This strategy has reduced operation time per cycle. Also, it doesn't give any importance to condition-based maintenance. Sometimes this strategy cannot be implemented due to operational restrictions.
- c) Condition Based Maintenance (Third Generation): This maintenance strategy provides a continuous risk assessment. It integrates with total resource planning. The focus is on higher plant availability and reliability, greater safety, better product quality etc. It accounts for all the disadvantages of Run-to-Failure and Fixed Frequency maintenance. But this strategy leads to higher implementation and operating costs for labour and condition monitoring system.

Whereas, RCM over comes the disadvantages of other maintenance techniques in which the maintenance strategies are optimized based on the reliability information and conditioning of the components. RCM is attributed as third





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Remediation of uranium with treated neem (*Azadirachta indica*) bark from environmental waters

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Abstract

Use of biomaterials is cost-effective and eco-friendly process with minimal waste generation, making it a sustainable alternative for metal remediation. The present study emphasizes the remediation of uranium using treated neem bark (TNB). TNB has been investigated for uranium sorption and parameters, such as pH, initial uranium concentration, equilibration time and temperature were optimized. The experimental results were evaluated for sorption kinetics and mechanism. It follows a pseudo second-order kinetics and Langmuir model of isotherm indicating monolayer sorption. The maximum sorption capacity at a pH 7.0 and temperature 27 °C for the remediation of uranium using TNB was 10.42 mg g⁻¹.

Keywords Uranium · Remediation · Bio-sorption · Treated neem bark

Introduction

In India, the level for uranium that is considered to be safe is 30 ppb in groundwater. It is confirmed from the Bureau of Indian Standards (BIS) and the World Health Organization (WHO). As per a recent report, in many parts of India uranium concentration is above the permissible limit [1]. The source of uranium in groundwater may be natural as well as anthropogenic. Natural source is leaching from natural deposits. Anthropogenic sources are many for example, release from phosphate fertilizers, mine tailings, emission from the nuclear power reactors, thermal power stations and other fuels. Uranium is radioactive and has both radiotoxicity as well as chemo-toxicity to living organism [2]. Uranium in trace concentrations is considered as significant risk to the environment due to its exceptional ability to form complexes with ligands [3]. Therefore; remediation of uranium from uranium contaminated groundwater effectively and thoroughly, has become the need of the time[1].

Literature survey reveals use of a variety of routes for the remediation of uranium from aqueous streams. Nano

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filtration using membranes has been used extensively for remediation of uranium from potable water, ground water, industrial wastewater and seawater [4-15]. Researchers also used co-precipitation [16, 17], ion exchange [18-21], phytoremediation [22-24]and solid phase extraction [18, 25-30] for separation of uranium. Recently, researchers are focusing on use of biodegradable waste products for theremediation of heavy metals and other pollutants. Bayuo et al. have used shea fruit shell as biomass for decontamination of Cd(II) [31]. He and co-workers have presented various low cost bio sorbents for heavy metal remediation purposes in his review article[32]. With an aim to recover uranium from seawater, Bilal et al. have investigated various bio-materials [33]. They emphasized that, biosorbents contain natural chelating agents or functional groups that can form complexes with uranium and showcase fast adsorption kinetics and ultrahigh selectivity against other competing ions. The characteristicsof biosorbent, such as the surface area, and number of functional groups, are one of the major factorsaffecting metal sorption behavior gaining attention. Biosorbents are biodegradable and allowsan environmentfriendly disposal, unlike inorganic/synthetic adsorbents, which have long-term environmental impact. In contrast, the preparation method of synthetic polymers, activated carbons and other organic/ inorganic materials are expensive. Jauberty et al. have used douglas fir barks, Deshmukh et al. have used Phyllanthus emblica bark and Mustafa et. al. have used eucalyptus bark for remediation of uranium from aqueous media [34-36].

In the present work, the neem bark(Azadirachta indica), a bio-material is taken as the raw material for the development of uranium sorbent. The sorption of uranium by treated neem bark was investigated for various experimental parameters such as equilibration time, pH, temperature, amount of sorbent and concentration of uranium. The experimental data were evaluated to understand the kinetics and sorption mechanism. Desorption studies were performed to recovery uranium to regenerate the sorbent. The applicability of this material is tested for uranium contaminated ground water samples from Punjab region of India. This study explores the novel application of neem bark as a natural sorbent for uranium, highlighting its fast sorption kinetics and ease of desorption. Its potential as an inexpensive, eco-friendly alternative to synthetic materials offers a sustainable solution for uranium removal in environmental and industrial contexts.

Material and methods

Reagents

AR grade phosphoric acid (5% v/v) was used as fluorescence enhancer during the fluorescence measurements. Stock solutions of desired concentrationswere prepared from AR grade salts for interference behaviour studies. De-ionised water of 18.2 μ S cm⁻¹ (Milli-Q, Italy) was collected and used for the experiments. AR grade, nitric acid (65%), sulphuric acid (98%) and sodium hydroxide (48%) (S.D. Fine Chemicals, India) were used.

Sorbent: treated neem bark (TNB)

Neem bark was collected from the local area of Trombay, Mumbai. It was washed with de-ionized water to remove soluble impurities and kept for drying at 50 °C temperature for 24 h.

After drying, neem bark was further crushed and sieved to required size (~ 1.0 mm). The neem bark particles are chemically treated with 1:10 sulfuric acid and washed with distilled water until its surface is free of acid and kept in oven at 70 °C for 24 h. It was stored in an airtight bottle for the adsorption studies.

Preparation of uranium standard

Known weight of uranium oxide was dissolved in concentrated nitric acid to prepare a stock solution of 1 mg mL⁻¹ uranium. Experimental solutions were prepared by serial dilution of stock solution using de-ionized water.

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Characterization of sorbent

The TNB was characterized using various characterization techniques. FTIR was used to identify the functional groups present in the sorbent. Energy dispersive spectroscopy (EDS) is used to detect the elements present in the developed sorbent and their composition in terms of the weight fraction. X-ray Fluorescence spectroscopy (XRF) is used to detect the extent of uranium sorption on TNB.

Batch mode sorption experiments

Batch sorption experiments were conducted a t27 2 °C by equilibrating 0.2 g of TNB with 50 mL uranium solution of required concentrations in 100 mL stoppered conical flask. The solution pH was maintained at 7. The equilibration was carried out for 1 h at 140 rpm using orbital shaker (Remi Engineering, India). The initial uranium concentration was varied from 0.01-100 mg L⁻¹. The data obtained were fitted into Langmuir and Fraundlich isotherm equations. To study effect of pH on sorption, pH of the solutions were adjusted using 0.1 M HCl or 0.1 M NaOH. The experiments were conducted to evaluate the effect of pH on optimum uptake of uranium. The sorption time was varied between 5 to 120 min for kinetic studies. Similar experiments were conducted at 27, 40, 50 and 80 °C. The concentration of uranium in supernatant solution was determined using a laser fluorimeter at fixed time intervals.

Metal uptake

Sorption percentage of uranium was determined using following Equation:

Percentage of uranium sorbed (%) =
$$\left[\frac{(C_o - C_t)}{C_o}\right] \times 100$$
(1)

Where, C_0 is the initial uranium concentration of testsolution in mg L⁻¹, C_t is the equilibrium uranium concentration in mg L⁻¹ of test solution at time (t).

The data obtained from batch equilibration experiments were subjected to Langmuir and Freundlich adsorption isotherm equation.

Desorption studies

To explore the possibility for reusability of sorbent, desorption experiments were performed. The uranium sorbed TNB was washed with deionised water for removal of any





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REVIEW ARTICLE



Role of alanine aminotransferase in crop resilience to climate change: a critical review

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Abstract

Alanine aminotransferase (AlaAT) is a crucial enzyme present in various isoforms. It is playing vital role in both humans and plants. This concise review focuses on the role of AlaAT in plants, particularly on preharvest sprouting, hypoxia, nitrogen use efficiency, abiotic and biotic stress tolerance. The molecular genetics of AlaAT, including gene identification and the impact on plant yield and its physiology, is discussed. Notably, the major dormancy gene *Qsd1/SD1* governing AlaAT synthesis has been characterized and cloned in various crops. This review emphasizes the current understanding of AlaAT and its influence on plants, covering mechanisms regulating preharvest sprouting, hypoxia, drought tolerance, salt tolerance, biotic resistance and nitrogen use efficiency. Identifying a protein with multidimensional roles in crop plants is very important. Modern biotechnological approaches can alter such candidate gene/protein for superior varieties development. Overall, the review gives an understanding of the uncovered area of AlaAT and the challenge of climatic change triggers in plants. In the future, the potential of genome editing in AlaAT through enhancer insertion and rapid stabilization through speed breeding will impart resilience to crop plants against climate change.

Keywords Biotic resistance · Climate change · Enhancer insertion · Genome editing · Hypoxia · Nitrogen use efficiency · Pre-harvest sprouting

Introduction

Alanine aminotransferase (AlaAT; L-alanine: 2-oxoglutarate aminotransferase; EC 2.6.1.2) is an enzyme that catalyses the reversible transamination of an amino group from glutamate to pyruvate to form 2-oxoglutarate and L-alanine (Welch 1975). The enzyme catalyzes the reversible transamination reaction between alanine and 2-oxoglutarate according to the Ping Pong Bi-Bi mechanism (Raychaudhuri 2015). In comparison, β -alanine aminotransferase (EC 2.6.1.18) forms β -alanine (D-alanine) from a pydridoxal-5-phosphate (PLP) dependent transamination reaction from L-alanine and malonate semialdehyde (Hayaishi et al. 1961; Stinson and Spencer 1969a&b). Initially, it was identified in a sub cellular fraction from bean cotyledons (Stinson and Spencer

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1969a). Alpha alanine or L-alanine is proteinogenic in nature while β -alanine is non- proteinogenic.

AlaAT is widely present in various plant tissues and organs. Many researchers documented that AlaAT plays an important role in hypoxia conditions by conserving carbon and nitrogen source in the form of alanine in Hordeum vulgare, Medicago truncatula, Arabidopsis thaliana and Lotus japonica (Good and Crosby 1989; Ricoult et al. 2005, 2006; Miyashita et al. 2007; Rocha et al. 2010). Splittstoesser et al. (1976) showed that AlaAT plays a key role in synthesizing alanine during germination in pumpkin cotyledons. Very recently, AlaAT activity was noticed in nectar, nectaries, and leaves of 30 Pitcairnia species and the highest concentration of alanine was found in nectar of reddish flowers (Göttlinger and Lohaus 2024). Studies on mammalian cells revealed that AlaAT is crucial in gluconeogenesis and amino acid metabolism and this familiar enzyme is used as a marker of liver function (Felig 1973). The ubiquitous presence of AlaAT in lower organisms (including archaea) to higher organism suggests that it is an ancient and highly conserved biomolecule (Sakuraba et al. 2004). AlaAT was initially isolated and purified from cotton seeds by Turano et al (1966) and

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later identified in various plant parts, including Atriplex spongiosa leaves, tomato fruit, and pumpkin cotyledons. This wide distribution across plant tissues suggests its vital role in plant life cycle. Plant-specific isozyme variations resulted in the detection of two to six isoforms of AlaAT enzyme located in different cellular compartments such as cytoplasm, mitochondria, and peroxisomes (Liepman and Olsen 2004). Wightman and Forest (1978) found similarities between plant and animal AlaAT in terms of molecular weight, sedimentation coefficient, subunit composition, pyridoxal phosphate requirement, pH and cation effects. While aminotransferase activity is abundant in the cytosol, there are suggestions that a-alanine aminotransferase might predominantly reside in mitochondria, facilitating the utilization of pyruvate produced through the Krebs cycle in plants (Bone and Fowden 1960; Yu and Spencer 1970). Apart from cytosol and mitochondria, this enzyme is also presents in peroxisome and plays a role in photorespiration (Liepman and Olsen 2003). In the present review, molecular understanding of this enzyme was highlighted initially. Later, we emphasize its importance in providing tolerance against pre-harvest sprouting hypoxia tolerance, nitrogen use efficiency, abiotic stress (drought, salinity and heat) tolerance and biotic stress tolerance in crop plants. There are several unique functions of β-alanine in plants. It is accumulated as a generic stress response molecule involved in protecting plants from temperature extremes, hypoxia, drought, heavy metal shock, and some biotic stresses (Parthasarathy et al. 2019). A novel cytosolic enzyme from Phaseolus vulgaris cotyledons showed that β-alanine could be converted into plant signalling molecule ethylene via the formation of malonate semialdehyde and/or β-hydroxypropionate (Stinson and Spencer 1969a, b). Moreover, involvement of β-alanine aminotransferases in drought and salinity stress response is also elaborated here. A detailed account of utilizing allelic variation or creating such variation through modern biotechnological tools is depicted for better use in agriculture.

Basic understanding of alanine aminotransferase

Molecular details of alanine aminotransferase

Wightman and Forest (1978) found that the aminotransferases or transaminases are pyridoxal-5'-phosphate dependent enzymes that catalyse reversible reactions between amino acids and α -keto (2-oxo) acids. Rech and Crouzet (1974) isolated AlaAT from tomato fruits for the first time. The Michaelis constants for alanine, 2-oxoglutarate, pyruvate, and glutamate were found to be 2.8 mM, 0.28 mM, 0.09 mM, and 2.3 mM, respectively. Good and Muench

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(1992) isolated the AlaAT enzyme from barley roots and found that molecular masses of the homodimer (native) and monomer are 97 kDa and 50 kDa, respectively. While, Son and Sugiyama (1992) characterized three isoforms of AlaAT from prosomillet (Panicum miliaceum) and found that it had 44.2-44.8% homology with rat and human liver AlaAT. The isoform AlaAT-2 is induced by light and function in the C4 cycle aspartate/alanine shuttle. Thereafter, Kikuchi et al. (1999) firstly isolated cDNA encoding plant AlaAT from rice and the primary structure of the enzyme was deduced with the nucleotide sequence of gene composed of 14 introns ranging from 66 to 1547 bp in length and has15 exons. Moreover, it was found that the rice cDNA was about 1.8 kb long, with an open reading frame of 1449 bp (483 amino acids), a 5'-UTR of 68 bp and a 3'-UTR of 280 bp. The deduced molecular mass of the protein was 52,590 Da, aligning closely with the 52 kDa determined by SDS-PAGE, which corresponds to an amino acid sequence of 482 residues (Muench and Good 1994). When the deduced amino acid sequences of AlaAT from rice, prosomillet (Son and Sugiyama 1992) and barley (Muench and Good 1994) were compared, the AlaAT from rice was found to be with 91% and 88% homology to AlaAT of prosomillet and barley, respectively. Duff et al. (2012) first crystallized plant-based AlaAT (from barley) in complex with PLP and L-cycloserine, resolving up to 2.7 Å. Their findings suggested a canonical aminotransferase fold similar to structures of Thermotoga maritima, Pyrococcus furiosus, and human. Cycloserine is a structural analog of alanine and is known to be a more effective inhibitor of AlaAT activity than other transaminases. The major activity for this crystallized enzyme was alanine aminotransferase rather than aspartate aminotransferase with a native homodimer (105,761 Da) comprised of two identical 53 kDa subunits.

AlaAT gene expression is regulated by various environmental factors like hypoxia (Diab and Limami 2016), temperature (Yamakawa and Hakata 2010), drought (Kendziorek et al. 2012) and biotic stress (Sempruch et al. (2012). Plants have different homologs of alanine aminotransferases. Apart from cytosolic and mitochondrial, few homologs are peroxisomal too. Three Arabidopsis homologs of alanine (Ala): glyoxylate aminotransferase 2 (AGT2) contain a putative type 1 peroxisomal targeting signal and participate in photorespiration (Liepman and Olsen 2003). Localization of mitochondrial AlaAT depends on the N-terminal targeting sequence for the transport of protein to the organelle (Metón et al. 2004). In addition to gene expression, protein activity is controlled through post-translational modification (PTM) that creates a fine-tuning between all regulatory networks (Pandey and Gayen 2024). PTM of aminotransferase is not an exception. Lysine methylation of aspartate aminotransferase from Sulfolobus solfaturicus was evident for the involvement in protein aging and turn over (Zappacosta et al.





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ORIGINAL RESEARCH ARTICLE

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Roles of Refractory Solutes on the Stability of Carbide and Boride Phases in Nickel Superalloys

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Abstract Nickel-base superalloys contain high amounts of solutes like Cr, Mo, W, Nb, Ti, etc. These solutes promote the formation of different types of carbide and boride phases that may contain multiple elements. Researchers have mostly discussed the roles of primary elements responsible for the formation of a given carbide/boride phase, often ignoring the role of other solutes on its stability. In the present work, thermodynamic stability of carbide and boride phases in seven commercial superalloys, namely, Alloy 625, Alloy 690, Alloy 718, MAR M246, Rene 100, Udimet 710 and Nimonic 80A, has been studied using the CALPHAD based Thermo-Calc software. The aim of the study was to understand the role of different alloying elements on temperature stability and chemical compositions of equilibrium phases in superalloys. As the accuracy of CALPHAD based predictions depends upon the database used, a detailed examination of its inadequacies has also been carried out to ascertain the limitations of the predicted data. From the calculated equilibrium chemical compositions, major and minor constituents promoting the formation of carbides and borides have been identified. The individual effect of a given solute as well as the synergistic effect of two solutes on the relative thermodynamic stability of carbide/boride phases has been identified using property diagrams and isothermal sections of the temperature-composition diagrams. Most of the simulated results have been found to be consistent with the experimental data available in the literature. From a comparison of the experimental literature and the simulated

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data of the stable carbide and boride phases in the studied alloys, the interplay of different solutes has been deduced to define conditions under which these phases form, within the limitations of the database used. This study has helped in better understanding of general tendencies of solutes to form different carbide and boride phases in nickel-based superalloys.

Keywords borides · CALPHAD · carbides · nickel superalloys · phase stability · thermodynamic simulation

1 Introduction

Superalloys contain a large number of refractory elements like Cr, Mo, W, Ti, etc. and carbon up to 0.15 wt.%, though some cobalt-base alloys may contain carbon even greater than 0.15 wt.%.^[11] The amount of carbon usually present in alloys is much more than its solubility (typically $< \sim 0.01$ wt.% at 500 °C^[2,3]) in the face-centered cubic (FCC) nickel solid solution matrix. Likewise, boron also has very limited solubility in the nickel matrix—a maximum of 0.07 wt.% can dissolve at 1000 °C.^[3] However, boron amount as high as 0.12 wt.% has been reported in alloys.^[11] The excess carbon/boron invariably causes the precipitation of carbide/boride phases by interacting with reactive refractory solutes.

Carbide and boride phases are very hard and may precipitate in varying sizes and shapes with different stoichiometry.^[4] The formation of carbide and boride particles may enhance or degrade an alloy's mechanical properties depending on their morphology and distribution. Small particles within the matrix are more effective in imparting strength and retaining ductility and fracture toughness, as

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dislocations can cross slip around them easily and avoid their pile-up and the formation of voids at precipitate/matrix interfaces. Precipitation of small discrete carbides at grain boundaries in thermally treated superalloys, like Alloy 600 and 690, and in age hardenable nickel-base alloys, like Rene 41 and Udimet 710, increase their creeprupture life^[5,6] by restricting the movement of grain boundaries that tend to slide under stress at temperatures above 0.5 $T_{\rm m}$. On the other hand, plate like particles provide a large precipitate/matrix contact area for dislocations to pile-up at the interface, which can easily cause cracking.^[1,7]

In most superalloys, the presence of strong carbide formers like Ti, Nb, Ta and/or Hf leads to the formation of MC phase during solidification. Carbides that form during solidification of the alloy melt are termed 'primary' carbides. On the other hand, many carbides can also form during thermo-mechanical processing of the alloy and such carbides are termed 'secondary' carbides. Though the precipitation of M23C6, M6C, M7C3 and MC secondary carbides during thermal annealing has been reported by various researchers,^[1,5,8,9] the precipitation of M23C6 secondary carbides is most commonly reported. The metal element "M" in all these carbides can be chromium, molybdenum, tungsten, tantalum, niobium, nickel or iron, or their combination, depending upon chemical composition of the alloy. In general, alloys containing high chromium, titanium and aluminium favour the formation of M23C6 carbides, high molybdenum and tungsten favour the M6C phase and high niobium, tantalum and titanium favour the formation of the MC phase.^[10] Although M₇C₃ is not widely encountered in superalloys, it forms in alloys like Alloy 600^[11] and Nimonic 80A^[12] that contain relatively low amounts of chromium and other refractory metals. In many cases, more than one type of carbides may co-exist. In general, the formation of MC is reported at high temperatures, and the formation of M23C6 and M7C3 is reported at relatively lower temperatures. M6C is reported to form in the intermediate temperature range.^[4]

Above the solubility limit, boron may combine with solutes like chromium, molybdenum, and tungsten, etc., as well as nickel to form borides. The commonly observed borides in nickel superalloys are M_3B_2 and M_5B_3 ,^[13–15] where element "M" can be any transition metal or their combination, as in carbides, depending upon chemical composition of the alloy.

The stability of carbides and borides in nickel alloys is influenced by the presence of not only carbide/boride forming elements but also by some other elements.^[1,5,8,9] Though any solute can affect the formation, dissolution, and stability of a phase, it remains often unclear about the roles of major solutes on the stability of various carbide and boride phases in spite of a large body of experimental

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work on their formation in nickel-based superalloys. For instance, Nimonic 80A alloy containing about 20 wt.% Cr forms only M_7C_3 , while alloys like 718 and 625 containing similar amounts of Cr form other carbide phases.^[16] Likewise, the formation of M_6C carbide, which is based on Mo and W elements, is reported in only some Mo/W bearing superalloys. Besides, only a few phases remain stable over a prolonged period, and a stable phase in a given alloy may be unstable in another. For example, M_6C transforms to $M_{23}C_6$ during prolonged ageing in alloys like Rene 41 and M252, while the reverse transformation occurs in MAR M200 alloy.^[17,18]

The observed inconsistencies in the roles of different elements still remain mostly unclear due to the lack of systematic studies on the formation of carbide and boride phases. Further, such studies are rather difficult to establish experimentally because of the involvement of many elements. However, systematic studies using computational tools can provide a better understanding on the inter-connected roles of different solutes in stabilizing these phases. In the present work, thermodynamic stability of carbide and boride phases in seven commercial alloys (Table 1) has been studied through computed phase equilibria using the Thermo-Calc software package. As the accuracy of CALPHAD based software depends upon the database used, a detailed evaluation of the inadequacies of the database has been carried out to ascertain the limitations of the predicted data. The equilibrium phases observed in the simulated study are compared with those reported in the experimental literature to deduce the roles of various solutes in stabilizing the two types of phases within limitations of the software and the database used.

Because all the superalloys studied in the present work are widely used commercial alloys, their compositions are mentioned in weight percent as a standard industrial practice unless and otherwise mentioned specifically.

2 Methodology

2.1 Computation Procedure

The roles of alloying elements in altering thermodynamic stability of carbides and borides in seven commercial nickel-based superalloys were studied through computed phase equilibria using Thermo-Calc software^[19] along with TCNI10 database.^[20] The nominal compositions of the seven alloys used in the study are given in Table 1. The relative stability of all the possible phases in the database was initially assessed as a function of temperature to identify equilibrium phases and their temperature stability range in each alloy. However, the results presented here are confined only to carbides and borides to retain the focus on





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ORIGINAL PAPER





Stable Isotope Ratio and Elemental Analysis (CNS) in Mangrove Leaves in the Creek Ecosystem: An Indicator of Coastal Marine Pollution

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Abstract: The stable isotopes ratio and elemental composition in the mangrove leaves are excellent indicators for coastal marine pollution. The present study investigated the composition of Carbon, Nitrogen, and Sulfur, \delta^{13}C and \delta^{15}N values in mangrove leaves to identify the source of pollution and energy to the mangroves in the creek ecosystem of Mumbai Harbour Bay. The oxygen and hydrogen stable isotope ratios (δ^{18} O and δ^{2} H) of leaf water were estimated to understand the relative contribution of freshwater and seawater to the mangrove's water source. The Carbon, Nitrogen and Sulfur contents were found to vary from 37.79 to 42.55% (Average: 40.06 1.54%), 2.13-3.79% (Average: 2.94 0.45%) and 0.37–0.81% (Average: 0.53 0.14%) in the mangrove leaves, respectively. The δ^{13} C and δ^{15} N values were found to vary from - 30.43 to - 28.41‰ (Average: - 29.46 0.74‰) and from - 2.67 to 5.54‰ (Average: 2.21 3.20%). respectively. The δ^{18} O and δ^{2} H values were found to vary from -2.7 to 0.83‰ and -6.86 to 5.43‰ with an average of 3.52% respectively. According to the observed δ^{18} O and δ^{2} H values, mangroves in the 0.83 and -2.03-0.94northern part had a relatively higher contribution of freshwater input compared to southern part of the study area. The lower values of δ^{15} N towards the northern end of the creek indicate a relatively higher contribution of nitrogen from industrial discharges. Similar values of $\delta^{13}C$ in mangrove in the region suggest a common source of carbon. Mangroves found near discharge locations have different elemental composition and $\delta^{15}N$ values compared to those mangroves that are not located near discharge location. These differences can be used as potential markers to identify the coastal marine pollution. The results of the present study may be used for developing rational approaches for protection and conservation of the mangrove ecosystem in the bay.

Keywords: Stable isotope; Mangrove; Creek ecosystem; Pollution source; Mumbai Harbour Bay

Introduction

Mangrove forests are highly productive ecosystem found at the interface between land and marine ecosystem [1]. The impact and consequences of high load of anthropogenic inputs to the marine environment can be minimized by mangroves in coastal area as their roots and leaves act as interceptor for terrestrial-derived nutrients, pollutants and terrestrial washouts, sediments etc., before they reach the coastal ocean [2]. Mangrove ecosystems are able to store large amounts of organic carbon, making them an important component when constructing any carbon budgets

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(e.g., Blue Carbon) in marine ecosystems [3]. They also stabilize and protect coastlines against hydrodynamic disturbances. Acting as nursery grounds, mangrove ecosystems provide shelter and protection for young marine life during development. The complex root structure mitigates challenges from highly polluted runoff or discharges and protects against predators. Additionally, mangrove systems supply important nutrients and organic carbon to tropical coastal oceans [4, 5]. Therefore, mangroves act as biochemical filters for land-derived inputs and can be used as ideal indicator matrices to study terrestrial pollution entering the marine environment [6].

It has been reported that main contributor of nitrate in the coastal environment viz. the agriculture fertilizer, animal faeces (domestic discharge) and treated urban effluents have significantly different isotope ratio signatures [7]. Nutrient cycling involves complex processes and isotopic changes [8-10]. However, plants integrate many of these variations, and the 815N of tree leaves represents the longterm nitrogen acquired over growing seasons [11]. Previous studies, [12, 13] including laboratory experiments [14-17] and field experiments [18-21] have demonstrated a very good correlation between the nutrient level (nitrogen and phosphorus concentration) in mangrove leaves and the concentration of nutrient input and/or natural variability in nutrient concentrations in the environment. Studies conducted in different parts of the world, such as northern New Zealand [22], three marshes along south Florida [23], and Hainan Island in southeastern China[24], have reported that mangroves in regions with higher exposure to humanderived sewage have leaves with higher nitrogen content (N(%)) and $\delta^{15}N$ values. Therefore, high values of N content and $\delta^{15}N$ in mangrove leaves are considered good bio-monitors of anthropogenic nitrogen loading.

Plants convert atmospheric CO₂ into energy via the photosynthesis process and have a lower ${}^{13}C/{}^{12}C$ ratio compared to that of atmospheric CO₂ due to isotopic fractionation [12]. The extent of fractionation depends on the enzymatic process used in photosynthesis. The Calvin cycle (C3), Hatch–Slack cycle (C4), and Crassulacean acid metabolism (CAM) photosynthetic processes significantly differ in terms of carbon fixation, which leads to different $\delta^{13}C$ values for different types of plants [25, 26]. Therefore, the $\delta^{13}C$ values in plant leaves are used as an indicator of their energy source.

The stable isotope ratios of oxygen and hydrogen (δ^{18} O and δ D) in water extracted from plant xylem are used as bio-markers to trace the source of plant water because these ratios remain relatively unchanged during uptake and transport within the plant [27, 28]. However, transpiration from plant leaves can fractionate the xylem water, causing leaf water to become enriched in the heavier isotopes [29]. If we assume a similar extent of transpiration (e.g., for the same type of mangrove under similar environmental conditions), then δ^{18} O and δ D values can still be used to understand the relative contribution of freshwater to the mangrove ecosystem [30].

There are previous studies in the Mumbai Harbour Bay dealing with multi-decadal changes of the mangrove forest in Thane Creek [31], mangrove mapping using remote sensing data [32], estimation of carbon content using CHN analysis, allometry, and remote sensing for aboveground biomass estimation [33], habitat-based diversity assessment of mangroves [34], the status of trace and toxic elements [35], and heavy metal concentration in mangrove sediments [36]. However, there is a scarcity of comprehensive data on the analysis of mangrove leaves, which can be used as an indicator for the long-term effects of

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anthropogenic input in the study area. To our best knowledge, previously published studies [11, 14–21, 23–26, 33] have dealt separately with isotope ratios (mainly $\delta^{15}N$ and $\delta^{13}C$) or C and N analysis in mangrove leaves to understand the sources of pollution from anthropogenic input in different coastal regions around the world.

In the present study multiple stable isotope ratio (δ^{18} O, δ^{15} N, δ^{13} C and δ^{2} H) along with the Carbon, Nitrogen and Sulfur composition (CNS composition) has been used to understand the relative contribution of discharges originating from domestic (human settlements) and industrial establishments in the creek ecosystem which is receiving both types of effluents along its both the coasts. Briefly, the objective of the present study is to understand the source of pollution, energy and water to mangroves using the stable isotope ratio (δ^{18} O, δ^{15} N, δ^{13} C and δ^{2} H) and CNS composition in the mangrove leaves.

Study Area and Sample Collection

The study area, Mumbai Harbour Bay (MHB), is located on the west coast of India Fig. 1. The bay, containing brackish water (TDS: 18,965-39,226 mg/L), opens into the Arabian Sea in the South and is fed by freshwater from Ulhas River in the north. The narrower, northern part of the bay, called Thane Creek, lies between the city of Thane and the Arabian Sea at Trombay, before the Gharapuri Islands. The Thane Creek Industrial Area houses several major, medium, and small-scale industrial units, primarily involved in the manufacturing, storage and use of chemicals, petrochemicals, pharmaceuticals and fine chemical products, pesticide formulation, etc. The creek receives effluents from various industrial and domestic establishments containing trace and toxic elements and acts as a sink for most of the pollutants [35] are different sewage inputs that are generally partially treated and released into creek using drainage outfalls [37]. The Mumbai and adjacent marine environment, though intensely polluted and heavily pressurized from various anthropogenic interference, harbors over 60% of total mangrove cover along the Central West Coast (CWC) of India [38] Mumbai Harbor Bay (MHB) is dominated by the Avicennia Marina species of mangroves along it's both the coast. Avicennia Sonneratia mangroves were also present to some extent in the Thane region [32]. Mangrove leaves were collected from 10 locations along the creek Fig. 1(D, E). Sampling locations 1 to 5 had both industrial and domestic establishments, particularly on the eastern side of the creek, which was dominated by industrial settlements. Locations 6 to 9, on the west side, had domestic settlements only; no industrial input was present at these locations [39, 40].





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Synthesis and performance evaluation of bio-derived and synthetic carbon as lithium-sulfur battery cathode

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ABSTRACT

The next-generation of batteries need be both energy dense and environment friendly. Lithium sulfur batteries (LSBs) satisfy both criteria but their practical implementation is marred by the highly resistive nature of sulfur. Carbon-based cathodes play a vital role in mitigating the issue because their high conductivity allows for effective electron transfer during electrochemical cycling. Synthesis and electrochemical evaluation of carbon-based cathodes from two different sources for LSBs was carried out. Herein, two kinds of carbon, namely bio-derived carbon from coconut shells (CC500) and N-doped carbon (NC) from polyacrylonitrile fibers were synthesized and sulfur was incorporated via the melt diffusion route. The composites are characterized by PXRD and TGA, which determined 80 wt% mass loading of sulfur. The higher intensity of G-band over D-band in Raman spectroscopy indicates greater graphitic character for CC500 compared to NC. SEM images show large macro-pore like tunnels in CC500 while NC appears are irregular chunks. EDAX spectra showed 20 wt% N content in NC while CC500 is largely carbon with some minor surface oxygen. In galvanostatic charge-discharge cycling of coin cells, bare CC500/S shows better specific capacity compared to NC/S samples but the trend flips once a separator modified with 4 mg of graphene oxide (GO) is introduced (indicated as NC/S/GO4 and CC500/S/GO4). This points towards synergy between N-doped carbon and GO layer in retaining the soluble polysulfides in the catholyte region. NC/S/GO4 exhibited better capacity i.e., 1453, 1024, 866, 787, 697 mAh/g versus 1016, 779, 672, 551, 441 mAh/g offered by CC500/S/GO4 when discharged at 50, 100, 200, 300 and 500 mA/g, respectively.

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1 Introduction

The meteoric rise in the utility and power of electronic devices has led to increasing demands for more energy dense batteries. In this context, lithium sulfur batteries (LSBs) are well poised to meet these demands with their high theoretical capacity (1675 mAh/g), high theoretical energy density (~ 2600 Wh/kg), environment friendliness and affordable characteristics. The theoretical capacity of LSB cathodes is ~ 6 times the theoretical capacity of LiCoO₂ and represents a significant jump in charge storage capacity.

Their wide-spread exploitation though, is mainly hindered by (i) the high electrical resistance of sulfur (~ 10^{-31} S/cm), (ii) the "polysulfide shuttle" due to dissolution intermediate polysulfides during cycling, leading to large capacity fade and (iii) large volume change (~ 80%) upon electrochemical charge/discharge. Thus, the practical implementation of LSBs requires the use of some conducting agent that can act as a host to enhance electrochemical utilization of highly resistive elemental sulfur.

Despite, the advantages afforded by the host, it is ultimately dead-weight from an electrochemical standpoint. It is imperative to develop cathode materials with low molecular weight and high sulfur loading, to maximize the specific capacity of the cathode. Ideally, the host should have (i) low molecular weight (ii) high surface area (iii) high loading of sulfur (iv) good conductivity (v) earth abundant (vi) non-toxic (vii) hetero-atom dopants/porous structure to restrain polysulfides viii) produced via facile synthetic route.

Carbon based conducting hosts satisfy most of the aforementioned qualities and have been actively researched for designing cost-effective and highcapacity cathodes for lithium sulfur batteries. A wide range of carbon materials (CNTs [1], rGO [2], carbon nanofibers [3], carbon aerogels, carbon spheres [4]) as well as carbon hosts with Co based single-atom catalysts (SACs) [5] have been explored as sulfur hosts in Li–S batteries, each offering unique advantages and characteristics.

A simple nanocomposite of sulfur wrapped with rGO sheets (77 wt% sulfur loading) exhibited a specific capacity of 823 mAh/g at 167 mA/g current density [2]. A freestanding carbon nanotube (both single walled and multiwalled) based composite sulfur cathode developed by Yahalom et al. [1], retained a capacity of 876 mAh/g after 100 cycles when cycled at 167 mA/g. Another composite utilizing an aerogel of rGO that

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are covalently bonded by polyethylenimine and multiwalled CNTs via a multistep route provides a high capacity of 933 mAh/g after 500 cycles at 1.6 A/g rate [6].

Heteroatom (N, P) co-doped mesoporous carbon wrapped with rGO has been demonstrated as an excellent sulfur cathode by Zhao et al. [7] The heteroatoms along with the porous structure inhibit the shuttle and accommodate volume changes during cycling, leading to an observed capacity of 1469 mAh/g at 167 mA/g. A sulfur cathode based on N-doped branched carbon nanofibers, which provide conductivity, polysulfide shuttle suppression as well as flexible structure to accommodate volume variation was developed by Zhou et al. [3] It retained a specific capacity of 1039 mAh/g after 200 cycles at 167 mA/g. A highly porous carbon sphere cathode host was fabricated by Zhao et al., [4] via a sol-gel based sacrificial template route, that loads about 52-72 wt% of sulfur via melt-diffusion route. The sample with 52 wt% sulfur, retained a capacity of 560 mAh/g retained after 200 cycles at 837 mA/g discharge rate.

In addition to having a conducting host for sulfur, incorporation of a secondary barrier layer between the cathode and anode has been found to be effective at suppression of the "polysulfide shuttle". Several materials like carbon nanotubes (CNTs) [8], graphene oxide (GO) [9, 10], metal organic frameworks (MOFs) [11] and several inorganic compounds (MXenes, CoP, SnO₂) [12–14] have been employed to this end. These chemical species are generally loaded onto the cathode facing surface of the separator and help to restrain the dissolved polysulfides to the catholyte region by means of physisorption/chemisorption.

In the subsequent sections, the synthesis, physical characterization as well as electrochemical evaluation of two different carbon-based hosts — a bio-derived carbon (CC500) and a synthetic N-doped carbon (NC) are discussed. Their performance is also evaluated with and without the introduction of a graphene oxide (GO) modified separator.

2 Experimental section

2.1 Synthesis of bio-derived carbon (CC500)

Coconut shells were dried in an oven at 80 °C for 2 days. Thereafter, they were broken into small pieces and heated in a tubular furnace under argon flow at





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ORIGINAL ARTICLE



Temperature driven n- to p-type conduction switching in SnSe and its mitigation through Zn doping with added advantage of Improved thermoelectric performance

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Abstract

Tin selenide (SnSe) has emerged as a surprising new p-type thermoelectric material with exceptionally low thermal conductivity, leading to impressive thermoelectric performance. However, the presence of thermally conducting & electrically insulating SnO₂ at the grain boundaries of SnSe supresses its desirable thermoelectric properties. In this work we report temperature dependence of Seebeck coefficient for polycrystalline SnSe which exhibits an unusual reversible change in conduction from n- to p-type at ~565 K. The n-type conduction near room temperature is attributed to the Se deficiency as well as SnO₂ present at grain boundaries. At high temperature formation of Sn vacancies leads to p-type conduction. The Zn doping at Sn site (Sn_{1-x}Zn_xSe) establishes the usual p-type conduction in the entire temperature range along with the lowering of thermal conductivity, resulting in a figure-of-merit of ~0.15 at 700 K, which is nearly 275% higher than that for pristine SnSe.

1 Introduction

Nearly 70% of the energy produced worldwide is lost as waste heat [1, 2]. Thermoelectric energy conversion technology and sustainable solution for directly converting this

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waste heat into usable electrical energy [2]. The conversion efficiency of a thermoelectric materials is directly related to a material, parameters known as dimensionless figureof-merit (*ZT*), which is defined as $ZT = \alpha^2 \sigma T/\kappa$, where α is the Seebeck Coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and *T* is the average temperature [3]. The ratio $\alpha^2 \sigma$ is known as power factor [4]. The total thermal conductivity (κ) consists of two terms governed by electronic contribution (κ_e) and lattice contribution (κ_i) [5]. All three thermoelectric parameters namely α , σ and κ are inter-connected therefore it puts a limit on the improvement of *ZT*. Isovalent doping of a thermoelectric material is most effective strategy to improve its *ZT* by the reduction of the lattice contribution (κ_i) of total κ [6, 7].

Chalcogenides, known for their intricate electronic structures and low intrinsic lattice thermal conductivity, have long stood out as top-performing thermoelectric materials [8]. In last decade one of the remarkable discoveries with respect to high performance thermoelectric materials is attributed to the tin selenide (SnSe) compound consisting of earth abundant environment friendly elements [9]. The pristine p-type SnSe single crystal exhibiting a high figure-of-merit (*ZT*) of 2.6 at 923 K [10] along the b axis attributed to intrinsic ultralow lattice thermal conductivity (0.20^{-1} K⁻¹), which

derives from strong anharmonic and anisotropic behaviour due to layered nature of the compound [11]. Despite the impressive ZT obtained for pure and doped SnSe single crystals their stringent growth conditions, poor mechanical strength, high fragility and production cost inhibits their use in the development of thermoelectric power generators [12]. Polycrystalline SnSe has emerged as a suitable alternative due to its ease of synthesis, machinability, and scalability [8, 13]. However, polycrystalline SnSe exhibit low ZT value due to its high thermal conductivity and low electrical conductivity. Such detrimental properties arise due to spontaneous oxidation at grain boundaries leading to the formation of SnO₂, having very high κ (140 times larger than the single crystal SnSe) and carrier scattering at the SnSe/SnO2 interface [14]. The true intrinsic ultra-low thermal conductivity in polycrystalline SnSe can be revealed through the removal of SnO₂ present at grain boundaries [15]. Undesirable SnO₂ can be removed by preparing the SnSe samples in reducing atmosphere of H2 gas [16]. Such polycrystalline SnSe samples with clean grain boundaries possess lower thermal conductivity then the single crystals due to additional phonon scattering at the grain boundaries leading to a high ZT of ~3.1 at 783 K and average ZT of 2.0 [17]. Another interesting property of SnSe is that it undergoes a phase transition in temperature range of 600-807 K, from low-temperature Pnma phase to high-temperature Cmcm phase with large enhancement of the carrier concentration. The defects chemistry calculations showed that the dominant defects in both phases are Sn vacancies which produces holes (p-type conduction) and these Sn vacancies strongly stabilises in high temperature Cmcm phase as compared to low temperature Pnma [18].

So far most of the temperature dependent experimental and theoretical transport properties were carried out for p-type SnSe having synthesis induced Sn vacancies. In the present work we have studied temperature dependent thermoelectric properties of polycrystalline SnSe bulk samples along with effect of Zn doping at Sn site. For pure SnSe we observed a temperature dependent n- to p-type transition in conduction at 565 K. Further substitution of iso-valent Zn at Sn site in the doped Sn_{1-x}Zn_xSe (x > 0.6) establishes usual p-type conduction along with lowering of thermal conductivity in the entire temperature range of 300–700 K.

2 Experimental details

Elemental Sn powder (99.5%, Alfa Aesar), Zn powders (99.5%, Alfa Aesar) and Se (99%, Alfa Aesar) powders were weighed according to the atomic ratio of $Sn_{1-x}Zn_xSe$ (x=0.00,0.04,0.06,0.08). The mixture was loaded into a single walled quartz ampoule sealed under vacuum at

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10⁻³ Pa, and then heated to 950°C over 8 h, soaking at that temperature for 5 h, followed by furnace cooling to room temperature which leads to minor cracks in the quartz tube. Such cracks usually appear due to sticking of SnSe material with quartz tube and during cooling due to thermal expansion mismatch cracking of ampoules takes place. Usually, to avoid such cracking of ampoule, SnSe was prepared in double layer of quartz ampoule. The ingot obtained after melting was ground into powders with an agate mortar. Then powdered materials is spark plasma sintered (SPS) at 480 °C for 10 min under the pressure of 40 MPa in a graphite die (hole dia: 13 mm). The crystal structure and phase purity of the powder and pellet samples were observed by x-ray diffraction (XRD) using a Rigaku diffractometer (RINT-2200, Japan, Cu Ka). Scanning electron microscope (SEM, SNE-4500 M PLUS) and energy-dispersive X-ray spectrometer (EDX) were used to analyse the surface morphology and elemental composition of the prepared material. The carrier concentration and mobility of the samples were examined at room temperature through four probe Pauw augmented Hall measurement (HL5500). A laser flash instrument (NETZSCH LFA 467) was used to measure the thermal diffusivity (D) and specific heat capacity (C_p) of the sample under an Ar atmosphere. The total thermal conductivity was determined using $\kappa = D \times C_p \times \rho$, where ρ is the density of the sample. The Seebeck coefficient and four probe electrical conductivity were measured using the ADVANCE RIKO ZEM - 3 instrument system under Helium environment on a 4 mm \times 2 mm \times 10 mm rectangular-shaped sample in the temperature range of 300-700 K.

3 Results and analysis

The XRD data of spark plasma sintered Sn1-xZnxSe samples are shown in Fig. 1. The diffraction peaks of pristine SnSe sample (x=0) could be indexed as per the JCPDS# 00-014-0159 and the extra peak present at $2\theta \sim 33.97^{\circ}$ which shows the presence of (101) plane of SnO₂ in the SnSe sample. The intensity of (101) SnO2 peak in Zn doped Sn1-Zn, Se samples decreases with increasing Zn doping in the sample (details given in supplementary information). The relative intensity of SnO2 (101) diffraction peak with respect to SnSe (400) diffraction peak is ~0.03 for pristine SnSe (x=0) sample, while for x=0.06 sample it is 0.01. In Sn1_,Zn,Se samples apart from SnSe and SnO2 diffraction peaks there are some additional peaks JCPDS# 00-037-1463 corresponding to ZnSe nano-inclusions. The analysis of the diffraction peak corresponding to the ZnSe reveals the presence of ZnSe crystallite having average crystallite size of -24 nm for x=0 sample and it increases to a value of ~ 50 nm in the sample having highest content of Zn





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Theoretical and experimental study on efficient thorium removal from aquatic environment using phosphate-modified graphene oxide polymeric beads

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Abstract

Thorium is an element of immense importance in nuclear industry due to lower environmental impact compared to fossil fuels and conventional nuclear power. In the present study, highly selective adsorption of Th⁴⁺ on phosphate modified graphene oxide polymeric beads was investigated. The interaction of $-PO_4$, -OH and -O- functional groups of graphene oxide with thorium ion was thoroughly investigated using Density Functional Theory. The adsorption induced density difference was utilized to investigate the bonding characteristics. The affinity of the Th⁴⁺ ions was obtained as $-PO_4 > -OH > -O$ - group of the phosphate modified graphene oxide. Phosphate modified Graphene oxide embedded in Calcium alginate matrix was characterized using ATR-FTIR, XRD, SEM and Raman spectroscopy. Highly efficient (>93%) uptake of thorium at pH 5 with fast rate of sorption (< 5 min) was observed in the batch sorption studies.

Keywords Modified graphene oxide · Thorium · Adsorption energy · Electron density difference

Introduction

Currently thorium is gaining attention due to its potential importance in various fields, particularly energy production [1, 2]. Apart from high abundant in the Earth's crust, thorium has several advantages over uranium, including reduced nuclear waste and increased safety margins. Countries like India with limited uranium reserves may find thorium a more attractive alternative for long-term energy security [3, 4]. Thorium can also find applications in other industries beyond energy, such as in high-temperature ceramics, welding electrodes, and as a catalyst in chemical reactions. Thorium is naturally present in low concentrations in both seawater (~0.1 ng mL⁻¹) and groundwater (≤ 1.8 ng mL⁻¹) [5, 6]. In both seawater and groundwater, thorium exists mainly in the form of dissolved thorium ions (Th⁴⁺). The extraction and concentration of thorium from these natural sources typically require advanced separation techniques and are not commonly practiced on a large scale due to the low concentrations involved. A set of adsorbents like activated carbon, graphene oxide, carbon nanotubes, natural clay minerals such as bentonite and kaolinite, iron oxide, aluminum oxide, and titanium dioxide for selectively binding thorium ions from solutions, typically in the context of environmental remediation or recovery processes were developed in current years [7-10]. But the separation of the adsorbents from the aquatic environment after highly selective and efficient thorium sorption without using electricity or filters for separation of used sorbent is still a big challenge. Thorium conventionally exists in conjunction with rare earth elements within mineral matrices and is frequently generated as a secondary product in the rare earth extraction industry. In recent years, comprehensive investigations into the extraction of thorium from lanthanides and other concomitant metallic ions have been conducted like metal-Organic Framework with Nanocavity Traps [11], ion excahne resins [12], layered metal sulfide [13] etc.

In previous studies graphene oxide was successfully utilized as sorbent of various radionuclides, heavy metals and precious metals due to its porous configuration, high surface area, structural stability and easily tunable structure

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modification by introducing various functional groups. But the effect of different oxygen inclosing functional groups of graphene oxide specially phosphate group for thorium sorption was not explored extensively. In search of highly selective and efficient sorbent of thorium, at first the interaction of Th4+ ions with various functional groups like -PO4, -OH and -O- in the graphene oxide flakes was studied using Density Functional theory [14, 15]. The adsorption energy was calculated for graphene oxide nano-flakes containing single functional group and Th4+ ions. In the next step, a new hybrid material was synthesized by embedding phosphate modified graphene oxide in calcium alginate matrix for adsorption of Th⁴⁺. The hybrid materials synthesis by impregnating inorganic material in organic matrices or vice versa shows enhances applicability in wastewater treatment [16-18]. Calcium alginate was created by cross-linking Ca²⁺ ions amid the polymer strands of alginate matrix. The sorbent was then captured within the intermolecular spaces of the calcium alginate [19, 20]. Hybrid materials are highly efficient for extraction of inorganic pollutants, radioactive and nanoparticle impurities. In general, Hybrid materials possess two different sorption sites enabling enhanced capability for removal. The hybrid materials do not leach into experimental solution due to low solubility in ground water in the neutral pH range. The newly synthesized hybrid material can easily be parted from water by decantation. The adsorbent is characterised using Attenuated total reflection Fourier transform spectroscopy (ATR-FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Raman spectroscopy. Batch sorption studies were carried out for optimization of various physicochemical parameters of the sorption process. The quantification of thorium was carried out using ICP-OES at 401.9 nm wavelength.

Theory section

DFT calculation

For the DFT calculations a graphene oxide sheet containing single functional group ($-PO_4/-OH/-O-$) was placed in the middle of a simulation box of dimension 20 Å × 25 Å × 30 Å. The electronic structure calculations were performed using VASP software (Version 5.4.4). The Perdew-Burke-Ernzerhof (PBE) functional [21, 22] was utilized to obtain an optimized geometry. PAW potential was utilised during all the simulations. The energy cut-off was 550 eV. VESTA software packages were used for visualisation of the optimised structures.

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Calculation of adsorption energy

In this study, initially a graphene oxide sheet containing single functional group ($-PO_4/-OH/-O-$) was optimised. In the next step, further optimisation of the structure was carried out with addition of Th⁴⁺ ion. The adsorption energy [23, 24] of different functional groups of functionalised graphene oxide for Th⁴⁺ ion was calculated using the Eq. 1.

Adsorption energy =
$$E_{\text{total}} - E_{\text{FG}} - E_{\text{Th}}^{4+}$$
 (1)

where, $E_{\rm total}$ is the total energy of the optimised, composite system of functionalized graphene oxide and Th⁴⁺ ion, $E_{\rm Th^{4+}}$ is the energy of only Th⁴⁺ ion and $E_{\rm FG}$ denotes the energy of the –PO₄/–OH/–O– functionalised graphene oxide sheet.

Calculations of adsorption induced electronic density difference

To understand the nature of the bonds, the electronic density differences [25, 26] due to adsorption was calculated for thorium ion using Eq. 2 given below.

$$\rho_{Final} = \rho_{total} - \rho_{FG} - \rho_{Th^{4+}} \tag{2}$$

where, ρ_{Final} is the difference in electron density due to interaction of thorium ion with functionalised graphene oxide, ρ_{total} is the total electron density of the optimised system, $\rho_{Th^{4+}}$ is the electron density of Th⁴⁺ ion and ρ_{FG} is the electron density of functionalised graphene oxide.

Experiment section

Reagents and materials

All the reagents consumed during the present study is of analytical grade and were procured from Merck. 1000 μ g mL⁻¹ thorium(IV) nitrate was used as thorium standard. For all the batch sorption tests demineralised water from MilliQ Millipore Ultrapure Water Purification System was used. For fine-tuning of the solution pH, 0.1 N HNO₃ and 0.1 N NaOH were used. For the calibration of ICP-OES, ICP standards in nitric acid medium were procured from Merck.

Synthesis of the adsorbent

Synthesis of phosphate modified graphene oxide

Synthesizing phosphate-modified graphene oxide involves a series of steps to introduce phosphate groups onto the





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Trend analysis of environmental radioactivity levels around Kaiga Generating Station, India

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Abstract

The study assessed the radiological impact of the Kaiga Generating Station (KGS) on the surrounding environment and the safety of the nearby population. Over a period of 15 years (2005–2020), the radiological monitoring detected only trace levels of ³H and ¹³⁷Cs (attributed to fallout) in the surrounding environment. The study utilized the non-parametric Mann–Ken-dall test to analyze the long-term trends, identifying either decreasing or no trend in the radioactivity levels across various environmental matrices such as air, water, biota, and dietary items. These findings indicate no significant accumulation of radioactivity, confirming the minimal environmental impact of the KGS operations.

Keywords Trend analysis · Mann-Kendall test · Environmental radioactivity · Radiological impact assessment

Introduction

Radiation naturally occurs and has been part of Earth's environment since its inception. It is found in Earth's crust, building materials, food, drinking water, and even the air we breathe. Humans have always been exposed to natural radiation sources such as Earth itself and cosmic radiation from space. Additionally, human activities also contribute to radiation exposure through X-rays for medical applications, the fallout from nuclear weapon testing, and the release of small amounts of radioactive materials from coal and nuclear power plants (NPPs) [1]. However, during the routine operation of a NPP, minimal amount of radioactivity, within regulatory limits, is discharged into the environment. Public exposure can occur internally through inhalation or consumption of radionuclides and externally from deposited activity or effluent plumes.

The safety of both occupational workers and the public is given the top priority in nuclear industries in India.

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² Environmental Monitoring and Assessment Division, Bhabha Atomic Research Centre, Trombay, Mumbai, Maharashtra 400085, India The Kaiga Generating Station (KGS) in Kaiga, Karnataka, operates four PHWR (pressurized heavy water reactor) type nuclear reactors, each with a capacity of 220 MWe, where rigorous protocols limit the discharge of radioactive materials. Liquid effluents are treated to significantly reduce contamination levels, ensuring they are well below permissible limits. Gaseous effluents are filtered through HEPA (highefficiency particulate air) filters before being discharged through a stack of height 100 m. Continuous emission monitoring from the facility ensures compliance with regulatory standards [2].

However, environmental radiological monitoring around NPPs is crucial to ensuring public and environmental safety. The Indian nuclear industry follows a systematic monitoring program, beginning with a comprehensive pre-operational survey around the NPP site. At KGS, a detailed pre-operational survey was conducted over a 30 km radius of the site to set baseline radioactivity levels [3]. Once operational, continuous environmental monitoring is conducted. The Environmental Survey Laboratory (ESL) equipped with highly sensitive instruments, operated by the Environmental Monitoring and Assessment Division, Bhabha Atomic Research Centre (BARC), oversees these efforts to ensure public radiation exposure remains within safe limits as set by national and international guidelines.

During normal or accidental operations, NPPs can release radioactive effluents in gaseous or liquid states. Tritium (³H; $t_{1/2}$ =12.3 years) is a major by-product of nuclear reactions

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in PHWR-type nuclear reactors at KGS, Kaiga, which use heavy water (D₂O) as its coolant and neutron moderator [4, 5]. It can enter into the atmosphere and water bodies, making its monitoring crucial for assessing environmental impacts and public radiation doses. Other significant radionuclides, like ¹³⁷Cs (t_{1/2}=30.2 years) and ⁹⁰Sr (t_{1/2}=28.7 years), are also rigorously monitored due to their high fission yields and long physical half-lives, which allow them to remain active in the environment for several decades [6]. Additionally, ¹³⁷Cs and ⁹⁰Sr possess significant radiotoxicity and can accumulate in muscle tissues and bones of the organisms upon ingestion [7]. Consequently, their presence in the environment is of critical concern, and monitoring their levels is vital for assessing radiation risks to the public and the environment [6, 7].

The monitoring covers various environmental matrices such as air, water, sediment, soil, vegetation, and food samples, to detect any radioactivity levels exceeding natural background levels due to KGS operations. The measurement of gross-alpha and gross-beta activity in the air primarily serves screening purposes and helps in the long-term monitoring of radionuclide behaviors [8]. Samples from terrestrial environments like soil, grass and other vegetation act as trend indicators and markers of events near a nuclear installation. Vegetation and food samples including crops, vegetables, milk, and meat are the main dose-contributing samples of terrestrial origin. Meanwhile, samples of aquatic origin such as surface water, fish, and sediments cover the aquatic aspects and assess the impact on water bodies due to discharges from the NPP. These indicators are selected based on their relevance in assessing radiation exposure and environmental contamination stemming from NPP operations. This holistic approach to environmental monitoring and radiation assessment helps enhance the understanding of the environmental implications of nuclear energy production.

Globally, extensive research has been conducted to examine the environmental radiological impacts of NPPs, with numerous studies examining the long-term trends in environmental radioactivity levels [9-17]. For instance, a study at Qinshan NPP in China monitored the radioactivity in drinking water and the surrounding environment, as well as cancer incidence rates among the residents, over 9 years from 2012 to 2020 [10]. Similarly, research conducted at the Wolsong nuclear power plant in Korea analysed environmental radioactivity data collected from 1998 to 2010 to understand long-term accumulation trends [17]. These long-term assessments often employ trend analysis methods to evaluate the ongoing trends in environmental monitoring data. Trend detection techniques can be categorized as parametric and non-parametric. Parametric tests assume a normal distribution of data and require a large sample size [18]. In cases where the underlying distribution is unknown, nonparametric methods are more appropriate [19]. The present

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study utilized the non-parametric Mann–Kendall test, considering the inadequate knowledge of the parent distribution, which is widely used in analyzing the time series data related to environmental radioactivity [10, 17, 20–22].

Site description

The KGS is situated in Kaiga village within the Indian state of Karnataka, at Latitude 14.86° N and Longitude 74.44° E. On India's southwest coast, this location is approximately 58 km east of the coastal town of Karwar. Kaiga is encircled by tropical forests, ranging in elevation from +20 to +700 m above mean sea level, and is home to a wide diversity of flora and animals. Rainfall in the area averages 3700 mm during 4 months from June to September. At Kaiga, the ambient temperature ranges from 13.3 to 41.0 °C, and the relative humidity varies between 17.7 and 99.9% [23]. Figure 1 shows the location of KGS, Kaiga.

Environmental monitoring programme

Monitoring environmental radioactivity poses significant challenges due to the spatial and temporal variations of radioactivity levels within environmental samples. Therefore, it is imperative to analyze numerous samples from various locations and time periods to establish a statistically significant concentration profile of radioactivity. The collected environmental samples were categorized into three groups:

- Samples such as food/crops, vegetables, drinking water, air, etc., relevant for the estimation of impact to the members of the public.
- Samples such as soil, grass, leaf, and sediment, serve as trend indicators, and
- Samples such as goat thyroid, accumulate specific radionuclides to a greater extent (e.g., ¹³¹I), serving as a sensitive indicator.

The sampling locations around KGS were identified based on considerations such as prominent wind direction, atmospheric dilution factor, proximity to the site, population centres, availability of samples, and accessibility. The region around KGS was divided into four different circular zones (beyond the exclusion zone of 2.3 km) namely zone-1 (Z1: 2.3–05 km), zone-2 (Z2: 05–10 km), zone-3 (Z3: 10–15 km) and zone-4 (Z4: 15–30 km). The samples were collected from various locations within these zones, covering a radial distance of up to 30 km from KGS. The zone-wise sampling map around KGS is shown in Fig. 2. All samples were collected and analyzed using standardized procedures [24].





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Abstract

The present work calculated the velocity of edge dislocations in the Ta–W system using molecular dynamics (MD) simulations and through machine learning (ML), identified the key parameters influencing the velocity. To achieve this, MD simulations were conducted at various values of the extrinsic parameters—temperatures and applied stresses (τ_{app}), and the intrinsic variables—slip systems and alloying contents of tungsten in tantalum. Configurations containing edge dislocations on {110}/(112)/{123} planes were employed, and dislocation velocities were subsequently estimated. The MD results were processed using ML models, specifically extreme gradient boosting and SHapley Additive exPlanations (SHAP). SHAP analysis identified τ_{app} as the most influencing parameter affecting velocity, followed by slip plane, temperature, and W addition. SHAP estimated the base velocity value (v_b) to be 1376 m·s⁻¹. v_b was calculated by training SHAP on a parameter-less model. v_b could be increased by applying τ_{app} of at least 1 GPa, through slipping on the {112} and {123} planes, at temperatures of 0 and 300 K, and in configurations with 0 wt.% and 5 wt.% W. The importance of v_b on deformation was established.

Keywords Dislocation · Slip planes {110} {112} {123} · Tungsten effect · Temperature · Resolved shear stress

1 Introduction

The plasticity of metals primarily depends on the mobility of dislocations. The velocity of dislocations is governed by temperature [1], strain rate [1], applied stress [2], and obstacles such as grain boundaries [3], solute atoms [4, 5], and cracks and voids [6–8]. Over the last few decades, several analytical and computational studies have been carried out to investigate the mobility of dislocations in different types of crystal systems, at different temperatures and with varying alloying content. In α -Fe, the glide of screw dislocation occurred on {110} between 0 and 100 K and on {112} at 300 K [1]. In a study on Al, dislocation velocity decreased with increasing temperature [2]. In another study on Al, the effect of local stress on dislocation motion showed that dislocation velocity can be constant with a gradual decrease in stress [9]. In Cu–Ni for the applied stresses between 10

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and 40 MPa, the dislocation motion showed two distinct regimes. At lower applied stress, Ni atoms slowed the dislocation motion while at higher applied stress, Ni atoms favored dislocation motion [10]. In Nb, dislocation velocity on {110} was lesser than that on {112}, while in Fe-Si an opposite effect was observed [11]. In Fe-Ni and Fe-Cu, solute hardening was observed at high temperatures and solute softening at low temperatures [4]. At high temperatures, the increase in the lattice resistance to dislocation motion has been explained through phonon drag [12]. In Cu-Fe, a nano-precipitate of Fe hindered the dislocation moving towards the precipitate [13]. A critical value of atomic misfit in the Cu-x (x = Ni, Ag, Pd, Pt) system was observed to change the dislocation mobility [14]. A lower misfit value does not affect the dislocation motion while a higher misfit value dragged the dislocation motion. In Ni-Al, the hardening was shown to be due to solute-solute repulsion during the motion of edge dislocations [5]. In Ni-10 wt.% Al, the screw dislocation motion was faster in short-range order than in random Al structure [15]. In Ni-Co, increased Co content and temperature decreased the dislocation motion [16]. The current study focused on Ta-W alloy for its excellent properties such as high-temperature strength, corrosion resistance, and good ductility among refractory metals [17]. In pure Ta,

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dislocation velocity was dependent on the activation energy for double kink formation [18]. In a W–Ta alloy, the solute–dislocation interaction energy was found to be negligible and hence the dislocation core structure in W due to Ta addition was minimally affected [19]. In Ta–10W, simulations using density functional theory showed that local variation in Peierls barrier of screw dislocation was larger in alloyed than in pure Ta [20].

Computational tools such as molecular dynamics (MD) and dislocation dynamics (DD) provided a reasonable understanding of the influence of the different parameters on the dislocation velocity. However, the individual effect of temperature, applied stress, alloying content, and slip planes on the dislocation velocity is still not clear. Bertin et al. laid out the areas of research for dislocation physics with data science being inevitable to gain insight into dislocation mechanisms [21]. The complex interplay of various parameters on the dislocation velocity can be understood using machine learning (ML) thereby providing insights into the plasticity of the materials. Graph-based neural network (NN) frameworks were developed to model dislocation mobility using data generated from MD simulations [22, 23]. These frameworks were implemented in large-scale discrete DD simulations to predict flow stress [24]. An NN model was developed to predict Peierls barrier in NbMoTa alloy using local atomic type and displacement as inputs [25]. An ML approach was developed to predict forces and energies of dislocations which was used to perform two-dimensional (2D) ML-based DD simulations [26]. The regression NN model used dislocation configurations from DD simulations to predict stress-strain curves [27]. SHapley Additive exPlanations (SHAP) analysis of the input parameters from DD simulations predicted specimen size to be the most important parameter affecting yield stress [28]. Artificial NN used MD stress-strain data to model the dislocation plasticity which was applied and verified on shock loading conditions [29]. Extreme gradient boosting (XGBoost) [30] model was used to predict critical resolved shear stress (CRSS) and ranked lattice distortion as the important parameter influencing CRSS [31]. SHAP used data from crystal plasticity with a DD-based hardening model and identified the Schmid factor as the significant parameter for the formation of stress and strain hotspots during various deformation states [32, 33]. A k-nearest neighbors ML model was used to study the plasticity in metallic glasses with the help of atomic dynamics data [34]. With these supporting references, the aim of this article revolves around the changes in dislocation mobility studied using MD and ML.

The aim of this article is to determine using MD, the dependence of the extrinsic parameters such as applied stress and temperature, and intrinsic parameters such as slip system and W content on the dislocation velocity of Ta–W alloy, and further, using ML, to find the significance and

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importance of each parameter. XGBoost model was trained and tested on the MD results. SHAP was used to interpret the XGBoost model.

2 Methodology

The dislocation mobility in Ta was simulated using an MD simulator LAMMPS [35], in three different orientations, such that their orthogonal directions were [111] along x direction, [110], [112], and [123] along y directions, and [112], [110], and [541] along z directions, respectively, as shown in Fig. 1. An extra half-plane of atoms was inserted into every single crystal using Atomsk to create three different configurations with edge dislocations with Burgers vector $\frac{1}{2}$ [111] on (110), (112), and (113) slip planes having their dislocation line direction along [112], [110], and [541] [36], respectively. The dimensions of the simulation box were 75×75×5 nm3 with 1.51 million atoms for {110} slip configurations, 75×75×5 nm3 with 1.46 million atoms for {112} slip configurations, and 75×75×4 nm³ with 1.34 million atoms for {123} slip configurations. Each configuration with a dislocation was energy minimized using microcanonical ensemble and conjugate gradient method. Atoms within a region of 1.5 nm on the top and bottom of the simulation box along y direction were fixed and allowed only for rigid movement. A constant shear stress along y direction on xy plane was applied on the fixed rigid region of atoms to simulate shear deformation. The shear simulations were carried out at 0, 300, 1000, and 2000 K with applied shear stress (τ_{app}) of 0.5, 1, and 1.5 GPa for 200 ps with 2 fs timestep. The velocity of the atoms was rescaled to obtain



Fig.1 Schematic illustration of dislocation and various parameters affecting its mobility. Three choices of directions are given for y and z





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Understanding the effect of experimental variables on the recovery of ²³¹Pa from siliceous cake using factorial design

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Abstract

Four-factor (oxalic acid concentration, contact time, temperature, ultra-sound), two-level experimental design was applied during the recovery of ²³¹Pa from siliceous cake—a solid radioactive-waste, produced in monazite processing. Oxalic acid (0.5 to 1.1 M) had the highest positive (F=1018.6) and ultrasound had the least (F=33.0) impact on recovery. All inter-factor interactions were significant, as $F_{calculated} < F_{critical}$ and P < 0.05. Enthalpy of protactinium-oxalate complexation was found to be -24.8 kJ mol⁻¹. The regression coefficient (0.9853), randomness and magnitude (< 2) of fitted residuals explicated the suitability of present statistical model for predictive analysis.

Keywords Experimental design · Oxalic acid · Protactinium · Recovery · Siliceous cake

Introduction

In India, development of ²³²Th-²³³U fuel cycle based nuclear reactor technology is being perused because of huge deposits of thorium (Th) compared to the modest reserves of uranium [1]. However, the back end of ²³²Th-²³³U fuel cycle poses several challenges, one being the radiotoxicity of ²³¹Pa ($t_{1/2}$ = 32,670 y) isotope produced from ²³²Th [2]. ²³¹Pa is a category (IV) high level waste that can have long-term radiological effect.

The knowledge of chemistry of protactinium (Pa) is important for the chemical processing of irradiated Th. The chemistry of Pa is not thoroughly investigated due to its low natural abundance and the tendency to hydrolyze even in strong acid leading to non-reproducible and complex behavior [3–5].

Therefore, macroscopic quantities of protactinium (²³¹Pa) are essential for studies related to processing of irradiated Th. Out of the several isotopes of Pa, ²³¹Pa is the most suitable for chemical studies, due to its better nuclear properties such as (i) long half-life (ii) alpha and gamma emitting

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radionuclide, and (iii) low specific activity that allow handling of microgram quantities of Pa.

In undisturbed geological formations, 231 Pa exists in secular equilibrium with 235 U at a concentration of about 0.34 mg kg⁻¹ of uranium. Recovery from natural sources is the most favorable approach for the production of useful quantity of 231 Pa [6–14].

Work had been initiated at our division for the recovery of ²³¹Pa from siliceous cake, a solid radioactive-waste, produced in monazite processing plant, Aluva, India [2]. The work consists of three stages namely (i) determination of ²³¹Pa in the siliceous cake (ii) recovery of ²³¹Pa from the siliceous cake using oxalic acid as leaching agent, and (iii) chemical/radiochemical purification of the ²³¹Pa. The determination of ²³¹Pa in siliceous cake has been previously reported from our laboratory [15].

Experimental design methodology is extensively used (i) to identify the parameters (termed as factor) which may affect the result of an experiment (termed as response factor), and (ii) to carry out statistical analysis to separate and evaluate the impact of the various factors involved; an experimental design study provides sufficient results of right kind, if the objective of the experiment is defined properly, with limited number of experiments as opposed to the conventional one-variable-at-one-time approach, saving resources, and time [16–19].

A two level full factorial methodology is widely adopted to understand the effect of experimental variables on the





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response factor [18, 20, 21]. In this work, a four factor and two levels experimental design study was carried out to evaluate the effect of concentration of oxalic acid, contact time, temperature, and ultrasound on (i) the percentage recovery of ²³¹Pa and (ii) the accompanying impurities (measured as the total dissolved solids) from siliceous cake using oxalic acid. The results of the experimental design study are presented and the fitness of a multiple regression model for predictive analysis is discussed. Thermodynamic data obtained is also discussed.

Experimental

Materials

Siliceous cake was obtained from Indian rare earths limited at Aluva in Kerala. HCl, Oxalic acid and sodium hydroxide (GR grade, Purity \geq 99%), were procured from Thomas Baker Chemicals, India.

Instrumentation

Gamma ray measurements were carried out using high purity germanium (HPGe) detector (Canberra, USA), coupled to 8 k channel analyzer. The detector specifications were: relative efficiency -30%; resolution—1.8 keV at 1332 keV gamma peak of ⁶⁰Co; Multichannel analyzer— APTEC 5000 series, version 6.3, Canberra, USA.

Chemometric analysis was performed using Minitab statistical software (trial version 20.2.0.0).

Procedure for recovery of Pa

About 10 g of siliceous cake was weighed and transferred to 500 mL polyethylene bottle containing about 100 mL of sodium hydroxide (1 M). It was agitated on mechanical shaker for a period of 2 h. The supernatant was discarded and the insoluble mass was thoroughly washed with deionized water. 30 mL of 2 M HCl solution was then added. After equilibration for about 2 h on a mechanical shaker, the supernatant was discarded by careful decantation. Finally, the cake was thoroughly washed with de-ionized water.

Recovery of ²³¹Pa was carried out by equilibrating this pretreated siliceous cake with oxalic acid on mechanical shaker. The siliceous cake to oxalic acid ratio was maintained at 1:5 (w/v). The concentration of oxalic acid and other experimental parameters were kept as per the design. The detailed flowsheet has been described earlier [22]. After equilibration, the supernatant was collected in a Teflon beaker. To this, concentrated HNO₃ (about 5 mL) was added. Decomposition of oxalic acid was carried out by heating the solution on sand bath with periodic addition

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of hydrogen peroxide (drop-wise). The residue obtained was then transferred to Pt crucible, ignited using Bunsen burner and heat sealed in polythene after weighing. 283.690 keV gamma ray peak was used for the determination of ²³¹Pa using the following equation [15]

$$C = \left(N_{sample} M t_{1/2} \right) / \left(0.693 N_a W Y \epsilon \gamma \right)$$
(1)

where,

Nsample_net counts under the peak at 283.690 keV.

M—atomic weight of ²³¹Pa.

t_{1/2}—half life of ²³¹Pa.

N_a—Avogadro number.

W-weight of siliceous cake (g).

ε-efficiency of detector at 283.690 keV.

 γ —gamma abundance of 283.690 keV (²³¹Pa).

The rationale for selecting 283.690 keV gamma line of 231 Pa (γ —0.017), for the quantification was:

- a. The interference free gamma line at 27.371 keV (γ—0.103) could not be utilized, as it suffered severe attenuation within the matrix (residue obtained after decomposition of oxalic acid).
- b. The peaks at 300.060 keV, 302.670 keV and 330.041 keV (γ —0.025, 0.022 and 0.014, respectively), had strong interference from the gamma rays due to ²¹²Pb and ²²⁷Th (daughter products of ²³²Th and ²³⁵U respectively).

Literature reported values of atomic weight, half-life, Avogadro number, and γ -ray abundance of ²³¹Pa [23] were used for calculating the concentration of ²³¹Pa.

The efficiency of HPGe detector (ε) at 283.690 keV was determined by counting¹⁵²Eu source (calibration source, procured from International Atomic Energy Agency, IAEA, Vienna) of known activity (disintegrations per second, dps) under identical geometry as that of the sample. The count rate (counts per second, cps) of photo-peaks arising from the gamma rays of.¹⁵²Eu, was converted into efficiency using Eq. (2) [24]

$$\varepsilon = \frac{cps}{dps * \gamma}$$
(2)

Here ' γ ' is the literature reported γ -ray abundances of ¹⁵²Eu. Efficiency curve was constructed by plotting natural logarithm of efficiency versus natural logarithm of gamma ray energies. Least squares fitting of the plotted points showed a 2nd order polynomial relationship. The fitted function was utilized to determine efficiency of the detector at 283.690 keV.

The recovery of ²³¹Pa from the siliceous cake was then calculated by comparing the measured concentration (C)





BRIEF COMMUNICATION



Understanding the Stress-Induced Movement of γ/ϵ Interfaces and Coalescence of ϵ Martensite Variants **Through Fractal Analysis**

ARPAN DAS

The influence of stress/strain on the movement/rearrangement of γ/ϵ interfaces and the coalescence of ϵ plates under a fixed location of a high Mn steel have been investigated through fractal measurement of ϵ plates. Image texture analysis has also been implemented to recognize the stored energy and configurational stability of such plates under γ matrix as a function of tensile deformation. Fractality of ϵ variants are correlated with their geometrical configurations at different directions with systematic increment of tensile strain.

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RECENTLY, high Mn steels have received significant attention for a variety of applications. Therefore, advanced research regarding high Mn steels with excel-lent low-temperature properties have been reported.^[1-3] These steels often show characteristics of TRansformation-Induced Plasticity (TRIP) and TWinning-Induced Plasticity (TWIP) effects. An in-depth understanding of Fe-Mn system is required for further evolution of such steels. Austenitic steels with the low stacking fault energy (Γ) markedly facilitate the formation of stacking faults, ϵ -martensite, slip bands, and understanding of γ (fcc) $\rightarrow \epsilon$ (hcp) transformation is indispensable.^[4] When the stress-assisted ϵ -martensite transformation (MT) takes place below M_d , plastic deformation is instigated by ϵ formation.^[5] Plastic deformation above M_d is driven by slip mechanism.^[5] Particularly, understanding the movement/rearrangement of γ/ϵ interfaces and ϵ variants' coalescence (during $\gamma = \epsilon$ transformation) under tension is extremely important for these steels.^[6] The performance of these steels strongly depends on ϵ characteristics resulting from different application of stress/strain and temperature. Jun *et al.*^[7] concluded that the rise in damping property is attributed to the contribution of movement of ϵ boundaries (variants), migration of the stacking fault boundaries in ϵ phase and movement of γ/ϵ interfaces. Therefore, interface characteristics/patterns are extremely important for

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such materials of any microstructural scale size to understand their complete mechanical responses under different stress/strain.^[8–10] Recently, Lee et al.[6] investigated the movement/

rearrangement of γ/ϵ interfaces and ϵ variants' coalescence (see Figure 1 in Reference 6) during tensile deformation of a Fe-24Mn alloy [24.1Mn-0.02C-0.015N-0.021Si-0.03S-0.015P-bal Fe (wt pct)] at different stress/strain based on the crystallographic relationship between γ and ϵ and some thermodynamic analysis. Finally, e-MT comprises a small volume change, it (geometry, volume, morphology, arrangement, pattern, and configuration) also depends on *sign of stress*.^[11] According to Nishiyama,^[12] the contraction in c-axis direction for $\gamma \rightarrow \epsilon$ transformation is about 0.7 pet when the c/a ratio of ϵ is 1.633. Lee^[6] reported the rearrangement of ϵ plates of systematically tensile deformed Fe-24Mn steel (at different strains: 0, 1.7, 3.5, 10.3, 20.6 pct) at room temperature. The configurations/patterns, rearrangements, and organizations of γ/ϵ interfaces are visually looking almost similar in 2D microstructure for all stressed/strained conditions (Figure 1). But they are not exactly similar in their dimensions/arrangements, rather complex in nature when quantified. The ϵ plate thickness (at different directions) and their lengths are also systematically plotted as a function of tensile strain by Lee.¹⁶

Formation of ϵ was found to be highly localized, and the parent γ had a high Schmid factor for active slip system during $\gamma \rightarrow \epsilon_{\cdot}^{[13]}$ Thus, such conditions offer the most favorable orientation for transformation to undergo.^[13] The faulted ϵ is also found presently, which is the characteristic of irregular overlapping process as discussed by Fujita and Ueda.^[14] The ϵ -martensite has 12 variants, since $\gamma \rightarrow \epsilon$ transformation occurs in three $\langle 112 \rangle$ directions on four $(111)_{\gamma}$ planes.^[15] Many observations were also performed by Takaki *et al.*^[16] to determine the crystallographic nature of ϵ resulting four kinds of ϵ plates: $(\overline{111})_{\gamma}[\overline{121}]_{\gamma}$, $(\overline{111})_{\gamma}[\overline{121}]_{\gamma}$, $(\overline{111})_{\gamma}[\overline{211}]_{\gamma}$, and $(11\overline{1})_{\gamma}[\overline{211}]_{\gamma}$, in general $\{111\}_{\gamma}\langle 112\rangle_{\gamma}$, exist in γ matrix. This orientation relationship (*OR*) corresponds with that of Shoji–Nishiyama.^[17,18] Consequently, four kind of ϵ plates on different $\{111\}_{\gamma}$ planes can be formed in one γ grain.^[16]

Statistical self-similarity of complex γ/ϵ networks generated at different deformations are the essential quality of fractals in 2D/3D micrographs. Interpreting the differences in complex arrangements of ϵ plates, fractal analysis has been used to represent the microstructural irregularities/rearrangements, mainly through measurement of fractal dimension (D_f) in 2D. Image texture analysis has also been done to comprehend the relative configurational stability and stored energy of/in ϵ and γ phases (and their complex-interfaces) as a function of tensile deformation. Currently, significant number of research articles reported by different scientists on the estimation of volume, crystallographic details, and morphologies of ϵ martensite as a function of stress/strain for high Mn steels, but the theme related to D_f and chaos rearrangements/patterns of such complex γ/ϵ interfaces as a function of extent of tensile deformation (correlating this with its respective geometries) are not available in open domain, which has been primarily aimed at in present investigation. This study also aims to develop a fundamental understanding of alteration of γ/ϵ interfaces' patterns (due to their complex movement/rearrangement and coalescence of ϵ variants under tension) at a fixed location of a microstructure through exhaustive fractal analysis in order to engineer these complex/irregular interfaces through systematic mechanical deformation. The pattern analysis of such complex interfacial characteristics at different stress/strain will help to understand the $\gamma \rightleftharpoons$ ϵ transformation, deformation, and fracture mechanisms of high Mn steels.

The $D_{\rm f}$, an intensive property measures the chaos (complexity), an idea related to certain key features of fractals: *self-similarity* and detail or irregularity which also act as a marker of microstructure.^[19] $D_{\rm f}$ of microstructural networks can often be measured by box-counting and Fourier transform, which are clearly based on self-similar character concepts.[20] For an exactly self-similar object, its length has a power-law correlation to length scale and $D_{\rm f}$ of the object can be derived from the exponential-term of power-law relation.^[20] Currently, box-counting fractal analysis has been employed for the understanding of statistical distribution of microstructural rearrangements/patterns, mainly through the measurements of $D_{\rm f}$. The complex movement of γ/ϵ interfaces and coalescence of ϵ plates (during $e \rightleftharpoons \epsilon$ transformation) as a function of tensile strain of a high Mn steel has been investigated though the measurement of $D_{\rm f}$ of ϵ -martensite plates and the basic image texture analysis.

Currently, the series of reported optical micrographs (OM, Figure 1) of systematically tensile deformed high Mn steel illustrating the rearrangements/organizations

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of ϵ variants under γ matrix have been extracted from Reference 6. The ϵ -martensite appears as thin/parallel bands that usually start at grain boundaries (*GB*) and terminate at either *GB*/twin of equiaxed γ . The length and thickness data of ϵ plates (for all directions) are also digitized from Reference 6. Deformation-induced ϵ -martensite or slip bands are nucleated at different {111}_{fice} planes. The ϵ plates' networks in 2D micrographs (Figure 1) are presumed to be an invasive *self-affine* fractal character in statistical sense. The ϵ -martensite evolves as long/straight, thin bands on {111} octahedral slip planes and is associated with atomic shifts of a/6 (112) in these planes, altering the stacking sequence to form an *hcp* structure.^[21]

All micrographs are first binarized using ImageJ software. Figure 2(a) schematically illustrates the direction and position of different ϵ plates under γ matrix. The microstructure consists of a mixture of ϵ -martensite (bright-area) under y-austenite (dark area) (Figure 1). The gray-scale histograms (Figure 2(b)) for all micrographs are achieved by plotting 'pixel-value' distribution. All data are then normalized, averaged, and plotted (Figure 2(b)). This shows the statistical analysis of the normalized/averaged gray-scale distribution of all micrographs as a function of strain. Bimodal kind of distribution patterns are noted (first peak: γ , second: ϵ) for all strains. Systematic shift of horizontal peak positions is noted for both the phases (Figure 2(b)). For zero strain, y peak is maximum and ϵ peak is minimum, contrarily when the strain is 20.6 pct, the γ peak is minimum and ϵ peak is maximum. Approximate 'area under curves' for γ and ϵ profiles as a function of strains are measured to be (0 pct strain: 2.04 and 1.54, 1.7 pct strain: 1.86 and 1.71, 3.5 pct strain: 1.89 and 1.62, 10.3 pct strain: 1.89 and 2.20, and 20.6 pct strain: 1.27 and 2.79 respectively). These variations may be attributed to the alteration in volume and arrangements/patterns of ϵ plates (i.e., its configurational stability) under γ matrix with the systematic increment of stress/strain. The complex movement of γ/ϵ interfaces and coalescence of ϵ plates as a function of extent of tensile deformation can be grossly understood from the differences in 'area under curves' and 'bimodal profile patterns' of the gray-scale distribution of corresponding two-phase micrographs.

Research shows that MT is a non-uniform and limited fractal.^[22] For computing $D_{\rm f}$ of ϵ plates, *box-counting* algorithm has been applied exhaustively. Based on the classical concept of covering dimension by Mandelbrot, the *box-counting* method allows to calculate $D_{\rm f}$ of lacunar and invasive fractal sets.^[23] To estimate $D_{\rm f}$, a series of square grids (*fine to coarse*) are properly laid over the micrographs exactly covering the region of 'representative constant portions' (big areas chosen when measurement) individually (Figure 1). The grids containing phase are defined as occupied grids (N_{ϵ} : bright region) are counted (exhaustive manual way) for the series of grids (with sizes, *s*) and kept in a spreadsheet. Since the ϵ -martensite network is a fractal object, the number of occupied grids has a *power-law* relationship

METALLURGICAL AND MATERIALS TRANSACTIONS A





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Uranium separation from urine matrix using amidoximated crosslinked polyacrylonitrile adsorbent

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Abstract

A rapid radiochemical separation method was developed for the assessment of uranium in urine using indigenously synthesised amidoximated crosslinked polyacrylonitrile (ACPAN) adsorbent. The synthesised adsorbent exhibited a high uranium adsorption capacity for urine samples conditioned at pH 2. The reusability of the ACPAN adsorbent was demonstrated by its stable adsorption capacity for ultra-trace levels of uranium over multiple cycles. The standardized method complied ANSI 13.30 radio bioassay performance criteria, validating the suitability of this novel technique for precise determination of uranium in urine. The method developed is rapid, sensitive, and can be applied for emergency bioassay of uranium in urine.

Keywords Emergency bioassay · Urine · Uranium · Amidoximated crosslinked polyacrylonitrile adsorbent · Liquid scintillation counting · LED fluorimetry

Introduction

Uranium is a significant radionuclide that can be released into the environment during radiation emergencies, posing health hazards due to its chemical toxicity and radiological properties once it enters the body. Once inside the body, uranium is mainly deposited in bones, kidneys and liver [1]. The health risks associated with uranium arise primarily from its chemical toxicity and radiological properties. Therefore, during emergencies, rapid assessment of internal contamination is crucial for identifying potentially contaminated individuals and facilitating early medical intervention. The assessment of internal contamination is carried out through in-vivo (direct measurement) and in-vitro (in-direct measurement) monitoring techniques. In case of uranium, in-vitro

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monitoring techniques are usually preferred over in-vivo monitoring, mainly due to higher sensitivity. Furthermore, in-vivo monitoring requires specialized systems, such as NaI(Tl) or HpGe detectors placed inside graded steel room [2]. The applicability of in-vivo monitoring during radiation emergencies [3] may be limited by these factors. As a result, in-vitro monitoring through spot urine analysis [4] is often preferred due to its higher sample throughput and enables rapid dose assessment of contaminated individuals [5]. Consequently, assessing internal contamination due to uranium and separating uranium from other radionuclides in a urine matrix is essential. Traditional techniques, such as solvent extraction, ion-exchange, and extraction chromatography, rely on commercially available resins and chemicals. In contrast, this present study aimed to separate uranium using an indigenously synthesized resin for emergency bioassay purposes.

Various separation methods have been reported in the literature for the separation of uranium from other radionuclides in urine matrix. These methods include solvent extraction [6–10], ion-exchange [5, 11–17] and extraction chromatography [18–22]. Although high radiochemical yields (approximately 80–100%) are obtained with these methods, they involve several sequential steps, and are labour-intensive. More recently, novel separation media such as advanced sorbents and nanomaterials, with improved

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performances, have been primarily utilized for uranium estimation in aqueous, seawater, and water samples [23, 24], with limited application in biological samples like urine [25–27]. For instance, Khayatian et al [25] synthesized magnetic iron oxide nanoparticles (MIONPs) modified with sodium dodecyl sulfate and utilized them for estimation of uranium (VI) in various samples, including granite rocks, water, blood serum and urine. Similarly, Paul et al [26] developed polymeric-based sorbent (TEHP: HDEHP@PP for plutonium and HDEHP@PP for uranium) and evaluated its effectiveness in estimation of Pu & U in seawater and urine samples at ppb range. Mandal et al [27] developed magnetic nanoparticles (Mn-doped Fe₃O₄) specifically for the adsorption of uranium (VI) ions from urine matrix,

In the present study, an effort was made to employ an indigenously synthesised amidoximated crosslinked polyacrylonitrile (ACPAN) adsorbent for selective uranium separation from urine matrix. A literature review revealed that researchers have utilized amidoxime-based adsorbents for uranium separation from aqueous matrices, primarily seawater [28-32]. Notably, Omichi et al [28], Kabay et al [29], Prasad et al [30] synthesised polyacrylonitrile (PAN) fibrous adsorbent with amidoxime as a functional group using the radiation grafting method for recovery of uranium from seawater. Omichi et al [28] reported that PAN fibrous adsorbent effectively concentrated uranium on the adsorbent, with a concentration factor of 1000 when compared with other alkali and alkaline earth metals present in seawater. Liu et al [31] utilized amidoxime polyacrylonitrile membrane for the extraction of uranium from uranium-containing simulated waste water, achieving a static adsorption rate of 96.96%. Tang et al [32] highlighted that amidoxime-based materials are among the most promising candidates for uranium extraction from aqueous systems. However, a thorough literature survey did not yield any previous studies on the use of amidoxime-based adsorbents for uranium separation from urine. Therefore, in the present study, a novel method utilizing prefilter resin for organic removal followed by uranium separation using indigenously synthesised ACPAN adsorbent has been developed from direct urine. The developed method eliminates the need for time consuming wet digestion, simplifying the radiochemical separation of uranium from urine matrix.

For the synthesis of the ACPAN adsorbent, the crosslinked polyacrylonitrile (CPAN) beads were prepared via suspension polymerization technique, followed by reaction with hydroxylamine hydrochloride (H₂N-OH. HCl) [33]. The characterization of the synthesized ACPAN adsorbent was carried out using various techniques. Subsequently, the factors affecting uranium separation from urine were investigated, including the effects of temperature, pH of urine, uranium (VI) concentration, contact time, and different desorption solvents. The kinetics, isotherms,

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and thermodynamics of adsorption were studied in detail to understand the adsorption mechanisms.

The quantification of uranium was carried out using Liquid Scintillation Counting (LSC) and LED fluorimetry technique. Earlier studies [34] have shown that the LSC technique can be directly applied to measure activity in urine samples, providing gross alpha (actinides) and gross beta activities. This enables its use as a screening technique to assess overall internal contamination. However, to facilitate appropriate medical intervention following significant radionuclide intake, it is essential to identify the specific type of radionuclide responsible for internal contamination. Therefore, in the current study, a methodology was developed using ACPAN to separate uranium from other radionuclides in urine matrix, with the aim of applying it in radiation emergency scenarios. Furthermore, the developed bioassay procedure was validated using the ANSI 13.30 acceptance criteria [35].

Experimental

Materials

The following chemicals were acquired from the specified sources: Acrylonitrile (AN) and hydroxylamine hydrochloride (H₂N-OH.HCl) from SD Fine Chemicals Limited, India. The cross linkers, ethylene glycol dimethacrylate (EGDMA) and divinyl benzene (DVB) from Sigma Aldrich and Merck, respectively. Calcium carbonate (CaCO₃), gelatin, sodium nitrite (NaNO₂), sodium sulfate (Na₂SO₄), azobisisobutyronitrile (AIBN), nitric acid (HNO₃), toluene, and methanol were purchased from Thomas Baker Chemicals, India. All the aforementioned compounds were of analytical reagent (AR) grade and were used without any additional purification.

In the present study, a prefilter resin was employed to remove organics from acidified urine samples, thereby avoiding conventional time-consuming acid digestion procedures using concentrated HNO₃ and H₂O₂ [36]. Triskem[®] Prefilter resin (particle size: 100–150 μ m) and Triskem[®] 10 mL reservoirs (PP) were used for prefilter column preparation.

Spot urine samples were collected from unexposed individuals in 100 mL plastic bottles. A U(nat.) solution was prepared by dissolving clean uranium metal (1.5 g) in 30 mL of 1:1 HNO₃ medium at 100–105 °C, which was further diluted to 100 mL in a standard flask using distilled water. The uranium concentration of this standard solution was 15,000 56 ppm (375.0 1.4 Bq g⁻¹) as determined using Hidex 300SL LSC. This stock solution was diluted to prepare various uranium standards of intermediate concentrations. A TARSONS ROTOSPIN apparatus was used to equilibrate solutions during adsorption/desorption experiments at 40






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REVIEW ARTICLE



Uranium standards in drinking water: An examination from scientific and socio-economic standpoints of India

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Abstract

The detection of uranium in drinking water has ignited concerns among the public, regulators, and policymakers, particularly as around 1% of the 55,554 water samples in India have shown uranium levels surpassing the 60 μ g/l guideline established by the Atomic Energy Regulatory Board (AERB) based on radiological toxicity. Further, the Bureau of Indian Standard (BIS), has given a limit of 30 μ g/l, which is derived from World Health Organization (WHO) guidelines. Besides the chemical and radiological aspects associated with uranium, factors such as technological constraints in water purification, waste management, environmental factors, and socio-economic conditions significantly influence these guideline values, which are often overlooked. This manuscript explores the variations in approaches for establishing guideline values and highlights the uncertainties arising from dependence on various variables such as intake and usage patterns, inter- and intra-species distinctions, and epidemiological data. A critical analysis indicates that adherence to global guidelines may result in some undesirable environmental issues. By considering factors such as population dynamics, socio-economic conditions, and geological influences, we suggest that limit of 60 μ g/l for uranium in drinking water is appropriate for India.

Keywords Uranium · Drinking water · Guideline values · Toxicity · Environment

Introduction

The Earth's ecosystem is an intricate and interconnected dynamic system that encompasses diverse components such as rocks, soil, water, plants, and animals. This intricate network of interactions plays a vital role in sustaining life on our planet. Uranium, a naturally occurring element, has been present on Earth since its formation 4.5 billion years ago. Natural uranium consists of three isotopes: ²³⁸U (99.28%), ²³⁵U (0.70%), and ²³⁴U (0.0054%), distributed in both biotic and abiotic components of the environment. Geochemical and environmental factors have led to the dispersion of

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uranium from its minerals into the lithosphere, hydrosphere, biosphere, and atmosphere, as illustrated in (Fig. 1). The average uranium concentration in the Earth's crust is approximately 2.8 ppm. In ground waters and seawaters, uranium concentrations range from ≤ 0.001 to 0.008 ppm and nearly 3 µg/L, respectively (Balaram et al. 2022). Drinking water is a crucial element of the human diet and is considered in dietary intake estimates.

Despite being a radioactive element, uranium is also recognized for its chemical toxicity. When consumed, uranium primarily impacts the kidneys, potentially leading to kidney damage at excessively high concentrations. Notably, uranium toxicity predominantly affects the renal tubules (Kurttio et al. 2006). To safeguard human health from the potential adverse effects of uranium intake through the drinking water pathway, national and international advisory organizations/ agencies, such as the International Commission on Radiological Protection (ICRP), the United States Environmental Protection Agency (USEPA), the World Health Organization (WHO), the Codex Alimentarius Commission (Codex), etc., establish guideline values or ensure their implementation through regulatory bodies. The frequent revisions in guideline values and discrepancies among different countries

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have heightened public concerns regarding the presence of uranium in drinking waters. It is important to note that the regulatory limits for uranium in drinking waters can vary between different countries due to several influencing factors. The driving force behind these inconsistencies include variations in the primary basis for formulating standards, encompassing the sensitivity of population groups, geological conditions, economic conditions, and more. In India, two different regulatory agencies, namely the Atomic Energy Regulatory Board (AERB) and the Bureau of Indian Standards (BIS), have stipulated distinct limits for uranium in drinking water. In the conventional approach based on dose limits, doses exceeding the limit are deemed intolerable, while doses below the limit are kept as low as reasonably achievable, a methodology differing from that employed in the case of exposure to hazardous chemicals. Generally, ensuring safe drinking water aims for a goal of zero risk to the public within technical and financial limitations.

The World Health Organization (WHO) releases manuals, handbooks, recommendations, and guidelines that address health-related concerns related to pollutants and are recognized as global advisories (WHO 2011). Since 1958, the organization has consistently issued specific guidelines for international drinking water standards, presenting limits for both chemical (in mg/l) and radiological (in Bq/l) pollutants. The critical consideration for uranium revolves around whether the existing guideline value is adequate to prevent chemical toxicity in the kidneys. This determination hinges on various factors, including the assumed threshold for chemical toxicity in the kidney, the appropriate selection of

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an uncertainty factor, and the relationship between uranium kidney burden and dose. In 1987, the Agency for Toxic Substances and Disease Registry (ATSDR) published toxicological profiles containing information on the toxicology and adverse health effects associated with uranium. The initial recognition of uranium as a chemical toxicant occurred in ATSDR (1999), with a revised version published in ATSDR (2013).

The scope of this paper is to compare the procedures adopted in deriving guideline values of uranium in drinking water. A glimpse of the nationwide survey of uranium in Indian drinking waters has also been presented. The paper also discusses the diversity in methodologies, uncertainties in the input parameters, absence of harmonization in country-specific guidelines, and various sources of information related to animal studies and human data. The counterproductive outcomes stemming from the adoption of WHO recommendations for uranium in drinking water, particularly concerning socio-economic considerations for India has also been emphasized.

Approaches for guideline values

The Compendium of Chemical Terminology Gold Book by the International Union of Pure and Applied Chemistry (IUPAC 2014) presents two definitions of 'dose.' In toxicology, 'dose' refers to the entire amount of a chemical delivered to, ingested by, or absorbed by an organism, organ, or tissue, measured in mass units (µg, mg, or g).



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ORIGINAL PAPER



Utilization of gamma irradiation for development of shelf-stable mint coriander sauce

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Abstract

The mint coriander sauce (MCS) prepared using fresh herbs is known to be heat-sensitive and highly perishable with a limited shelf life (less than 2 days). Therefore, in the current study, the aim was to develop a shelf-stable MCS utilizing gamma radiation without the use of thermal processing. The D_{10} values for yeast and mold (Y&M) and total viable counts (TVC) were observed to be 1.18 and 6.70 kGy, respectively. The gamma radiation at a dose of 25 kGy successfully achieved microbial sterility in MCS. No microbial growth was observed in irradiated samples during the entire storage period of 180 days. Significant (P < 0.05) increase in content of phenolic acids was observed during storage. After storage of 180 days, the amount of caffeic acid, vanillic acid and ferulic acid increased by 1.35, 5.71 and 2.14 fold, respectively. In comparison with fresh samples, the irradiated samples after storage showed a significant (P < 0.05) increase of 0.6 and 0.9 fold in total antioxidant activity and total phenolic content, respectively. Although, irradiation did not show significant effect on volatile aroma constituents, however, during storage a significant (P < 0.05) loss in aroma compounds was noted. During color analysis, a marginal loss in greenness and an increase in browning index (BI) were observed. MCS samples subjected to radiation treatment maintained acceptable sensory quality during the entire storage period of 180 days. These results suggested that radiation treatment can be a practical proposition for preparing a shelf-stable MCS with excellent sensory quality.

Keywords Aroma · Gamma radiation · Mint coriander sauce · Phenolic acids · Shelf-stable

Introduction

The Indian sauces (traditionally known as chutneys) are prepared using unique ingredients and spices with distinct flavors and have varied composition [1]. These are served in small quantities as accompaniments to the main dishes to enhance palatability. Mint coriander sauce (MCS) prepared using fresh mint and coriander leaves with additional seasonings that are ground together, provides a refreshing chili and tangy flavor [2]. It is widely consumed as a dip or a spread with several snack preparations. MCS is a good

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Food Technology Division, Bhabha Atomic Research Centre, Mumbai 400085, India source of functional nutrients such as vitamins, minerals and phytochemicals [3]. Mint has been consumed for years as a remedy for the treatment of fever, liver ailments, digestive disorders, and ulcerative colitis [4]. Coriander is used in traditional remedies for gastrointestinal maladies, respiratory ailments, loss of appetite, as an aphrodisiac, and an antibiotic [5, 6]. These herbs have diverse bioactive compounds including phenolic acids such as gallic, ferulic, caffeic, chlorogenic, syringic, vanillic, p-coumaric, rosmarinic and cinnamic acid along with flavonoids such as quercetin-3-rhamnoside, luteolin, coumarin, quercetin, rutin, apigenin and amentoflavone [7-9]. Owing to these nutritional benefits, MCS can be utilized as a functional food and has huge growth potential in the global market. However, freshly prepared MCS is only available at street/local shops in South Asian countries including India. The short shelf life and microbial safety concerns (due to the use of raw uncooked herbs) are the major roadblocks that need to be addressed. A previous study has demonstrated safety concerns in MCS and other street snacks available in the Indian market [10]. Fresh herbs, like mint and coriander leaves, are prone to

microbial contamination due to poor pre and post-harvest handling practices and storage conditions. High total viable count, yeast & mold count, Enterobacteriaceae and total coliforms were reported in fresh mint leaves [11]. In Northern India, Salmonella species was reported in 3% and 2.4% of the tested coriander and mint samples, respectively [12]. The preparation of MCS does not involve cooking, as heating in any form unfavorably affect the aroma and flavor of fresh herbs [2, 13]. In previous attempts, thermal processing along with the use of preservatives such as potassium metabisulfite (KMS) and sodium benzoate has been employed to increase the shelf life of MCS [2]. Thermal processing resulted in a loss of color and bioactive components such as phenolic acids in coriander puree [14]. Therefore, there is a need to apply alternative non-thermal processing methods for the shelf life extension of MCS. Microwave processing was recently reported for the shelf life extension of coriander paste, which was successful for a limited time of 15 days of storage [15]. High pressure processing (600 MPa) did not lead to complete microbial sterilization when applied for preservation of coriander puree.

Gamma irradiation is one of the non-thermal processing methods offering the advantage of ensuring microbial sterility without altering sensory and nutritional properties [16]. Radiation processing also did not affect several quality attributes such as appearance, flavor, texture, and nutritional properties of fresh cut fruits, vegetables, and green leafy vegetables [17, 18]. Irradiation was reported to reduce microbes, including pathogens, and thus could prevent food borne illnesses [19]. Radiation processing by gamma radiation has been established to eliminate food borne pathogens such as E. coli O157:H7, Salmonella spp. and Listeria innocua at doses up to 2 kGy in fresh mint and coriander samples [20, 21]. Gamma radiation at a low dose (2 kGy) was shown to improve visual quality by inhibiting browning of mint leaves, improving microbial quality and extending shelf life during storage [21]. Gamma radiation has demonstrated its utility in various applications of food preservation including the hygienization of food for shelf life extension by many international statutory bodies and organizations such as Food and Agriculture Organization (FAO), World Health Organization (WHO), Codex Alimentarius Commission (CAC), International Atomic Energy Agency (IAEA) and Food Safety and Standards Authority of India (FSSAI). These agencies have accepted the wholesomeness, safety and commercial benefits of food irradiation [22]. A Joint Study Group (JSGHDI, 1999) of FAO/IAEA/WHO found that food irradiated at higher doses in the range of 25-45 kGy remains safe for consumption, which was included in the revision of the Codex General Standard for Irradiated Foods [23, 24].

The objective of the current study was to apply gamma radiation to mitigate the problems associated with the preservation of MCS, such as the heat-labile nature of fresh

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herbs, proneness to microbial contamination, and a very short shelf life. This study aimed to develop a microbiologically safe and shelf-stable MCS having acceptable organoleptic properties. The study also demonstrated the effect of irradiation on the antioxidant activity, phenolic acids, aroma, and color characteristics of MCS during its storage at ambient temperature.

Materials and methods

Chemicals and reagents

Phenolic and benzoic acid standards such as benzoic acid, m-methylbenzoic acid, o-hydroxybenzoic acid, m-hydroxybenzoic acid, p-hydroxybenzoic acid, p-hydroxyphenylacetic acid, 2,3-dihydroxybenzoic acid, 2,4-dihydroxybenzoic acid, vanillic acid, p-coumaric acid, ferulic acid, caffeic acid, catechin, quercetin, kaempherol, kojic acid, rosmarinic acid, chlorogenic acid, dihydrocaffeic acid, phloretic acid, 4-coumaric acid, naringin, gallic acid, thymol and trans-2, cis-6-nonadien-1-ol used in this study were obtained from Sigma Chemicals (St Louis, MO, USA). BSTFA (N,Obis(trimethylsilyl)trifluoro-acetamide, and trichloro acetic acid (TCA) were procured from Sigma Aldrich (St. Louis, MO, USA). Trolox was procured from Aldrich Chem Co. (Milwaukee, WI, USA). Plate count agar and potato dextrose agar were purchased from HiMedia Laboratories (Mumbai, Maharashtra, India). DPPH (2,2-diphenyl-1-picrylhydrazyl) radical and ferric chloride were procured from HiMedia Laboratories, Mumbai, India. Potassium ferricyanide, sodium carbonate, sodium dihydrogen-orthophosphate and disodium hydrogen orthophosphate were procured from Thomas Baker Private Limited, Mumbai, India. All the chemicals utilized in the study were of high purity (99.9%) analytical grade.

Sample preparation and packaging

All the ingredients were procured from the local market of Mumbai, India. Mint leaves, coriander leaves, fresh ginger and green chilies were washed thoroughly in potable water to remove all adhering dust. The ingredients in the following composition were used for MCS preparation. Mint or spearmint leaves (*Mentha spicata*, 38.75% w/w), coriander (*Coriandrum sativum*, 13.37% w/w) leaves, fresh ginger (*Zingiber officinale*, 3.10% w/w) rhizome, cumin (*Cuminum cyminum*) seed powder (0.7% w/w), food grade citric acid (0.7% w/w), black salt (3.4%), groundnut (*Arachis hypogaea*) seed (Dehusked and powdered, 3.8% w/w), green chili (*Capsicum annuum*) (2.7% w/w). The prepared MCS of 1 kg contained fresh mint leaves (400 g), fresh coriander leaves (200 g), fresh peeled ginger (32 g), cumin





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FOOD SAFETY AND QUALITY - SHORT COMMUNICATION



Virulent and multidrug-resistant *Aeromonas* in aquatic environments of Kerala, India: potential risks to fish and humans

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Abstract

Aeromonas inhabit diverse aquatic habitats and are recognized as both opportunistic and primary pathogens of fish and humans. This study delineates the biochemical and *gyrB* sequence-based molecular identification of 14 *Aeromonas* strains isolated from aquatic environments in Kerala, India, identifying them as *A. dhakensis* (50%), *A. hydrophila* (28.6%), and *A. jandaei* (21.4%). These strains exhibit a high prevalence of virulence genes (*act, flaA, ser, gcat, lip, and ela*) implicated in pathogenesis in both fish and humans. These findings underline the emergence of *A. dhakensis*, often misidentified as *A. hydrophila*, as a potential pathogen, highlighting the necessity for comprehensive identification methods. Significantly, all strains demonstrated beta-hemolysis and moderate to strong biofilm formation, enhancing their infectivity potential. Moreover, all isolates exhibited multidrug resistance, with a multiple antimicrobial resistance (MAR) index ranging from 0.39 to 0.56, and a significant presence of class 1 (500–1100 bp) and class 2 (250–700 bp) integrons, indicating their potential risk to both fish and human populations. Our results underscore the role of aquatic environment as a repository for virulent and multidrug-resistant *Aeromonas* spp., emphasizing the imperative for prudent antimicrobial usage and regular monitoring of antimicrobial resistance (AMR) in these environments.

Keywords Aeromoniasis · Water bodies · Virulent determinants · Antibiotic resistance · Biofilm · Integrons

Introduction

The genus *Aeromonas*, comprising 36 gram-negative aquatic species, represents a diverse group with notable implications for aquatic ecosystems and public health. These species are significant fish pathogens, causing diseases like haemorrhagic septicemia and furunculosis, leading to large-scale outbreaks in aquaculture farms [1]. Additionally, they are recognized as emerging opportunistic pathogens, transitioning from environmental sources to humans and

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causing various intestinal and extra-intestinal infections [2]. *Aeromonas* plays a critical role in the One Health concept, being associated with economic losses in aquaculture, the spread of antibiotic resistance genes, and infections related to leech therapy in humans [3].

Aeromonas species are ubiquitous, found in aquatic environments, soil, and food, posing significant public health challenges [4]. Among them, A. hydrophila, A. dhakensis, A. caviae, and A. veronii (biovar veronii and sobria) are responsible for over 95% of human intestinal infections caused by Aeromonas [5]. However, A. dhakensis is often misidentified as A. hydrophila, leading to an underestimation of its cases [6, 7]. Research shows that A. dhakensis is predominant in tropical and subtropical regions and exhibits greater virulence than A. veronii, A. caviae, and A. hydrophila [5, 8]. Recently, virulent and antibiotic-resistant A. dhakensis strains have been increasingly reported from various environmental sources, causing numerous infections in fish and humans [6, 9]. Species-level identification of Aeromonas is complex and challenging due to the lack of standardized phenotypic tests, discrepancies between phenotypic and genotypic methods, genetic heterogeneity, and the increasing number of new species [4]. Recent studies have utilized housekeeping genes (*gyrB*, *rpoD*, and *rpoB*) as molecular markers for precise species-level identification and to establish phylogenetic relationships [2, 6, 10].

The virulence potential of *Aeromonas* is complex, dependent on host susceptibility, and not fully understood [3]. Various virulence factors, including cell-associated structural components, extracellular products, toxins, and biofilm formation, enable *Aeromonas* cells to colonize and destroy host cells [11]. In recent years, antibiotic resistance among *Aeromonas* strains has become a significant public health concern, particularly in developing countries where the use of antibiotics is often unregulated and uncontrolled [5]. Pathogens affecting humans, animals, and the environment face the dual challenges of increased virulence determinants and growing antimicrobial resistance. Therefore, this study aimed to identify *Aeromonas* strains, isolated from aquatic environments of Kerala, India and examine their pathogenicity, biofilm formation, and resistance potential.

Materials and methods

Aeromonas cultures and biochemical identification

Fourteen presumptive *Aeromonas* strains, previously isolated from both healthy and moribund finfish exhibiting symptoms such as exophthalmia, abdominal distention, haemorrhagic spots, necrotic fin rot, and ragged fins, were collected from aquaculture farms and river water samples in Ernakulam and Thrissur, Kerala, India (Suppl Table 1). The affected animals, including species such as Catla (*Catla catla*), Rohu (*Labeo rohita*), and Gourami (family *Osphronemidae*), were brought to the laboratory by farmers. These farms utilized traditional intensive freshwater aquaculture ponds, either for food fish production or for rearing ornamental fish. The isolates were identified to the species level using comprehensive biochemical tests [12–14]. The strains' hemolytic activity was assessed on blood agar plates (HiMedia, India) incubated at 30 °C for 18 h [15].

Molecular Identification and phylogenetic analysis

All biochemically identified *Aeromonas* species were confirmed through gyrB (~1100 bp) gene sequencing, following the primers and procedures of Soler et al. [16]. The amplified products were purified, sequenced, and compared against GenBank database entries using the BLASTN program (www.ncbi.nih.gov/BLAST/). These sequences were then uploaded to GenBank (Accession numbers: OQ743456-64, OQ789562-65, and OQ920270). The gyrB gene sequences were aligned, and sequence similarities were estimated for a

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920 base segment (positions 852,606–853,528, according to *E. coli* ATCC 25922 numbering, NZ_CP009072). A phylogenetic tree was constructed using the UPGMA method and Kimura two-parameter model in MEGA 11 [17].

Virulence genes

Virulence genes, including aerolysin (*aer*), cytotoxic enterotoxin (*act*), hemolysin (*hly*), lipase (*lip*), elastase (*ahyB*), glycerophospholipid cholesterol acyltransferase (*gcat*), cytotonic enterotoxins (*ast*, *alt*), serine protease (*ser*), polar flagella (*fla*), and lateral flagella (*lafA*), were amplified from chromosomal DNA using previously described primers and PCR conditions [18, 19].

Biofilm formation and analysis

Biofilm formation was evaluated by culturing various *Aeromonas* strains in TSB within 96-well flat-bottomed microtiter plates (Falcon, BD Biosciences, NJ, USA) and quantified using a modified crystal violet (CV) assay [19]. The biofilm-forming ability was classified using the specific biofilm formation (SBF) index, calculated for each isolate by normalizing biofilm accumulation (OD_{570nm}) relative to cell growth (OD_{600nm}) with the formula SBF = (B - NC)/G, where B represents the OD_{570nm} of the attached and stained bacteria, NC is the OD_{570nm} of the control wells containing bacteria-free medium, and G is the OD_{600nm} of cell growth in the medium [20]. The extent of biofilm formation was categorized into three groups: no biofilm (SBF < 0.1), weak ($0.1 \leq SBF \leq 0.5$), moderate ($0.5 \leq SBF \leq 1$), or strong (SBF > 1) [21].

Antimicrobial susceptibility and integron analysis

The antimicrobial resistance patterns of these strains were determined against 18 commonly used antibiotics from 11 classes, using the disc diffusion method on Mueller-Hinton Agar, as specified by the Clinical and Laboratory Standards Institute (CLSI) [22]. Resistance profiles were assigned based on zone diameters according to CLSI breakpoints [23]. Multi-drug resistance and multiple antibiotic resistance (MAR) indices were calculated following Magiorakos et al. [24] and Krumperman [25], respectively. The MAR index for a single isolate is calculated as the ratio of *a* to *b*, where *a* is the number of antibiotics the isolate is resistant to, and *b* is the total number of antibiotics it has been exposed to. The presence of class 1 and class 2 integrons was assessed under conditions described by Nagar et al. [19].



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