BARC NEWSLETTER

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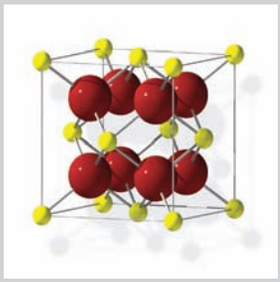

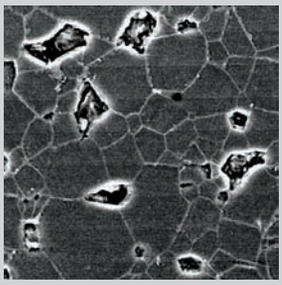

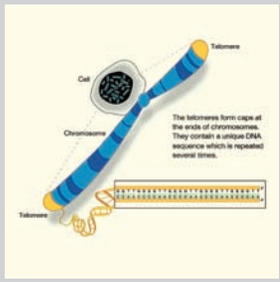

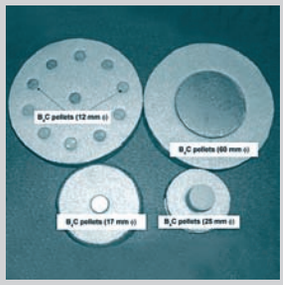

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From the Editor's Desk

We would like to thank you, for all your emails and words of appreciation which we received, for the new look of the BARC Newsletter. We have also received several suggestions for further improving the quality of the newsletter. We assure you that these would be discussed in our regular meetings of the Editorial Committee and suitable action would be taken.

In this issue, we are also including articles of general interest from Senior Scientists of the Centre. Dr. V. Venugopal, Director, Radiochemistry & Isotope Group has contributed the article "Innovations and Recent Trends in Radiochemistry Research" for this issue.

We would like to inform you, that as suggested by Director, BARC, we are also accepting research articles, technology development and related articles, for inclusion in the newsletter. You may send your articles directly to the Editorial Board, after approval from respective Group Directors/ Associate Directors and Heads of Divisions.

Hope that you all continue to give your support to your publication.

K. Bhanumurthy
On behalf of the Editorial Committee

Innovations and Recent Trends in Radiochemistry Research

V. Venugopal,
Radiochemistry & Isotope Group

Introduction

The founding of Atomic Energy Establishment at Trombay (AEET) witnessed a whole gamut of research activities in basic as well as applied research in nuclear science and technology in the country. With the commissioning of India's first nuclear research reactor, APSARA, the nuclear and radiochemistry programme received a fillip. A large number of diverse research activities related to nuclear chemistry, nuclear fission, spectroscopic investigations, development of radioanalytical techniques and other analytical methodologies for chemical quality control (CQC) of nuclear fuel materials, process chemistry of actinides, spectroscopic and X-ray studies, mass spectrometry, thermodynamic investigations, recovery of actinides from analytical waste solutions and post irradiation studies on irradiated nuclear fuel were undertaken. This diverse research field has made us scientifically very confident in making collaborations with other research institutes in different countries. In the years to come, BARC will be playing major role in Nuclear Material Safeguards related activities, when more facilities coming under IAEA safeguards.

Role of Chemistry in fuel development Program

The challenges in this program will be: (i) augmenting the existing analytical methodology base for CQC of nuclear materials, (ii) understanding thermal and thermodynamic behavior of various fission product systems and their interactions with fuel and clad, (iii) developing new analytical techniques for understanding the ageing management of nuclear reactor components (iv) carrying out post irradiation examination of new fuels for burn-up as well as fission gas release (v) augmenting the database for nuclear properties of actinides and (vi) development of special materials for strategic program of the Department.

Conventional powder-pellet fuel fabrication processes are not well suited for remote handling of Pu and ^{233}U based fuel materials inside the shielded facilities as they involve a large number of mechanical steps. Sol-Gel process is amenable for such fuel preparation. Studies have to be carried out in a shielded facility on the preparation of $(^{233}U,Th)O_2$ and $(ThO_2\text{-}PuO_2)$ microspheres using the sol-gel process. Test fuel pins have to be fabricated for the irradiation studies to understand irradiation behavior. This program involves various experts such as, radiochemists, metallurgists, reactor physicists and fuel designers.

Future program includes the development of coated particle fuels for high temperature gas cooled reactors, SGMP process for the Th-^{233}U based fuels and irradiation behavior studies of the vibro-compacted fuel pins etc.

Analytical Methodologies for Chemical Quality Control of Nuclear Materials

For optimum performance of nuclear fuel inside a nuclear reactor, the nuclear fuel material should meet stringent requirements in terms of its chemical composition, purity, stoichiometry, and many other physical and chemical properties.

Presence of a number of elements as impurities in trace amounts is detrimental to the performance of the fuel. Boron, cadmium or rare earth elements are of larger interest and their quantification in sub–ppm level is very critical. Chemical quality control of these elements in nuclear materials is determined employing a number of techniques and methodologies.

Several methods with new redox reagents have been standardized for the determination of uranium with improved precision and accuracy. Many of the methods developed are confined to the applications in safeguards laboratory. Newer methods with minimum sample size have to developed with new instrumental methods. Multielemental analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) and GD-MS will have to be developed for this purpose. The advantages of this method include the reduced time of analysis, reasonable precision and accuracy and large sample throughput.

Gaseous impurities in nuclear fuels such as H, C, N, O and S are routinely determined employing commercially available instruments. The techniques are based on thermal conductivity (CO_2), IR detection (SO_2), Inert gas fusion and Kjeldahl distillation followed by spectrophotometry for nitrogen. Halogens such as fluorine and chlorine are separated from the sample matrix by pyrohydrolysis and determined either by ion selective electrodes, spectrophotometry or by ion chromatography. Ion chromatographic technique has also been developed recently to determine nitrogen in uranium and uranium alloy samples. The advantages of this method are (i) elimination of Kjeldahl distillation (ii) reduced time of analysis (iii) requirement of small sample size (10 mg) and (iv) increased sensitivity.

A new method based on the vacuum combustion extraction-quadrupole mass spectrometry has been developed for the determination of sulfur in nuclear fuel materials. It involves the combustion of the sample in presence of oxygen supplier like UO_3 in static vacuum conditions, extraction of the gases released into a known volume and determine the the composition by on-line quadrupole mass spectrometer.

An XRF method was standardised for the determination of Th in (total U+Th) sintered UO_2-ThO_2, with UO_2 varying from 1-3% in powder samples. Another method based on the same principle was developed for the determination of Ga and U present in the mixture of their solid oxides.

Chelation ion Chromatography technique was developed for the separation and determination of lanthanides in different nuclear materials.

Studies on sulphur speciation employing Ion chromatography were carried out with different mobile phase concentrations to reduce the retention time of thiosulphate without compromising the resolution between sulphite and sulphate peaks. Experiments were carried out with industrial effluents and water samples received from different locations. The sulphide content in these samples was determined by iodimetric titration for comparing with ion chromatographic values.

Ageing management of coolant channels in PHWRs and Post Irradiation Studies

The life of zircaloy coolant channel used in Pressurised Heavy Water Reactors depends mainly on the extent of hydride formation. Since the solubility of hydrogen in zirconium is very much limited, slight excess of hydrogen leads to the precipitation of zirconium hydride and is highly brittle. A hot vacuum-quadrupole mass spectrometry (HVE-QMS) technique has been developed for the determination of hydrogen/ deuterium in samples received from zircaloy coolant channels. The entire system has been conceived, designed and fabricated indigenously at BARC.

Procedures were established for the analysis of fission gases Kr and Xe from test fuel pins of MOX fuel as a part of post irradiation examination of irradiated fuels employing quadrupole mass spectrometry (QMS). The isotopic ratios of $^{131}Xe/^{134}Xe$ and $^{132}Xe/^{134}Xe$; $^{83}Kr/^{86}Kr$ and $^{84}Kr/^{86}Kr$ were very near to those from Pu-239 fissions indicating that majority of fissions are from Pu-239.

Thermal ionization mass spectrometry has been employed to determine burn up of nuclear fuels. Triple spike isotope dilution mass spectrometry has been employed for this purpose.

Mass spectrometry and Alpha Spectrometry

Isotopic mass of an element determines its nuclear properties including fission and absorption cross sections. Measurement of isotopic composition of materials used in nuclear technology is therefore very important. Considerable effort and time has been spent in developing analytical methodologies for the determination of isotopic composition and concentration of different elements from Li to Cm.

Nuclear fission is one of the fundamental characteristic features in nuclear chemistry. Each fissioning nuclide breaks into two fission products (one with mass less than 100 and another mass greater than 100) and a few neutrons accompanying by large release of energy. Comprehensive data on the fission yields of stable isotopes in neutron induced fission of ^{233}U, ^{235}U, ^{239}Pu and ^{24l}Pu were obtained using mass spectrometric studies.

In a reprocessing plant it is necessary to carry out precise measurements of U and Pu content in the dissolver solution for input accountability. Special tracer techniques MAGTRAP and LEADTRAP were developed for measuring not only the volume of solution in the accountability tank but also the amount of plutonium .

Alternate spikes ($^{239}Pu/^{240}Pu$) in lieu of conventionally used and difficult to procure ^{242}Pu for Pu determination by TIMS have been developed.

^{238}Pu spike has also been identified as a suitable spike for Pu determination by Isotope Dilution Alpha Spectrometry (IDAS). Necessary methodology for correcting the degradation of alpha spectrum to measure accurate alpha activity ratios needed for Pu determination was also developed.

New analytical methodologies were developed for carrying out precise and accurate measurements on isotopic ratios of lighter elements such as Li, B, Mg etc.

Precise and accurate measurements on half-lives of a number of transactinide isotopes (^{232}U, ^{233}U, ^{238}Pu, ^{241}Pu, ^{242}Pu, ^{241}Am, ^{243}Am, ^{242}Cm, ^{244}Cm) have been carried out employing TIMS and alpha spectrometry.

The expertise achieved in the field of mass spectrometry was demonstrated by the successful participation in three international experiments (IDA-72, PAFEX- I and PAFEX-II) organised by the international agencies to evaluate precision and accuracy achievable on measurements of U and Pu.

High Temperature Thermodynamics

Solid Oxide electrolyte galvanic cells, Knudsen effusion mass loss and Knudsen effusion cell mass-spectrometric methods were used to determine vaporization behavior of UC, (U,Ce)C, UN, stainless steel, Pd, Rh, Tellurides of U and Th and molybdates of alkali metals. The noteworthy feature of all the investigations was that all thermodynamic properties were determined by the same laboratory using a variety of techniques.

For the FBTR at Kalpakkam, a fuel, which could provide high fissile content without the use of enriched uranium, was required. $(U_{0.30}Pu_{0.70})C$ with

5-15% sesquicarbide content and very small amounts (< 1000 ppm) of O_2 and N_2 was required. However, it was observed during the fabrication that it was not possible to achieve low N+O content with out significant loss of Pu by volatilization. With proper optimization of parameters, a fuel having 5000-6000 ppm of oxygen and 500 ppm of nitrogen could be obtained. The compatibility of the fuel with S.S cladding could not easily be established on the basis of available literature. Investigations carried out could establish the chemical compatibility of the fuel fabricated with SS cladding. It is heartening to note that this has borne out by actual experiment on the FBTR fuel, which has reached a burn up of 140,000 MWD/T.

For the second core of FBTR, there was a proposal at one time to use mixed nitride fuel. Theoretical calculations established that good chemical compatibility could only be achieved if the fuel has very low carbon content and a separate mixed oxide phase.

(U, Th)O_2 is a nuclear fuel proposed to be used in the advanced heavy water reactors. Hence, it is necessary to investigate the thermophysical properties of this fuel in the reactor operating conditions. In this context, the C_p values of this alloy were determined employing DSC with a predefined heating programme. The C_p values were determined for the mixed oxide containing 0%, 2%, 4%, 6%, 10% and 20% uranium. The experimental values were similar to those of thorium oxide (ThO_2).

Thermochemistry of interoxide compounds in the system M- Te-O where M is a fission product is of considerable interest to understand the internal chemistry of the oxide fuel pins in an operating nuclear reactor.

X-ray and Solid State Chemistry

X-ray, thermal, IR and NMR techniques have been employed to study the structural aspects of uranium and plutonium compounds to understand the nature of structure-property relation. The single crystal X-ray structure of the complex $[UO_2(TTA)_2.H_2O]$ crown shows that two of the $[UO_2(TTA)_2.H_2O]$ molecules are bridged by the crown ether ligand to give a dinuclear complex $[UO_2(TTA)_2.H_2O]_2$(Crown). Two such dinuclear complexes are stabilized by the intermolecular hydrogen bonding to give a stable tetra nuclear cluster.

Thermogravimetry and X-ray powder diffraction procedures have been used to study the solid solubility of Pu^{3+} and Pu^{4+} oxides in the stabilized zirconia, a fluorite matrix, in air.

The crystal structure of $Pu_2Zr_2O_7$ was derived from the analysis of X-ray powder diffraction data by Rietveld analysis. The systematic absence in X-ray reflections required by the pyrochlore structure [Fd3m] were observed in the indexed pattern with cubic cell parameter of a= 10.5719 (1) Å and Z =8. In the structure, each Zr cation has 6 oxygen anions in octahedral coordination.

Actinide Chemistry

The basic research programme on actinide chemistry included investigations on the interconversion of their oxidation states with a view to arriving at suitable conditions for stabilizing each of the oxidation states, studies on the complexing abilities of actinides with different inorganic and organic anions, studies on the solvent extraction behaviour of actinide ions into different types of solvent-diluents combinations and from different aqueous environments and studies related to both cation and anion exchange behavior of actinides etc. The understanding of their chemistry forms the backbone in developing methods for their estimation as well as their recovery and purification from different complex matrices.

Detailed investigations were carried out for the recovery of neptunium as a byproduct of plutonium-

uranium extraction (Purex) process. Large data generated in our laboratory on neptunium behavior in Purex Process has found a place in the standard textbook on nuclear chemical engineering by Benedict and Pigford. Extensive studies on the complexation behavior of neptunium carried out in our laboratory resulted in publishing a review article on the coordination complexes of neptunium in the journal "Coordination Chemistry Reviews" in 1978, which is a unique source material on neptunium complexes even to this day.

Studies on irradiation of Neptunium-237 targets and their processing for the recovery of ^{238}Pu enabled in establishing methods for the making of ^{238}Pu sources, which has many applications as an isotopic power generator.

Large scale plutonium recycling operation was carried out for meeting the Pu required for FBTR fuel fabrications. A novel method has been developed to recover gram quantities of americium, which has many applications in gamma radiography, smoke detectors etc from the waste solution. This americium could be used in measuring the uranium concentration profile in reprocessing plant streams with on-line detection.

An anion exchange studies on plutonium recovery with a large number of gel type and macroporous resins conducted in our laboratory has widened the scope of plutonium recovery from different sources yielding a pure and concentrated plutonium product.

Stability constants of the fluoride complexes of lanthanides were determined by ion selective potentiometry and the data are comparable with the estimated values obtained by interpolation from the general trend of stability constants of the lanthanide fluorides in aqueous solution. Correlation of the stability constants with their fundamental properties like ionic charge, coordination number, ionic radius and electronic configuration was studied.

Reliable thermodynamic data are of prime importance to predict radionuclide speciation in biological as well as natural environments.

Conclusion

A number of dedicated Radiochemists and Radioanalytical chemists are involved in this task. The expertise generated has provided enough confidence to take on fresh challenges to meet the future requirements of the Department. The Programme has a vital role to play to address many of the issues related to chemical and physico-chemical aspects of thorium based fuel technology thus fully utilizing our country's vast resources of thorium to satiate the ever increasing energy demands to realize a self sufficient and prosperous India.

RESEARCH ARTICLE

Pyrochlores: Potential multifunctional materials

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Chemistry Division

Abstract

Pyrochlores are important class of materials from the point of view of diverse technological applications like in luminescence, ionic conductivity, nuclear waste immobilization etc. It has been found that $Gd_2Zr_2O_7$ is the most suitable pyrochlore for nuclear waste immobilization because it is extremely stable under radiation environment. An optimum size difference between Gd^{3+} and Zr^{4+} facilitates antisite formation in $Gd_2Zr_2O_7$, which renders exceptionally high radiation stability to it. Immobilization of Nd^{3+} and Ce^{3+}, which are surrogate materials of Am^{3+} and Pu^{3+}, respectively, in $Gd_2Zr_2O_7$ lattice has been discussed in the article. Advanced Heavy Water Reactor (AHWR) will generate Al, Th, F in addition to other nuclear wastes. Immobilization of Th and Al in $Gd_2Zr_2O_7$ is also described in this article.

Introduction

Among the ternary metallic oxides, compounds of the general formula, $A_2B_2O_7$ (A and B are metals), represent a family of phases isostructural to the mineral pyrochlore, (NaCa)(NbTa)O_6F/(OH)[1]. The space group of the ideal pyrochlore structure is $Fd\bar{3}m$ and there are eight molecules per unit cell (Z=8). In $A_2B_2O_7$ pyrochlores, A is usually a trivalent rare earth ion, but can also be a mono, divalent cation and B may be 3d, 4d or 5d transition element having an appropriate oxidation state required for charge balance to give rise to the composition $A_2B_2O_7$ [2]. The pyrochlore crystal structure also tolerates vacancies at the A and O sites to a certain extent with the result that cation and anion migration within the solid is feasible. Recently, it has been shown by our group that anion rich pyrochlores like $Ce_2Zr_2O_8$ are also possible [3]. The pyrochlore structure is closely related to the fluorite structure AX_2, except that there are two cation sites and one-eighth of the anions are absent as shown in the Fig. 1[4]. For the ordered pyrochlore, $A_2B_2O_7$, the phase stability of the superstructure is basically determined by the A and B site cation radius ratio. It is worth noting here that compounds with similar cationic radii are more likely to form as disordered fluorites than ordered pyrochlores, for instance, $Er_2Zr_2O_7$ having $r_A/r_B \sim 1.39$ crystallizes as a disordered fluorite structure whereas $Er_2Ti_2O_7$ with $r_A/r_B \sim 1.66$ crystallizes as a ordered pyrochlore structure.

Since more number of (3+, 4+) ions are possible, therefore, large number of pyrochlores having (3+, 4+) cations are reported in literature compared to pyrochlores having (2+, 5+) cations. Recently, (1+, 6+) pyrochlores like KOs_2O_6 are reported in the literature [5]. In general, pyrochlores exhibit a wide variety of interesting physical properties because a diverse range of constituent ions can be chosen to obtain the desired properties. The electrical properties of the pyrochlores vary from highly insulating through semiconducting

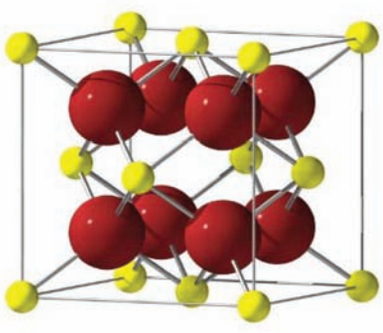

Fig. 1a: Unit cell of fluorite (*Fmm*), yellow atoms represent A^{4+} cations and the red O^{2-}.

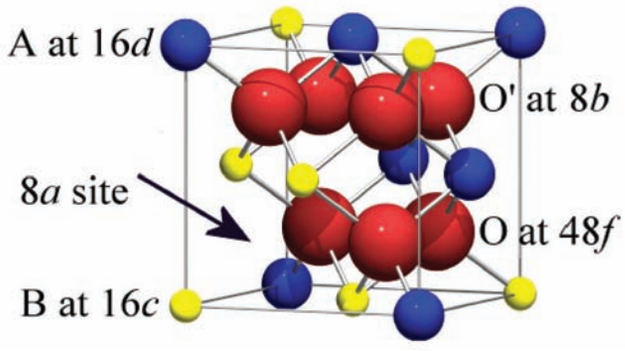

Fig. 1b: Unit cell of pyrochlore (*Fdm*), Blue spheres represent A^{3+} cations, yellow B^{4+} and red O^{2-}.

to metallic behaviour. It has been reported that few rare-earth molybdate and ruthenate pyrochlores show semiconductor to metal transition. Pyrochlores like $Cd_2Re_2O_7$ exhibit superconductivity at lower temperature [6]. The system where the A and B ions are in the maximum possible oxidation states, exhibits excellent dielectric properties. The electrical properties of the pyrochlores having Bi ion, like $Bi_2Ru_2O_7$, are interesting, because the lone pair of electron on Bi contributes to the electrical property of the compound. Many of the pyrochlores like $La_2Zr_2O_7$ act as thermal barrier coating whereas some other systems like $Y_2Sn_2O_7$ act as excellent host matrices for photoluminescence. Oxide ion conduction is also possible in pyrochlores if the compositions are tuned properly [7, 8]. High pressure response of pyrochlore is also worth mentioning. Mostly researchers have found that pyrochlores transform to fluorite phase or some other phases at higher pressure. Recently, it has been found that they can transform to starting reactants too [9]. In addition, pyrochlores are excellent host matrices for nuclear waste immobilization because it can dissolve various lanthanides, actinides and other elements which are generated from nuclear reactors. It has been found that stability of the pyrochlores under radiation environment increases with decrease in radius ratio. This can be explained on the basis of antisite defect formation. The energy deposited due to irradiation can be dissipated by swapping the A and B cations and the structure transforms to defect fluorite form. However, in case of pyrochlores having large difference in ionic radii of A and B cations cannot exchange their sites. Therefore, these pyrochlores amorphize under high irradiation dose to dissipate the extra energy [10]. Hence, $Gd_2Zr_2O_7$ was chosen as a suitable host material for fixation of some of the nuclear waste products.

Sample Preparation

Few samples were prepared by standard solid state route. The constituent oxides were preheated at 900°C overnight to remove moisture and other volatile impurities. Stoichiometric amounts of the reactants were weighed to get the various compositions. The homogenized mixtures were then subjected to a three-step heating protocol with intermittent grindings. The XRD patterns of samples were recorded on a Philips X'pert Pro XRD unit in static air condition with monochromatized Cu-Ka radiation. Since the starting materials are high melting point solids, therefore to complete the reaction high temperature is required. Raman spectra were recorded using a 632.8nm line from a He–Ne

laser and the scattered light was analyzed using a single-stage spectrograph. It can be mentioned here that few samples were prepared by gel combustion method also. In this method the nitrates of the constituent elements and glycine were mixed in desired ratio and then heated till 100°C, which ultimately gives rise to transparent gel. The gel undergoes combustion at higher temperature. The formed powder is then calcined to remove carbon and unreacted organic materials.

Result and Discussion

1. Solubility of Nd^{3+} in $Gd_2Zr_2O_7$ and $Y_2Zr_2O_7$ pyrochlores

A series of compositions having nominal compositions $Nd_{2-y}Gd_yZr_2O_7$ ($0.0 \leq y \leq 2.0$) was prepared by standard solid state route and analyzed by XRD and Raman spectroscopy. It has been found that with increase in Gd^{3+} content in the series the lattice parameter decreases, which is attributed to the relative ionic size of Nd^{3+} and Gd^{3+}. This also establishes the monophasic nature of all the products in this series. Structural analysis has been done by using Rietveld refinement programme Fullprof-2005. The most important observation of the present investigation is that, with increase in Gd content in the series, the system undergoes change from ordered pyrochlore to disordered pyrochlore. Originally, in pyrochlore structure all the oxygens are not equivalent. The oxygen at *48f* position is surrounded by two A and two B cations and *8a* position has four B neighboring atoms, and *8b* position is surrounded by four A cations. The coordinate of 48f oxygen is (x, 0.125, 0.125). The x-parameter of *48f* oxygen is indicator of the degree of disorder in the system. The x parameters of 48f oxygen in perfect pyrochlore and highly disordered pyrochlore are 0.3125 and 0.375, respectively. Initially the value of the x parameter increases linearly on incorporation of Gd in $Nd_2Zr_2O_7$, which indicates an increase in disorder in the system. However, there is a distinct change in the slope at $Nd_{0.2}Gd_{1.8}Zr_2O_7$ composition, which suggests that the degree of disorder increases abruptly from that composition onward.

XRD studies are more sensitive to disorder in the cationic sublattice compared to anionic sublattice, whereas, Raman spectroscopy is primarily sensitive to oxygen-cation vibrations and is an excellent probe for local disorder. The Raman spectroscopic investigation has been found to provide unequivocal information to distinguish between a pyrochlore, disordered pyrochlore and a defect fluorite material, because these phases differ essentially with respect to local disorder around the A or B cations. Therefore, all the compounds were further investigated by Raman spectroscopy over the frequency range 200–800 cm^{-1} to investigate the exact composition at and beyond which a distinct pyrochlore lattice undergoes a transformation to disordered pyrochlore.

The six Raman active modes of pyrochlore are distributed as $A_{1g} + E_g + 4F_{2g}$. The observed Raman spectrum of the pyrochlore structure of $Nd_2Zr_2O_7$ and the different mode frequencies, agree quite well with the values reported in literature. The width of different modes also increases with increasing Gd concentration (not shown). As mentioned earlier, a gradual increase in the 48f oxygen x-parameter was observed till $y \approx 1.8$ beyond which there is sudden change in the slope even though the radius ratio r_A/r_B changes linearly. The change in slope observed in the frequency vs Gd content curve and the sudden increase in width in the Raman modes for $y \geq 1.8$ can be related to this discontinuous change in the 48f oxygen x-parameter. As the size difference between "average" A cation and B cation decreases with increase of Gd content, the system has a tendency to transform from perfect pyrochlore to defect pyrochlore [11, 12].

In another attempt, Nd was incorporated in $Y_2Zr_2O_7$, which was expected to be a stable material under radiation environment. The samples were prepared

following the same protocol. Structural analysis on $Nd_{2-y}Y_yZr_2O_7$ ($0.0 \le y \le 2.0$) series has also been done by using Rietveld refinement programme Fullprof-2008. It has been found that with increase in Y^{3+} content in the solid solution, the structure transforms from ideal pyrochlore to defect fluorite through a biphasic region. The decrease in lattice parameter with increase in Y^{3+} content in the series, is due to lower ionic radius of Y^{3+} (0.93Å) than that of Nd^{3+} (1.02Å) in eight fold co-ordination. It is noticeable that the lattice parameters remain unchanged for the two compositions in the region from $Nd_{0.8}Y_{1.2}Zr_2O_7$ to $Nd_{0.4}Y_{1.6}Zr_2O_7$, which indicates that these two compositions are a biphasic mixture of pyrochlore and defect fluorite. During refinement it has been assumed that in $Nd_2Zr_2O_7$, the *8a* site remains totally vacant. With increase in Y^{3+} content in the series, the *8a* site also gets populated with concomitant depopulation at *48f* site. The occupancy at *8b* site remains almost constant. The involvement of *8a* oxygen and *48f* oxygen in disordering also has been verified by Raman spectroscopy. Another end member i.e. $Y_2Zr_2O_7$ crystallizes as defect fluorite structure.

In order to further substantiate the present work, Raman spectroscopic investigation has been performed on all the samples. All the six modes of pyrochlores have been found in the Raman spectra. The qualitative nature of the Raman bands remain similar till $Nd_{1.2}Y_{0.8}Zr_2O_7$ (y=0.8) which suggest that these compositions are pyrochlore only. Beyond this, the Raman spectra show huge broadening for the biphasic samples y = 1.2 and 1.6. The Raman spectra of another end member i.e. $Y_2Zr_2O_7$, which has been found as disordered fluorite by XRD, is also too broad [13].

2. Solubility of Ce in $Gd_2Zr_2O_7$ pyrochlore

It is well known that cerium and plutonium share many common properties specially thermophysical ones. So in order to investigate the solubility of plutonium in $Gd_2Zr_2O_7$ matrix, cerium has been chosen as surrogate material. Reduction of Ce^{4+} to Ce^{3+} has been done, by heating the powder samples in the presence of Zr sponge and low oxygen partial pressure.

In order to investigate the structural aspects of the compositions in the series $Gd_{2-x}Ce_xZr_2O_7$ ($0.0 \le x \le 2.0$), XRD data has been recorded and analyzed. All the products were found to have pyrochlore type lattice, which is characterized by the presence of typical super-lattice peaks at for 14° (111), 27° (311), 37° (331), (using Cu-Kα as radiation source) etc. A shift of the diffraction peaks towards lower angle on Ce incorporation clearly indicates, that the cell parameters of the doped pyrochlores increase as the content of Ce increases. The cell parameters for each composition, along with both the end members were calculated using POWDERX programme. The lattice parameter of these solid solutions increases on incorporation of cerium. The ionic radii of Gd^{3+} and Ce^{3+}, in 8-fold coordination, are 0.98 Å and 1.04 Å, respectively. Therefore, based on the relative ionic size considerations, one can explain the increasing trend in the lattice parameter of pyrochlore, upon incorporation of cerium ion at the Gd sites.

The pyrochlore phase exists throughout the homogeneity range and could be attributed to r_A/r_B (r_A and r_B are the ionic radii of the A and B cations, respectively) ratio which varies from 1.46 (in $Gd_2Zr_2O_7$) to 1.58 (in $Ce_2Zr_2O_7$), which is within the limiting radius ratio, required for the stabilization of pyrochlore structure. Another interesting observation was that, the intensity of characteristic super-structure peaks for pyrochlore systematically increases on going from $Gd_2Zr_2O_7$ to $Ce_2Zr_2O_7$ in the series. This observation can also be explained based on the radius ratio. As the radius ratio increases, the structure becomes more and more ordered and subsequently, the intensities of the super-structure peaks increase.

In order to investigate the thermal behaviour of these

pyrochlores, XRD data has been recorded at higher temperature. In case of $Gd_2Zr_2O_7$, the lattice parameter increases almost linearly with increase in temperature. The samples having the compositions x=0.3 to x=1.2 also show increasing trend in lattice parameter with temperature. The lattice parameters, calculated after cooling to room temperature from 1273K show that it is smaller than the initial lattice parameter room temperature calculated at room temperature. In case of these samples, the increase in lattice parameter due to thermal effect predominates over the decrease in lattice parameter due to aerial oxidation. It is interesting to observe the change in lattice parameters of heavily cerium substituted samples (x=1.5, 1.8, 2.0). Initially, the lattice parameters show a decreasing trend till the temperature reaches 673K, and then it starts to increase as the temperature increases. The reason is that, all the substituted samples undergo aerial oxidation of Ce^{3+} to Ce^{4+} at elevated temperature, which leads to decrease in lattice parameter. Interestingly, after formation of Ce^{4+}, it remains in the solid solution only. The ionic radius of Ce^{4+} is smaller than that of Ce^{3+}, hence the lattice parameter decreases upon heating. The samples having x=1.5 to 2.0, show an increasing trend in lattice parameter after 673K, because the solid solution starts to expand with increase in temperature. Another interesting aspect is that, though Ce^{4+} has formed in the solid solution, but it does form any secondary phase. The phase, $Ce_2Zr_2O_8$, can be considered as anion rich pyrochlore. In the present study, it has been found that $Gd_2Zr_2O_7$ and $Ce_2Zr_2O_7$ form a solid solution over the entire homogeneity range. The oxidation state of cerium could not alter the degree of solubility of cerium in $Gd_2Zr_2O_7$. During oxidation of Ce^{3+} to Ce^{4+}, extra oxygen is introduced into the lattice but still the pyrochlore lattice remains undisturbed.

3. Solubility of Th and Al in $Gd_2Zr_2O_7$ pyrochlore

It has been stated earlier that Al and Th are expected to be generated from Advanced Heavy Water Reactors (AHWR). An attempt has been made to show the dissolution of Th and Al in $Gd_2Zr_2O_7$ by substituting Gd by Th and Zr by Al of $Gd_2Zr_2O_7$. The substitution of Al^{3+} at Zr^{4+} site can compensate for the extra oxygen formed due to the incorporation of Th^{4+} at Gd^{3+} site, which is expected to increase the solubility of Th^{4+} in $Gd_2Zr_2O_7$ [14].

The samples having nominal composition $Gd_{2-x}Th_xZr_{2-x}Al_xO_7$ ($0.0 \leq x \leq 2.0$) were prepared by gel-combustion method. The XRD patterns of all the products in $Gd_{2-x}Th_xZr_{2-x}Al_xO_7$ ($0.0 \leq x \leq 2.0$) series were recorded and analyzed. A few representative XRD patterns are shown in Fig 2. Pure $Gd_2Zr_2O_7$ crystallizes as pyrochlore, which is evident by the presence of super-lattice peaks at $2\theta \approx 14^o(111)$, $27^o(311)$, $37^o(331)$, $45^o(511)$ (using Cu Kα as radiation source). It is observed from that, the compositions corresponding to x=0.0 to x=0.4, adopt pyrochlore structure. A systematic shift of the diffraction peaks towards lower angle on Th and Al incorporation clearly indicates, that the cell parameters of the substituted pyrochlores increase as the content of Th and Al increase.

The cell parameters of all the compositions were calculated using POWDERX programme which

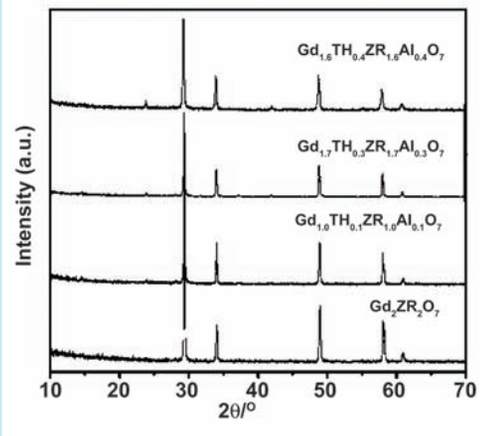

Fig 2: XRD patterns of single phasic compositions in the $Gd_{2-x}Th_xZr_{2-x}Al_xO_7$ systems in the range $0.0 \leq x \leq 0.4$.

show an increasing trend as a function of Th and Al content upto x=0.4. An interesting result has been observed in the trend of cell parameters of the samples. The ionic radii of Gd^{3+} and Th^{4+}, in 8-fold coordination, are 0.98Å and 1.05 Å and the ionic radii of Zr^{4+} and Al^{3+} are 0.72Å and 0.54Å in six fold coordination. Thus the average increase of cationic radii at A site will be smaller than the average decrease in cationic radii at B site. Therefore, a simultaneous incorporation of Th^{4+} and Al^{3+} at Gd^{3+} and Zr^{4+} site, respectively, should result in a decrease in cell parameters. However, the cell parameter increases in $Gd_{2-x}Th_xZr_{2-x}Al_xO_7$ series on increasing x. The probable reason could be that part of Al^{3+} resides at some interstitial sites of the host pyrochlore.

The cations and anions in pyrochlore structure become more and more ordered with increase in r_A/r_B ratio. The planes like (220), (422) etc. consist of anions and planes like (622) are made of metal ions only. The interesting observation is that the intensity of all the superstructure peaks increases with increase in Th^{4+} and Al^{3+} content. The increase in intensity of the peaks corresponding to oxygen only planes like (220), (422) etc., with increase in r_A/r_B ratio, is a rare observation in pyrochlores. The plausible reason could be that with increase in r_A/r_B ratio, the degree of order increased to such an extent that even the intensity of oxygen ordered peaks becomes stronger. From the composition x=0.5 onward, biphasic region comprising of pyrochlore phase and F-type phase starts to appear.

4. Radiation stability of $Gd_2Zr_2O_7$ and $Nd_2Zr_2O_7$ under low energy ion beam

It has been mentioned earlier that these pyrochlore materials could be used for waste immobilization. In order to investigate their stability in radiation environment, $Gd_2Zr_2O_7$ and $Nd_2Zr_2O_7$ pellets were irradiated with 300 KeV Ar^+ ions at fluences ranging from 1×10^{16} to 5×10^{17} ion/cm^2. It was observed,

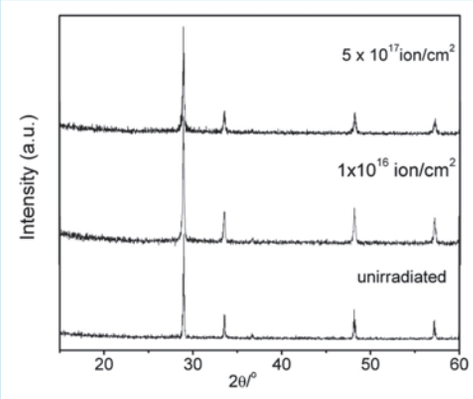

Fig. 3: XRD pattern of unirradiated and irradiated $Nd_2Zr_2O_7$ samples at different fluences

that with an increase in fluence, there is only a broadening of the diffraction lines. No signature of amorphization was observed even at the highest fluence. Fig. 3 shows the Grazing Incidence X-Ray Diffraction (GIXRD) plots for virgin $Nd_2Zr_2O_7$ and the irradiated $Nd_2Zr_2O_7$ at different fluences. The broadening is attributed to the disorder caused by irradiation. The peak positions of the pyrochlore do not change, which means that there is no change in the size of the lattice. One more interesting observation is that, the superstructure peaks get diminished. This suggests that the extra energy due to irradiation, gets dissipated due to swapping (i.e. anti-site formation) of the ions since the radius ratio (r_A/r_B) of the ions was close to that of defect fluorite. Even the sample with the highest fluence shows no signature of amorphization.

The Raman spectra of the samples appear quite similar which suggest that no major change in structure of $Nd_2Zr_2O_7$ has taken place due to irradiation, except minor broadening (not shown). As it has been stated in XRD analysis, that it is probably due to disorder caused by ion irradiation. No amorphization has occured even at highest fluence which suggests that $Nd_2Zr_2O_7$ is also an exceptionally stable material, under low energy irradiation.

In case of $Gd_2Zr_2O_7$ also, the peaks are broadened and the superstructure peaks also disappear, which means the structure turns to defect fluorite (Fig. 4). The broadening is due to disorder as a result of

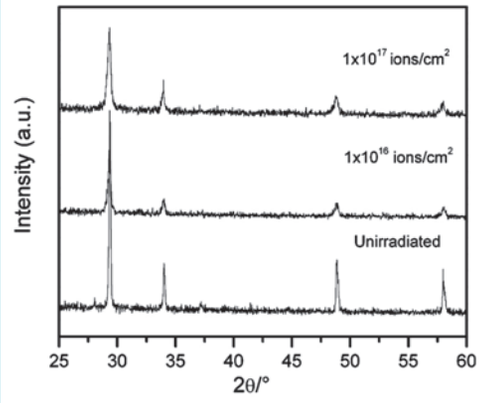

Fig. 4: XRD pattern of unirradiated and irradiated $Gd_2Zr_2O_7$ samples at different fluences

irradiation. Since the size of the cations does not differ much it favours antsite defect formation.

The huge broadening in Raman spectra is due to inherent disorder in $Gd_2Zr_2O_7$ system, even in the absence of irradiation (not shown). Upon irradiation, the disorder increases but the systems remain crystalline only.

Conclusions

It can be concluded that Nd, the surrogate of Am, can be completely dissolved in $Gd_2Zr_2O_7$ and partially in $Y_2Zr_2O_7$. It has again been shown, that an element like Ce which is a simulant of Pu can be completely dissolved in $Gd_2Zr_2O_7$. The other two elements Th and Al also show 20mol% solubility in $Gd_2Zr_2O_7$ matrix. The ion beam irradiation study reveals, that $Gd_2Zr_2O_7$ and $Nd_2Zr_2O_7$ are extremely stable under radiation environment.

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References

1. M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, *Prog. Solid State Chem.* 15 (1983) 55.
2. B. P. Mandal and A. K. Tyagi. *J. Alloys & Comps.* 437 (2007) 260.
3. S. N. Achary, S. K. Sali, K. Kulkarni, P. S. R. Krishna, A. B. Shinde, A. K. Tyagi, *Chem. Mater.* 21 (2009) 5848.
4. A. R. Cleave, Thesis "Atomistic Scale Simulations for Waste Form Applications", Imperial College of Science (2006).
5. Jan Kuneš, W. E. Pickett, *Phys B: Cond. Matter*, 378 (2006) 898.
6. Kazuyoshi Yoshimura, Hironori Sakaia, Hiroyuki Ohno, Shinsaku Kambe, R. E. Walstedt, *Physica B* 329 (2003) 1319.
7. B. P. Mandal, S. K. Deshpande, and A. K. Tyagi. *J. Mater. Res.* 23 (2008) 911.
8. B. P. Mandal, A. Dutta, S. K. Deshpande, R. N. Basu and A. K. Tyagi, *J. Mater. Res.* 24 (2009) 2855.
9. N. Garg, K. K. Pandey, C. Murli , K. V. Shanavas, B. P. Mandal, A. K. Tyagi and S. M. Sharma, *Phys. Rev B* 77, (2008) 214105.
10. K.E. Sickafus, L. Minervini, R.W. Grimes, J.A. Valdez, M. Ishimaru, F. Li, K.J. McClellan, T. Hartmann, *Science* 289 (2000) 748.

11. B. P. Mandal, N. Garg, S. M. Sharma and A. K. Tyagi *J. Solid State Chem* 179 (2006)1999.

12. B. P. Mandal, A. Banerji, V. Sathe, S. K. Deb and A. K.Tyagi *J. Solid State Chem.* 180 (2007) 2643.

13. B. P. Mandal, P. S. R. Krishna, A. K. Tyagi, *J. Solid State Chem.*, 183, (2010) 41.

4.B. P. Mandal, N. Garg, S. M. Sharma, A. K. Tyagi, *J. Nucl. Mater.* 392 (2009) 95.

Forthcoming Symposium

Third Asia-Pacific Symposium on Radiation Chemistry APSRC 2010
&
Trombay Symposium on Radiation and Photochemistry TSRP 2010

The third Asia-Pacific Symposium on Radiation Chemistry (APSRC-2010) incorporating tenth Trombay Symposium on Radiation & Photochemsitry (TSRP- 2010), organized by BARC in association with the Indian Society for Radiation and Photochemical Sciences (ISRAPS), will be held from September 14 (Tuesday) to September 17 (Friday) at Treasure Island Resorts, Lonavala, INDIA. The scientific program of the symposium will consist of key note addresses and about 50 invited lectures of 20 to 30 minutes duration in the field of Radiation and Photochemistry, and about 150 contributory poster papers. The main topics include:

a. Fundamental Radiation Chemical Issues for Advanced Nuclear Energy Systems
b. Advanced Techniques in Radiation and Photochemistry
c. Chemical and Biological Applications of Radiation and Photochemistry
d. Role of Radiation and Photochemistry in Nano Sciences and Radiation Processing e.
e. Radiation and Photochemistry in Ionic liquids and Supercritical Fluids
f. Ultrafast Spectroscopy & Dynamics of Radiation and Photoinduced Chemical Processes
g. Gas Phase Reaction Kinetics, Dynamics and Atmospheric Photochemistry
h. Single Molecule Spectroscopy and Fluorescence Microscopy
I. Theoretical Aspects of Radiation and Photochemistry.

Important Dates

Submission of manuscript for contributory papers	15 Jun 2010
Submission of manuscript for invited papers	15 Jun 2010
Intimation of acceptance to authors	30 Jun 2010
Final Confirmation of participation including request for accommodation (by the delegates) against Payment of Registration Fee	15 July 2010

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TECHNOLOGY DEVELOPMENT ARTICLE

Development of Boron-based materials for nuclear applications

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Materials Group

Abstract

Due to high neutron absorption cross section, boron and its compounds find extensive application in the nuclear industry. The former Metallurgy Division and the present Materials Processing Division have developed processes for the production of boron, its compounds and components for application as control/shutoff rods in nuclear reactors, sensors for neutron counting, shapes for neutron shielding etc. Some of the technologies have been transferred to other units, Ministry of Defense and private industries for regular production. This article traces the research and development activities, carried out on boron based neutron absorber materials.

Introduction

One of the basic requirements associated with the development and operation of nuclear reactors is control and containment of neutrons that sustain, and are also produced during fission reaction. Boron is one of the few elements to possess nuclear properties, which warrant its consideration as neutron absorber material. Boron and its compounds boric acid, boron carbide, rare-earth and refractory metal borides find extensive applications in the nuclear industry as neutron sensors, human and instrument shielding against neutrons, nuclear/neutron poison, control/shutoff rods and in nuclear material storage, due to their high neutron absorption cross section. Boron has two principal isotopes, ^{10}B and ^{11}B and the effectiveness of boron as neutron absorber is due to the high absorption cross sections. of ^{10}B isotope (thermal neutron absorption cross-section for ^{10}B and ^{11}B are 3837 barn and 0.005 barn respectively). The neutron absorption of natural boron containing ~19% ^{10}B is sufficiently high (752 barn) in the low neutron energy range to make it an excellent candidate for use in thermal reactors. At higher energies, the cross section of most other elements becomes very small, often abruptly as in the case of cadmium, whereas that of ^{10}B decreases monotonically with energy and the absorption cross-section is sufficiently high at 1 barn for 1 MeV energy neutrons. Absolute values along the entire energy spectrum are of sufficient magnitudes to make it very effective in the intermediate and fast energy range also. In addition to a high absorption cross section, boron has another advantage over other potential neutron absorber materials. The reaction products, helium and lithium, are formed as stable, non-radioactive isotopes. As they do not emit nuclear radiation, decay heating problems during reactor shutdowns and transfer of depleted control rods are minimal.

The (n, α) reaction

$$_5B^{10} + {}_on^1 \rightarrow {}_2He^4 + {}_3Li^7 + 2.4\ MeV$$

however leads to release of helium, posing problems in the design of control rods. With fast neutrons (E>1.2MeV) there is a secondary reaction as given below

$$_5B^{10} + {}_on^1 \rightarrow 2\ {}_2He^4 + {}_1H^3$$

Though this reaction has a very less probability compared to n,a reaction, it has great importance from the viewpoint of reactor waste, since it constitutes one of the major sources of tritium production in the reactor core.

Some of the actual applications of boron and its compounds in Indian nuclear industry are as follows: Boric acid is used as poison in moderator/coolant of research reactors. Boric acid and boron carbide powder have been used in concrete while constructing reactor buildings. Natural as well as ^{10}B enriched elemental boron are used as neutron detectors. Boral (boron carbide in aluminium matrix), Bocarsil (boron carbide in silicon rubber), Polyboron (boric acid in polyethylene) are used as neutron shields in reactors, nuclear materials storage and nuclear instrumentation. Boron carbide powder is used as control rod material in BWR (Boiling Water Reactor at Tarapur) and dense pellets of ^{10}B enriched boron carbide in PFBR (Prototype Fast Breeder Reactor at Kalpakam). TiB_2 and B_4C+ZrO_2 composites are useful in control and shielding of packaged reactors.

Boron carbide and refractory metal borides in addition have an attractive combination of properties such as low density, high melting point and hardness, chemical inertness and excellent thermal and electrical characteristics making them potential materials for many advanced applications. In the recent past, the Materials Processing Division has been engaged on synthesis, consolidation and composite fabrication of various refractory/rare earth metal borides.

1. Boron powder

Due to it's high reactivity, it is extremely difficult to prepare pure boron, which is further complicated by the fact, that the impurities are mainly present within the crystal lattice combined with boron or combined together. Due to its extreme hardness, pulverization of boron introduces impurities from the crushers and causes a superficial oxidation of the grains. In view of these difficulties, the electrolytic process was chosen for the extraction of pure boron where no reductant is used, the deposit is in fine form and the process itself is very selective to obtain boron of high purity. Two different methods 1) namely extraction of boron by fused salt electrowinning from KCl-KF-KBF_4 electrolyte and 2) electroextraction from soluble B_4C anodes in NaCl-KF-KBF_4 melt were developed.

In the electrowinning of boron, the following overall reaction can be assumed to take place.

$$4KBF_4 + 2KCl \rightarrow 4B + 6KF + 5F_2 + Cl_2$$

Under optimum electrowinning conditions, a current efficiency of about 84% and a boron yield of >90% were obtained. The purity of boron was high at B - 96.8%; Fe - 0.52%; SiO_2 -1.25%; C-0.26%; Mg-0.62%; $N_2 + O_2$ - 0.55%.

In the other process, B_4C is used as a soluble anode; the following two reactions take place during electro deposition at the electrodes.

At the anode: $B_4C \rightarrow x\ B^{3+} + B_{4-x}C + 3\ ne^-$
At the cathode: $x\ B^{3+} + 3\ ne^- \rightarrow x\ B$ where $x = 4$.

Hence, this deposition is conducted at sufficiently low voltage of just above 1 V. In this process, the current efficiency is high at 98% and boron yield about 82% under the optimum conditions. Boron of much higher purity (B - 99.8%; Fe - 0.06%; Si - 0.08%; C - 0.06%; Na - 0.04%; N_2+O_2 - 0.03%) is obtained. A sketch of the electrolytic cell used for

these studies is shown in Fig.1 and electro deposit of boron in Fig. 2. For preparation of ^{10}B enriched boron, electrowinning from KBF_4 is the most suitable process.

The technology for production of enriched boron was transferred to IGCAR, Kalpakkam. A few electrolytic cells were operated at IGCAR to produce ^{10}B erniched boron in kilogram scale. Regular production of enriched boron has recently started at HWB, Manuguru by this method. Technology for production of natural boron from boron carbide was transferred to the Ministry of defense (for use in pyrochemical formulations in a wide range of military explosives) and a plant with a capacity of 200 kg/year of boron was set up at Jabalpur.

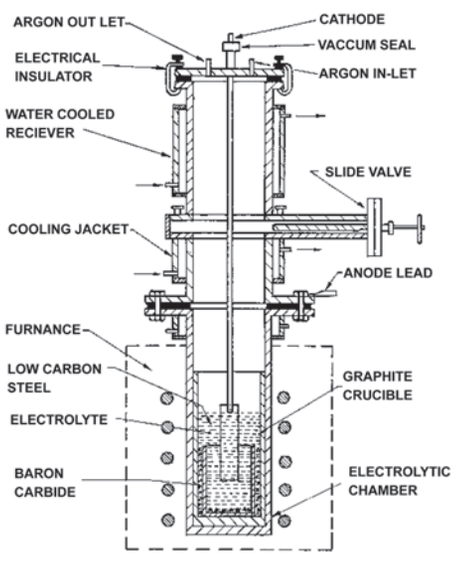

Fig.1: Sketch of electrolytic cell for electroextraction

Coating of natural and enriched boron on aluminium as well as stainless steel material have been carried out by dip coating method from fine suspension of boron in an organic medium. These coated elements have been used as sensors in neutron counters for measurement of neutron flux in various reactors at different locations.

Fig.2: Electrodeposit of boron

2. Boron carbide

Boron carbide is usually prepared from its oxide by carbothermic or magnesiothermic reduction in the presence of carbon. Carbothermic reduction route was developed in our laboratory using commercially available boric acid in place of boron trioxide as per the following reaction.

$$4H_3BO_3 + 7C \rightarrow B_4C + 6H_2O + 6CO$$

This process requires a temperature of >1500°C to start the formation of boron carbide and is generally carried out at temperatures in the range of 1900°C - 2500°C. A photograph of the furnace used in our laboratory for the production of B_4C is shown in Fig. 3.

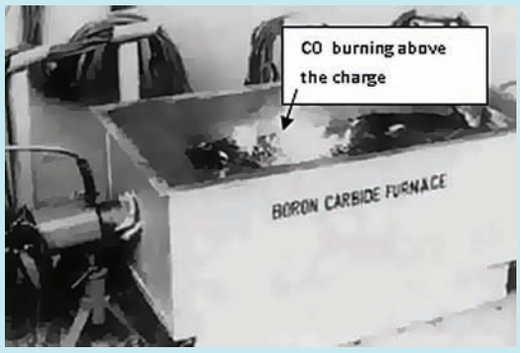

Fig. 3 : Graphite resistance furnace

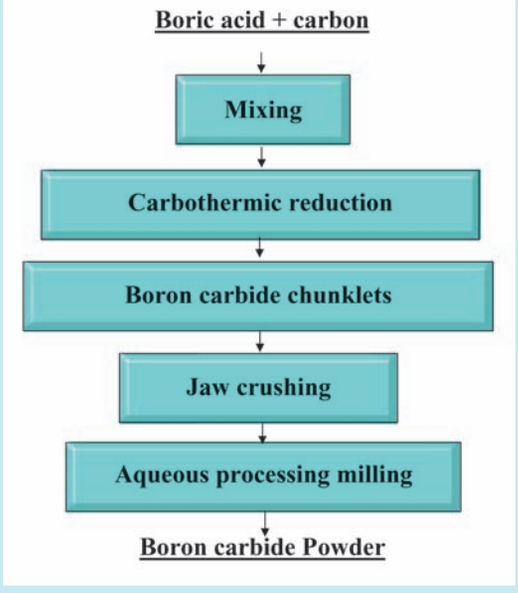

Fig. 4: Flow sheet for production of B_4C

The boron carbide lumps, as obtained from the furnace, varying in size upto 80-100mm, are further crushed to small pieces in a jaw crusher and then to a fine powder in a pulveriser using multiple hammer heads lined with hardened manganese steel. This powder needs further purification to remove the small amounts of unreacted / partially reduced charge and the contaminants picked during the process of size reduction. The aqueous processing of boron carbide powder to remove the impurities is carried out in polypropylene lined fiber reinforced plastic tanks using hydrochloric acid for the dissolution of impurities and silica lined heaters for heating the solution. Agitation of the solid liquid mixture is effected by passing air under pressure through the bed. The flow sheet for the production of boron carbide powder from boric acid is given in Fig. 4. Graded powder mix filled in stainless steel tubes is used as control rods in TAPS.

3. Boral sheets

Boral is a composite made up of boron carbide and aluminium where aluminium provides the bonding between the particles. This material is fabricated by powder metallurgy route. Powders of boron carbide and aluminium in the required ratio are mixed thoroughly and hot pressed at temperatures close to the melting point of aluminium. The sintered compact is sandwiched between aluminium sheets and picture framed all around, using aluminium sheet. This block is then hot rolled to produce boral sheets of required thickness. Boral sheets with a maximum boron carbide content of 50-60 wt% could be produced with good adhesion. Boral sheets produced in our laboratory were used in the construction of Dhruva reactor for neutron shielding in beam hole inner gate and other locations.

4. Bocarsil sheets

Bocarsil is a composite of silicon rubber, using boron carbide as the filler material. Silicon rubber was specially chosen for its longer shelf life. Fine boron carbide powder of median particle size in the range of 10-20μm is thoroughly mixed with silicon rubber in a sigma kneader. The mixed dough is rolled into sheets of required thickness and then cured at a temperature of 150°C. Some of the properties of these composite sheets (Boral and Bocarsil) are given in Table 1. Bocarsil sheets are used as neutron shield in online fuelling machines of power reactors, for storage of nuclear materials and also in nuclear instrumentation.

Table 1: Properties of Boral and Bocarsil sheets

Boral		Bocarsil	
Boron carbide content	- 45-55 %	Boron carbide content	- 45-55 %
Density	- 2.5 g/cc	Density	- ~ 1.5g/cc
Thickness	- 6-8 mm	Hardness	- 80 shore
Absorption cross section, Σa	- 40 cm^{-1}	Flexibility	-Excellent
Sp.heat cal/^oC	- 0.175	Working temperature	- 200^0C
		max.Absorption cross section, Σa	- 30 cm^{-1}

5. Poly boron blocks

Poly boron is a composite, made up of boron compound in High Density PolyEthylene (HDPE) matrix. For neutron shielding surrounding instruments using various radioactive isotopes, composites with boron content of less than 10 % are also useful. The procedure for fabrication of Polyboron shapes consists of mixing of the polymer with the chosen compound of boron, melting the mixture and casting into moulds of requisite shapes. These cast blocks can be easily cut, drilled, worked in lathes etc. to form complex final shapes. Hydrogen content of the polymer also acts as a good moderator for neutrons.

6. Enriched boron carbide

The second generation nuclear reactors in India are proposed to be fuelled by Plutonium containing materials and the energy of neutrons in such reactors is much higher than the present reactor systems. Boron enriched in ^{10}B is the only available suitable material for control rod application in such systems. As the enriched boron material is prohibitively costly, the extraction processes should consider the recovery of boron to a very high extent and also suitable techniques to be developed for in house scrap reclamation, recovery from effluent and reprocessing of used materials. Keeping this in view, investigations have been carried out for the development of suitable processing schemes for the extraction of enriched boron and fabrication of dense pellets of enriched boron carbide to be used as control rod materials.

Boric acid containing enriched boron is the raw material available for extraction of enriched boron. Carbothermic reduction of boric acid or boron trioxide, as they are carried out commercially, gives a very poor yield of 60-65% only in boron terms. Hence a different route for the preparation of enriched boron carbide was adopted. In the new scheme, enriched boric acid is first chemically converted to potassium fluoroborate and extraction of boron from this potassium compound is carried out by fused salt electrolysis. Enriched boron prepared by this method is further converted to its carbide by reacting with carbon.

Synthesis of boron carbide by solid - solid reaction between its elements was studied, which can be represented by the following equation:

$$4B + C \rightarrow B_4C$$

Since B_4C is in equilibrium with free carbon and is only boundary between B_nC and B_nC+C (where $4<n<10$), synthesis of B_4C without free carbon is extremely difficult. With the view to produce pure B_4C without graphite, experiments were carried out by varying Boron/Carbon ratio from 4.0 (stoichiometric) to 4.6. XRD of the products revealed the presence of B_4C only when B/C ratio is 4.0 but boron rich B_8C and B_4C with higher B/C ratios. In all the experiments, the product in addition to boron carbide contained graphite. These clearly show that

by simply increasing the boron content of the charge, one cannot avoid the presence of carbon in the product as shown in Table 2.

6.1 Densification

6.1.1 Pressureless sintering

Though boron carbide in powder form is used for control rod application in BWR, Fast breeder reactors need dense boron carbide pellets containing ^{10}B enriched boron due to high neutron flux. Consolidation of B_4C is complicated due to its high melting point, low self diffusion coefficient and high vapour pressure. Very high sintering temperatures are required for densification due to the presence of predominantly covalent bonds in B_4C. Boron carbide particles generally have a thin coating of surface oxide layer which also hinders the densification process. At temperatures >2000°C, surface diffusion and evaporation condensation mechanism occur, which result in mass transfer without densification. Densification is achieved only at temperatures >2000°C, by grain boundary and volume diffusion mechanisms. At higher temperature exaggerated grain growth also takes place, resulting in poor mechanical properties. One

Table 2: Effect of B/C ratio in the charge (Temperature: 1850°C, Duration: 3 hours)

S.No.	B/C	Phase present
1	4.0	B_4C and Graphite
2	4.2	B_4C and Graphite B_8C
3	4.4	B_4C and Graphite B_8C
4	4.6	B_4C and Graphite B_8C

more observation at temperatures >2150°C is volatilization of non-stoichiometric boron carbide, leaving minute carbon behind at the grain boundaries. Densification of boron carbide powder was studied by pressureless sintering with and without additives and also by hot pressing. Particle size of boron carbide powder and the sintering temperature are two key parameters in densification. While pressureless sintering of B_4C powder, though compaction can be done under an inert gas cover, use of vacuum appears to have beneficial effects. By pressureless sintering upto 2300°C, a maximum density of 85%ρ_{th} was obtained when the carbide starting particle size was in the range of 0.5—2.0 μm. Compact densities of above 90%ρ_{th} could be achieved by sintering at 2375°C using finer particles of median diameter 0.5/ 0.8 μm. SEM image of pressureless sintered boron carbide is presented in Fig.5. Hardness of the samples sintered with ZrO_2 additive was higher at 30–31.5 GPa, compared to 27 GPa of B_4C obtained without additive. Variation of hardness with ZrO_2 addition and back scattered image of dense B_4C+ZrO_2 are presented in Figs. 6 and 7. Both carbon and zirconium are neutron transparent, hence could be used with boron carbide for nuclear applications.

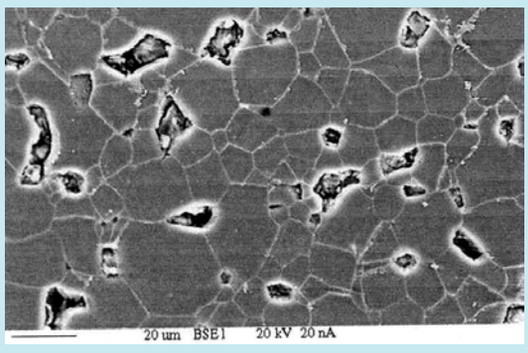

Fig. 5: SEM of pressure-less sintered B_4C

6.1.2 Hot pressing

As the required density of ³95% could not be obtained by pressureless sintering, hot pressing method was chosen for compaction of ^{10}B enriched boron carbide. Density of pellets obtained by hot pressing method is a function of temperature,

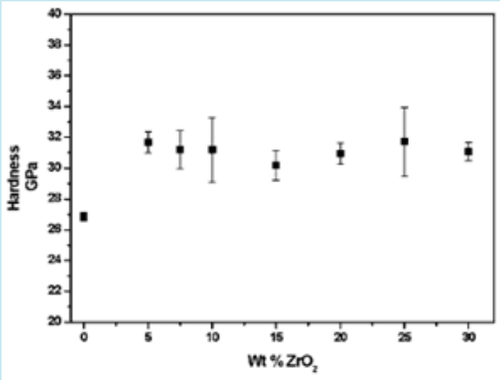

Fig. 6: Variation in hardness of B_4C with ZrO_2

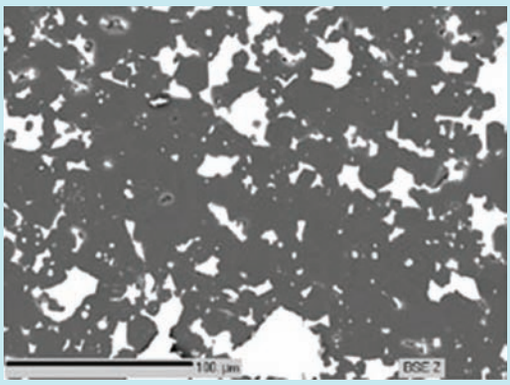

Fig. 7 Back scattered image of dense B_4C+ZrO_2

pressure, particle size of powder and length to diameter ratio (L/D) of the pellet. Effect of these factors on densification process was studied. Hot pressing of boron carbide powder was carried out in a graphite resistance heated vacuum furnace using high density graphite dies. Effect of particle size on pellet density was studied by conducting experiments at 1850°C under 35 MPa pressure. It was observed that density (measured using Archimedes principle) improved from 83% to 95% ρth with the decrease in particle size from 12.73 µm to 2.98 µm. Fig.8 presents the progress of densification with time while hot pressing. A high temperature high vacuum hot press was indigenously developed for this purpose. A photograph of the hot press and the products are shown in Fig.9 and Fig.10.

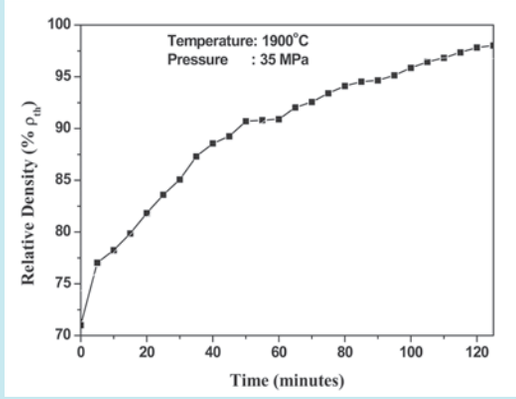

Fig. 8: Progress of densification with time

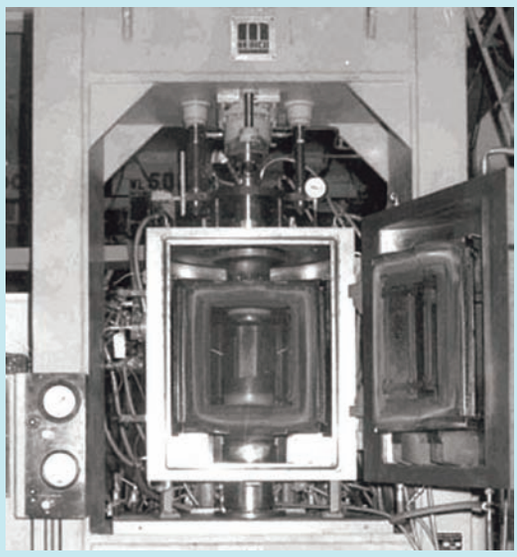

Fig. 9: Vacuum hot press

Fractured surface of the high density boron carbide is presented in Fig.11. Density, mechanical (hardness, young's modulus, shear modulus, bulk modulus, flexural strength, fracture toughness) and physical properties (coefficient of thermal expansion, electrical resistivity, thermal conductivity) of dense (95% TD) boron carbide pellets prepared by the above methods were measured and found to be comparable to the literature values and meets the requirement of intended application. This data is given in Table 3.

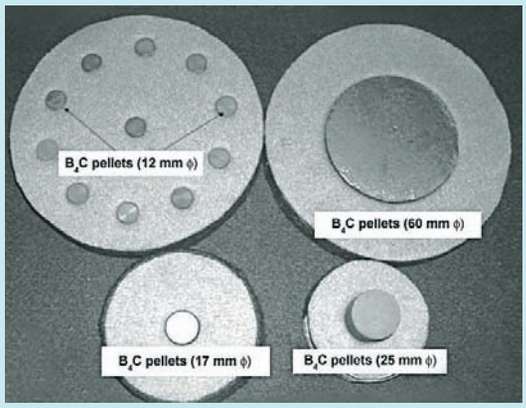

Fig.10: Boron carbide pellets of various sizes compacted by hot pressing

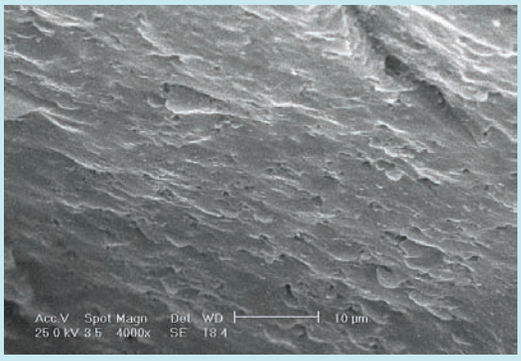

Fig.11: Fractured surface of high density B_4C

7. Summary

Research and development activities carried out in Materials Group, BARC have made a strong base for the production of boron based neutron absorber materials.

1. Technology for the production of natural boron carbide powder has been established and transferred to private industry. M/s. Boron carbide India have been successfully producing and marketing this material for the last 15 years. Major requirements of neutron shielding material for the proposed PFBR at Kalpakam have been successfully met due to the pioneering work of the former Metallurgy Division.

Table 3: Properties of dense B_4C pellet

Property	Value
Density (gm/cc)	2.42
Hardness (GPa)	2S-2
Young[1] Modulus (GPa)	420
Shear modulus (GPa)	171
Bulk modulus (GPa)	261
Flexural Strength at RT (MPa)	363
Flexural Stiength at 600°C (MPa)	271
Fracture toughness K_{IC} (MPa.$m^{1/2}$)	4.06
Coefficient of thermal expansion (ppm/K) @900° C	*53*
Electrical Resistivity @ RT (-crn)	1.27
Electrical Resistivity @ 600°C (-crn)	8.42 x 10^{-2}
Electrical Resisitivity @ (£ 1000° C (-crn)	6.15 x 10^{-2}

2. Elemental boron production plant of 200 kg/ annum has been set up at Jabalpur to meet the defense requirements.
3. A process for the production of ^{10}B enriched elemental boron has been established. Based on this, a bench scale facility at IGCAR and a plant by Heavy Water Board at Manuguru have been set up.
4. Method for synthesis and densification of ^{10}B enriched boron carbide has been established and a trial production run of PFBR control/ shutoff rod material has been completed.
5. Process for boron coating has been established and boron coated sensor elements for neutron detectors supplied as and when required.

8. Acknowledgement

The authors gratefully acknowledge the contribution of many of their colleagues who have nurtured this programme from inception to the present stage. Amongst the many who have made significant contribution, special mention may be made of Dr. C.K. Gupta who has admirably led this programme from the front and many others who have implemented such as Late Shri B.R. Mahindra, Dr. T.K. Mukherjee, Dr. D.K. Bose, Dr.M.K.Totlani, Shri.A.K.Grover, Dr. K.U. Nair, Shri C. Narayanan, Shri S.M. Shetty, Smt. T.K. Roy, Shri. Shaikh Baba,

Shri R.D. Bedse and Shri C.D. Singh. The authors also wish to acknowledge the contributions of Shri R.K. Fotedar, Shri. A.L.Pappachan, Shri. Jitendra Sonber, S. Patiram, S.B.Chavan and others from Materials Processing Division, who are presently participating in the programme. The authors also wish to express their sincere gratitude to the Head and staff members of Analytical Chemistry Division and Post Irradiation Examination Division for characterization of these materials.

9. References

1. A. K. Suri, C. Subramanian, J. K. Sonber and T. S. R. Ch. Murthy; Synthesis and consolidation of boron carbide: A Review; *International Materials Review*, 2010, 55[1], 4-40.

2. F. Thevenot: 'Boron carbide – a comprehensive review', *J. Eur. Ceram. Soc.*, 1990, 6, 205–225.

3. V. I. Matkovich: 'Boron and refractory borides'; 1977, *Heidelberg/New York,* Springler-Verlag Berlin.

4. D. K. Bose, K. U. Nair and C. K. Gupta: 'Production of high purity boron carbide', *High Temp. Mater. Proc.*, 1986, 7, (2–3), 133–140.

5. G. Goller, C. Toy, A. Tekin and C. K. Gupta: 'The production of boron carbide by carbothermic reduction', *High Temp. Mater. Proc.*, 1996, 15, (1–2), 117–122.

6. A.K.Suri and C.K.Gupta: "Studies on the fabrication of aluminum bonded boron carbide rings", *J. Nucl. Mat.* 1978, 74, 297-302

7. K. U. Nair, D. K. Bose and C. K. Gupta: 'The production of elemental boron by fused salt electrolysis', *Miner. Proc. Extract. Metall. Rev.*, 1992, 9, 283–291.

8. D.N.Prasad, K.R.Prasad, S.K.Khataria, S.N.Athavale, A.L. Papachan, C. Subramanian, A.K. Grover and A.K. Suri; Indigenous development of gamma compensated boron lined neutron chamber; *Journal of Scientific and Industrial research* 2003,62, 1057-1062.

9. C. Subramanian and A. K. Suri: 'Development of boron based neutron absorber materials', *Met. Mater. Process.*, 2004, 16, (1), 39-52.

10. C. Subramanian and A. K. Suri: 'Development of Boron and other Boron compounds of Nuclear Interest', *IANCAS Bulletin.*, July 2005, 237-244.

11. T.K. Roy, C. Subramanian and A.K. Suri: "Pressureless sintering of boron carbide", *Ceram. Int.* 2006, 32, 227-233

12. C Subramanian., T.K. Roy, T.S.R.Ch. Murthy, P.Sengupta, G.B.Kale, M.V.Krishnaiah, A.K.Suri, Effect of Zirconia addition on Pressureless Sintering of Boron Carbide; *Ceram. Inter.* 34[6] 1543-1549 (2008)

13. `A. Jain, S. Anthonysamy, K. Ananthasivan, R. Ranganathan, V. Mittal, S. V. Narsimhan and V. Mittal: 'Charecterization of electrodeposited elemental boron', *Mater. Charact*, 2008, 59, 890-900.

14. M.P.L.N. Rao, G.S. Gupta, P. Manjunath, S. Kumar, A. K. Suri, N. Krishnamurthy and C. Subramanian: "Temperature measurements in the boron carbide manufacturing process-A hot model study", *Int. J. Refract. Met. and Hard Mat.*, 2009, 27[3], 621-628.

15. M.P.L.N. Rao, G.S. Gupta, P. Manjunath, S. Kumar, A. K. Suri, N. Krishnamurthy and C. Subramanian: "Core temperature measurement in carbothermal reduction process", *Thermochimica Acta* 482 (2009) 66-71

Isotope Correlations for Determination of Isotopic Composition of Plutonium

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Fuel Chemistry Division

Abstract

Isotope correlations were developed using the experimentally determined isotopic composition data of Pu produced in Indian PHWRs. Thermal Ionization Mass Spectrometry (TIMS) and alpha spectrometry were employed for obtaining the data on abundances of different Pu isotopes. Linear correlations were obtained between $^{238}Pu/(^{239}Pu + ^{240}Pu)$ alpha activity ratio vs. $^{240}Pu/^{239}Pu$ atom ratio as well as between $^{240}Pu/^{239}Pu$ atom ratio vs. $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ atom ratios. The correlations can be used to obtain data on the abundances of different Pu isotopes with an accuracy of 2 to 10% which is useful for radiometric assay of Pu samples. Principal component analysis is shown as a useful tool for the classification of the source of Pu.

Introduction

Determination of isotopic composition of different elements, is a prerequisite in many areas of science and technology. Mass Spectrometry plays an important role in obtaining isotopic composition of various elements with high precision and accuracy. Alpha Spectrometry is also useful to obtain the data on nuclides emitting alpha particles, in particular for nuclides with low abundance (e.g. ^{232}U, ^{238}Pu etc.), high alpha specific activity and relatively short half lives.

Isotope correlations are highly useful to verify and validate the isotopic composition data, provided the database is generated after careful analysis of data collected over a period of time. Isotope correlations can be valuable in checking the internal consistency of the data, when a large number of samples are analyzed. They are also useful in the development of non-destructive analysis techniques such as gamma spectrometry and neutron counting techniques. A few correlations developed based on gamma spectrometry [1-3] and neutron counting techniques [4] were previously reported in literature. These isotope correlations are useful for obtaining the isotopic composition as well as the alpha specific activity of Pu required for radiometric assay of Pu as well as for the determination of ^{241}Am in any Pu-based nuclear fuel sample.

During the present work, isotope correlations were developed, for determining the isotopic composition of plutonium from Indian Pressurized Heavy Water Reactors (PHWRs) and research reactors. Using the data on the atom ratios $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ obtained by Thermal Ionization Mass Spectrometry (TIMS) and the $^{238}Pu / (^{239}Pu + ^{240}Pu)$ alpha activity ratio obtained by alpha spectrometry, isotope correlations were developed. A correlation based on the ratio of counts observed in beta channel to the alpha channel in a liquid scintillation counting system was also developed, to determine accurately the $^{241}Pu/^{239}Pu$ atom ratio for its correlation with the other isotope ratios. An agreement of 1-5 %, depending upon the abundance of the Pu isotope,

was observed with the data obtained by TIMS for different Pu isotopes.

Formation of Plutonium Isotopes

The various Pu isotopes namely ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu are formed from successive absorption of neutrons by the U isotopes, namely ^{235}U and ^{238}U.

The formation of the different Pu isotopes depends on many factors such as

i. Initial content of ^{235}U in the fuel
ii. Type of moderator used
iii. Neutron energy spectrum in the reactor
iv. Burn-up of the fuel
v. Design features of the reactor such as material and position of control rods etc.

The properties of the different isotopes of Pu are listed in Table 1.

Experimental

Data on different isotopes of Pu were obtained using thermal ionization mass spectrometry. Alpha spectrometry was used for the determination of ^{238}Pu. In order to eliminate the isobaric interference of ^{241}Am at ^{241}Pu during plutonium analysis by mass spectrometry as well the interference of the alpha peaks of ^{241}Am at ^{238}Pu alpha peaks during alpha spectrometric analysis, the plutonium solution was purified from americium by employing the anion exchange separation procedure using DOWEX 1 x 8 in HNO_3 medium [6]. In order to reduce the uncertainties due to the build up of ^{241}Am in the purified Pu fraction, the experiments were completed within a day or two after separation.

^{238}Pu/(^{239}Pu + ^{240}Pu) alpha activity ratio was obtained by alpha spectrometry using the alpha spectrometric system consisting of a passivated and ion implanted detector mounted in a vacuum chamber (pressure $< 10^{-2}$ torr). In order to account for the tail contribution due to the energy degradation of high energy alpha peak (^{238}Pu) at the low energy peak (i.e. ^{239}Pu & ^{240}Pu), (a method based on geometric

Table 1 : Nuclear characteristics of different Pu isotopes [5]

Isotope	*Half-life (Years)*	*Mode of decay*	*Energy (KeV)*	*% Abundance*
^{238}Pu	87.7 ± 0.1	α	5499.03 ± 0.20	70.91 ± 0.10
			5456.3 ± 0.3	28.98 ± 0.10
			5357.7	0.105 ± 0.005
^{239}Pu	24110 ± 30	α	5156.59 ± 0.14	70.77 ± 0.14
			5144.3 ± 0.8	17.11 ± 0.14
			5105.5 ± 0.8	11.94 ± 0.07
^{240}Pu	6561 ± 7	α	5168.17 ± 0.15	72.80 ± 0.10
			5123.68 ± 0.23	27.10 ± 0.10
^{241}Pu	14.290 ± 0.006	β(–)	20.78 ± 0.13	99.998 ± 0.002
^{242}Pu	(3.75 ± 0.02) x 10^5	α	4902.2 ± 0.9	76.49 ± 0.17
			4858.1 ± 0.9	23.48 ± 0.17

progression (G.P.)) decrease of the counts in the far tail of the alpha peak was employed [7].

$^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ atom ratios were obtained by thermal ionization mass spectrometry. A double rhenium filament assembly was used and the multi Faraday cup detector system was employed, to eliminate the time dependent fluctuations in the ion current. The overall performance of the system was checked using NIST certified isotopic reference material CRM-947 Pu. The range of data used for the development of the correlations for Pu from different research and power reactors is given in Table 2.

Results and Discussion

The following correlations were developed using the data in the range given in Table 2.

1. $^{238}Pu/(^{239}Pu + ^{240}Pu)$ alpha activity ratio Vs. $^{240}Pu/^{239}Pu$ atom ratio
2. $^{240}Pu/^{239}Pu$ atom ratio Vs. $^{241}Pu/^{239}Pu$ atom ratio & $^{242}Pu/^{239}Pu$ atom ratio.

The linear correlations obtained between $^{238}Pu/(^{239}Pu + ^{240}Pu)$ alpha activity ratio and $^{240}Pu/^{239}Pu$ atom ratio, $^{240}Pu/^{239}Pu$ atom ratio and $^{242}Pu/^{239}Pu$ atom ratio for Pu produced in PHWR reactors are shown in Figs. 1 and 2, respectively.

Correlation for the determination of $^{241}Pu/^{239}Pu$

Correlation between $^{241}Pu/^{239}Pu$ atom ratio and $^{240}Pu/^{239}Pu$ atom ratio obtained using the range of data shown in Table 2 is given in Fig. 3.

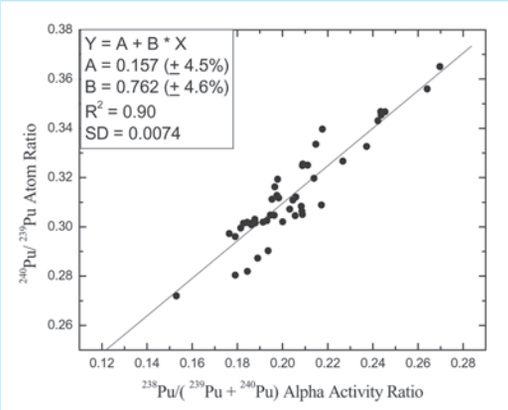

Fig. 1 : Correlation between $^{238}Pu/(^{239}Pu+^{240}Pu)$ alpha activity ratio and $^{240}Pu/^{239}Pu$ atom ratio

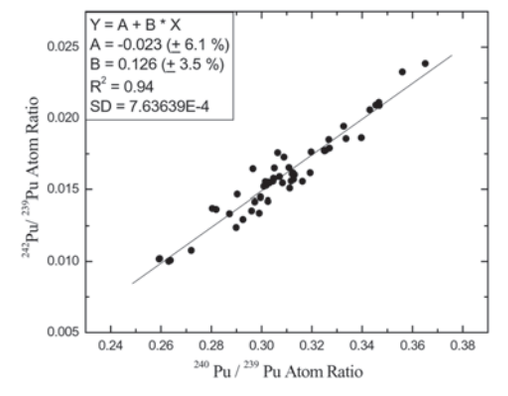

Fig. 2 : Correlation between $^{240}Pu/^{239}Pu$ atom ratio and $^{242}Pu/^{239}Pu$ atom ratio

Using the correlations developed and shown in the figures above, the different atom ratios of Pu namely $^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ can be obtained with an accuracy of about 2%, 0.5%, 5% and 5%, respectively. Similar linear correlations were obtained for the Pu samples from research reactors, namely Cirus and Dhruva [8]. The

Table 2 : Range of the isotopic composition data used

Reactor type	*Range of atom % abundances*				
	^{238}Pu	*^{239}Pu*	*^{240}Pu*	*^{241}Pu*	*^{242}Pu*
Research	0.003-0.031	89.93 - 94.54	5.18 - 8.98	0.243 - 0.796	0.013 - 0.154
PHWR	0.072 - 0.160	69.57 - 77.64	19.14 – 25.40	1.917 - 3.475	0.702 – 1.659

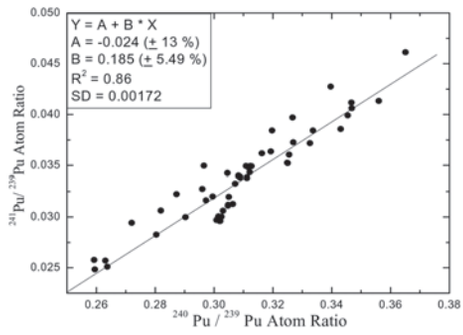

Fig. 3 : Correlation between $^{240}Pu/^{239}Pu$ atom ratio and $^{241}Pu/^{239}Pu$ atom ratio

Pu isotopes in the sample. Fig. 4 shows the correlation developed for the determination of $^{241}Pu/^{239}Pu$ atom ratio using the X value calculated from ratio of total beta counts to total alpha counts obtained by Liquid Scintillation Counting (LSC) and the atom ratios obtained from TIMS as discussed above.

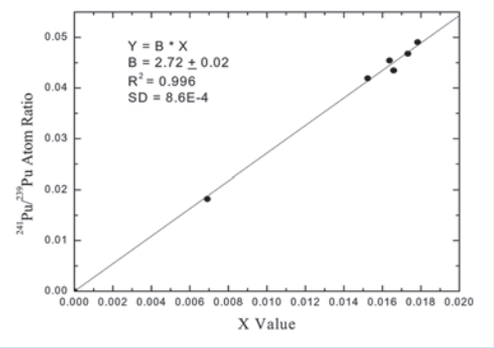

Fig. 4 : Correlation between X-value and $^{241}Pu/^{239}Pu$ atom ratio
(X-Value = $[t_\beta / t_\alpha].[(R_{8/9}.\lambda_8) + \lambda_{89} + (R_{0/9}.\lambda_{80}) + (R_{2/9}.\lambda_{82})] / \lambda_{81}$,
Where R is the atom ratio of two isotopes of Pu and t_α and t_β, are the observed α and β count rates in LSC, respectively.)

Chemometric analysis of Pu isotopic composition data

The isotopic composition data of Pu obtained from irradiated samples, over a long period, was employed for this work. Data of over 150 samples was compiled for chemometric analysis. The data from research reactors and power reactors in India (PHWR) are used in this work, the details of which are shown in Table 2. Auto-scaling of the isotopic composition data was performed, in order to provide equal weights for all the isotopic composition data since the isotopic composition data from the reactors varies significantly by more than an order of of of of magnitude. The covariance matrix and the Eigen values and Eigen vectors of the covariance matrix of the transformed data were evaluated using the commercially available MATLAB (version 7.0.1 Release 14) software, from M/s. Math Works Inc. The Principal component scores were then calculated using the transformed data. For the data under study, the PC1 accounted for 98 % of the variance in the data, while 99.5 % of the variance in the data was explained using the two principal components.

Fig. 5 shows a plot of the scores of PC1 & PC2. It can be seen that using PC1 scores, it is possible to differentiate the PHWR Pu samples from the research reactor Pu samples. It is highly encouraging since this is the first study of this kind reported on the use of chemometry for the classification of Pu using experimentally determined Pu isotopic composition. The full capability of this chemometric analysis work can be ascertained using the data from other types of reactors which are in operation worldwide.

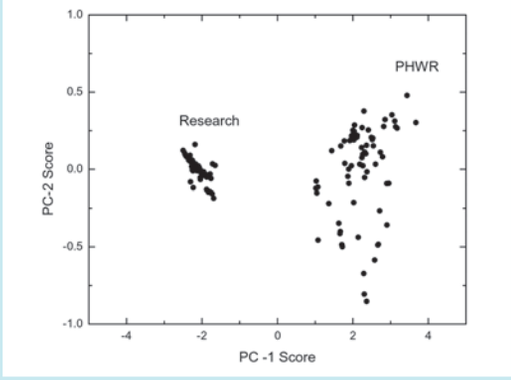

Fig.5. Plot of the principal component scores for the Pu isotopic composition data

which can be due to the different cooling histories of the Pu samples used in this work. The chemometric methodology discussed is highly encouraging and promising for its use in nuclear forensics, though limited data was available.

Conclusions

Using the isotope correlations, the isotopic composition of plutonium from PHWR and research reactors samples can be determined. By determining $^{238}Pu/(^{239}Pu + ^{240}Pu)$ alpha activity ratio by alpha spectrometry, the isotopic composition of Pu can be obtained. Such correlations are quite useful when the amount of sample is very small, or when highly sensitive techniques such as Resonance Ionization Mass Spectrometry (RIMS) [10] and Accelerator-based Mass Spectrometry (AMS) [11] are used due to extremely small quantities of samples being available. For example, in RIMS, the isotopic composition of Pu was obtained using 10^5 atoms of Pu. In such cases, the data on the major isotopes ^{239}Pu and ^{240}Pu can only be obtained with reasonable accuracy and the correlations can be employed for determining the other isotope ratios. These correlations are also useful when employing gamma spectrometry for determining Pu isotopic composition for the determination of $^{242}Pu/^{239}Pu$ atom ratio, since ^{242}Pu has no significant gamma decay scheme. Also the correlations are useful for the determination of fissile content of Pu. The correlations can provide data to obtain the alpha specific activity of Pu, required for the determination of ^{241}Am content in Pu employing alpha/gamma method [12]. These correlations can also be employed for determining Pu concentration by Isotope Dilution Alpha Spectrometry (IDAS) [13] in which the data on the atom % abundances of ^{239}Pu & ^{240}Pu isotopes are necessary.

It must be noted that, although the formation of Pu isotopes is non-linear, it can be approximated to a linear function, over the limited range of data (from research & power reactors).

References

1. S.B. Manohar, S.K. Aggarwal, S.M. Deshmukh, A.R. Parab, P.P. Burte, H.C. Jain, S. Prakash : *J. Radioanal. Chem.,* **63** (1981) 145.
2. Software for Nuclear Spectrometry, IAEA-TECDOC-1049, International Atomic Energy Agency, **103** (1998).
3. G. Bignan, W. Ruhter, H. Ottmar, A. Schubert, C. Zimmerman: *ESARDA Bulletin* No. **28**, 1 (1998)
4. A. Klett: *IEEE Trans. on Nucl. Science,* **46** (1999) 877.
5. http://www.nndc.bnl.gov.
6. J.J.Ryan and E.J. Wheelbright: *Ind. Eng. Chem.,* **51** (1959) 60.
7. S.K. Aggarwal, S.A. Chidambar, V.D. Kavimandan, A.I. Almaula, P.M. Shah, A.R. Parab, V.L. Sant, H.C. Jain, M.V. Ramanaiah: *Radichim. Acta,* **27** (1980) 1.
8. S.K.Aggarwal and D.Alamelu: *Int. J. Nucl. Energy Science and Technology*, **1** (2005) 215.
9. D.Alamelu and S.K.Aggarwal: *J. of Alloys and Compounds,* **444-445** (2007) 652.
10. N.Trautmann, G.Passler, K.D.A.Wendt: *Anal. Bioanal. Chem.,* **378** (2004) 348.
11. C.Vockenhuber, I.Ahamd, R.Gosler, W.Kutschera, V. Liechtenstein, A.Priller, P.Steier, S.Winkler: *Int. J. Mass Spectrom.,* **223/224** (2003) 713.of
12. N.N.Mirashi, P.M.Shah and S.K.Aggarwal: *J. of Radioanal & Nucl. Chem.,* **275** (2008) 479.
13. M.V.Ramaniah, H.C.Jain, S.K.Aggarwal, S.A. Chitambar, V.D. Kavimandan, A.I. Almaula, P.M. Shah, A.R.P arab and V.L. Sant: *Nucl. Tech.,* **49** (1980) 121.

FEATURE ARTICLE

Genetic studies on human population residing in High Level Natural Radiation Areas of Kerala coast

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Abstract

For the past few decades, the monazite bearing coastal belt of Kerala in South West India is under investigation, to study the biological and health effects of natural chronic low dose exposure of background radiation, on human population residing in that area. The level of background radiation varies from >1mGy per year to 45 mGy per year and the areas with a dose level of ≤1.5 mGy per year are considered as Normal Level Natural Radiation Areas (NLNRAs), whereas areas having the background dose >1.5mGy per year are High Level Natural Radiation Areas (HLNRAs). The non-uniform distribution of radiation level in this coastal belt provides a unique opportunity to study in vivo dose response of biological parameters. A number of studies have been conducted in this area, including cytogenetic investigation on newborns and adults for chromosomal aberrations, monitoring the newborns for congenital malformations and genetic disorders, Health Audit Survey to find out prevalence of late onset diseases and DNA mutation rate of the families using hyper-variable markers such as mini- and microsatellites. In the present paper, the findings obtained from two recently published reports dealing with spontaneous frequency of micronuclei among newborns and telomere length of adult population from high and normal level radiation areas have been highlighted. The spontaneous frequency of micronuclei (MN) was estimated in 271 newborns, whereas telomere length was determined from 310 adults. Our data did not reveal any significant difference in HLNRA as compared to NLNRA in both the parameters studied. No dose response was observed. In conclusion, the elevated background radiation prevailing in Kerala coast has no significant effect on the induction of micronuclei in newborns and telomere length in adults, which is in agreement with other studies conducted so far. Using advanced molecular biological techniques, further studies are in progress, to understand the cellular and molecular response of human cells to low dose radiation exposure.

Introduction

Studies on biological and health effects of the human population living in High Level Natural Radiation Areas (HLNRAs) provide an important source of information on the effects of chronic low dose rate exposures to ionizing radiation. There are many areas in the world, where the natural background radiation level is high (sometimes 10 -100 times the normal levels) either due to high levels of radioactivity in soils, rocks and hot springs or due to high levels of indoor radon and its decay products. For instance, the level of background radiation is high in the hot springs at Ramsar (Iran) due to high Radium content and because of Thorium content of monazite containing sand in Yangjiang (China), Guarapari (Brazil) and the coastal belt of Kerala

in South West India. These areas give unique opportunity to study the effect of natural chronic low level radiation directly on human population at all stages of life.

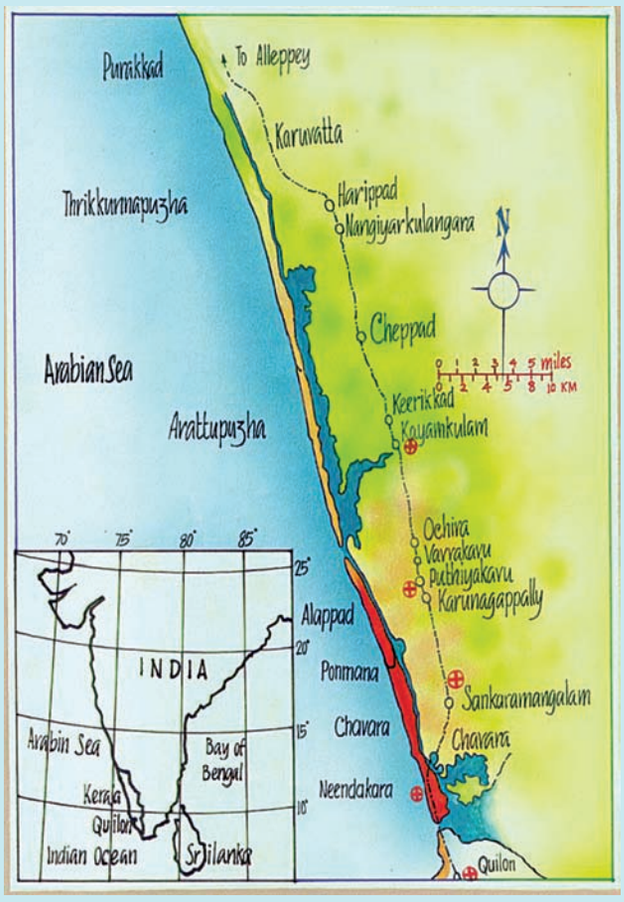

Fig. 1: Kerala coastal belt showing High Level Natural Radiation areas extending from Neendakara in south to Purrakad in north.

The monazite bearing coastal belt of Kerala is a strip of about 55kms, extending from Neendakara (Kollam district) in south to Purakkadu (Alapuzha district) in north (George et al. 1976). The radioactive component of this beach sand is monazite, which contains thorium (8-10%, highest in the World) and its radioactive daughter products. Due to non-uniform distribution of monazite in the beach sand, the level of background radiation in this area varies from <1.0 mGy to 45 mGy per year and in some areas it is as high as 70mGy per year. The per capita average dose received by the population residing in HLNRA is ~ 4mGy/year (Bharatwal and Vaze, 1958, Sunta, 1993). The areas with a dose range of ≤1.50 mGy/year are considered as Normal Level Natural Radiation Areas (NLNRA), whereas dose range of >1.50mGy/year is considered as HLNRA. This area is densely populated which is approximately 1000 years old. It is a difficult task to delineate the effect of natural background radiation, if any, on humans as there are many confounding factors such as age, gender, habits, diet, life style etc. in a population. But this area is unique as compared to other HLNRAs of the world, due to a great deal of variation in the level of background dose exposures, which allows the study of dose response.

Studies conducted in the past

A number of studies have been undertaken in the past including genetic studies in wild rats based on skeletal and dental variants (Grunberg, 1964 ; Grunberg et al. 1966) and a demographic study covering 70,000 individuals, to find out reproductive parameters, infant mortality etc. between high and normal level radiation areas (Gopal-Ayengar et al. 1971). Since 1975, the Bio-medical Group, BARC has its field laboratory at Kollam [presently Low Level Radiation Research Laboratory (LLRRL)] in order to carry out detailed genetic and epidemiological survey of the entire population. Studies conducted in this area include cytogenetic investigations on adults and newborns for chromosomal aberrations (Cheriyan et al. 1999, Thampi et al. 2002, 2005),

screening of the newborns for congenital malformations (Jaikrishan et al. 1999, Thampi et al. 2005), house-to-house Health Audit Survey (Thampi et al. 2005) and DNA mutation rate in the families using mini and microsatellite markers (unpublished data).

Initially, chromosome aberration analysis was carried out on adults using peripheral blood lymphocytes. Dicentrics (chromosomes with two centromeres) are considered as indicators of radiation-induced damage. The frequency of dicentrics in HLNRA adults was not significantly different as compared to NLNRA. From 1986 to 1996, cytogenetic investigation was carried out on newborns to establish the frequency of chromosomal aberrations (such as dicentrics, translocations, inversions, rings, chromosome breaks, gaps, etc.) as well as constitutional anomalies (both structural and numerical). Umbilical cord blood samples were collected from four local Government hospitals and lymphocyte cultures were set up at LLRRL, Kollam, Kerala. Cells with well spread metaphase were analysed for chromosomal aberrations. The frequency of chromosomal aberrations was reported per 10,000 cells. The frequencies of dicentrics were 1.87± 0.14 in HLNRA and 1.88± 0.34 in NLNRA, which were not significantly different from each other. Similarly, the frequency of stable aberrations (translocations, inversions) had a frequency of 3.46 ± 0.34 in HLNRA as compared to 3.26 ± 0.45 in NLNRA, which were not significantly different from each other. No significant difference was observed in the frequency of unstable aberrations (fragments, minutes and rings) in HLNRA (2.29 ± 0.17) and NLNRA (2.88± 0.42). Dose related increase in the frequency of any type of chromosomal aberrations was not observed in these samples (Cheriyan et al. 1999 and Thampi et al, 2005). Karyotype analysis of 23, 844 newborns (8004 from NLNRA and 15,840 from HLNRA) revealed the overall incidence of karyotype anomalies to be 4.86 ± 0.45 per 1000 newborns (HLNRA: 4.80 ± 0.55; NLNRA: 5.00 ± 0.79). The data is comparable with the published UNSCEAR reports (UNSCEAR, 1993).

Screening of newborns in hospital-based studies is one of the major programmes in this area, in order to establish the frequency of various congenital malformations including Downs Syndrome. So far, our data based on approximately 1,00,000 newborns did not show any significant increase in the frequency of any type of congenital malformations in HLNRA as compared to NLNRA (Jaikrishan et al. 1999, Thampi et al. 2002, 2005). The overall incidence of still births was 0.51% and that of malformations was 2.03%. Our statistical analysis of malformations and still births showed dependence on maternal age, gravida status, ethnicity, gender of the newborn and consanguinity, but does not suggest any correlation with radiation levels. The frequency of Downs Syndrome is also similar in both the areas with an overall frequency of 1 in 1471. The relatively lower incidence of still birth, malformations, Downs Syndrome could be due to the fact that our study group having ~85% mothers from the younger age group of 20-29 years.

The Health Audit Survey was initiated in collaboration with the Department of Health and Social Welfare, Government of Kerala to find out the prevalence of late onset diseases such as diabetes, hypertension, asthma etc. and malformations. The study also collects information on socio-demograpy, life style and reproductive history of married women. All these basic data is collected with the help of anganwadi workers, who have good rapport and interaction with the inhabitants. So far, Health Audit Survey carried out on six panchayats revealed that the pattern of both birth defects and late onset diseases was similar in both the areas (Thampi et al. 2005).

In addition to the above studies conducted in the field laboratory at Kollam, molecular genetic studies were initiated in 1995 at Low Level Radiation Studies Section (LLRSS), Radiation Biology and Health Sciences Division, Bio-Medical Group, Mumbai. For that purpose, human genomic DNA was isolated from blood samples of over 200 families (Father, mother and child trio) residing in that area. Over 40 hypervariable DNA markers such as minisatellites (autosomal) and microsatellites (includes autosomal and Ychromosomal) were analysed, to determine heritable mutation rate. No increase in the mutation rate at autosomal as well as Y-chromosomal markers was observed in HLNRA as compared to NLNRA. The data has not shown any dose response, suggesting that mutation rate at the mutational hot spots of human genome has not been affected due to natural chronic low dose exposure to radiation (unpublished data).

In the present article, the findings of two recently published reports in this study area have been discussed in detail. In one of the studies, we have determined and compared the spontaneous frequency of micronuclei among the newborns from HLNRA and NLNRA in order to assess the effect of elevated level of background radiation, if any, on the induction of micronuclei (Das and Karuppasamy, 2009). In the other study, telomere length was determined from HLNRA and NLNRA adults to find out the effect of natural background radiation, if any, on telomere length (Das et al. 2009).

I. Spontaneous frequency of micronuclei in newborns (published in IJRB, 2009):

The most frequently used biomarkers to study radiation-induced damage both *in vitro* and *in vivo* are chromosome aberration analysis in metaphase spreads or scoring micronuclei (MN) in binucleated (BN) cells. Micronucleus is a small nucleus present in the cell in addition to the main nucleus, indicating the presence of chromosomal damage. It may arise from a whole lagging chromosome (aneugenic event leading to chromosome loss) or an acentric chromosome fragment detaching from a chromosome after breakage (clastogenic event) which do not integrate in the daughter nuclei. Cytochalasin-Blocked Micronucleus (CBMN) assay is one of the most reliable and precise methods for assessing radiation-induced chromosome damage (Fenech & Morley 1985, 1986). It is also used as a biomarker to evaluate the utero effects to environmental exposures on umbilical cord blood samples (Milosevic-Djordjevic et al. 2007). In order to determine and compare the spontaneous frequency of MN among the newborns, cord blood samples were collected from 271 newborns (61 from NLNRA and 210 from HLNRA), born to mothers aged between 17 and 37 years (mean maternal age: 24.08 $\pm$ 4.23 years). Analysis of micronuclei was restricted to Cytochalasin Blocked binucleated (BN) cells only and the frequency of micronuclei was calculated per 1000 BN cells.

The frequency of BN cells with MN was observed to be 1.17 $\pm$ 0.04, in HLNRA newborns as compared to 1.23 $\pm$ 0.07 in NLNRA. These values are not statistically significant ($p>0.2$). In order to find out any dose-related changes in chromosomal/ DNA damage if any, we have categorized the samples into six different dose groups (NLNRA : d"1.5 mGy/year and five dose groups of HLNRA: 1.51 to 3.00 mGy/year, 3.01 to 6.0 mGy/year, 6.01 to 12.00 mGy/year, 12.01 to 18.00mGy/year and 18.00 to 28.12 mGy/ year. Odds ratios (OR) and confidence intervals (CI) have been calculated, to find out statistical significance, if any, in the mean MN frequency among the newborns from various dose groups with respect to control. It did not reveal any significant difference ($P>0.05$).

As shown in the Fig. 3, MN frequency did not show any increasing trend with respect to the dose groups studied. The baseline frequency of micronuclei in HLNRA newborns is not statistically different from NLNRA newborns, suggesting that, elevated level of naturally occurring radiation has

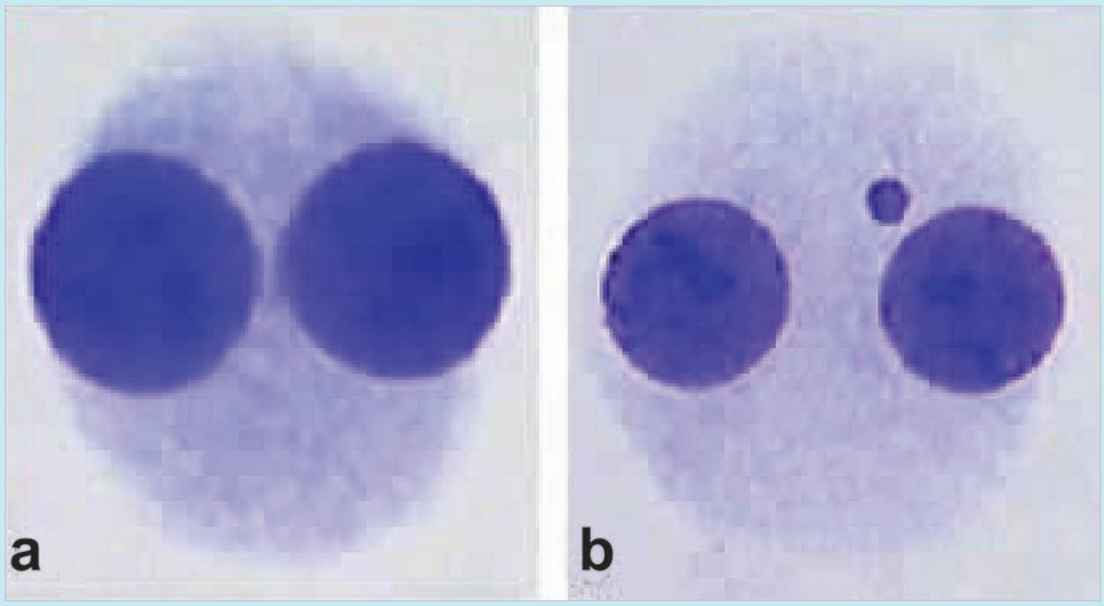

Fig. 2 : (a) Binucleated cell (b) Binucleated cell with a micronucleus

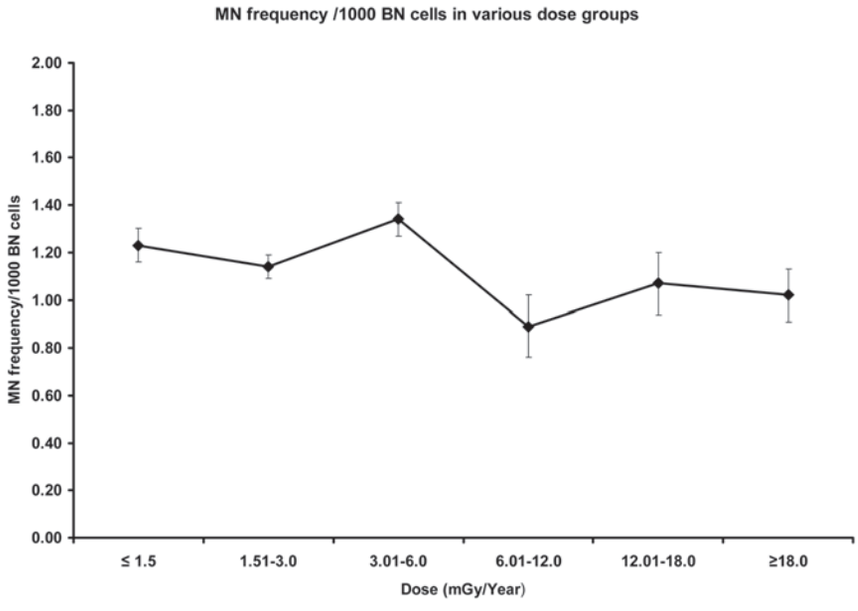

Fig. 3: The line graph represents the frequency of micronuclei/1000 BN cells in six different background dose groups [d"1.5mGy/year (N=61), 1.51-3.0 mGy/year (N=90), 3.01-6.0 mGy/year (N=69), 6.01-12.0 mGy/year (N=14), 12.01-18.0 mGy/year (N=16) and 18.01-28.1 mGY/year (N=21)]. N = The number of individuals studied in each dose group.Each point represents the mean frequency of micronuclei per 1000 BN cells for that particular dose group. For each point, the error bars indicate the standard error of the mean (SEM).

no significant effect on the induction of micronuclei frequency among the newborns. There is a maternal age-dependent increase, though not significant, in the frequency of MN among HLNRA and NLNRA newborns, except the age group >30 years (study samples consisted of ~85% mothers from the age group < 30 years). The MN frequency observed in females did not show any statistically significant difference as compared to males. The data was also in agreement with other reported studies.

In conclusion, due to elevated level of background radiation, there is no increase in the frequency of MN in HLNRA of Kerala coast as compared to the adjacent control area. Moreover, lower levels of micronuclei frequency observed among the newborns of HLNRA of Kerala coast could be indicative of adaptive response. The decreased frequency of MN at dose group of 6.01-12.00 mGy/year supports the phenomenon of hormesis, which needs to be explored further. To our knowledge, this is the first report which estimates the spontaneous frequency of MN among the newborns using cord blood samples from a natural high background radiation area.

II. Telomere length in adults (published in PLoS ONE, 2009):

The long, thread-like DNA molecules that carry our genes are packed into chromosomes and telomeres are the caps on their ends. There is a unique DNA sequence (TTAGGG)n in telomeres, which protects the chromosomes from degradation. Telomere length gets reduced with each round of cell division in normal human somatic tissues. It also shows inter-individual variation. Shortening of telomere length has been reported to be associated with aging, stress, diabetes, hypertension, obesity, dementia and many other age-related diseases.

So far, using cell lines, few *in vitro* experiments have shown telomere length variation in response to ionizing radiation. Till date, no *in vivo* data on

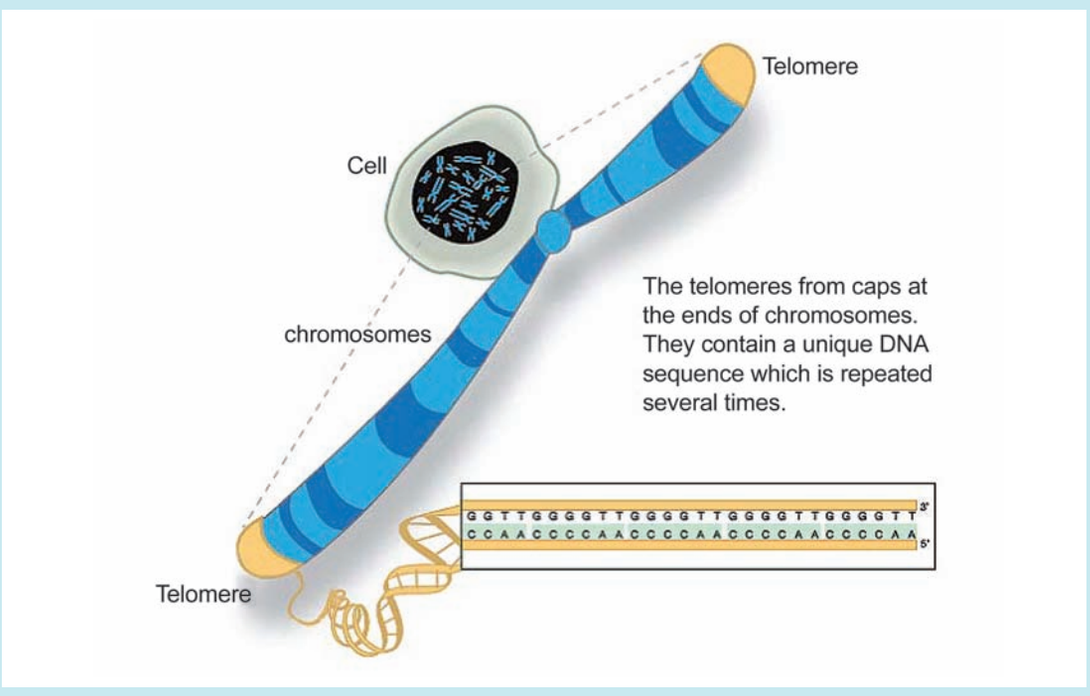

Fig. 4: Human chromosome showing telomere at the ends.

telomere length in human population exposed to elevated level of natural background radiation is available. We have determined telomere length in peripheral blood lymphocytes of 310 random, normal and healthy, age matched adult individuals (141 males and 169 females) of which 233 individuals were from HLNRA and 77 individuals were from NLNRA [mean maternal age in HLNRA; 26.24 ± 4.52 years and 25.69 ± 4.38 years], respectively. Genomic DNA was isolated from venous blood samples and telomere length was determined by using real time quantitative polymerase chain reaction. This method measures the factor by which the ratio of telomere repeat copy number to single gene copy number differs between a sample and that of a reference DNA sample. PCR amplification was achieved using telomere (T) and single copy gene, 36B4 (encodes acidic ribosomal phosphoprotein) primers(S) which serves as a quantitative control. The mean telomere repeat gene sequence (T) to a reference single copy gene (S) is represented as T/S ratio which is calculated to determine the telomere length.

The samples from HLNRA were stratified into four different dose groups on the basis of natural background dose level, which were as follows: ≤1.50mGy per year (NLNRA) and three HLNRA dose groups such as (1.51-3.00, 3.01-5.00 and >5.00 mGy per year). Telomere length was correlated with background dose groups. As shown in Fig.4, the telomere length observed in HLNRA adults was not significantly different from NLNRA. Our data did not show any dose dependent changes in the length of the telomere.

Inter-individual variation in the length of the telomere was observed among the samples. Longer telomere length is an indication of lesser

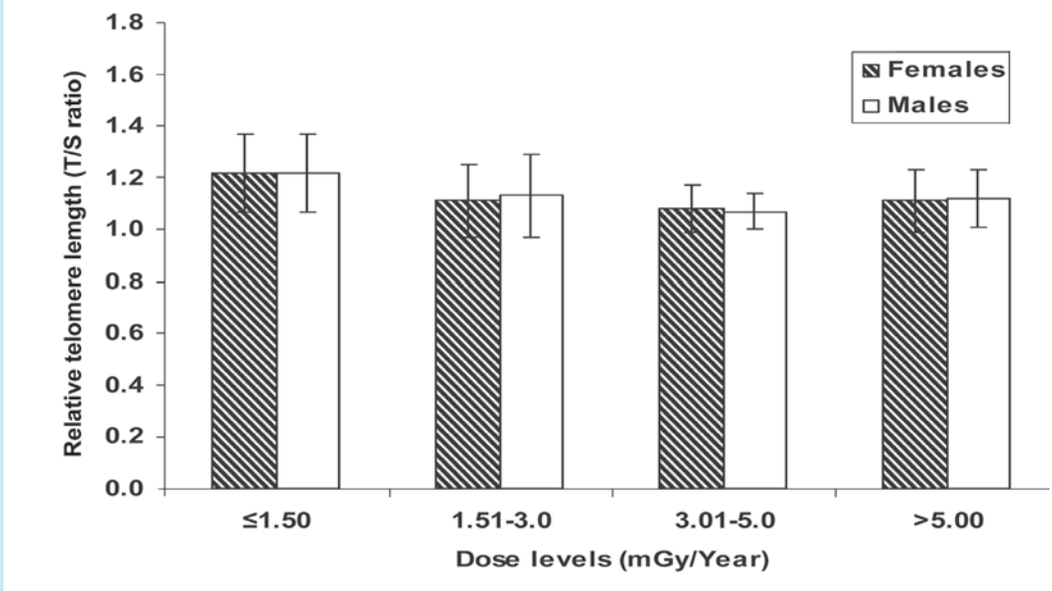

Fig. 5: Telomere length among male and female adults with respect to various background dose levels. [(d"1.50 mGy/year : 34 males + 43 females, 1.51-3.0 mGy/year: 67 males + 80 females, 3.01-5.0 mGy/year : 23 males + 27 females, >5.00 mGy/year : 17 males +19 females)].

DNA damage at the telomeric ends. Data analysis was done to compare the individuals from each group with shorter telomere length (defined as relative T/S ratio below the median) versus longer telomere length (defined as relative T/S ratio above the median). Logistic regression was used to compute the odds ratios (OR) and 95% confidence intervals (CI), for individuals with shorter and longer telomere lengths in all the three HLNRA dose groups (> 1.5mGy per year) with respect to the NLNRA (dose group ≤1.5 mGy per year), where odds ratio was taken as 1.00. The OR values found in various dose groups in HLNRA were not statistically different as compared to NLNRA, indicating that, elevated level of natural background radiation has no significant effect on telomere length in high background radiation areas of Kerala coast. There were no significant differences in telomere length between male and female adults in both the areas. Association of telomere length with aging has significant implications for human health. Data was correlated with age and indicated a negative correlation between the telomere length and the age in both NLNRA and HLNRA, with the limited sample size which is relatively from a younger age group.

In conclusion, the elevated level of natural background radiation has no significant effect on telomere length among the adult population residing in HLNRAs of Kerala coast. This could be an indication of better repair capacity of HLNRA individuals at telomeric ends. To our knowledge, this is the first *in vivo* study, addressing the dose response relationship between natural chronic background radiation and telomere length in human peripheral blood mononuclear cells. Telomere length attrition between males and females, association of telomere length and age, telomere length loss during different stages of life and contributions from genetic and environmental factors give rise to the large amount of variation of telomere length in a population. Efforts are in progress to collect data from older population and from each of the background dose groups, in order to provide a clearer picture of the association between telomere length, age and natural background radiation.

Future prospects

From this data, it is evident that it would be interesting and essential to understand the molecular and cellular mechanism occuring in human cells, in response to natural background radiation. It is worth pursuing the use of newer molecular biology techniques, in order to throw new light on this area of research. It might provide a deeper understanding of the phenomenon such as adaptive response, hormesis etc.. Perhaps, research in Kerala high background radiation area will contribute substantially towards Linear Non threshold (LNT) hypothesis, a well debated topic in radiation biology. At present, other ongoing studies in this area are Health Audit Survey covering 12 panchayats, DNA damage and repair studies using comet assay in adult population, adaptive response study using cytogenetic parameters like chromosomal aberration and micronuclei, global gene expression profile using microarray technology and structural or copy number variation study on selected malformations.

Contributors

Presently this work is being carried out under the supervision of Dr. M. Seshadri, Head, Radiation Biology and Health Sciences Division. The team members include researchers from LLRRL, Kollam, Kerala and LLRSS, RB&HSD, Bio-Medical Group, Trombay, Mumbai. [Mr. V. D. Cheriyan, Dr Birajalaxmi Das, Dr. G. Jaikrishan, Dr. Anu Ghosh, Mr. E.N. Ramachandran, Mr. C. V. Karuppasamy, Mrs. Shazia Ahmad, Mr. D.C. Soren, Dr. Sudheer K. R, Mr. P.K.M. Koya, Dr. Vivek Kumar P.R, Mr. Vinay Jain, Mr. V. J. Andrews, Mr. V. Anil Kumar and Mrs. Divyalakshmi Saini.

References:

1. George KP, Sundaram K, Mistry KB, Gopal-Ayengar AR (1976) Investigations on human populations residing in high background radiation areas of Kerala and adjoining regions. Reprint from ''Biological and environmental effects of low level radiation." Vol. II, IAEA, Vienna, SM - 202/703:325–329.

2. Bharatwal DS and Vaze GH (1958) Radiation dose measurements in the monazite areas of Kerala state in India. In: proceedings of the 2nd UN International conference on Peaceful uses of Atomic energy. United Nations, NewYork 23:156.

3. Sunta CM (1993) A review of the studies of high background areas of the S-W coast of India. In: Sohrabi M, Ahmed JU, Durani SA, editors. Proceedings of the International conference on high levels of natural radiation, Atomic Energy Organization of Iran, Tehran.

4. Grunberg H 1964. Genetic research in an area og high natural radioactivity in south India. *Nature* 204, 222-224.

5. Grunberg H, Bains GS., Berry RJ., Riles L, Smith CAB and Weiss RA (1966) A search for genetic effects of High Natural Radioactivity in South India. Report SRS 307. Medical research Council, Her Majesty's Stationery Office, London.

6. Gopal-Ayengar AR, Sundaram K, Mistry KB, Sunta CM, Nambi KSV, Kathuria SP, Basu AS and David M (1971) Evaluation of the long term effects of high background radiation on selected population groups of Kerala coast. In Proceedings of the IV International Conference on Peaceful uses of Atomic energy, Vol II. Pp. 31-61. United Nations, New York.

7. Cheriyan VD, Kurien CJ, Das Birajalaxmi, Ramachandran EN, Karuppasamy CV, Thampi MV, George KP, Kesavan PC, Koya PKM, Chauhan PS (1999) Genetic monitoring of the human population from high-level natural radiation areas of Kerala on the Southwest coast of India. II. Incidence of numerical and structural chromosomal aberrations in the lymphocytes of newborns. *Radiation Research* 152:S154–S158.

8. Thampi, MV, Cheriyan VD, Kurien CJ, Ramachandran EN, Karuppasamy CV, Koya PKM, Das Birajalaxmi, George KP, Rajan VK and Chauhan PS (2002) " Cytogenetic studies in the high level natural radiation areas of Kerala. International Congress Series, 1225:207-211.

9. Thampi MV, Cheriyan VD, Jaikrishan G, Das B, Kurien CJ, Ramachandran, EN, Karuppasamy CV, Ravikumar B, Soren D, Vijayan Usha, Koya PKM, Andrews VJ, Anilkumar V, Mitra A, Madhusoodhanan M, Aravindan KV, Seshadri M (2005) Investigations on the health effects of human population residing in the high level natural radiation areas in Kerala in the southwest coast of India. International Congress Series 1276 : 8–12.

10. Jaikrishan G, Andrews VJ, Thampi MV, Koya PKM, Rajan VK, Chauhan PS (1999) Genetic monitoring of the human population from high-level natural radiation areas of Kerala on the Southwest coast of India. I. Prevalence of congenital malformations in newborns. *Radiation Research* 152 : S149–153.

11. United Nations Scientific Committee on the Effects of Atomic Radiations (UNSCEAR) (1993) Sources, Effects and risks of Ionizing Radiation. Report to the General Assembly, United Nations, New York.

12. Das Birajalaxmi and Karuppasamy CV (2009) Spontaneous frequency of micronuclei among the newborns from high level natural radiation areas of Kerala in the southwest coast of India. *International Journal of Radiation Biology* 85 (3) : 272–280.

13. Das Birajalaxmi, Divyalakshmi Saini and M. Seshadri. 2009. Telomere length in human adults and high level natural background radiation. *PloS ONE* 4(12): e8440.

14. Fenech M and Morley AA 1985. Measurement of micronuclei in lymphocytes, *Mutation Research* 147:29 - 36.

15. Fenech M and Morley AA. 1986. Cytokinesis block micronucleus method in human lymphocytes:effect of in vivo ageing and low dose X- irradiation. *Mutation Research* 161:193 - 198.

16. Milosevic-Djordjevic O, Grujicic D, Arsenijevic S, Brkic M, Ugrinovic S and Marinkovic D. 2007. Micronuclei in cord blood lymphocytes as a biomarker of transplacental exposure to environmental pollutants. *Tohoku Journal of Experimental Medicine* 213: 231-239.

Forthcoming Conference

International Conference on Physics of Emerging Functional Materials (PEFM-2010)

The above conference sponsored by BRNS, will be held at BARC, Mumbai, between Sep. 22-24, 2010. The conference focuses on the physics of emerging functional materials of 21st century, including organic semiconductors (both molecular and polymeric), materials at nanoscale, spintronic materials, novel superconducting and magnetic materials, soft matter etc. Contributed papers for poster presentation are invited on the following topics:

1. Organic semiconductors: Charge transport; photovoltaic, lighting and field effect transistors; flexible devices; molecular electronics 2. Soft matter: liquids, colloids, foams, polymers 3. Electronic and lattice phenomena in crystalline solids: semi- and superconductivity, magnetism, 4. Ferroelectricity, multiferroics, heavy fermions etc. 5. Non-crystalline solids: glass and ceramics, granular materials, quasicrystals 6. Biophysics 7. Experimental techniques: neutron, synchrotron, x-rays, positron, ions as probes 8. • Low dimensional structures: quantum dots, clusters, nanostructures, thin films. The template and guidelines for the preparation of manuscript can be downloaded from the AIP
website: http://proceedings.aip.org

Important Dates

Paper submission :	July 15, 2010.
Acceptance notification :	August 1, 2010
Registration form submission :	August 10, 2010
Accommodation form submission :	August 10, 2010

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FEATURE ARTICLE

Physics-of-Failure Based Approach for Predicting Life and Reliability of Electronics Components

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Abstract

Enhancing functional performance while at the same time continuing with the miniaturization of electronic systems are the main drivers for electronic industries world over. The phenomenal growth of VLSIs and embedded systems is testimony to these developments. Development of complex embedded systems using components like FPGA, CPLD, etc, where not only the transistor densities but current densities of interconnects have almost been optimized to the limits, pose reliability issues that need to be addressed. Even though the material properties, design and construction features are better understood than ever before, further research is required to understand root causes of failure so that failure in the field conditions can be further minimized.

The traditional method of reliability prediction, Like MIL-217 approach, have some inherent limitations which include, a) it does not allow simulations with projected component load profiles, b) no provisions to assess the root cause(s) of component failure, c) basis and science behind the considerations of base failure rate and other modifying factors are not clear.

The physics-of-failure approach is based on first principles of science and technology and provides the insight into not only life and reliability aspects of the component, but also provides details about the various degradation mechanism(s) and thereby improved understand of the associated root cause(s) of the failure. This approach extends Accelerated Life Testing philosophy to investigate the basic failure mechanism. The role of statistics in this methodology is to predict the uncertainty in the estimates of life and reliability. This paper brings out the salient feature of this approach.

1. Introduction

In the last more than four decades, electronics systems and their applications have revolutionised the industrial and domestic scene. It all started with application of vacuum tube-based systems in fifties and solid state systems in sixties to the present VLSI (Very Large Scale Integration) based digital systems. Even though the embedded technology has entered the market and finding wider applications; there are reliability issues primarily due to higher current densities of the order of 106 A/cm^2 in the interconnects and new modes of failure viz, Electromigration, gate oxide breakdown and hot carrier effects. These developments posed a challenge to reliability specialists to devise new methods for reliability prediction which should be effective in estimating not only the likelihood of the failure but also provide adequate understanding of associated failure mechanisms, such that, the

re-engineering / root cause analysis can be done to avoid recurrence of such failures.

Reliability of a component, system or structure has two components. The first one is probabilistic, where the likelihood of failure and uncertainty in parameters is estimated, while the second one is deterministic and deals with finding various modes and causes of failure. These two aspects together make reliability prediction more accurate and complete.

Traditionally, the reliability estimates for electronics components are obtained by one of the three approaches, viz., one, using standard handbook; two, statistical analysis of operating & maintenance data and third, by performing life testing experiments. Generally, the reliability of electronics components is estimated using standard handbooks, the most prominent among these include MIL-HDBK-217 (American Military Handbook 217), TELCORDIA (or Bellcore, developed for Telecommunication applications), PRISM (Developed by Reliability Analysis Center, USA for US Air force), etc. These handbooks are based on data and model derived from simulated engineering tests of the individual components. Amongst these the American Military Handbook 217 is being most widely used for predicting reliability of electronic components [1]. In MIL-217 approach the individual component failure rate is estimated using the base failure rate of the component. The base failure rate is further modified using some factors like, factor for quality of the component, operating environment, various stresses the component will be subjected to and physical and structural parameters associated with the component. The second approach for reliability estimation involves statistical analysis of the operational and maintenance experience data collected from plant records. One more approach that is used for assessing the life / reliability of the component is through accelerated life testing of the components. It is a well established fact, that stress has influence on the life and reliability of the component. As the stress, which may include operating stress or the environmental stress, increases; the failure rate also increases. This principle forms the basic tenet of the life prediction through accelerated life testing methods.

The MIL-217 approach is most widely used while the plant specific statistical modelling and Life testing methods have limited applications. The major limitation of the MIL-217 approach includes, a) it provides assessment of only one aspect of reliability, i.e. likelihood of the failure and cannot indicate basic failure mechanisms, b) relatively large uncertainties that are associated with various parameters and hence, in the final results; c) often this method tends to provide very optimistic estimates of reliability as it does not take into account the life cycle loads particularly modelling of wearing phenomenon, d) MIL217 approach is based on constant failure rate assumptions which may not reflect the true life cycle failure trends, and e) no reference to the basic material properties or constructional features for predicting the reliability, f) it is not effective in predicting reliability of new components, like, embedded electronics, FPGA / CPLD, or new design of conventional components like control connectors, etc.

2. The Component Life Cycle

Reliability prediction includes both the likelihood estimates for Mean Time To Failure and the competing root causes of the failure. Hence, it is important that the life cycle model should address both probabilistic and deterministic aspects of component life cycle. Probabilistic aspect is required to predict the life with acceptable level of uncertainty and deterministic approach to analyze the competing failure mechanisms and identify the dominant failure mechanism that limits the functional capability of the component. Fig. 1 can be interpreted as modified form of traditional bath tub curve depicting three regions, viz, early failure, useful life and ageing end of life along with the competing failure mechanisms.

3. Competing Failure Mechanisms

As shown in Fig. 1, there could be more than one failure mechanism associated for a given mode of failure. As shown, the failure of type one could be due to failure mechanism 1a or 1b etc. Similarly, for other modes of component failure can also have more than one failure mechanisms. For example, consider life testing of electrical connectors. In an electrical connector the increase in contact resistance beyond threshold can be considered as failure criteria.

The mechanism for increase in contact resistance could be due to deposition of oxide layer due to environmental corrosion, particularly under the influence of temperature and humidity. The mechanical relaxation of connectors pins due to prolonged usage may also contribute to increase in contact resistance. Hence, it is important to understand the root cause of each failure and identify amongst the competing failure mechanisms the dominating failure mechanism(s). To model the competing failure mechanisms in life testing, it is important to create synergy of operational and environmental stresses, by defining appropriate acceleration factors for each stress. Testing / experiments performed under such condition will facilitate proper modelling of not only individual effect but also the net effect of the synergy, created by combining stresses on component life. The dominant failure mechanism plays decisive role in naming the life of the component. The physics-of-failure approach incorporates this theory of competing failure mechanisms, towards assessing the root cause of failure and mean time to failure (MTTF), as part of reliability assessment of not only electronic but mechanical and electrical components too.

4. The Approach

The physics-of-failure approach is based on the fundamental principles of science and engineering.

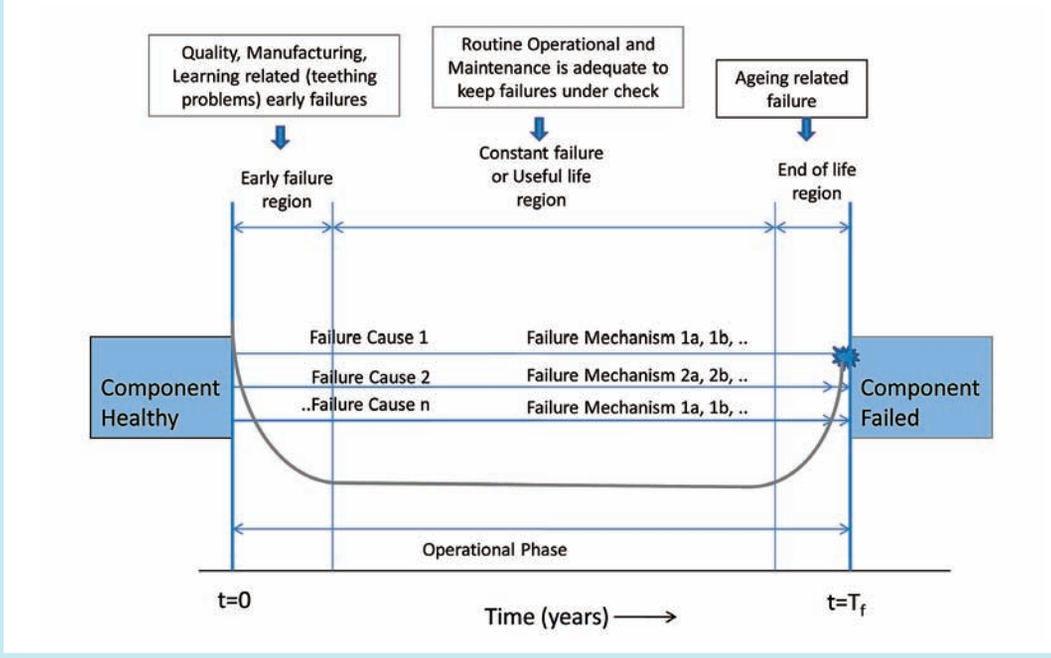

Fig. 1: Depiction of competing failure causes / mechanisms along the component life cycle

The associated component failure mechanisms are evaluated, considering basic phenomenon involved in degradation / failure of components. These models recreate the life of the component with operating stresses and load profiles. The existing physics-of-failure (PoF) for electronics components in general and embedded systems in particular, is becoming the most sought after approach, for reliability professions all over the world. This approach tends to overcome the limitations that are inherent in traditional approaches as it facilitates; a) estimation of life and root causes of failure, employing models that are based on first principles of science and engineering, which address deterministic as well as probabilistic applications, b) incorporation of operational load profiles of the component, c) evaluation of associated failure mechanisms and detailed modelling for identified dominant failure mechanisms, among more than one failure mechanisms, and d) modelling for wear out phenomenon as part of life cycle loads. Fig. 2 depicts the broad features of the procedure followed to implement (PoF) approach for predicting the reliability of electronics components and systems. The following sections deal with the major features of PoF:

4.1 Input Data

The first step is collection of input data which includes material properties, design and constructional features of the component, and operational load profiles, like number of cycles of operations, test and maintenance provisions, current and voltage characteristics, power supply quality, etc. It is also required to establish the failure criteria of the component, based on the operational and engineering requirements of the system.

4.2 Design of Experiment

For effective planning and execution, for characterizing the reliability attributes of the components, it is very important to optimize all

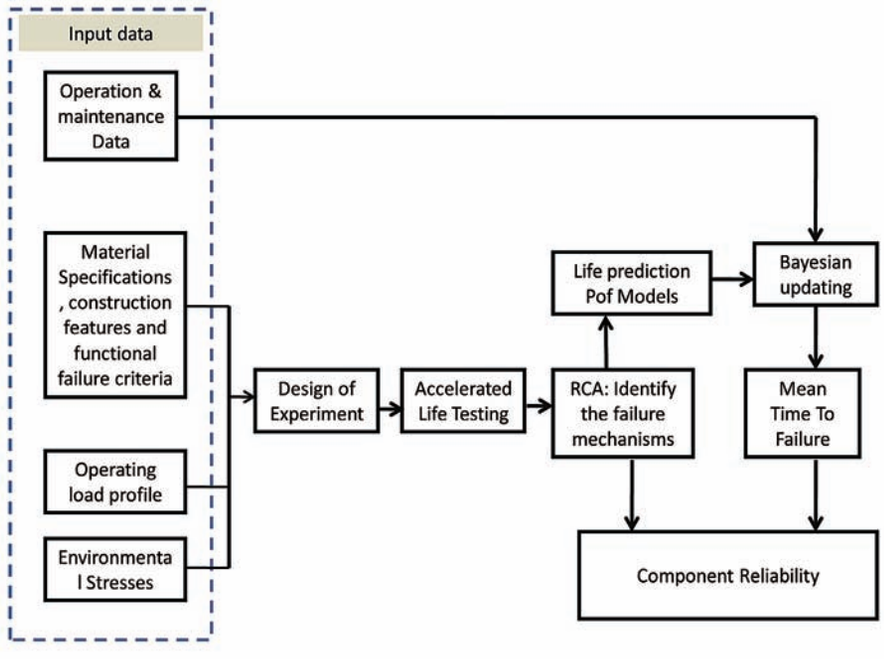

Fig. 2: Depiction of Physics failure approach for electronics component cycle

the test parameters. Published literature shows that most of the life testing experiments choose arbitrary sets of parameters, like sample size, level of tests, test duration, stress values like temperature, humidity, radiation, etc. The net outcome is the result of the test with relatively large uncertainty bound.

The design of experiment (DoE) approach enables estimation of these parameters based on sound statistical basis [2]. This approach ensures that selection of the test parameters is such that, it helps reveal the hidden failure mechanisms under considerations and at the same time not induce any failure mode that will not be encountered in the actual use condition.

As shown in Fig. 1, the parameters of the life testing experiments, such as number of samples to be tested, the stress levels the components are subjected to (Maximum temperature or humidity level at various stress levels), operational stress levels like current and voltage levels and other features like number of operations to be performed on the component during the test (like actuation of relays or make and break operation for connectors). Once the parameters of the experiments are worked out, the component is subjected to accelerated life testing in life test chambers.

4.3 Accelerated Life Testing

The influence of stress in reducing the life of the component, forms the basic principle of accelerated life testing of components or systems. Fig. 3 depicts how stress vs life relationship is utilized, for predicting the life of the component at the working stress level. Often it is required to design the electronic circuit, to monitor and log the test parameters in on-line mode. For example, if the contact resistance of the control contacts forms the failure criteria for the component, then the circuit is designed to monitor the contact resistance in on-line mode, with an alarm and provision for recording, such that, these criteria can be monitored and recorded. Provision of trip on the chambers power supply and alarm to alert the operator, form part of the preparation of accelerated testing.

As shown in Fig. 3, the component was subjected to two stress levels. The applicable probability distribution is determined using the test data as input to the conventional statistical methods, like probability plotting (for approximations), $\div^2$ (Chi-square) method, or any other method that the analyst feels adequate, for interpolation of the life test results to use stress level. The research on life test data modelling and analysis shows, that the modelling of data using Weibull distribution, provides an effective and useful way to interpret the life test data. The estimates of shape parameter β, in Weibull distribution, while on one hand provide information on applicable distribution; the Characteristic life parameter α on the other hand, provides the estimate of characteristic life of the component. The next is Interpolation of this data to estimate the life of the component at use stress level as shown in Fig. 3.

The accelerated test also provides the information on degradation of the components and its constituting part and material. The root cause analysis is performed on the component, to understand the underlying degradation mechanism(s).

4.4 Root cause analysis

The cause-effect analysis based on logical and chronological reasoning of the successive antecedents, associated with any event at any point of time, forms the basic tenet of root cause analysis approach. This approach assumes, that every event that is being investigated has roots, that if properly addressed, can avoid the recurrence of the event. The investigation of component failure is carried out at two levels. One at system level where a systematic analysis is carried out employing

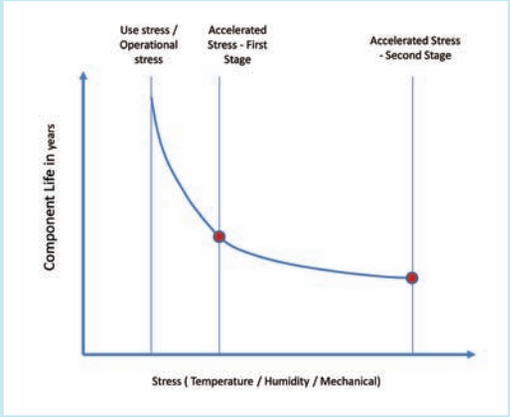

Fig. 3: Reprensentation of Stress Vs Life relationship

various logic models, like logic tree, cause-effect diagram, what-if analysis, binary decision diagram, etc. to arrive at the basic causes of failure. These causes may include, human error, component failure, or procedural failure which is subset of institutional failures, etc. However, when the root cause of failure indicates that the basic cause of the system failure is component failure; further analysis is required as to why the component failed. This is where the role of PoF approach comes into play.

4.5 Pof Models

The salient features of physics-of-failure approach have been discussed in respect of semiconductor based microelectronics devices. There are three basic degradation mechanisms for semiconductor devices, viz., Electromigration, Gate–oxide breakdown and Hot carrier effect, mostly discussed as hot carrier injection [3]. The following section will bring out in brief, the role of deterministic and statistical model, in prediction the life / reliability for respective failure mechanism.

4.5.1 Electromigration

Exhaustive research has documented on physics of failure, involving EM process. Electro-migration involves migration of metal atoms in interconnect, through which large dc current densities pass. The factors responsible for EM include, grain structure, grain texture, interface structure, stresses, film composition, physics of voids nucleation and growth, thermal and current density dependence, etc. [4]. The model proposed by Black [5] shows the dependence of median life on temperature, T and current density, J, as follows;

$$t_{50} = \frac{A}{J} Exp\left(\frac{E_a}{kT}\right)$$

Where A is a material process dependent constant and E_a is activation energy of the diffusion process.

The momentum transfer between electron and metal atom, forms the governing consideration in understanding the physics-of failure of interconnects. The metal atoms get activated by the electron current called 'electron-wind'. The positively ionized metal atoms move against the electron-wind force. The net result is the movement of vacancies and interstitials. The vacancies form voids or micro cracks and interstitials form hillocks. Further the creation of voids results in reduction in cross-sectional area and thereby increases circuit resistance and current density at the affected locations. The synergy of increase in current and temperature increases EM effect. This positive feedback cycle can result into thermal runaway and catastrophic failure. Apart from the semiconductor material, the microstructure of the interconnect also dictates / governs the Electromigration process. In this respect, the grain boundaries play a vital role in forming potential defect sites and thereby conduit for electron flow. Hence, the challenge lies in working out a criterion or model that enables optimization of electron current density, for a given circuit configuration.
The quantum theory in respect of electron transport in a metal shows, that the ion current depends on the effective charge on the ions, the density of the ion available for transport, the ion mobility, and the electric field. Based on the quantum theory, the ion current density is given by the following

model as:

$$J = (eN)(C_i'\rho_e - 1)\left(\frac{eD}{kT}\right)E$$

Where J : the ion current, N : density of ion available for transport, E : the electric field, ρ_e : the electron resistivity, C_i : proportionality constant, T : temperature and k: Boltzmann's constant. There are other physical affects that might accelerate the net ion currents, like temperature gradient, stress in the conducting strip, material structure in homogeneities, etc. which further result in the formation of voids and consequent defects. There is a reasonably good understanding of effect of these factors, on microchip reliability.

4.5.2 Hot Carrier Degradation

When either 'electron' or a 'hole' under certain conditions gains kinetic energy (more than 3.3 eV for SiO_2 dielectric) in semiconductor devices, such that it overcomes a potential barrier, it is referred to as 'hot carrier'. Hot carrier injection phenomenon is associated with MOSFET devices where the hot carrier is injected from the silicon substrate to the gate dielectric [6]. The presence of mobile hot carrier in oxides induces various physical damage processes, that degrade the device performance characteristics and pose critical reliability issues and are hence, referred to as 'hot carrier degradation'. Even though extensive research is being carried out to understand this degradation mechanism, the physics behind this degradation mechanism is not as well understood as Electromigration. Based on the 'lucky' electron approach (supply of opportune electron to be available as hot carrier) the device life time can be computed from the following model [7].

$$\tau^{-1} = \frac{B}{T_c}\int_0^{T_c} I_D\left(\frac{I_{Sub}}{I_D}\right)^m dt,$$

Where t is the device life time, T_c: full cycle time, I_{sub}: Substrate current, I_D; drain current; $m=\phi_b/\phi_i$ (ϕ_b = Si-SiO_2 energy barrier and ϕ_i = electron energy for ionization impact); B= constant.

There are many empirical models for estimation of device life time, however, the degradation model which is straightforward and simple proposed by Takeda [8] is as follows:

$$t \propto I_{sub}^{m}$$

Where the value of m lies between 3.2 and 3.4.

4.5.3 Time-Dependent Dielectric Breakdown

This degradation involves phenomenon of leakage current and finally leads to short circuits due to failure of transistor gates. The degradation mechanism involves creation of charge traps within the gate di-electrics, diminishing the potential barrier. The understanding of trap generation mechanism is the key, to evaluating oxide degradation. There are many models given in literature to estimate the 'time to breakdown' (T_{BD}) of oxide layer, however, the one which is commonly employed is 'anode hole injection' (AHI) model [9].

$$T_{BD} = \tau_0(T)\exp\left(\frac{G(T)}{\varepsilon_{ox}}\right)$$

Where, ε'_{oX} is electric field across the dielectric in MV/cm $\tau_o(T)$ and G(T) are temperature dependent constants and T; absolute temperature.

As discussed earlier, even though the physics behind the failure of semiconductor devices is now better understood, in each of the failure mechanisms, the role of statistical methods is still relevant in estimating the time to failure. However, better estimates can be obtained, by conducting the accelerated life tests / experiments, to narrow down the uncertainty band.

4.5.4 Statistical data Modelling

The modelling of data is crucial to the quality and

accuracy of the results of the analysis. The traditional approach involves either assuming a distribution for the set of data based on common practices or assessing the applicable distribution by conventional techniques like probability plotting or using the methods like Chi-square tests, etc. Taking a decision based on parameter evaluation like, employing the Weibull distribution selecting a particular distribution based on β-value (shape parameter) also forms a popular method for data trending. However, it is known that a single distribution alone may not be adequate represent to the entire set of data. The reason is that the data trend changes due to changes in operational or maintenance practices like, major modification in the system, major change in overall maintenance practices, or repair / replacement. There are models available which facilitate single change point, like poison process model etc. It is possible to accommodate single and more than one change points using models like hazard model. However, the prediction capability of these models is determined by their capability to accurately predict the change point location. Other limitations of these change point models is that, it is not possible to incorporate the effect of change in environment in the analysis and thereby the accuracy of prediction can always be argued. Segmented point process model for multiple change point has been developed and shown that accuracy of prediction can be improved significantly [10].

5. Conclusions

This article discusses the experience and observations on reliability and life prediction of components. Even though traditional approaches, like MIL-217 approach and Accelerated Testing form the mainstay of reliability prediction, it is a well recognized fact that these methods provide only one component of reliability i.e. failure rate estimates. Apart from this, it is also recognized that these approaches tend to provide, at times, optimistic estimates of life and reliability. One of the possible explanations is that, these approaches do not consider component load profile, which is an additional feature against which the life or reliability predicted should be carried out. The above observations corroborate with the insights available on reliability modelling of conventional components of electronic channels of nuclear plants and industrial systems. Hence, there is a need to focus R&D efforts on development of PoF based simulation approach, for reliability & life prediction of electronic components.

6. References

1. Military Handbook (1991). Reliability prediction of electronic equipment. MIL-HDBK-217F, Department of defense, Washington.
2. Condra, L.W., (1993). Reliability improvement with design of experiments. Marcel Decker, New York, 1993.
3. White Mark & Joseph B. Bernstein (2008) "Microelectronics reliability : Physics-of-Failure based modelling and Lifetime evaluation, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, JPL publication.
4. Pierce, D.G. and Brusius, P.G., (1997). Electromigration: A review," *Microelectron Reliability,* Vol. 37, pp1053-1072.
5. Black, J.R. (1967). "Mass transport of aluminium by moment exchange with conducting electrons", 6th Annual Int. Reliability physics Symposium, pp. 148-159.
6. http://en.wikipedia.org/wiki/Hot_Carrier_injection, 22/05/(2009).
7. Weber, W, (1998). Dynamic stress experiments for understanding hot carrier degradation phenomenon. *IEEE Transactions on Electronics Devices*, Vol. 35, pp1476-1486.

8. Takeda, E., Yong, C.Y., & Miura-Hamad (1995). Hot carrier effects in MOS devices, Academic devices. Academic Press.

9. Schuegraf and Hu, C., (1994). Hole injection SiO_2 breakdown model for very low voltage lifetime extrapolation. *IEEE Transactions on Electronics Devices,* Vol. 41, pp. 761-767.

10. Syansundar,A., Naikan, V.N.A. (2007) "Segmented point process models for maintained systems, *Int. Journal of reliability, quality and safety engineering,* 14, 5, 431-458.

New Publication

Thermodynamic properties of solids: experiment and modeling,
Edited by S. L. Chaplot, R. Mittal and N. Choudhury
(Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010)

ISBN 978-3-527-40812-2

Recent years have seen a growing interest in the field of thermodynamic properties of solids, due to the development of advanced experimental and modeling tools. Predicting structural phase transitions and thermodynamic properties, find important applications in condensed matter and materials science research as well as in interdisciplinary research, involving geophysics and earth sciences. The present book, with contributions from leading researchers around the world, is aimed at meeting the needs of academic and industrial researchers, graduate students and non-specialists working in these fields. The book covers various experimental and theoretical techniques relevant to the subject. The wide range of topics include:

- Thermodynamic Properties of Solids: Experiment and Modeling
- Optical Spectroscopy Methods and High-pressure-high-temperature Studies
- Inelastic Neutron Scattering, Lattice Dynamics, Computer Simulations and Thermodynamic Properties
- Phonon Spectroscopy using Inelastic X-ray Scattering
- Heat Capacity of Solids
- Diffraction and Thermal Expansion of Solids
- Electronic Structure and High-pressure Behaviour of Solids
- Ab-initio Lattice Dynamics and Thermodynamic Properties

Electricity From Footsteps

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Reactor Control Division, Electronics & Instrumentation Group
and
T.K. Basu
IPR, Gandhinagar

Introduction

Walking is the most common activity in day to day life. When a person walks, he loses energy to the road surface in the form of impact, vibration, sound etc, due to the transfer of his weight on to the road surface, through foot falls on the ground during every step. This energy can be tapped and converted in the usable form such as in electrical form.

In order to develop a technique to harness foot step energy, a foot step electricity generating device was developed in the Reactor Control Division, BARC. This device, if embedded in the footpath, can convert foot impact energy into electrical form. The working principle is simple. When a pedestrian steps on the top plate of the device, the plate will dip down slightly due to the weight of the pedestrian. The downward movement of the plate results in rotation of the shaft of an electrical alternator, fitted in the device, to produce electrical energy. The top plate reverts back to its original position due to negating springs provided in the device.

If such devices are embedded in places where there is continuous human traffic such as in city malls, railway platforms, city footpaths etc., the electricity generated from these devices can be used for street lights.

The device developed at the Reactor Control Division is shown in Fig. 1. The device was tested and it was demonstrated that the energy generated by this device can be stored in a 12 V lead acid battery. A 100 watt, 230 volt bulb was connected to the battery through an inverter. The device was operated by persons walking over to it. The bulb automatically lights up when the battery reaches its full voltage. The bulb remained lighted till the battery was exhausted. However, if there is continuous movement of pedestrians over the device, the bulb can be kept lighted continuously.

Fig. 1: Foot Step Electric Converter Device

Operation

The working of the Foot Stop Electric Converter (FSEC) is demonstrated in photographs in Fig. 2. The right side photograph shows the foot touching the top plate without applying weight. The left side photograph shows the foot when full weight of the body is transferred to the top plate. A 6 W, 12 V bulb connected to the output of the alternator glows, to indicate the electric output when foot load is applied. The unit is designed to generate full power pulse when actuated by a person weighing nearly 60 kg. An experimental plot of voltage vs time was generated, by using an oscilloscope. Using voltage data and the load (a resistor), a typical plot of power vs. time was generated. The plot is shown in Fig. 3.

Fig. 2: Operation of Foot Step Electric Converter
(a) After applying weight (Bulb lights up)
(b) Before applying weight (No light)

Energy storing

The power generated by the foot step generator can be stored in an energy storing device. The output of the generator was fed to a 12 V lead acid battery, through an ac-dc converter bridge. Initially, the battery was completely discharged. Then, the FSEC was operated by applying foot load and energy was stored in the battery. A 100 W, 230V bulb was connected to the battery through an inverter. The arrangement is shown in Fig. 4. The duration of lighting, the bulb for number of footsteps and corresponding energy stored, are given in Table 1.

The main objective of developing the FSEC was to demonstrate the technology of harnessing

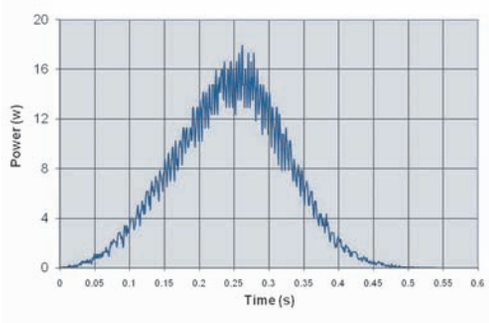

Fig. 3: Power vs. Time Plot
for Single Step

Table 1: Energy Storage by Foot Steps

No. of foot steps	Duration of lighting a 100 watt 230 Volt bulb (s)	Total energy (J)	Energy /step (J)
250	6	600	2.4
500	12	1200	2.4
750	18	1800	2.4
1000	25	2500	2.5

energy from human walk. However, multiple unit clusters may be more useful for producing useable power. A single cluster with 5 FSEC devices was developed for experimental purpose.

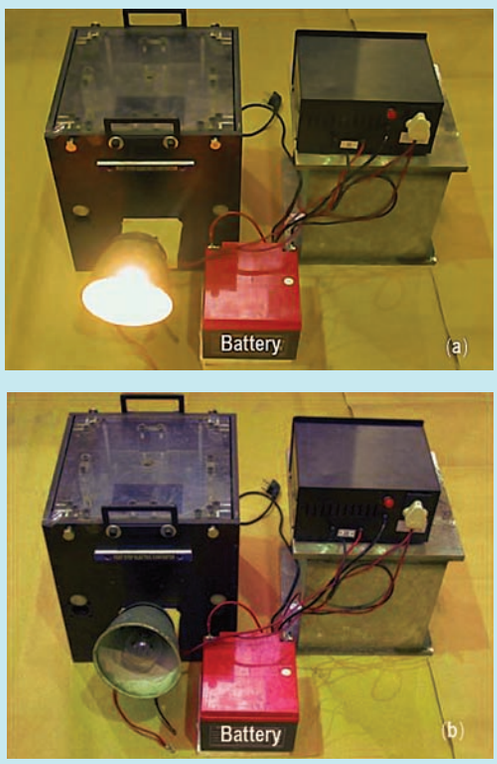

Fig. 4: Storing Device for Foot Step Electric Energy
(a) Bulb on (after charging battery)
(b) Bulb off (before charging battery)

Multi FSEC unit platform

A cluster of 5 FSEC devices mounted on a wheeled platform was developed. A view of the internal components of a typical FSEC device used in the cluster is shown in Fig. 5. The electrical output of all five FSEC devices is stored in 2 batteries provided in the platform. An electronic digital energy meter is fitted on the platform. The energy generated in each of the five FSEC units fitted in the mobile platform is integrated and displayed on the energy meter. The energy meter shows a total integrated value of electrical energy in KJ generated in all FSECs fitted in the platform.

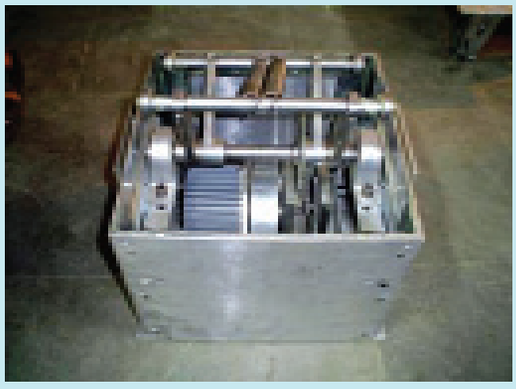

Fig. 5: Internal View of the FSEC Mechanism

The platform is shown in Fig. 6. The platform is provided castor wheels, and can be placed at any public place where there is continuous movement of people. This unit is designed for persons weighing 50 Kg and above. However, persons below 50 kg weight can also operate but the power produced will be low. The unit is fitted with two 12 V, 26 AH lead acid batteries for storing the output energy from this unit. Also, an inverter is provided to convert 12 V DC from battery to 230 V AC supply for general use.

When a person walks over to the platform, the reading on the energy meter was observed to be incremented by 3-5 J per step, depending on the weight of the person. The output may be further increased by increasing the efficiency of the FSEC device. As millions of people are on the move in cities, significant amount of electricity can be generated by installing these devices at places where public walk through.

The economic viability aspects of these units will be studied, after sufficient data is collected. There is a plan to put the platform for public use, for testing and collecting data.

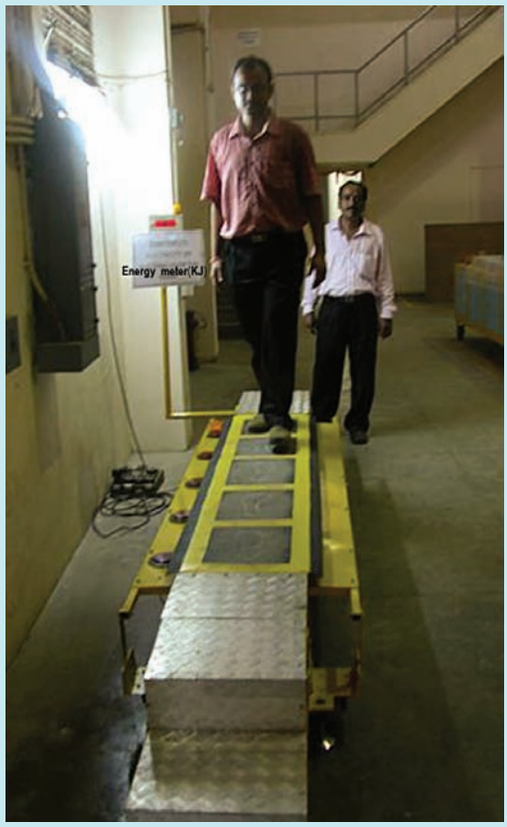

Fig. 6.: Multi Unit FSEC Platform

DAE Solid State Physics Symposium 2009 (DAE-SSPS-2009) : a brief report

The 54th DAE Solid State Physics Symposium organized jointly by BARC and The Maharaja Sayajirao University of Baroda was held during December 14-18, 2009 at the Maharaja Sayajirao University of Baroda, Vadodara. This annual conference is a prestigious national event drawing an overwhelming participation from researchers from various universities and national institutions across the country.

The symposium was inaugurated by Dr. S. Banerjee, Chairman, Atomic Energy Commission and Secretary, DAE. In his inaugural speech, Dr. Banerjee while appreciating the wide variety of the papers presented at the symposium (that cut across subjects like molecular magnets to spintronics, irradiation study of thin films to amorphous glasses and material synthesis to microscopic calculations) also raised his concerns regarding the quality of research

Dr S. Banerjee, Chairman, Atomic Energy Commission and Secretary, DAE, releasing the Proceedings of DAE-SSPS-09 at the inaugural function. Others from left: Prof. A.C. Sharma, Local Co-Convener, SSPS-09, Dr G. P. Kothiyal, Convener SSPS-09, Prof. Ramesh K. Goyal, Vice Chancellor, M.S. University, Dr. J.V. Yakhmi, Associate Director, Physics Group, BARC and Chairman Basic Sciences of BRNS, Dr. A. K. Rajarajan, Secretary, SSPS-09.

by Indian Scientists.Dr. Banerjee also released the Proceedings of the DAE-SSPS 2009.

Prof. Ramesh Goyal, Honorable Vice-Chancellor of MS University of Baroda in his presidential speech elucidated the role of universities in creating great citizens of this country.

Prof. A.C. Sharma, Local convener and Head of Department of Physics, The MS University of Baroda delivered the welcome address.

Dr. J.V. Yakhmi, Associate Director, Physics Group, BARC and Chairman Basic Sciences of BRNS in his special remarks on DAE-SSPS, presented the role of the Board of Studies in Nuclear Sciences in spreading scientific knowledge by conducting symposia and encouraging the participation of students, young scientists and faculty from the universities.

Dr. Kothiyal, Convener, DAE-SSPS 2009, highlighted the scope of the symposium.

The inaugural session was concluded with a formal vote of thanks by Dr. A.K. Rajarajan, Secretary, DAE-SSPS 2009.

The following is the distribution of the registered contributory papers under various subject categories.

A. Phase transitions:31, B. Soft Condensed Matter including Biological Systems & Liquid Crystals:24, C. Nano-materials:86, D.Experimental Techniques & Devices:14, E. Liquids,Glasses & Amorphous Systems: 31, F. Surfaces, Interfaces & thin Films: 76, G. Electronic Structure & Phonons: 47, H. Superconductivity: 23, I. Transport Properties:50, J. Semiconductor Physics: 27, K. Magnetism including Spintronics: 65, L. Novel Materials:26.

In all there were eight sessions of invited talks by eminent speakers covering a wide spectrum of topics related to condensed matter physics.

Dr. S.M. Yusuf of BARC and Prof. K. Suresh of IIT Mumbai presented their results on studies of magnetism. Excellent results on nanostructures of Carbon nanotubes to quantum dots were presented by Prof. K.K. Chattopadhyay of Jadhavpur University, Prof. C. S. Jayanthi Univ. of Louisville, USA and Dr.Achanta Venugopal of TIFR, mumbai. In the session on experimental methods, Dr. A. Lausi of the Italian National Synchrotron Radiation Facility, Italy presented the status report of the MCX Powder Diffraction beamline at ELETTRA. Prof. I Zizak Elektronenspeicherring BESSY II, Germany presented X-Ray Micro-Spectroscopy at BESSY II and Prof. K.L. Yadav presented the properties of Pr doped Bismuth ferrites. In the session on thin films, Prof. B. N. Dev of IACS, Kolkata, Prof. K. S. Narayan of JNCASR, Bengaluru and Prof. Arnab Bhattacharya of TIFR, Mumbai presented their work on Epitaxial Structures on Single Crystal Surfaces, Recent Strategies to Gain Insight in Polymer based Solar Cells N-lightenment: Nitride based optoelectronic materials and devices. Sessions on electronic structures was covered by G.P. Das (SINP, Kolkata) and Arindam Ghosh (IISc, Bengaluru).

Lectures on X-ray Spectroscopy and lattice structures were delivered by Prof. M. Mukherjee (SINP, Kolkata) Prof. R. K. Singh (MATS University, Raipur) and Dr. B.R. Shekhar (IOP, Bhubneshwar). Invited talks on glassy materials were delivered Prof. M. Zannetti (Università di Salerno, Italy) on Aging in Domain Growth, Prof. Arun Pratap (M. S. University of Baroda, Vadodara) on Thermodynamics of amorphous phase formation and thermal stability of meta-stable phase in metallic glasses and Dr. S.K. Tripathi (Punjab University) on Optical Studies in Chalcogenide Glasses. The subject of Superconductivity was covered by Prof. S. S. Banerjee (IIT, Kanpur) and Dr. Ranjan Mittal (BARC, Mumbai). Prof. Banerjee talked on Novel large amplitude low frequency velocity fluctuations in the elastic phase of driven vortex matter and Dr. Mittal talked about Phonon Dynamics in Parent and Superconducting FeAs Compounds.

Dr. V. Sivasubramanian (IGCAR, Kalpakkam) delivered a lecture on Acoustic anomalies and central peak in relaxor ferroelectric materials.

In addition to the invited talks, two interesting evening lectures were held – one on Computing Reality by Prof. Sushil Auluck, (IITK, Kanpur) and the second by Prof. Arup Kumar Raychaudhuri, (Director, S.N. Bose National Centre for Basic Sciences) on Resistive switching in nanoscale: Basic and conceptual issues of new type of Random Access Memory.

Five hundred contributed papers were presented in the form of posters in four poster sessions on four days of the symposium. Ten select contributions were presented as oral presentations in three oral sessions.

A half day session during the symposium was devoted to the Young Achiever award and thesis presentation, judged by a panel. A notable feature of the symposium was the institution of a special award for two Post Graduate students recognizing their extraordinary contribution in M.Sc. project work in the subject of Solid State Physics. Twelve nominations from various universities across the country were received, out of which the two were selected by a panel of judges. The students were then invited to make oral presentations of their project work. All the M.Sc project manuscripts were included for publication in the Proceedings.

On first day a cultural programme was also organized, which was presented by the students and Faculty of the Department of Performing Arts of the M.S. University, Baroda.

The symposium was a grand success with a widespread participation. The concluding session of the symposium was presided over by Prof. R.K. Singh, Dr. S.L. Chaplot, Head Solid State Physics Division, BARC and Dr. S.K. Gupta, Head, Thin film Devices Section, BARC. This session started with the distribution of awards and certificates for Young Achiever, M.Sc. Project, Best Thesis and twenty Best Posters. A brief summary of the symposium was given by Dr. Alka Garg, Secretary, DAE-SSPS 2009. The symposium was concluded with a formal vote of thanks delivered by Prof. Arun Pratap, Local Co-Convener, DAE-SSPS 2009, appreciating the well coordinated team work of all the members and volunteers.

11th ISMAS Triennial International Conference on Mass Spectrometry: highlights

The 11th ISMAS Triennial International Conference on Mass Spectrometry (11th ISMAS-TRICON-2009) was organized by the Indian Society for Mass Spectrometry (ISMAS) and was co-sponsored by Scientific Departments (BRNS, CSIR) of the Government of India. The Conference was held at Hyderabad, during November 24 – 28, 2009.

The Conference was inaugurated by Prof. P. Balaram, Director, IISc, Bengaluru on November 24, 2009. Prof. V. Venugopal, Director, Radiochemistry and Isotope Group, BARC, Mumbai presided over the function and delivered the Presidential address. Dr. H.C. Jain, President, ISMAS delivered the welcome address and briefed about the activities of ISMAS. Prof. S.K. Aggarwal, Chairman of the Organizing Committee of the Conference, highlighted the scope of 11th ISMAS-TRICON-2009 and proposed a vote of thanks. During the inauguration function, the bound volume of the Proceedings of the 11th ISMAS-TRICON-2009 was released by Prof. Balaram. A special ISMAS Souvenir cum Bulletin brought out to commemorate the occasion, was released by Prof. V. Venugopal.

During the inauguration function, three mass spectroscopists from within the country were honoured with "*EMINENT MASS SPECTROSCOPIST*" awards. The awards were conferred upon Prof. A.K.Chakraborty (NIPER, Mohali), Dr B.R. Chakraborty (NPL, Delhi) and Dr R.K. Vatsa (BARC, Mumbai). Each of the award winners presented a brief account of his research work.

Around 200 participants including many guest speakers participated in the 11th ISMAS-TRICON-2009. The scientific programme of the Conference covered in 12 technical sessions was spread over a period of 5 days. The Conference opened with a Plenary lecture by Prof. P. Balaram on the "Role of Mass Spectrometry in the Analysis of Peptides and Proteins" in view of significant contributions made by Prof. Balaram and his Group in the last 2-3 decades. There were 36 Invited talks by distinguished

At the Inaugural Function: On the dais from left to right: Prof. S.K. Aggarwal, Chairman, Organising Committee & Head, FCD; Dr. V. Venugopal, Director, Radiochemistry & Isotope Group, BARC; Prof. P. Balaram, Director, IISc, Bengaluru and Dr. H.C. Jain, President, ISMAS

mass spectroscopists from within the country and from overseas.

Invited speakers from overseas included Prof. I.B. Brenner (Israel), Prof. Naoki Furuta (Chuo University, Japan), Dr. Evgeny Gurevich (ISAS-Institute for Analytical Sciences, Germany), Prof. Mats Lennart Larsson (Stockholm University, Sweden), Dr. David S. McPhail (Warwick University, UK), Dr. Richard David Thomas (Stockholm University, Sweden), Dr. Hans Clemens Justus Walther (Institut fur Nukleare Entsorgung, Germany) and Dr. Ian Stuart Williams (Australian National University, Australia).

Speakers from India included Prof. D. Mathur (TIFR, Mumbai), Dr. S.K. Raza (DRDE, Gwalior), Dr. Y.J. Bhaskar Rao (NGRI, Hyderabad), Prof. Saranjit Singh (NIPER, Mohali), Dr. S. Kailas (BARC, Mumbai), Dr. M.V.S. Suryanarayana (DRDE, Gwalior), Prof. P. Chakrabarty (SINP, Kolkata), Dr. R.D. Deshpande (PRL, Ahmedabad) Dr. A.S. Sarpal (IOC, Faridabad), Dr. B. Kumar (Ex-NGRI, Hyderabad), Dr. M.V. Jagannadham (CCMB, Hyderabad), Dr. V. Sabareesh, (JNCASR, Bengaluru), Prof. A.K. Choudhury (IIT Roorkee), Dr. Sunil K. Singh (PRL, Ahmedabad), Mr. V. Nataraju (BARC, Mumbai), Dr. Narendra M. Raut (Piramal Life Sciences, Mumbai), Dr. M. Joseph (IGCAR, Kalpakkam), Dr. M. Vairamani (IICT, Hyderabad), Dr. R. Ramesh (PRL, Ahmedabad), Dr. V. Ramaswamy (NIO, Goa) and Prof. S.K. Aggarwal (BARC, Mumbai).

There were 90 papers presented as posters in three poster sessions. These sessions covered various fields of research such as Atomic & Molecular Physics, Biological & Environmental Science, Earth & Planetary Science, Instrumentation, Isotopic Composition & Concentration Measurements, Nuclear Technology and Organic Chemistry. There were 8 presentations by instrument suppliers showcasing the latest developments in the field of Mass Spectrometry Instrumentation. Five Research Scholars, who completed their Ph.D. or M.Sc. in the last three years, were provided with the opportunity to make oral presentations of their research work. The presentations made by the research scholars and the poster presentations of the contributory papers were evaluated by different panels of judges for awards.

The Conference was preceded by two parallel short courses, each of two days duration, during Nov. 21-23, 2009 on "Elemental Mass Spectrometry" at NGRI, Hyderabad and on "Biomedical Mass Spectrometry" at CCMB, Hyderabad. These short courses included visits to the mass spectrometric laboratories at NGRI and CCMB.

11th ISMAS-TRICON-2009 concluded with a Valedictory Function on November 28, 2009. During this function, prizes were awarded to the authors of the best posters in each discipline and to the best oral presentation among research scholars. The delegates expressed their satisfaction over the technical contents and scientific discussions held during the Conference. A need was felt to have a dedicated "*Accelerator based Mass Spectrometry (AMS)*" facility as well as "*Electromagnetic Separator for Producing Stable Enriched Isotopes*" in view of their increasing requirements and applications in Life Sciences for societal benefit.

'Thermo Physical Property Evaluation Laboratory'

A new laboratory entitled "Thermo physical Property Evaluation Laboratory" has been set up in the Radiometallurgy Division premises, Nuclear Fuels Group, RLG, for evaluation of thermo physical properties of nuclear fuels and structural materials. Some of the facilities available in this laboratory are high temperature TMA/dilatometer, combined TG/DTA/DSC, thermal conductivity/thermal diffusivity/specific heat measurement using TPS method, a battery of furnaces to conduct chemical compatibility experiments, metallographic examination including cut-off machine, grinding and polishing machine and optical microscope. Thermo-physical property data is important for evaluating the usefulness of fuel, structural materials in the reactor, predicting in-pile performance of fuel, fission gas release, fuel-clad mechanical interaction, whole core accident analysis etc. Work related to the development of metallic fuel for fast reactor and ceramic fuels based on U-Pu mixed carbide, oxide, nitride fuel and thoria based Th-Pu and Th-U fuels, will be carried out in this facility. Experimental studies related to chemical compatibility between fuel-clad and fuel-clad-coolant could also be carried out. This laboratory was inaugurated by Dr Srikumar Banerjee, Chairman, Department of Atomic energy and Director BARC on 3rd March, 2010. Mr. H. S. Kamath, Director, NFG, Mr. Arun Kumar, Head, RMD, Dr. G. J. Prasad, Head, MFD and Dr. A. K. Sengupta, Head, Fuel Property Evaluation Section, RMD and his colleagues were also present on this occasion. Dr Sengupta explained to the chairman the facilities available in this laboratory and their utility in evaluating different thermo-physical properties of fuels and structural materials.

Dr Srikumar Banerjee inaugurating the Laboratory

Hand-held Tele-ECG instrument for rural health care: transfer of technology

The technology of "**Handheld Tele-ECG Instrument for Rural Health Care**" developed by the Electronics Division, BARC was transferred to M/s Chess Medicare Pvt. Ltd., Mumbai, on 30th November, 2009.

The technology consists of a low cost, hand-held and compact Tele-ECG Instrument. It is operated and controlled with a mobile phone or laptop/ desktop via bluetooth and thus has mobile as well as LAN connectivity. In the hospital environment it can be used with LAN connection and in rural area with mobile phone for sending ECG of the patient to the expert. The Handheld Tele-ECG acquires, saves and transfers the electrocardiographic signal to the expert's mobile for his advice, in dealing with cardiac emergencies. This saves crucial time, which is otherwise lost in transporting the patient to the nearest cardiac care centre. This makes it highly suitable for isolated rural populations.

The Technology Transfer and Collaboration Division coordinated all activities related to the transfer of this technology, such as preparation of technical documents including brochure, leaflet, technology transfer document, advertisement of the technology and evaluation of party, technology transfer agreement, preparation and the signing of the agreement. Team of developers from Electronics Division and other officials were also present during the occasion.

Dr. Srikumar Banarjee, Director, BARC (third from left) and Mr. Nitin Desai (fourth from left), Managing Director, M/s Chess Medicare Pvt. Ltd., Mumbai signing Agreement. Other dignitaries seen from left to right are Mr. C. K. Pithawa, Head, ED, Mr. R. K. Patil, AD (C), E&IG, Ms. Smita Mule, TT&CD, Ms. Manjusha Desai & Mr. V. J. Shetty, Directors, M/s Chess Medicare Pvt. Ltd., Mumbai, Dr. R. B. Grover, Director, KMG, BARC, & Director SPG, DAE and Mr. A. M. Patankar, Head, TT&CD (extreme right).

International Symposium on Nuclear Physics - 2009: a report

The International Symposium on Nuclear Physics sponsored by the Board of Research in Nuclear Sciences, DAE was held at BARC, Mumbai during Decemeber 8 to 12, 2009. The symposium was part of the annual Nuclear Physics Symposium (54th in the series), which was organized as an international event. The symposium had 50 invited speakers from India and abroad and a total 338 (328 papers by individual contributions and 10 for PhD theses) research papers were presented in the form of posters. The symposium covered key areas of Nuclear Physics: a) Nuclear structure, b) Low and medium energy nuclear reactions, c) Physics with radioactive ion beams, d) Intermediate energy nuclear physics, e) Physics of hadrons and QCD, f) Relativistic nuclear collisions and QGP, g) Nuclear astrophysics and nuclear matter, h) Accelerators and instrumentation for Nuclear Physics. The conference proceedings, which included one page abstracts of invited talks and two page abstracts of contributed papers, were published in advance to facilitate discussions among the participants on different topics, covered during the conference.

Dr. R. K. Choudhury, Head, Nuclear Physics Division and Chairman, Symposium Organizing Committee welcomed the delegates coming from various parts of the country and abroad. He deliberated on the importance of this series of symposia, which were initially started by Dr. Homi J. Bhabha in the early fifties and has since served as a platform for the young researchers in Physics to interact with the nuclear physics community from India and abroad. The symposium was inaugurated by Prof. S.S.Kapoor, Senior Honorary INSA Scientist and Ex-DAE Homi Bhabha Chair Professor. Dr. Kapoor spoke on overall nuclear physics research scenario and its spin offs to applications for society. Dr. S. Kailas, Associate Director, Physics Group, BARC gave the introductory remarks. and Dr. A. K. Mohanty proposed the vote of thanks. As part of the inaugural session, there were two invited talks of general interest, one by Prof. Dieter Ackermann from GSI, Darm statt, Germany on super heavy elements-investigating the properties of exotic high Z nuclear matter and the other by Prof. Volker Metag, Univ. of Gieslem, Geneva on properties of hadrons in strongly interacting matter. Prof. Ackermann, GSI, Darmstaadt, Germany described the experimental efforts to synthesize nuclei of closed proton and neutron shells beyond ^{208}Pb , in particular the development of efficient experimental setups

Dr. R. K. Choudhury welcoming the delegates

Prof. S. S. Kapoor delivering the inaugural address

Prof. Volker Metag, Univ. of. Giessen, Geneva delivering the invited talk

Prof. Dieter Ackermann, GSI, Darmstaadt, Germany delivering the invited talk

including mass separators and particle detection arrangements which allow structure study of nuclei around and beyond Z=100. Among the most interesting features of these studies is the observation of K-isomeric states in the region of Z=100 to 110. Prof. Metag, Univ. of Giessen reviewed the results obtained in a series of experiments to study the in-medium properties of the hadrons. Properties of the hadrons in strongly interacting matter provide a link between quantum chromo-dynamics in the strong coupling regime and experimental observables.

The invited talks presented during the symposium covered a wide range of topics starting from low to high energy nuclear physics and associated accelerator and detector programmes. On the first day, a special session was held on various accelerator facilities including beam development and utilization programmes at superconducting cyclotron, Kolkata, heavy ion linear accelerator programme at Delhi and Mumbai, radioactive ion beam factory project at RIKEN, Japan and plans for rare isotope beams at TRIUMF, Canada.

In keeping with the tradition of the symposium, a one day pre-symposium orientation programme was held on 7th December 2009, on "Reactions with loosely bound nuclei". The theses posters were presented at TIFR and three best theses were selected for oral presentation on 11th December 2010. Mr. Ritesh Kshetri of SINP was given the C V. K. Baba award for Best Thesis presentation.

National Laser Symposium (NLS-09): a report

The National Laser Symposium (NLS-09), the ninth in the series organized annually since 2001, was held at the BARC, Trombay, Mumbai during January 13 to 16, 2010. The ninth symposium, sponsored by the Board of Research in Nuclear Sciences, Department of Atomic Energy, Government of India, was organized the Laser & Plasma Technology Division, BARC in collaboration with the Indian Laser Association (ILA). Incidentally, NLS-09 is the first major event in India in this calendar year to celebrate 50 years of the invention of laser. The four day symposium was inaugurated on January 13, 2010, by Dr. Srikumar Banerjee, Chairman, Atomic Energy Commission and Secretary, Department of Atomic Energy. In his inaugural speech, the Chairman highlighted the applications of lasers in various programmes of DAE in general and in the nuclear programme in particular, including the first use of lasers for machining of spent fuel bundles in radiation shielded enclosures, which generated keen interest among the international nuclear industry community. The symposium keynote address was delivered by Prof. Swapan Chattopadhyay, Director, International Centre of Accelerator Science & Technology, The Cockroft Institute, UK and Sir John Cockroft Chair of Physics at Universities of Liverpool, Manchester and Lancaster. In his address, Prof Chattopadhyay gave a glimpse of the recent developments in lasers and accelerators and innovations in the conception, production and control of pulses of light and charged particle beams.

The symposium was attended by over 500 delegates from all parts of India, as well as by a number of foreign nationals. About 210 research papers were presented and 25 invited talks delivered during the symposium, covering frontline research in basic laser physics and significant advances in development and application of laser technology, in various disciplines of science.Ten Ph.D theses were selected for presentation by young research scholars at the conference. Financial support was provided to over 70 deserving research students to facilitate their participation at the symposium.During Symposium, an expert panel discussion was conducted, to explore the National Photonics scene in India, in order to identify and focus R&D particularly on a few high impact areas in research institutes/ universities.Prof. Van Den Bergh, Institute of Bio-engineering, Lausanne, Switzerland and Dr. P. K. Gupta, President, ILA gave away the awards for the best thesis and poster during the concluding session on January 16.

Dr. Gantayet, Chairman, SOC welcoming the Chief Guest Dr. Swapan Chattopadhyay with a bouquet

National Symposium on BARC Technologies for Development of Rural India (BTDRI-2009)

On the occasion of Dr Bhabha's centenary year celebration, the BARC Officers' Association (BARCOA) in association with the Board of Research in Nuclear Sciences (BRNS), organized a two-day National Symposium on BARC Technologies for Development of Rural India (BTDRI-2009) on November 25-26, 2009. In the seminar, Farmers, Scientists, NGOs and industrialists gathered together for exchanging ideas on promoting technologies, which are the wealth and employment generators, in rural areas. Farmers, who have been benefited by BARC technologies, were felicitated.

Mr. R.K. Mishra, Convenor, BTDRI-2009 and President BARCOA welcomed the audience. The symposium was inaugurated by Mr. Sudhir Thakare, Secretary, Ministry of Rural Development, Govt. of Maharashtra. He referred to political, social and economic development in rural areas, where the thread of science and technology was common to all sectors. He urged the need for affordable science, so that the benefits percolate to a wider cross section. He also said that the government would encourage those technologies which are affordable to people.

At the release of the Proceedings Volume of BTDRI-09 (from left to right): Mr. M.C. Goel, Secretary, BARCOA, Dr. Srikumar Banerjee, Chairman AEC and Director, BARC, Dr. Anil Kakodkar, Homi Bhabha Chair, Mr. Sudhir Thakre, Secretary, Ministry of Rural Development, Govt. of Maharashtra and Mr. R.K. Mishra, President, BARCOA.

The keynote address was given by Dr. Anil Kakodkar.In his inaugural address, he referred to the multi faceted personality of Dr. Homi Bhabha. He complimented the quality of research work carried out in BARC where the power of technology is such that the beneficiaries create a market. He said that "We need to work with external stakeholders and the end users directly in order to push the technologies developed at Bhabha Atomic Research Centre (BARC) for wealth and employment generation in rural India,". Centre should promote all the useful technologies for the benefit of the rural masses, he said giving examples of technologies like biodigester 'Nisargruna' for processing wet garbage, solar dryers, water purifiers, Trombay oilseeds, pulses varieties, Nisargruna (the Bio-Gas Plant) and BHABHATRON-II (the teletherapy machine). He also referred to the radioisotope hydrology technique which has brought water to the villages in hilly areas. "To take technology successfully to society, we need to engage with society, end users and other institutes pursuing similar programmes. The symposium organized by BARCOA is unique and will be a turning point in the years to come," said Kakodkar. He asked BARCOA to encourage members to take up social causes apart from their R&D output.

Dr. Srikumar Banerjee, Director, BARC referred to the development brought out in rural India through application of science. Techniques such as tissue culture and cut flowers have tremendous potential. He referred to initiating decentralized power programme through harnessing solar energy and said, that the centre was taking efforts to make available Solar Tower for power generation and solar collector for heating pipes in rural areas. It was a maiden attempt to take the fruits of technology to the grassroots level and empower villages with science and technology based eco-friendly work plan.

Farmers from Amrawati, Pune & other parts of Maharashtra and Uttar Pradesh, Punjab, Guwahati and Gujarat spoke on the usefulness of BARC technology for their farms. They explained the improvement of the quality and quantity of their crops. NGOs and Heads of educational institutes expressed their wish to coordinate with the farmers. Head, TT&CD and the key person of Aakruti programme presented data on technology transfer to farmers and its utility.

Mr. M.C. Goel, Secretary, BTDRI-2009 and Secretary BARCOA, gave vote of thanks.

BARC Scientists Honoured

Name of the Scientist:		**Srikumar Banerjee, Director, BARC & Chairman, AEC**
Award	:	Excellence in Science & Technology Award
Awarded by	:	The Prime Minister of India at the inauguration of the 97th Indian Science Congress Association, held at Kerala University, Thiruvananthapuram, during Jan. 3-7, 2010
Name of the Scientist	:	**T. Mukherjee, Director, Chemistry Group**
Award	:	Acharya Prafulla Chandra Ray Memorial Award 2008 for Life Time Achievement in Chemical Research
Awarded by	:	Indian Chemical Society.
Name of the Scientists	:	**A.K. Bera and S.M. Yusuf, Solid State Physics Division**
Title of the Poster	:	Magnetic Structure of the Layered Square-lattice Spin System Zn_2:$VO(PO_4)_2$
Award	:	Best Poster Award
Awarded at	:	54th DAE-Solid State Physics Symposium, held at Maharaja Sayajirao University of Baroda, Vadodara, during December 14-18, 2009.
Name of the Scientist	:	**D. Datta** Head, Computational Radiation Physics Section (CRPS), Health Physics Division
Award	:	Millenium Plaques of Honour
Awarded by	:	The Prime Minister of India at the inauguration of the 97th Indian Science Congress Association, held at Kerala University, Thiruvananthapuram, during Jan. 3-7, 2010.
Name of the Scientist	:	**D.K. Aswal, Technical Physics Division**
Honour	:	MRSI-Medal by the Materials Research Society of India. He has also been featured as Nano-technologist by *India Today* (Hindi edision)
Name of the Scientists	:	**Kaushal Jha, K. Bhanumurthy, G.K. Dey and K.N. Mahule Materials Group, Knowledge Management Group, Nuclear Fuels Group**
Award	:	Best Poster Award (1st prize) in Materials Science
Awarded at	:	The International Conference on Advances in Electron Microscopy and Related Techniques & XXXI Annual Meeting of EMSI organized by the Electron Microscope Society of India (EMSI) & BARC, at Mumbai, during March 8-10, 2010.
Name of the Scientists	:	**Kaushal Jha, K. Bhanumurthy, G.K. Dey and K.N. Mahule Materials Group, Knowledge Management Group and Nuclear Fuels Group**
Title of the paper	:	Microstructural characterization of Al-based metallic form developed by novel FSP technique
Award	:	Best Poster- 3 Award in Materials Science
Awarded at	:	The International Conference on Advances in Electron Microscopy and Related Techniques & XXXI Annual Meeting of EMSI organized by the Electron Microscope Society of India (EMSI) & BARC, during March 8-10, 2010 at Mumbai.

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