Recovery of Wealth from Radioactive Waste and its Utilization

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Abstract

Since its discovery in the late 19th century, the field of radioactivity has developed from one of the pure research interests to a broad field combining engineering and basic sciences to realize technological applications such as nuclear reactors for power, radioisotopes for medical and space applications and crop sciences, to name a few. Of these, the flagship of nuclear technology remains nuclear power generation using fission reactors. Over the decades, fission reactors have developed into reliable, efficient power generation sources and are providing an environmentally friendly base-driver for rapidly developing nations such as India.

By virtue of nuclear fission reaction, nuclear reactors can produce large amount of electricity from relatively small amount of nuclear fuel. As a result, the amount of waste getting generated from the nuclear industry is very small in comparison with fossil fuel-based power plants. India follows "closed fuel cycle" and considers spent nuclear fuel as a material of resource rather than waste. This further reduces the amount of radioactive waste to a very small percentage of residual material present in spent nuclear fuel, which requires due care for their management. Besides nuclear fuel cycle and nuclear research facilities, other facilities using radioisotopes for various applications also generate radioactive wastes. Even though, radioactive waste volume generated from nuclear industries are small, it necessitates judicious management. The radioactive waste are conventionally classified as low level waste (LLW), intermediate level waste

(ILW) and high level waste (HLW) based on the concentration of radioactive constituents present in the waste. As a standard practice, the radioactive wastes are isolated, after suitable conditioning in a desired matrix, to mitigate dispersal concerns.

Recently, it has been appreciated that radioactive waste is host of many valuable radionuclides which can be recovered for various applications in other fields. The concept of wealth from radioactive waste is vindicated by the development of advanced separation techniques and plant systems capable to recover the useful radionuclide from radioactive waste and covert them in suitable form for desired applications. These processes and equipment allow selective separation of useful radionuclides from radioactive waste, thereby making them available for societal benefit in medical and industrial applications.

This article presents the origin of High Level Liquid Waste (HLLW), separation processes for various radionuclides and a few salient case studies on recovery of wealth from radioactive waste and its utilization.

Keywords: *High level waste, radioisotope recovery, Cesium, Strontium, Ruthenium, Yttrium*

1. Introduction

Nuclear reactors facilitate nuclear fission to produce energy. Uranium, either in natural or enriched form, is commonly used as fuel in nuclear power plants for nuclear fission. When neutron bombards on it, uranium-235 (fissile isotope of natural uranium) split into two lighter atoms, called fission products and generates large amount of energy. The energy, thus liberated, is utilized to generate steam, which rotates the turbine for production of electricity. Small amount of nuclear fuel can generate relatively large quantity of energy. For example, a nuclear power reactor requires only one ton of natural uranium to produce as much electricity as produced by a conventional thermal power station using 25,000 tons of coal. Thus, nuclear power reactor generates small quantities of waste and hence associated adverse environmental impacts are also very small. Besides fission reaction, another important reaction also takes place inside nuclear reactor. This involves capture of neutron by uranium-238 (fertile isotope of natural uranium) to produce plutonium-239. Plutonium can be utilized as fuel in another reactor for production of electricity.

After extraction of energy equivalent to 'burn-up of fuel', the fuel gets depleted in its fissile content and it becomes difficult to sustain the nuclear fission chain reaction for production of the desired power. At this point, the used fuel is replaced with fresh fuel. The used fuel is called 'Spent Nuclear Fuel' (SNF) which also contains many valuable components such as plutonium and unused uranium. For most countries, which are following 'open fuel cycle', SNF is considered a waste for suitable disposal. SNF contains about 95-99% of unutilized uranium besides newly generated plutonium. Recovery of uranium and plutonium from SNF and their use in next generation reactors in form of mixed oxide (MOX) fuel, helps in overall optimisation of fuel usage. In India, as part of "closed fuel cycle" philosophy, plutonium and unused uranium are

separated for their utilization in upcoming fast neutron reactors. Besides this, recovery of bulk amount of fuel materials from SNF also helps in reducing radioactive waste volume to a great extent which requires due care during their management.

2. High Level Liquid Waste (HLLW): A source of valuable radioisotopes

Reprocessing of SNF has been a key component for successful implementation of Indian three stage nuclear power program based on a closed fuel cycle. This aims for not only optimal utilization of uranium fuel but also paves ways for utilization of large resources of thorium in India for its long term energy security. Reprocessing of SNF leads to a significant reduction of final waste volume and also opens up possibilities for recovery of valuable radionuclides for social applications.

During reprocessing, valuable material like Pu and U are extracted from spent fuel using solvent extraction based PUREX process (Figure 1). The Pu and U are recycled back for fuel fabrication.

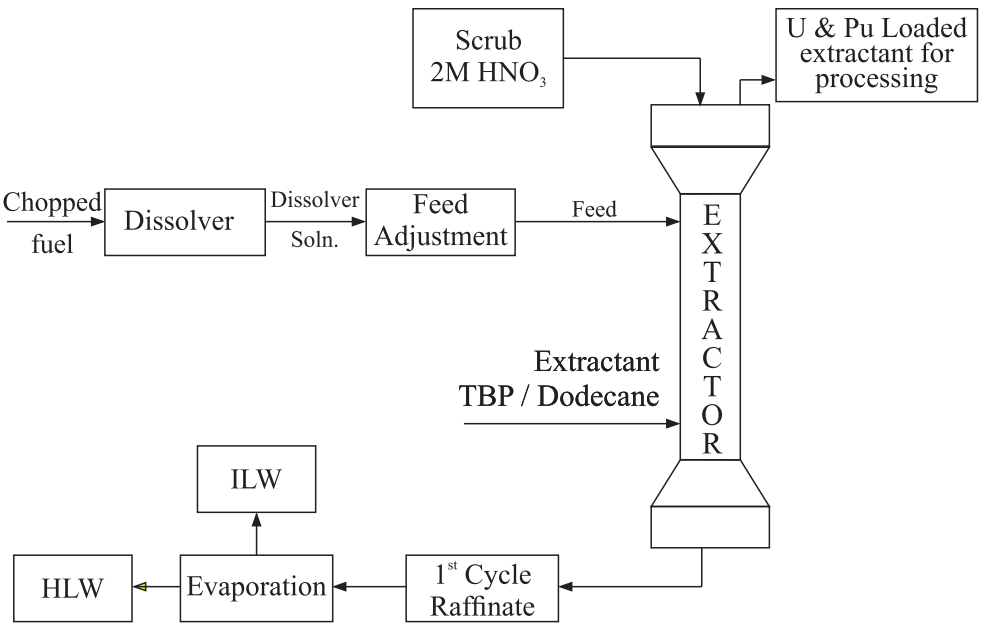


Figure 1: Flow chart for recovery of Pu and U from Spent Nuclear Fuel

After extracting Pu and U, remaining materials including fission products, minor actinides etc. emerge as a first cycle raffinate. The first cycle raffinate is concentrated further for volume reduction and is termed as High Level Liquid Waste (HLLW). It contains bulk of fission products and minor actinides generated in the reactor. Majority of radioactivity (about 99%) of SNF reports in HLLW.

HLLW contains fission products, minor actinides, traces of uranium & plutonium, corrosion products and chemicals added during reprocessing. HLLW is immobilized in inert glass (vitreous) matrix, stored for a few decades in air cooled vault and then planned to be disposed in deep repository. Conditioning of HLLW in vitreous matrix immobilizes the radioactivity in a

chemically durable form and ensures isolation of radioactivity from biosphere for larger time frame.

Composition of a high-level waste arising from reprocessing plants depends on various factors including type of reactor, nature and burn-up of the fuel, cooling period of the SNF, amount of waste volume and reprocessing methodologies applied. The inventory of a fission isotope can be calculated from the knowledge of fission yield, burn-up, cooling period and the volume of the generated waste. For example, around 240 g of ^{137}Cs (fission yield: 6%) is obtained for a five-year cooled fuel irradiated in a Pressurized Heavy Water Reactor (PHWR) having 6.7 GWd/tonne burn-up . This corresponds to about 20,000 Ci of ^{137}Cs. It is, one of the prominent radioisotopes present in the HLLW & useful in radiation technology applications. Similarly, there are many other radioisotopes present in the HLLW. A short list of radioisotopes and their potential area of applications are illustrated in Table 1. Considering the application potential of each of the useful radioisotope and inventory, Table 1 shows categorically that HLLW is no longer a waste material. Rather, it is a valuable resource of national importance with great societal impact.

Table 1: A list of valuable radionuclides present in the HLLW

Radioisotopes	Half life	Radiation type	Energy (MeV)	Major area of Application
Cesium (^{137}Cs)	30 y	Gamma (after emitting a Beta radiation)	0.66	Blood irradiation Food Irradiation
Strontium/Yttrium (^{90}Sr/^{90}Y)	28 y	Beta	0.5 and 2.28	Power source
Yttrium (^{90}Y)	64 hr	Beta	2.28	Bone pain palliation Radio-pharmaceutical
Ruthenium/Rhodium (^{106}Ru)	373 d	Beta	3.54	Eye cancer (Brachytherapy)
Americium (^{241}Am)	432 y	Alpha	5.48	Power source (Such as Radioisotope Heater Unit (RHU) & Radioisotope Thermoelectric Generator (RTG) for space applications)

3. Value recovery from HLLW

Towards utilization of a radioisotope, first and foremost, it must be separated from HLLW in a radio-chemically pure form. The extent of purity, though application specific, should be in conformity with stringent regulatory limits. Further, excluding the therapeutic applications, the radioisotope is to be converted to a non-leachable form, so that no inadvertent release of radioactivity occurs during its use. For therapeutic applications, the recovered radioisotope is tagged with a suitable carrier molecule before applications.

India has taken special efforts for recovery of valuable species from HLLW to deploy the same for societal benefit, such as large-scale recovery of ^{137}Cs and converting them into non-dispersive glass form for gamma irradiation applications. The efforts made by BARC in this regard are pioneering since Cs was traditionally deployed globally in the form of CsCl based source, which is water-soluble and therefore, presents a dispersal hazard. The use of a glass-

based gamma source greatly increased the applicability of the source while minimizing dispersal concerns. India has also demonstrated the separation of purified form of ^{90}Sr to recover ^{90}Y of clinical grade for radio-pharmaceutical applications. In addition to this, recovery of ^{106}Ru from HLLW has also been successfully demonstrated to prepare ^{106}Ru plaques for eye cancer treatment.

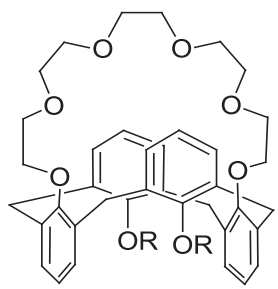
Indigenously developed processes, including novel extractants and technologies are deployed for the recovery of three important radioisotopes, viz., ^{137}Cs, ^{90}Sr and ^{106}Ru from HLLW followed by their conversion to a suitable form for end user applications.

3.1 Recovery of ^{137}Cs from HLLW

Solvent extraction-based processes are the most promising for the large-scale separation of ^{137}Cs from highly radioactive acidic solutions. Technologies for large scale applications of the process are also well established. In this process, an organic stream containing solvent, traces of selective extractant and the aqueous waste are kept in intimate contact by employing strong agitation. During agitation, the metal ions interact with the extractant and are extracted into the organic phase by formation of an organic phase soluble metal-extractant complex. On standing, the organic phase separates out and the metal ion is stripped from the organic to the aqueous phase by disturbing stability of the metal-extractant complex.

In India, solvent extraction-based facility has been deployed at Waste Immobilisation Plant, BARC, Trombay, where three cycle based solvent extraction process has been established. In the first cycle, residual uranium and plutonium are recovered from HLLW. While cesium recovery is aimed in the second cycle, Strontium-Actinide-Lanthanide combined separation is achieved in the third cycle from HLLW. Utilising the facility, large amount of ^{137}Cs recovery could be demonstrated from HLLW. 1, 3-di-n-octyloxy Calix [4] arene-Crown-6 (CC6) is being used for recovery of ^{137}Cs in bulk amount from high level waste of acidic nature[1]. The molecular structure of the Cs selective solvent, CC6 is presented in Figure 2.

The process involves recovery of cesium using selective extractant Calix Crown 6 in isodecyl alcohol (IDA)-Dodecane solution post removal of residual uranium and plutonium from HLLW. Cesium is stripped out from loaded organic to aqueous phase using dilute nitric acid as stripping agent. A pair of specially developed Continuous Air Lift based Mixer Settler Unit (CALMSU) are deployed for removal of cesium from HLLW using solvent extraction system at Waste Immobilisation Plant of BARC, Trombay. Each mixer settler contains around 12 equilibrium stages. Each stage has one mixer, for effective mixing of aqueous phase with organic phase, and one gravity settler for density segregation of the aqueous and organic phases. Air lift based mixing units are used for effective mixing of aqueous phase and organic phase.



Where R = n-Octyl

Figure 2: 1, 3-di-n-octyloxy Calix [4] arene-Crown-6 (CC6)

The cesium rich product stream is further concentrated and is used for making of Cs glass pencils for gamma irradiation applications. A thumbnail view of Cs pencil making process is shown in Figure 3. Concentrated cesium solution is fed to Induction Heated Metallic Melter (IHMM) along with glass making additives to produce cesium rich glass using vitrification process. Special glass matrix has been developed and deployed for making cesium glass with activity up to 5 Ci/g. The bulk cesium rich glass is drained into a dispenser, which is a smaller capacity pot for cesium re-melting furnace. Cesium glass containing dispenser is assembled remotely to dedicated re-melting furnace for making Cs glass pencils with precise control of Cesium glass in each pencil.

The re-melting furnace is a smaller capacity induction heated metallic melter and specially designed with mechanical plug to ensure controlled draining of Cs glass into SS pencils. The dispenser is heated to the melting point of Cs glass. Pre-determined quantity of Cs glass is drained in SS pencil, called the inner pencil. Cs glass containing SS pencil is sealed by remote welding of lid on it. The sealed pencil is subjected to hot water bubble test to ensure leak tightness and placed inside another SS pencil, called the outer pencil. The outer pencil is subjected to stringent quality assurance test including hot water bubble test to ensure leak tightness and finally it is externally decontaminated using an ultrasonic decontamination vessel. Stringent quality assurance program, as mentioned by Atomic Energy Regulatory Board (AERB) Guide – SS3, is followed for ensuring their qualification as a sealed radiation source. 10 such Cs glass pencils, post quality assurance, are placed in a cage and transported to Board of Radiation & Isotope Technology (BRIT), Mumbai in shielded casks for further use as radiation sources.

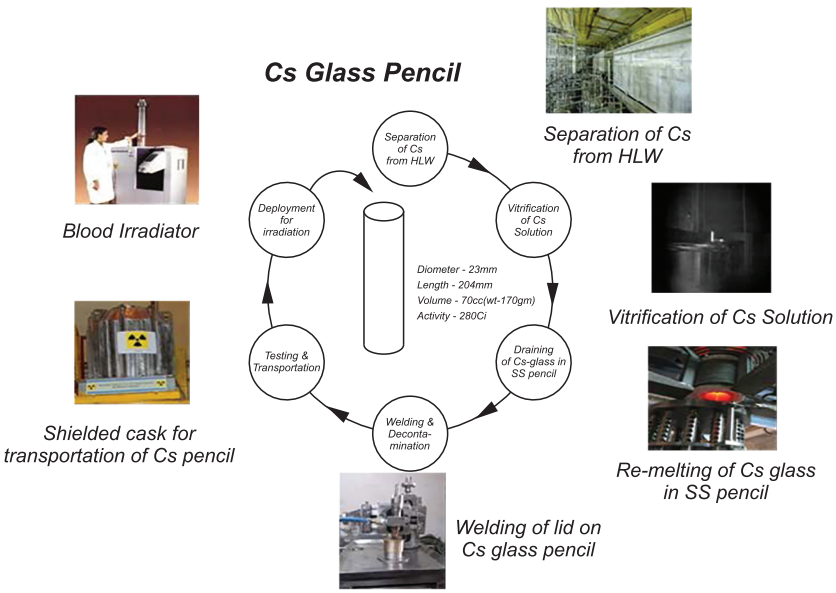


Figure 3: Cs glass pencil making process

The Cs glass pencils, having specific activity of cesium ranging from 2 Ci/g to 5 Ci/g, are under use for gamma irradiation applications (Figure 4). Presently, gamma irradiation of blood pouches is targeted by utilizing Cs glass pencils in blood irradiator (replacing ^{60}Co sources) to prevent Transfusion Associated - Graft Vs Host Disease (TA-GVHD). The Cs glass pencils, with

high specific activity of cesium, have potential to be used in various other gamma irradiation applications such as food irradiation, gamma chamber etc. Its use for irradiation to enhance the shelf life of food grains will be demonstrated at BARC, Trombay.

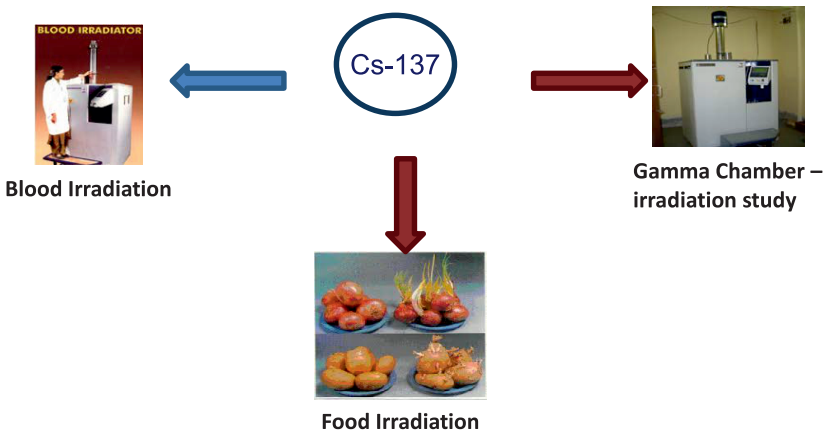


Figure 4: Applications of Cs glass pencils

3.2 Recovery of $^{90}Sr/^{90}Y$

Though ^{90}Sr has several applications, the major demand is due to its daughter ^{90}Y. It is used as a radiopharmaceutical in the treatment of liver cancer and neuroendocrine tumors. ^{90}Sr - ^{90}Y are in secular equilibrium and half-life of the daughter is only 64 hours. Therefore, separation of ^{90}Sr must be carried out first. Further challenges lie in meeting stringent radiopharmaceutical purity requirement of ^{90}Y for use as nuclear medicine.

Recovery of ^{90}Sr from HLLW is being carried out in India by employing solvent extraction based process. As indicated earlier (Section 3.1), solvent extraction system is deployed for recovery of Cesium. The same system is subjected to separation of Strontium-Actinides-Lanthanides using extractant Tetra Ethyl Hexyl Di-Glyco Amide (TEHDGA) in IDA-Dodecane solution from raffinate stream generated after extraction of cesium. It is to be noted that TEHDGA is used for co-extraction of actinides (An) and lanthanides (Ln) along with strontium (Sr) from high active acidic streams. The stripping of the radionuclides from loaded TEHDGA phase is carried out using dilute HNO_3 (0.01 M). The product, rich in Sr-An-Ln , is further concentrated and used for recovery of bulk amount of strontium. Multistep separation processes involving ion exchange process, membrane-based process, chemical precipitation etc. are employed to recover purified form of strontium, devoid of other radio-nuclides as per desired product quality. The recovered strontium product is subjected to two-step Supported Liquid Membrane (SLM) system for milking out Yttrium-90 (^{90}Y). The SLM based milking process for generation of pure ^{90}Y is done using three chamber glass assembly cell as presented in Figure 5. Acidity of mixture of ^{90}Sr and ^{90}Y is brought down to pH 1-2 and is placed in the first chamber (feed chamber). The second chamber (intermediate compartment) and third chamber (receiver chamber) contain 4 M HNO_3 and 1 M Acetic Acid (CH_3COOH), respectively. Between the feed and intermediate chamber, 2-ethylhexyl phosphonic acid (KSM-17) based SLM is inserted, whereas SLM containing carbamoyl methyl phosphine oxide (CMPO) is placed between intermediate and receiver chamber [2]. ^{90}Y is selectively transported from feed chamber to aqueous phase of receiver chamber containing acetic acid via intermediate chamber containing 4

M HNO_3. Production of pharmaceutical grade ^{90}Y to 150 mCi per batch with separation yield of >90% has been established using this system. ^{90}Y, in the form of Yttrium Acetate, is supplied to Radiation Medicine Centre (RMC) for radio-pharmaceutical applications.

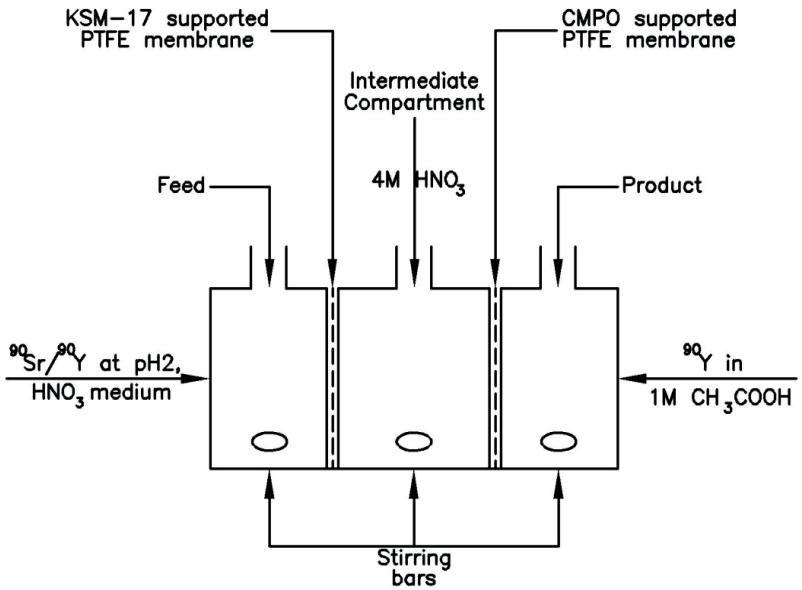


Figure 5: Schematic diagram of ^{90}Sr-^{90}Y SLM radiochemical generator

3.3 Separation of ^{106}Ru

^{106}Ru (half- life of 373 days) is an important fission product produced during thermal fission of uranium. It is a low energy beta emitter (Figure 6). However, its daughter, ^{16}Rh emits high energy beta radiation which is very useful for brachytherapy applications, particularly for the treatment of eye cancer.

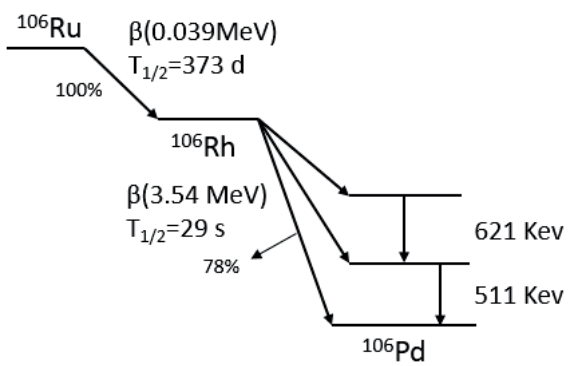


Figure 6: Decay characteristics of ^{106}Ru

Separation of ^{106}Ru is carried out from raffinate obtained after three cycle solvent extraction process as discussed above. The process utilizes oxidation of Ru-nitrosyl nitrate to RuO_4 by addition of KIO_4 followed by extraction of RuO_4 in chlorinated CCl_4. Finally, the extracted Ru is stripped from CCl_4 using acidic hydrazine solution [3]. A process flow-diagram is presented in **Figure 7**. The scheme has been used to recover around 100 mCi of ^{106}Ru for preparation of brachytherapy sources.

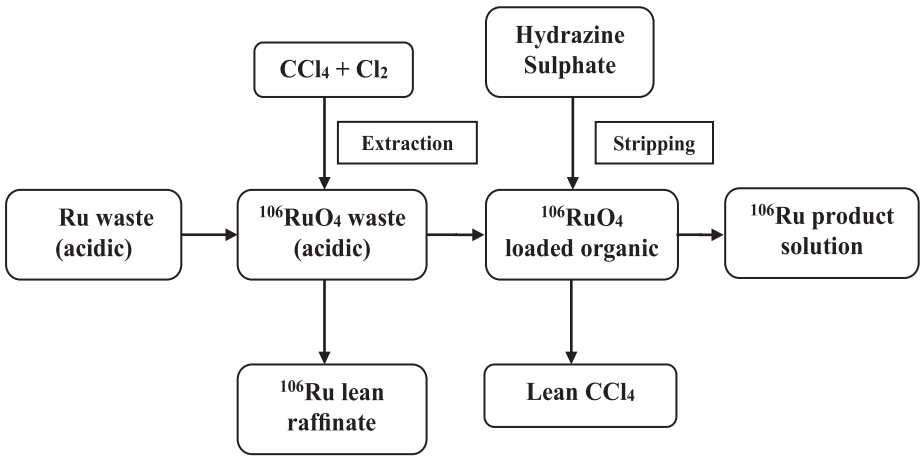
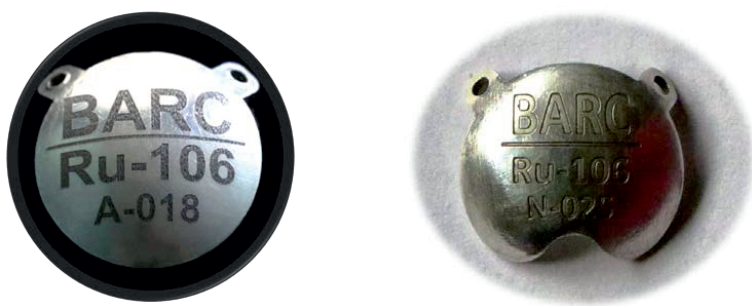


Figure 7: Flow chart developed to purify ^{106}Ru from high level waste

Preparation of brachytherapy source from purified ^{106}Ru solution includes electro-deposition of ^{106}Ru on a silver substrate followed by preparation of sealed source in the form of a plaque. Two types of Ru plaques have been developed by BARC (Figure 8). The notched plaque has been designed for treatment of eye cancers near the optic nerve. A number of ^{106}Ru bearing plaques have already been sent to different hospitals in India and are being used in treatment of eye cancer. The feedback from various hospitals (Figure 9) confirms that Ru plaques indigenously developed by BARC ensures affordable eye cancer treatment.

4. The way ahead

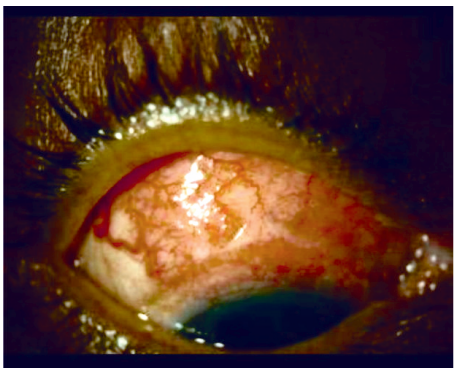
In summary, utilization of three radioisotopes as discussed in this article clearly justifies that HLLW is a true source of wealth of national importance. Nevertheless, there are many more



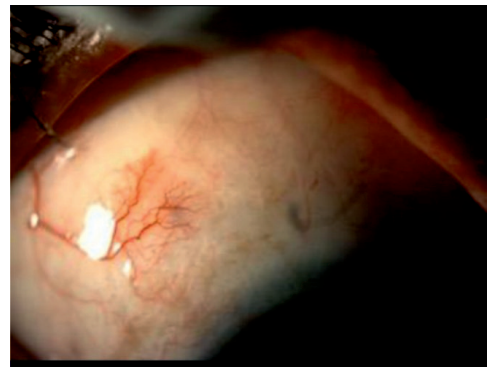
Type A (Round) Plaque Type N (Notched) Plaque

Figure 8: Different types of Ru plaques developed by BARC

valuable radioisotopes and some non-radioactive isotopes present in HLLW with potential applications. Efforts are also being made to establish large scale recovery of them. Successful implementations of some of the processes open up the true potential of HLLW towards serving mankind.



Conjunctival lymphoma before treatment



Regressed lesion after treatment

Figure 9: Eye cancer cure using Ru plaque developed by BARC

[Courtesy: Sankara Eye Hospital, Bengaluru]

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