

Advanced Treatment Process

Process Development in Back-end of Fuel Cycle

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Alpha Demonstration Facility in Waste Immobilisation Plant in Trombay

ABSTRACT

The activities in the back-end of nuclear fuel cycle demand sustained process development for meeting various challenges faced during spent fuel reprocessing and radioactive waste management. Adaptation of innovative process schemes and novel solvents has not only simplified the management of HLLW but also opened up a new dimension towards the beneficial applications of many of these radioactive isotopes in various medical and industrial radiation technology applications in concurrence with our mission of serving the nation and society through peaceful uses of nuclear energy. This article highlights some of the recent developments in the back-end of nuclear fuel cycle.

KEYWORDS: Pyrolysis, Incineration, Advanced oxidation, Decontamination, Novel solvents, Functionalized resin.

Introduction

The back-end of the Indian nuclear fuel cycle involves essentially spent fuel reprocessing and associated waste management activities. Process development in the back-end assumes greater importance to meet evolving requirements of higher productivity, improved product quality and enhanced safety. The reprocessing technology in the country has reached maturity at the industrial level with a very high recovery rate. Safe and economically efficient back-end operations that can further minimize waste generation and environmental impact are essential to the sustainable development of nuclear energy programmes. Sufficient scope exists to improvise processes and technologies with innovative approaches for significant reduction in radio-toxicity and hazard posed by radioactive substances to humans and the environment.

Process Development for the Management of Alpha-Contaminated Waste

Various types of cellulosic, polymeric and metallic wastes are generated during the glove box operations at fuel fabrication as well as at the back-end facilities. These wastes are currently stored at interim storage facilities pending treatment. Recovery of valuables and reduction in the waste volume are quite challenging while developing suitable treatment methods. Significant efforts have been geared towards process development for the treatment of aged cellulosic waste. To make the decontamination process more energy-efficient for treating polymeric and cellulosic waste, pyrolysis-incineration is envisaged prior to the decontamination step. Glove box adaptable modules for the pre-treatment step consisting of shredding, homogenizing and conveying of non-metallic waste in a continuous mode to the pyrolyzer and incinerator followed by combustion of off-gas in

an afterburner. Performance of these modules have been demonstrated by feeding the shredded waste comprising 10% cellulose, 35% rubber and 55% PVC to a pyrolyzer followed by an incinerator to produce ash with an overall volume reduction factor of 25 (Fig. 1).

Process Development for Combined Removal of Ruthenium and Antimony

The philosophy followed for the management of waste streams containing short-lived fission products like Ruthenium (¹⁰⁶Ru) and Antimony (¹²⁵Sb) is either delay and decay by storage or dilute and disperse by discharging to water bodies meeting the regulatory criteria. A chemical precipitation process was developed for simultaneous removal of Ruthenium and Antimony with a DF > 300 for the acidic Intermediate Level Waste (ILW) generated during high-level waste management at Trombay. An international patent has been applied for the developed process. The same process was tried for Low Level Waste (LLW) generated from DHRUVA. Experiments carried out using deca waste containing citrate showed Ru removal of 50%, while deca waste without citrate resulted in ~95% removal.

Ozone-based Treatment of DBP-bearing Simulated Carbonate Waste

Ozone-based advanced oxidation processes use ozone to destroy a variety of organic compounds mainly to CO₂ and H₂O [1]. These processes offer a salt-free treatment of a given waste stream, thus minimizing the secondary waste volumes. One such process has been developed for pre-treatment of di-butyl-phosphate (DBP) bearing carbonate waste and is demonstrated on a 50 L scale. Ozone generated from air is used to destruct the DBP content of simulated waste from 4.3 to 0.3 g/L in 14 hours as shown in Fig. 2. A slight decrease in pH during the treatment was also observed, which could be attributed to the formation of equimolar quantities of H₃PO₄ during ozonation.

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Fig.1: Pyrolysis-incineration process for management of GB waste. (Left: Shredded feed to pyrolyzer and Right: Ash product from incinerator)

Sequestration Process for Tc Removal from LLW

It is well known that TcO_4^- removal from the LLW is difficult and challenging due to the presence of other monovalent anions like, NO_3^- and OH^- , which competes with TcO_4^- during separation processes. In this regard, a novel process for Tc sequestration by in-situ formed corrosion products of mild steel was developed and patented [2]. Based on the encouraging results on active and inactive studies at BARC, engineering scale studies were carried out at LWTP, Tarapur jointly by NRG & NRB. Tc sequestration process was demonstrated on a plant scale with 90-95% ^{99}Tc removal. After carrying out a few runs for fine-tuning, DF of 200 was obtained for ^{99}Tc . Decant activity after sequestration treatment was found to be in the order of 10^{-4} mCi/L.

Electro-Brush Method for Removal of Fixed Contamination

Removal of fixed alpha contamination on metal surfaces requires aggressive chemical/mechanical techniques. Secondary waste generated by these methods is difficult to manage by conventional routes [3]. To address this issue, an inherently safe electrolytic decontamination method using a movable cathode (electro-brush) was developed. By this method, effective decontamination was obtained with minimal secondary waste generation. Initial inactive trials were carried out using various nitric acid concentrations and current densities. The optimum corrosion rate was observed at 4M HNO_3 concentration and 200 mA/cm² current density. Active trials were performed with alpha planchets having fixed contamination, and up to 99% decontamination was recorded in 10-20 min. Based on these, active decontamination studies were jointly carried out between NRG & NRB. Stainless Steel surfaces were successfully decontaminated by removing all loose & fixed contaminations to a level of alpha activity < 0.037 Bq/cm².

Chemical precipitation process developed for simultaneous removal of Ruthenium and Antimony can be effectively used for the management of acidic Intermediate Level Waste.

Development of New Solvents and Resins with Chemically-bonded Ligands

Development of novel solvents and their successful deployment at the back end of the nuclear fuel cycle established an innovative strategy for managing high-level liquid waste (HLLW). The use of such highly specific solvents was aimed at better waste management, and the recovery of some radioactive isotopes deemed beneficial for societal applications. The current radionuclide partitioning process followed in India is based on the application of two crucial solvents, viz., (i) 1,3-dioctylcalix[4]arene-18-crown-6 (Calix-Crown-6) for the recovery of ^{137}Cs and (ii) Tetra-2-Ethylhexyl-

Diglycolamide (T2EHDGA) for bulk separation of trivalent actinides and lanthanides [4, 5]. Further, the separation between trivalent actinides and lanthanides from TEHDGA strip products is carried out by an improvised TALSPEAK process for obtaining pure actinide products.

Consequent to the successful deployment of the above two solvents, recent R&D has been focused on the development of newer solvents with the objectives of process simplification and recovery of valuable radioisotopes with better product purity. Towards this, work has been taken up for the commercial synthesis of 4',4''(5'')-di-tertiary-butyl-dicyclohexano-18-crown-6 (DtBuDCH18C6). DtBuDCH18C6 is a solvent that is highly selective for Strontium [6]. Laboratory scale evaluation of the solvent has conclusively confirmed that DtBuDCH18C6 extracts ^{90}Sr directly from HLLW. This ^{90}Sr is used to generate ^{90}Y , which has tremendous applications as radiopharmaceuticals for cancer treatment. In a similar approach, a new solvent Camphor Bistriazinyl Pyridine (CA-BTP), has been investigated for trivalent lanthanide-actinide group separation. Process evaluation utilizing CA-BTP has shown very high separation factors (~90) for trivalent lanthanide-actinide group separation. The synthesis and purification of this solvent have been carried out in-house, and the procedures for its scale-up have been optimized.

A functionalized resin has been synthesized with ligand chemically bonded upon a supporting material. The resin has been tested in batch mode. It shows a very high uptake for trivalent (Am^{3+} , Eu^{3+} & Y^{3+}), tetravalent (Pu^{4+}) and to some extent, hexavalent (UO_2^{2+}) metal ions but almost

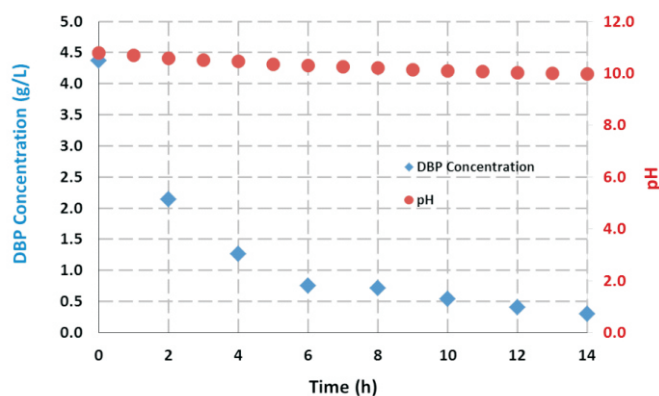


Fig.2: Di-butyl-phosphate (DBP) concentration. pH versus time plot.

negligible uptake for divalent metal ion (Sr^{2+}) from a feed acidity of 4.0 M nitric acid. The K_d values for the resin is in the range of ~3500 - 4000 mL/g for Am & Eu, Y and ~8 - 10 mL/g for Sr. Elution of Eu-loaded resin has also been carried out at pH~2 and 60% was eluted in 1st contact. Cumulative stripping of 98% was obtained in three successive contacts. The stability of the resin in the nitric acid medium was assessed by keeping the resin in nitric acid for 10 days continuously and was found to hold the same initial texture, colour and mass. The initial screening of the resin with respect to the extraction & elution behaviour of different metal ions shows potential for separation of Sr from TEHDGA-strip solution and for milking of ^{90}Y , from recovered ^{90}Sr from HLLW.

Conclusions

Process development is a continuous activity to meet the evolving requirements in the back-end of nuclear fuel cycle. Pyrolysis and incineration system has been developed for effective treatment of alpha contaminated polymeric and cellulosic wastes. Engineering scale demonstrations of ozone-based treatment process and Technetium sequestration process confirm their amenability for industrial deployment.

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