



# In-situ causticization, a new process for management of DBP containing alkaline low level radioactive liquid waste



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## ABSTRACT

The di-butyl phosphate (DBP) containing alkaline low level radioactive waste generated during PUREX solvent cleanup with  $\text{Na}_2\text{CO}_3$  was decontaminated using a new process called “in-situ causticization” where NaOH was produced in-situ by addition of  $\text{Ca}(\text{OH})_2$  resulting from precipitation of  $\text{CaCO}_3$ . Alpha activity from the carbonate free solution was quantitatively precipitated by NaOH leading to a high alpha decontamination factor (DF) of  $\sim 240$  in the supernatant solution. DF for  $\beta$ -activity was low ( $\sim 3$ ) due to partial precipitation of cesium and ruthenium. DBP remained in the solution as Na-DBP. XAD-4 resin was used to remove Na-DBP and any other dissolved organic. The remaining cesium was removed by resorcinol–formaldehyde resin and the solution containing only ruthenium was suitably diluted and discharged to sea. The calcium carbonate sludge was solidified with ordinary Portland cement, the activity load, compressive strength and leach rate of cement waste product (CWP) was within the acceptable limits of our near surface disposal facilities. The final volume of CWP obtained by this process is at least 2.5 times less than the volume obtained by direct cementation of the waste.

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## 1. Introduction

During reprocessing of spent nuclear fuel by PUREX process, the solvent, tri-*n* butyl phosphate/*n*-dodecane exposed to intense radiation in contact with nitric acid, undergoes chemical and radiolytic degradation forming varying amount of acidic degradation products like mono and di-butyl phosphates (MBP and DBP) among various other degradation products of solvent [1,2]. The acidic degradation products form stable complexes with Pu and U which leads to various difficulties during reprocessing steps like loss of extractability, poor stripping and third phase formation. Therefore, in order to make the solvent suitable for recycle, it needs to be washed with dilute sodium carbonate solution to remove the acidic degradation products as water soluble sodium salts [2,3]. However, during this process, stripping to a lesser extent of actinides and fission products present in the solvent phase also takes place thereby contaminating the aqueous carbonate solution with actinides and fission products [4–13]. This aqueous waste containing radioactivity concentration close to  $37 \times 10^6$  Bq/L is categorized as low level waste and requires removal of actinides, fission products and organic matter prior to discharge through sea route

and final disposal of solidified chemical sludge containing actinides and fission products in near surface disposal facilities (NSDF) as cemented waste form [14]. A large number of strategies have been investigated, however, difficulties like formation of emulsions, floating masses, cruds and precipitates are the major issues encountered while processing this type of waste stream [4,8].

The routine procedure to manage this kind of waste is by chemical precipitation where actinides are removed from the bulk solution as sludge by addition of sodium hydroxide. But, due to presence of actinides in stable carbonate complexes, addition of sodium hydroxide does not result in their quantitative precipitation. In view of this, carbonate needs to be destroyed by addition of acid before precipitation with sodium hydroxide. But, addition of acid results in foaming, formation of floating masses, cruds and dirty organic precipitates which hinder further processing of the liquid waste. Alternate methods like co-precipitation of U, Pu and Np from carbonate wash solution using sodium hydroxide, ammonium hydroxide and hydrolyzed Fe(III) ions have been tried for high burn up fast reactor fuel [8,9]. DBP extraction in long chain alcohols was also tried [4] but due to presence of other degradation products, formation of some floating organic mass hindered the process. Inorganic and organic ion exchangers, sorbents like silica gel, alumina, XAD-resins have been used to treat this kind of waste but poor elution and low decontamination factor for alpha emitters due to presence of sticky organic mass were always an issue [15].

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The present work reports a new process of removal of carbonate and actinides from the solution by addition of calcium hydroxide, where sodium hydroxide was generated in-situ resulted by precipitation of carbonate as calcium carbonate. This process called “in-situ causticization”, doing both the jobs together just by adding calcium hydroxide to the waste, first, removing total carbonate from the solution by precipitating carbonate as calcium carbonate and second, precipitating actinides quantitatively as their hydrous oxides by in-situ liberation of sodium hydroxide. Further reduction in actinides concentration in the waste solution was achieved by carrier precipitation reaction with ferric hydroxide. Flocculating agent, polyacrylamide (PAM), a water soluble polymer, has been used to reduce the volume of the calcium carbonate sludge [16]. Optimization of calcium hydroxide, PAM and Fe(III) concentrations were done to enhance alpha DF and improve settling behavior of sludge. Cementation of the sludge was also studied as a means for its management before final disposal at near surface disposal facility. Based on the results, a process flowsheet has been proposed for demonstration on larger scale for plant scale implementation.

## 2. Experimental

### 2.1. Chemicals and methods

All the chemicals used in the study were of commercial grade. pH was measured using Cyberscan pH-1100 from Eutech instrument pH meter. Gross  $\alpha$ ,  $\beta$  and  $\gamma$  activities were measured by ZnS/Ag scintillation detector, GM counter and NaI/Tl scintillation detector. Radiometry assay of  $^{106}\text{Ru}$ ,  $^{125}\text{Sb}$  and  $^{137}\text{Cs}$  was carried out by gamma counting employing an HPGe detector coupled with 4 K MCA at 511, 599 and 661 keV respectively. For determination of alpha activity, an aliquot of the filtered solution was diluted with 1 M nitric acid, placed on SS planchet, dried under IR lamp, fired in a flame and counted using alpha counter. Uranium concentration was determined by spectrophotometry using both ammonium thiocyanate and bromo-PADAP reagents [17]. For DBP analysis, the waste was acidified and extracted with three volumes of benzene, the combined extract was titrated with ethanolic sodium hydroxide using bromo-cresol purple as indicator [18]. Carbonate was analyzed by acid-base potentiometric titration. All the experiments were carried out at room temperature. The analysis by all the methods were within the error limits of  $\pm 5\%$ .

### 2.2. Experimental procedure

Few liters of actual waste generated from reprocessing plant, stored for 8–10 years, were collected for the experimental studies. The radiochemical composition of the waste is shown in Table 1. Different quantities of calcium hydroxide (0.05–0.50 M) were added to a fixed volume of radioactive waste and the supernatant was analyzed for depletion of carbonate, uranium, DBP, gross alpha and beta activities after filtration at different time intervals. Decontamination factor (DF) was calculated as the ratio of initial specific activity ( $\alpha$  or  $\beta$ ) to the final specific activity of the solution (Eq. (1)).

$$DF = \frac{\text{Initial activity } (\alpha \text{ or } \beta) \text{ per unit volume present in the feed waste}}{\text{Final activity } (\alpha \text{ or } \beta) \text{ per unit volume left in the supernatant}} \quad (1)$$

Settling behavior of the sludge and DF were improved by addition of PAM and  $\text{Fe}(\text{NO}_3)_3$ . The supernatant solution was decanted and dissolved organic was removed by Amberlite XAD-4 resin packed in 0.6 cm diameter and 10 cm bed height column. 10 g of resorcinol-formaldehyde (RF) resin packed in a 0.6 cm diameter column was used for cesium removal. The chemical sludge generated was taken

**Table 1**  
Characteristics of the waste.

Sr. no.	Property	Value
1	Color	Light yellowish-brown
2	pH	9.0–9.5
3	Gross $\alpha^*$ (Pu)	0.18 mCi/L
4	Gross $\beta$	0.6 mCi/L
5	$^{241}\text{Am}$	Not detected
6	$^{137}\text{Cs}$	0.27 mCi/L
7	$^{90}\text{Sr}$ – $^{90}\text{Y}$	0.2 mCi/L
8	$^{106}\text{Ru}$	0.07 mCi/L
9	$^{125}\text{Sb}$	0.05 mCi/L
10	DBP	30 g/L
11	Uranium	3 g/L
12	Sodium	15 g/L
13	Carbonate	18 g/L (0.3 M)
14	Total dissolved salts	80–90 g/L

BDL: below detection limit, minimum detection concentration for  $\alpha = 5 \times 10^{-6}$  mCi/L and  $\beta = 3 \times 10^{-5}$  mCi/L.

\* Gross  $\alpha$  activity is mainly due to plutonium.

in a plastic container for fixation in cement matrix. Ordinary Portland cement (OPC) at a waste to cement ratio of 1:1 w/w was slowly added in sludge under continues stirring. After complete addition of cement, the stirring was further continued for 15–20 min to remove entrapped air. The mixed paste was kept for curing under humid conditions for 28 days. The block was then removed from plastic container and taken for chemical durability and compressive strength evaluation. The chemical durability study of the cement block was tested by conventional Leaching methods using distilled water as leachant at ambient temperature following the method described by Ojovan et al. [19] and compressive strength was measured using a hydraulic compression testing machine as per procedure established in ASTM C39 [20]. For Leaching test, the cement blocks were tied with stainless steel wire and then submerged in requisite quantity of de-mineralized water. The ratio of leachant volume to surface area of cement block maintained throughout the leach test was 10.9 cm. The leachate was removed periodically and the water was replenished at predefined time intervals for a total period of 365 days. The leachate was analyzed for gross  $\beta$  activity after every removal and normalized leach rate was calculated using following equation.

$$\text{Normalized leach rate (g/cm}^2\text{day)} = \frac{\text{Normalized mass loss of } \beta \text{ radionuclides (g/cm}^2\text{)}}{\text{test duration in days}} \quad (2)$$

where normalized mass loss is the ratio of amount of  $\beta$  radionuclides leached from the cement block to the multiple of specific radioactivity (37,000 Bq/g) and surface area (41.25 cm<sup>2</sup>) of the cement block.

The overall error in the measurement was within 10%. Typical pictures of settled sludge and Leaching of the CWP are shown in Fig. 1a and b. The sludge was obtained on addition of 25 g Ca(OH)<sub>2</sub>, 2 mg PAM, and 50 mg Fe(III) to 1 L of waste solution and settling time of 8 h.

## 3. Results and discussion

### 3.1. Kinetics of decontamination

After addition of calcium hydroxide to the waste, the supernatant was analyzed for carbonate at different time intervals. As shown in Fig. 2, rate of depletion of carbonate from the solution increases with increase in calcium hydroxide concentration, it was maximum in two hours and then reduces slowly and remained constant after 6 h. Reduction in carbonate concentration was

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