SYNTHESIS OF DICYCLOHEXANO 18 CROWN 6 LIGAND ON BENCH SCALE & DEVELOPMENT AND DEMONSTRATION OF SELECTIVE RECOVERY OF STRONTIUM FROM THORIUM LEAN RAFFINATE (TLR) WASTE IN THE BACK END OF NUCLEAR FUEL CYCLE USING THE LIGAND

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Dr. K.T. Shenoy and his team received the DAE Group Achievement Award for the year 2011

Abstract

Chemical Engineering Division (ChED) has successfully developed the process for synthesis of Di-Cyclo Hexano 18 Crown 6 ether (DCH18C6) ligand, which is selective for strontium, on bench scale. Initial extraction experiments were carried out in ChED with simulated waste solution and later by radiometric analysis in FRD and WIP laboratories. Finally, quantitative recovery of strontium was successfully demonstrated from the actual Thorium Lean Raffinate (TLR) using the in-house synthesized solvent in five stage mixer – settler experimental facility set up in a fume hood of WIP laboratory. The details of these developmental studies are described in this paper.

Introduction

The crown ether, DCH18C6, has a very important application in back end of the fuel cycle for recovery of strontium from the actinide–free waste streams. TLR stream is generated at FRD during the processing of J-rods of CIRUS reactor. The composition of the raffinate stream after recovery of uranium and thorium are given in Table – 1. Major radioactive elements are Cs and Sr in acidic medium. There is a good demand for Sr$^{90}$ which is required for generation of Y$^{90}$ which is an important radionuclide for therapy in nuclear medicine. Sr$^{90}$ finds use as heat source in radio isotope thermoelectric generators and as radioactive tracer in medicine & agriculture. It is proposed to recover Sr from the active waste stream first by solvent extraction with DCH18C6 followed by recovery of Cs with Resorcinol Formaldehyde resin.

Synthesis of DCH18C6 on bench scale

The bench scale synthesis set up has a batch size of 1 kg of the crown ether DCH18C6 and its precursor DB18C6. The set up consists of 85 liter hastelloy reactor, 25 and 10 liter glass reactors for solvent recovery, 25 liter SS autoclave for hydrogenation, electrode boiler, 5 TR chiller unit etc. The bench scale synthesis runs were conducted through round the clock shift operations. The DB18C6 was synthesised in a ventilated enclosure with about 35% yield and more than 98% purity. Bio Organic Division, BARC has assisted in improving the yield of product. DCH18C6 was synthesized through high pressure catalytic hydrogenation in 25 liter SS autoclave in a semi open area, custom made for this purpose from safety point of view. DCH18C6 was synthesized with more than 90% yield and more than 98% purity.
Strontium extraction – Batch experiments

A set of experiments involved batch contacts of aqueous and organic samples intimately contacted at least for 10 min for attaining the equilibrium condition before separation for analysis. All the strontium analyses were carried out by doping with necessary amounts of active Sr85+89. Pure component data for distribution coefficient of strontium and various impurities likely to be encountered in waste streams, effect of nitric acid concentration, etc. were studied.

Effect of molarity of nitric acid in the feed solution:

Experiments were conducted to optimize the concentration of nitric acid in the feed to achieve maximum uptake of Sr using 0.1M DCH18C6 in the mixture of 20% Octanol + 80% Toluene. It was found that Sr extraction increases with increase in conc. of nitric acid upto 4 M, thereafter, it remains more or less constant. Hence, optimized concentration of 4 M is used for further studies.

Studies on pure components:

The major elements present in the HLW matrix were studied for their extraction by the DCH18C6 and the distribution coefficients were evaluated. It was noted that most of the constituents of the HLW like Cs, Ru, Ce, Eu, Am, U, etc are not extracted to any significant level. It was also noticed that Pu is significantly extracted especially at higher acidities (Kd=25 at 3N and 26.5 at 4N).

Studies on selectivity of DCH18C6 in octanol diluent for Sr in presence of competing actinide elements:

The effect of major elements which are likely to be present in HLW or TLR like Pu, U, Th and Na were studied for their effect on Sr extraction and to find any limiting concentration for better selectivity. It was noticed that thorium is extracted to a small extent at 4.0M acidity in feed. But upto a concentration of 2000 ppm, no significant effect is seen on D$_{Sr}$ (2.8 to 3.2 at 4M). Less than 3 mg/l Pu content in HLW does not affect Sr extraction.

Strontium extraction – Continuous contact experiments

Continuous counter current studies were carried out using 5 stage mixer settler, each stage having 125 ml mixer and 375 ml settler (Fig. 2). All the experiments were carried out in one of the fume hoods having adequate shielding at Process Control Laboratories of WIP with the DCH18C6 synthesised in ChED.

<table>
<thead>
<tr>
<th>Properties</th>
<th>TLR waste</th>
<th>Adjusted TLR Feed to MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molarity (M, H+)</td>
<td>2.0</td>
<td>3.7</td>
</tr>
<tr>
<td>Specific Activity, mCi/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gross Beta</td>
<td>16.64</td>
<td>15.07</td>
</tr>
<tr>
<td>Gross Alpha (Th)</td>
<td>1.56×10²</td>
<td>1.3×10²</td>
</tr>
<tr>
<td>Isotopic Constituents, mCi/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs-137</td>
<td>7.00</td>
<td>6.0 (0.0697 ppm)</td>
</tr>
<tr>
<td>Sr-90</td>
<td>4.60</td>
<td>3.92 (0.0284 ppm)</td>
</tr>
<tr>
<td>Sb-125</td>
<td>1.37×10³</td>
<td>1.22×10³</td>
</tr>
<tr>
<td>Tc-99</td>
<td>5.0×10³</td>
<td>4.44×10³</td>
</tr>
<tr>
<td>Ru-106</td>
<td>3.2×10³</td>
<td>2.84×10³</td>
</tr>
<tr>
<td>Al (g/l)</td>
<td>2</td>
<td>1.77</td>
</tr>
<tr>
<td>F (ppm)</td>
<td>300</td>
<td>267</td>
</tr>
</tbody>
</table>

Table 1: The composition of TLR used for mixer settler experiments
Since the TLR waste had free acidity of about 2M, the same was adjusted to about 3.7M by the addition of conc. nitric acid to exploit the higher distribution coefficient. The details of extraction and stripping parameters are given below:

Feed activity of Sr: 3.92 mCi/l  
Concentration of Sr = 0.0284 ppm (based on specific activity of Sr$^{90}$ as 138Ci/g)  
Flow rate of Aqueous: 25 ml/min; Flow rate of Organic: 25 ml/min  
Volume of organic: 7l (0.1M DCH18C6)  
Activity of loaded Organic (based on activity balance during extraction): 3.86 mCi/l

Only aqueous streams could be analysed for Strontium. Strontium in organic was estimated based on average D value of 3.2. Cumulative raffinate was found to contain 6 x 10^{-2} mCi/l of Sr and 5.8 mCi/l of Cs. Based on Sr and Cs activity in the feed and raffinate, the Decontamination Factor (DF) with respect to Sr works out to be 65.

More than 99% strontium was stripped in 3 stages. Activity balance shows complete stripping of the loaded organic. Concentration profiles of strontium in various stages of mixer settler for extraction and stripping are given in Fig. 3. Product solution showed 3.86 mCi/l of $^{90}$Sr and 0.12 mCi/l of $^{137}$Cs indicating negligible crosstalk of Cs during extraction and stripping cycle.

**Conclusion**

The demonstration of the extraction experiment has shown overall recovery of strontium from TLR is more than 98.5% based on the feed activity and cumulative raffinate activity. Three diluent combinations were tested namely Octanol, Octanol + Toluene and Octanol + Xylene. All were found suitable for strontium recovery. Octanol is better suited for feed streams, which does not have impurities like Ba, K, etc. from the point of view of lower volatility. The vapor pressure and flash point of octanol are close to dodecane. The only impurity identified in the product is Cs which is about 3% of the total product activity. Purity of the product can be improved to the desired extent by incorporating acidic scrubbing step. The Sr$^{90}$ content can be concentrated from the final product strip solution by evaporation followed by carbonate precipitation. The recovery of Sr$^{90}$ from feed stream to strip is more than 98%. DCH18C6 solvent system is also suitable for strontium recovery from actinide-free HLW. The flowsheet finalization may require some experimental work with HLW.