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TREATMENT OF ACIDIC INEEL WASTE USING A COUNTERCURRENT COBALT DICARBOLLIDE-BASED UNIVERSAL SOLVENT EXTRACTION PROCESS

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ABSTRACT

A tertiary solvent containing chlorinated cobalt dicarbollide, diphenylcarbamoylmethylphosphine oxide and polyethylene glycol in different diluents was evaluated for the separation of cesium, strontium, actinides and rare earth elements from acidic liquid radioactive waste in countercurrent solvent extraction processes. This universal solvent extraction process has been demonstrated in 24-stage centrifugal contactor pilot plants, using simulated acidic tank waste, at the Khlopin Radium Institute (KRI), St. Petersburg, Russia, and at the Idaho National Engineering and Environmental Laboratory (INEEL). Demonstration of the universal extraction process with actual tank waste is scheduled at the INEEL in 1998.

I. INTRODUCTION

The Idaho Chemical Processing Plant (ICPP) located at the INEEL, formerly reprocessed spent government-owned nuclear fuel to recovery uranium. A modified PUREX process was used to separate the uranium from the high-activity fission products and non-active fuel components. Subsequent uranium purification was accomplished in two cycles of a REDOX-type solvent extraction process. Liquid raffinates were temporarily stored in underground storage tanks, as acidic waste, and ultimately solidified into a granular calcine. High-activity liquid waste was also produced as the result of decontamination activities, solvent cleanup, and low-activity waste evaporation. This acidic waste is typically high in sodium content (about 1.3-1.8*M*) and is not amenable to direct calcination. Historically, this waste was blended with first-cycle raffinates and calcined, however, reprocessing activities were halted in 1992 and all stored raffinate solutions were calcined. The remaining liquid waste, approximately 5.6 million liters, is currently stored in underground tanks at the ICPP. The storage of these waste does not meet current regulatory requirements, and therefore the waste must be treated and removed from the INEEL in the near future.

An aggressive development effort has been underway since 1992 to evaluate technologies for processing and immobilizing the liquid and calcine radioactive wastes. The recommended treatment method for the calcine is to dissolve it in nitric acid and then separate the radionuclides from the bulk waste components. The liquid tank waste is highly amenable to treatment using the same processes.

The cobalt dicarbollide solvent extraction process, originally developed in the mid-1970's by Czechoslovakian researchers,[1,2] and later developed and implemented in Russia[3,4] has been demonstrated to be effective at removing cesium from acidic solutions. Strontium removal can also be achieved by the addition of polyethylene glycol to the solvent. A collaborative development program has been ongoing for the past four years between the Idaho National Engineering and Environmental Laboratory and the V. G. Khlopin Radium Institute in St. Petersburg, Russia. The focus of this program has been the development and demonstration of the cobalt dicarbollide process on simulated and actual INEEL acidic waste streams.[5]

Most of the original work with cobalt dicarbollide was performed with nitrobenzene derivatives as the solvent diluent. A non-aromatic diluent was developed by KRI researchers and used in batch contact tests and countercurrent demonstrations of the cobalt dicarbollide process at INEEL. Recently, a tertiary solvent containing chlorinated cobalt dicarbollide, polyethylene glycol and diphenylcarbamoylmethylphosphine oxide (dϕ-CMPO) was developed for the simultaneous removal of cesium, strontium, actinides and rare earth elements from acidic wastes. The removal of theses radionuclides from the waste in a single unit operation offers significant potential capital and operating cost savings.

This paper will describe the results of countercurrent flowsheet tests performed with the universal extraction process using simulated acidic wastes. Two tests were performed in centrifugal contactor pilot plants; one test performed at KRI in Gatchina, Russia, and the other at the INEEL. Another test, using actual tank waste, will be performed in a shielded hot cell facility at the INEEL, in June 1998.

II. EXPERIMENTAL

A countercurrent test of the universal extraction process was performed at the V. G. Khlopin Radium Institute (Gatchina), with simulated INEEL tank waste spiked with actual concentrations of radionuclides. The test was performed in two extraction cascades of 12 stage centrifugal contactors (type MZE 12-30). The centrifugal contactors are configured in a circle, with one electric motor drive for all 12 stages, via a gear mechanism. Flexible tubing connects each stage and interconnects both cascades to facilitate solution transfer. The radionuclides were extracted from the sodium-bearing waste simulant in stages 1-8. The solvent was then washed in stage 9 and the rare earths, Sr, and actinides were stripped in stages 10-14. Cesium was stripped in stages 15-20, and the solvent was washed in stages 21-24. The solvent used for the test was comprised of chlorinated cobalt dicarbollide, polyethylene glycol and dϕ-CMPO in metanitrobenzotrifluoride.

Based on the results of universal solvent development studies performed at the Khlopin Radium Institute and at the INEEL, a flowsheet was developed and recommended for countercurrent flowsheet testing in 3.3-cm diameter centrifugal contactors. This flowsheet, as shown in Figure 1, consists of eleven stages of extraction, one stage of scrub, six stages of Cs/Sr strip, three stages of actinide strip, and five stages of solvent wash.

Flowsheet testing was performed using 3.3-cm diameter centrifugal contactors procured from the Research and Development Institute of Construction Technology (NIKIMT) in Moscow, Russia. The 3.3-cm Centrifugal Contactor Pilot Plant consist of 26 stages of 3.3-cm diameter centrifugal contactors, feed and receiving vessels, feed pumps, and an air purge system for the feed and product vessels. Centrifugal contactor rotor speed is adjustable from 0 to 2700 rpm using a variable speed motor drive. The centrifugal contactors were designed for operation with a wide range of solvent extraction technologies. Application to different organic/aqueous systems is accomplished by length adjustment of the two light phase overflow tubes, or nozzles, located near the top of the separating chamber. The length of the tube is altered as function of the densities of the two phases.

Forty liters of tank waste simulant was prepared to emulate the average composition of the waste currently stored in the INEEL tank farm. The components used as surrogates for the fission products (stable Cs and Sr) and actinides (Eu) were added to the simulant at higher concentrations than found in the actual wastes to facilitate detection limits for analytical chemistry.

Samples from testing were analyzed for Eu, Cs, Sr, Ba, Zr, Fe, Pb, Hg, H^+, Mo, Na, and K. Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) was used for Eu, Pb, Mo, Zr, Ba, Cs, Sr, and Fe analyses, atomic absorption spectrophotometry (AAS) was used for Na and K analyses, and atomic fluorescence spectroscopy was used for Hg analyses.

A second flowsheet was also tested at the INEEL. The second flowsheet was modified to prevent problems encountered during testing of the first flowsheet. Modifications made for the second flowsheet included

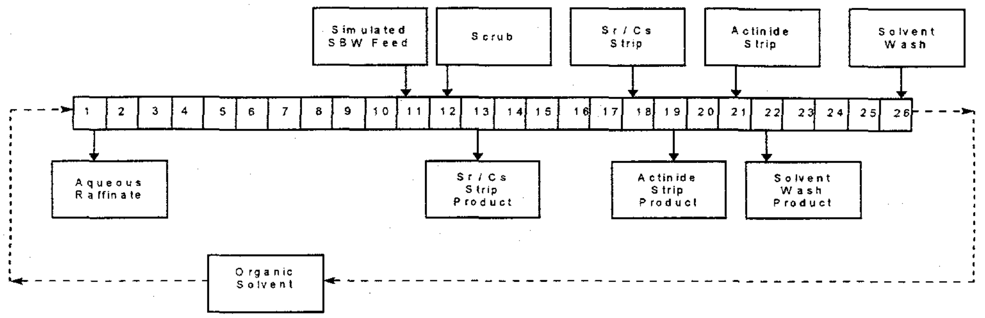

Figure 1. Universal Solvent Extraction Process Flowsheet

the addition of citric acid to the aqueous feed, the addition of citric acid to the scrub stream, the addition of citric acid to the Cs/Sr strip solution, and the increase of the Cs/Sr strip flowrate. The flowsheet modifications were necessary in order to reduce the quantity of Zr extracted by the solvent and to prevent the formation of a precipitate in the Cs/Sr strip section.

The composition of INEEL tank waste is shown in Table 1. The compositions of the wastes used in the tests performed at KRI and at the INEEL had slight variations, but, in general were very similar to the compositions shown in Table 1.

Table 1. INEEL tank waste composition

Component	Units	Concentration
H^+	*M*	1.7
Al	*M*	0.55
B	*M*	0.02
Ca	*M*	0.03
Cd	*M*	0.001
Fe	*M*	0.05
Hg	*M*	0.004
K	*M*	0.08
Na	*M*	0.74
NO_3	*M*	5.1
Pb	*M*	0.001
Zr	*M*	4.2E-4
gross α	Bq/L	2.41E+7
^{137}Cs	Bq/L	8.61E+9
^{90}Sr	Bq/L	6.84E+9

III. EXPERIMENTAL RESULTS

A. KRI Flowsheet Test

The universal solvent tested at KRI (Gatchina) using simulated INEEL tank waste with actual concentrations of radionuclides was completed with no observation of flooding, third phase formation or precipitation. The removal efficiencies obtained for the radionuclides are shown in Table 2. Excellent decontamination of the tank waste was achieved.

Iron was equally distributed between the aqueous raffinate and the Sr/actinide strip streams. Approximately 4% of the potassium, 15% of the zirconium and 100% of the lead were recovered in the Sr/actinide strip stream.

Table 2. Radionuclide removal efficiencies for KRI countercurrent flowsheet test.

Radionuclide	Removal Efficiency
^{137}Cs	99.92%
^{90}Sr	99.84%
^{152}Eu	99.8%
^{238}U	99.99%
^{237}Np	>99.93%
^{239,240}Pu	99.99%
^{241}Am	>99.2%

The organic solvent was recycled for about 3 cycles total, with no apparent decrease in extraction efficiency over the duration of the test.

B. INEEL Flowsheet Tests

In the first countercurrent flowsheet test (see Figure 1), flooding was observed in the aqueous solution exiting the Cs strip section. This flooding was not observed until approximately 2 hours after the start of solvent flow, and got progressively worse as the run continued.

Inspection of the Cs strip stages after completion of the test revealed large quantities of precipitate in each of the stages. The quantity of solids in the contactors was sufficient to prevent or impede the flows of solvent, resulting in flooding of the aqueous phase. X-ray diffraction analysis of the precipitate indicate it was likely an insoluble zirconium complex.

While no meaningful data could be obtained for the overall recovery of the radionuclides, the extraction section of the flowsheet operated without problems and removal efficiencies for the radionuclides could be determined. The removal efficiencies Cs, Sr, and Eu (Am surrogate) were 99.7%, >99.98%, and >99.92%, respectively.

The second flowsheet test was performed without flooding or precipitate formation in the contactors, however, some precipitate formation was observed in the solvent feed vessel and tubes leading to the contactors. Samples of the precipitate were not obtained, or subsequently analyzed, therefore the composition of the precipitate cannot be known with certainty. It is known that dϕ-CMPO compounds have a very limited solubility in organic solvents, and it is suspected that the precipitate may have been the CMPO component of the solvent. The solvent used in the second flowsheet test was the same solvent used in the first flowsheet test, but had undergone extensive solvent washing procedures between tests. These washing procedures may have altered the composition of the solvent, resulting in lower solubility of the CMPO, or the precipitate formed in the first flowsheet test could have also changed the composition of the solvent .

Removal efficiencies of 99.7%, 99.97% and 10% for Cs, Sr and Eu, respectively, were obtained. These results support the hypothesis that CMPO precipitated in the solvent, since it is the primary extractant responsible for Eu extraction and such a low removal efficiency for Eu was observed. The use of citrate in the feed, scrub and strip solutions appears to have been effective at complexing zirconium, and subsequently avoiding the precipitation observed in the first flowsheet test.

The effluents streams were also analyzed for Zr, Ba, Pb, Fe, Hg, Mo, Na, and K. Of these components, Ba and Pb were nearly completely extracted. Only 4% of the Pb was stripped in the Cs/Sr strip section and the remainder was stripped in the actinide strip section. For Ba, 2.2% exited in the Cs/Sr strip product and most of the remaining Ba exited with the actinide strip product. However, 12.7% of the Ba was not stripped and remained in the solvent.

Significant amounts of Zr, Fe, Hg, and K were also extracted. Approximately 50% of the Zr was extracted and exited in both the Cs/Sr and actinide strip sections. The Zr was not completely stripped, with 6.2% remaining in the solvent. Approximately 10% of the Fe was extracted and exited with the actinide strip product. Hg was slightly extracted (7.1%0 and exited with the Cs/Sr strip product. Finally, 20% of the K was extracted and exited with the Cs/Sr strip product.

IV. CONCLUSIONS

Preliminary testing of the tertiary universal solvent extraction process in countercurrent flowsheet tests with simulated waste shows promise. It has been demonstrated that acidic tank waste can be successfully decontaminated using the universal solvent process. Additional testing to establish operational parameters and limiting process conditions is needed.

Countercurrent testing in 2-cm centrifugal contactors using actual tank waste is planned for summer 1998. If adequately developed and successfully demonstrated, the universal extraction process could save significant capital and operating costs for the treatment of radioactive acidic tank wastes stored at the INEEL.

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