ABSTRACT

Chemical separation technologies for the treatment of radioactive wastes, including highly radioactive liquid wastes and solid calcined wastes, mixed wastes, and contaminated groundwater have been under development at the Idaho National Engineering and Environmental Laboratory (INEEL) since 1992. The INEEL Environmental Management (EM) Chemical Separations Program has successfully developed and demonstrated numerous technologies on simulated and actual radioactive wastes to support the INEEL High Level Waste Program. These technologies have repeatedly shown that the tank waste and dissolved calcine at the INEEL can be decontaminated to levels below NRC Class A Low Level Waste Criteria.

The technologies used to separate radionuclides from INEEL radioactive wastes include solvent extraction and ion exchange technologies. Solvent extraction technologies tested at the INEEL include the transuranium extraction (TRUEX) process for the removal of U, Pu, Am and Tc; the strontium extraction (SREX) process for the removal of Sr and Pb; the cobalt dicarbolide process for the removal of Cs and Sr; and the universal extraction (UNEX) process for the simultaneous removal of U, Pu, Am, Cs, and Sr from acidic waste solutions. Ion exchange processes using inorganic ion exchange sorbents such as hexacyanoferrates, silicotitanates and ammonium molybophosphate to remove cesium have been demonstrated on actual waste solutions. Other ion exchange sorbents to remove contaminants from groundwater or drinking water have been developed and tested.

Successful development and testing efforts by the INEEL EM Chemical Separations Program have included numerous national and international collaborations. These collaborations have led to numerous demonstrations of novel technologies as well as the generation of intellectual property.

INTRODUCTION

The Idaho National Engineering and Environmental Laboratory historically reprocessed spent Naval and government-owned reactor fuels with a PUREX-type solvent extraction process. Reprocessing raffinates were stored in underground tanks as an acidic liquid, on an interim basis, then calcined into a granular solid material. Incidental wastes from evaporator operation and decontamination activities, which were high in alkaline metal
concentration (Na and K) were difficult to calcine and were blended with raffinates to facilitate calcination in a fluidized bed process. The reprocessing mission at the INEEL was ended in 1992 by the U. S. Department of Energy. After all first-cycle raffinate solutions were calcined, the remaining tank waste required significant dilution of alkaline metals using non-radioactive chemical additives (e.g. aluminum nitrate) to calcine the incidental wastes. This dilution significantly reduced the overall efficiency of the calcination process.

A radioactive waste management and technology development program was initiated to evaluate approaches to treatment of the residual 5 million liters of acidic liquid waste stored in stainless steel tanks and the 4000 m$^3$ of high-level waste solid calcine stored in stainless steel bins. Priority was given to the treatment of the liquid waste, because of a Notice of Noncompliance, filed by the State of Idaho. The tank waste was categorized as hazardous by the Resource Conservation and Recovery Act (RCRA) and therefore required compatible double containment. The tanks at the INEEL have secondary containment in the form of concrete vaults, but it was determined that the vaults do not qualify for secondary containment of acidic waste. The radioactive waste management and technology development program began evaluation of a number of technologies to treat the existing tank waste, including improved calcination methods, separation of radionuclides followed by grouting of the bulk waste constituents, and direct immobilization of the tank wastes.

The current INEEL baseline approach is to directly vitrify the tank waste and to evaluate separations and direct vitrification for the treatment of calcine. The separations work presented in this paper was performed for both tank waste and calcine, as baseline approaches have evolved over time.

**APPROACH**

One key aspect of the newly formed Waste Management Program at the INEEL was the establishment of a group of scientists and engineers to evaluate separation technologies for the treatment of waste streams. Experience from previous spent nuclear fuel reprocessing development activities formed the basis for this group. Separation experts from within the DOE community participated in a peer review process of identifying applicable separation technologies and ranking them as to their potential for meeting INEEL separation requirements for calcine treatment (1). The recommendations from the peer review group formed the basis for prioritizing separation development tasks. Solvent extraction technologies ranked high for removal of TRU, Sr and Cs as well as ion exchange technologies for the removal of Cs. Precipitation and extraction chromatography technologies were ranked lower, literature reviews performed, and these technologies were not pursued further as part of the INEEL development program.

Extensive development of solvent extraction and ion exchange technologies has been underway since 1992. Preliminary work was focused on laboratory studies to provide sound chemical data for the development of process flowsheets. Emphasis was placed early in the program on validating chemical data with tests using actual waste samples.
Similarly, pilot-plant flowsheet testing was initially performed using simulated waste solutions and later flowsheet performance verified using actual waste solutions. The INEEL has led the DOE National Laboratories in demonstration of viable separation technologies for nuclear waste; performing nearly 40 countercurrent solvent extraction flowsheet tests, including 10 tests with actual highly-radioactive tank waste, and performing numerous ion exchange column tests with actual tank waste and dissolved calcine solutions. Six solvent extraction processes have been tested in pilot plants, as well as extensive column testing of three inorganic ion exchange processes. An overview of the technologies tested and the results of testing will be provided.

SOLVENT EXTRACTION

Solvent extraction technology provides for high throughput and efficient separation of radioactive components from acidic liquid wastes. The technology is mature, having been in practice in the nuclear industry for nearly 50 years, although new extractants have been recently developed. The benefit of using such separation processes is based on potential cost savings by handling the majority of the waste as low-level waste, as opposed to high-level waste. This potential cost advantage is partially offset by the capital costs of separation facilities and the uncertainty of waste disposition paths and actual disposal costs for repositories.

Flowsheet testing of solvent extraction processes at the INEEL has been performed in 3.3-cm and 5.5-cm centrifugal contactors using non-radioactive waste surrogates and in 2-cm centrifugal contactors using radio-traced waste surrogates and with actual tank waste. A and a view of the 2-cm centrifugal contactor pilot plant inside a shielded hot cell and the 3.3-cm centrifugal contactor pilot plant are shown in Figures 1 and 2, respectively. A summary of each technology and results from the flowsheet tests follows:

TRUEX Process

The Transuranic Extraction (TRUEX) process, developed by Horwitz and Schulz, effectively removes +3, +4 and +6 valance lanthanide and actinides from acidic solutions (2). The process solvent is similar to the Plutonium Uranium Extraction (PUREX) solvent, in that it contains tri-n-butyl phosphate (TBP) in a paraffinic hydrocarbon diluent. The TRUEX solvent also contains a powerful extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO). The TBP in the TRUEX solvent functions as a phase modifier, increasing the solubility of metal ions in the organic solvent.

The TRUEX process was demonstrated on actual tank waste in the 24-stage 2-cm centrifugal contactor pilot plant installed in a remotely-operated hot cell facility at the INEEL (3). Gross alpha activity of the waste was reduced from 457 nCi/g to 0.12 nCi/g. The NRC Class A LLW requirement is <10 nCi/g for the actinides and the criteria for non-transuranic (TRU) waste is 100 nCi/g. It is apparent that the TRUEX process could easily be implemented to remove the TRU components of the tank waste. The TRUEX process has also been shown to effectively extract Hg, which is easily removed from the
solvent in the solvent wash process using sodium carbonate. In an extended pilot plant
test (operated for ~70 hours) using a non-radioactive surrogate feed, the TRUEX process
successfully removed >99.999% of europium (surrogate for Am) and 96.3% of mercury
from the feed. No buildup of feed components in the solvent over the duration of the test
was observed (4).

![2-cm centrifugal contactor pilot plant in shielded hot cell facility](image)

Additional actinide separation flowsheets using similar processes, with different
extractants such as dihexyl-diethylcarbamoylphosphinate (DHDECMP) or tri-alkyl
phosphine oxide have also been demonstrated in countercurrent pilot plant tests,
however, these processes have disadvantages as compared to the TRUEX process and
were not evaluated further.

**SREX Process**

The Strontium Extraction (SREX) process, developed by Horwitz and co-workers at
Argonne National Laboratory effectively separates strontium from acidic liquid wastes
(5). The SREX solvent consists of the crown ether 4, 4 (5), di-(t-butylocyclohexano)-18-
crown-6 (DtBuCH18C6) in TBP and a paraffinic hydrocarbon diluent. As in the TRUEX
process, the TBP serves as a phase modifier in the SREX solvent.

The SREX process was also demonstrated on actual tank waste in the 24-stage
centrifugal contactor pilot plant installed in a remotely-operated hot cell facility at the
INEEL (6). Strontium-90 activity was reduced from 7.38E+06 Bq/mL in the feed to 326
Bq/mL in the aqueous raffinate. This corresponds to a removal efficiency of 99.994% for
$^{90}$Sr, which is sufficient to reduce the activity to below the NRC Class A LLW limit of
1,480 Bq/mL. The SREX process has also been shown to effectively extract Pb, which is
easily removed from the solvent and partitioned from the strontium by a separate strip
operation using 0.1 M ammonium citrate. In an extended pilot plant test (operated for
~78 hours) using a non-radioactive surrogate feed, the SREX process successfully removed 99.9% of strontium and >99.89% of Pb from the feed. The buildup of feed components in the solvent over the duration of the test was not observed, which included recycling of the solvent approximately 45 times (4).

![Figure 2. 3.3-cm centrifugal contactor pilot plant](image)

### Cobalt Dicarbollide Process

Chlorinated cobalt dicarbollide (ChCoDiC) was developed as an extractant for Cs from acidic waste solutions in the Czech Republic and Russia (7,8). With the addition of polyethylene glycol (PEG) to the solvent, Sr can also be partitioned from acidic waste streams (9). Due to the acid form of cobalt dicarbollide being completely dissociated in the organic phase, a polar solvent, such as nitrobenzene, has been used. Safety, environmental, and technical considerations associated with the use of nitrobenzene led to the development of acceptable alternatives to nitroaromatic diluents used in the cobalt dicarbollide process (10).

A joint research program with the Khlopin Radium Institute in St. Petersburg, Russia was initiated in 1993 to develop the ChCoDiC process for the removal of $^{137}$Cs and $^{90}$Sr from acidic radioactive waste at the INEEL. Numerous laboratory batch contact testing with simulated and actual tank waste solutions, as well as countercurrent pilot-scale flowsheet testing with simulated tank waste have been performed (11, 12). This testing has culminated in the development of ChCoDiC flowsheets (with and without polyethylene glycol (PEG) for the extraction of Sr) which have been demonstrated using actual tank waste solution in a centrifugal contactor pilot plant (13,14).
The actual tank waste flowsheet demonstration of the ChCoDiC process (without PEG) reduced the activity of $^{137}$Cs from 8.66E+06 Bq/mL in the feed to <97.9 Bq/mL in the aqueous raffinate. This corresponds to a removal efficiency of >99.998% which is sufficient to reduce the $^{137}$Cs activity to well below the NRC Class A LLW limit of 3.7E+04 Bq/mL for $^{137}$Cs. Results for the ChCoDiC process (with PEG) indicate that the activity of $^{137}$Cs was reduced from 4.56E+06 Bq/mL in the feed to 1.99E+04 Bq/mL in the aqueous raffinate. This corresponds to a cesium removal efficiency of 99.3%, which is sufficient to reduce the $^{137}$Cs activity to below the NRC Class A LLW limit of 3.70E+04 Bq/ml for $^{137}$Cs. The $^{90}$Sr activity was reduced from 4.05E+06 Bq/mL in the feed to 1.03E+05 Bq/mL in the aqueous raffinate.

Universal Extraction Process

The use of a single solvent extraction process to remove the desired radionuclides, as opposed to a combination of processes in separate unit operations that remove these same radionuclides in sequential steps, evolved from the previous collaborative work with the Khlopin Radium Institute (15). A solvent mixture containing ChCoDiC with PEG to remove $^{137}$Cs and $^{90}$Sr, and a carbamoylmethylphosphine oxide derivative (diphenyl CMPO) to remove the TRUs was developed. Numerous laboratory batch contact tests with simulated and actual waste solutions, as well as countercurrent pilot-scale flowsheet testing with simulated waste have been performed. This testing has culminated in the development of a universal solvent extraction flowsheet, which has been demonstrated using actual waste solution in a centrifugal contactor pilot plant (16).

The universal extraction process (UNEX) demonstration using actual tank waste reduced the activity of $^{137}$Cs from 6.78E+06 Bq/mL in the feed to 2.76E+03 Bq/mL in the aqueous raffinate. This corresponds to a removal efficiency of 99.95%, which is sufficient to reduce the $^{137}$Cs activity to below the NRC Class A LLW limit of 3.70E+04 Bq/mL for $^{137}$Cs. The activity of $^{90}$Sr was reduced from 6.62E+06 Bq/mL in the feed to 800 Bq/mL in the aqueous raffinate. This corresponds to a removal efficiency of 99.98%, which is sufficient to reduce the $^{90}$Sr activity to below the NRC Class A LLW limit of 1,480 Bq/mL. The total alpha activity was reduced from 2.15E+04 Bq/mL in the feed to 821 Bq/mL in the aqueous raffinate. This corresponds to a removal efficiency of 95.2%, which is sufficient to reduce the TRU activity to below the NRC Class B and C requirement of 3,700 Bq/g but not the Class A requirement of 370 Bq/g. The extraction of some inert waste matrix components by the universal solvent effectively “loaded” the diphenyl CMPO in the solvent, reducing the extraction of the actinides.

Extended testing of the UNEX process for several days (~70 hrs) using simulated waste has also been performed (17). The UNEX solvent was recycled a total of 89 times during the testing. The buildup of metals in the solvent or degradation of the solvent during operation was not observed. Removal efficiencies of 97.5% to 98.6% were obtained for Cs, >99.993% were obtained for Sr, and 17.2% to 34.1% were obtained for Eu (Am surrogate). Laboratory experiments using individual stage process solutions and Am and Pu tracers indicate >99.99% of the Pu and very little of the Am (<2%) would be removed from actual waste solutions with this flowsheet. This would result in the total alpha
activity of concentrated SBW being reduced to approximately 65 nCi/g, which is below the 100 nCi/g limit for non-TRU waste. The total alpha activity in a grouted low-activity waste (LAW) form would be approximately 30 nCi/g assuming the waste is concentrated in an evaporator, neutralized, and solidified with a grout mixture at a waste loading of 49 wt.%. The removal efficiencies obtained for Cs and Sr are sufficient to reduce the activity of the waste, and the subsequent LAW grout, to below NRC Class A LLW requirements.

**ION EXCHANGE**

Ion exchange technology is applicable in the treatment of dilute waste streams where sufficient selectivity and capacity can be achieved. In the treatment of acidic radioactive wastes, the most practical application is the removal of cesium with the use of highly selective inorganic ion exchange media. Cesium concentrations in the INEEL tank waste are less than 10 ppm, which makes the utilization of solvent extraction solely for cesium removal less cost effective than ion exchange. One of the primary challenges in the use of inorganic ion exchange media, is the very fine particle size of the media, which requires some process to put it into a form suitable for use in a large column. Different methods of preparing “engineered forms” of sorbents are available and each has different advantages and disadvantages.

**Ammonium molybdophosphate-polyacrylonitrile composite**

Ammonium molybdophosphate (AMP) is a well known inorganic cesium sorbent (18); however, like metal ferrocyanides, it is not alone suitable for column operation. Šebesta, et al., recently developed an engineered form of AMP using polyacrylonitrile (PAN) (19), and extensive studies by the Czech scientists have shown this material to be very promising (20). This matrix is very porous and allows for high throughputs and sorption capacities, but introduces a relatively stable organic component into the final radioactive waste matrix. The AMP can be efficiently dissolved from the PAN, if desired.

In small-scale (1.5 cm$^3$) column tests performed at the INEEL with actual tank waste and dissolved calcine, AMP-PAN demonstrated high selectivity for cesium over the other waste matrix components and high cesium sorption capacity (21). Cesium breakthrough was 0.15% after processing 1000 bed volumes of actual tank waste and 0.2% breakthrough after processing 1270 bed volumes of actual dissolved calcine. Dynamic sorption capacity at 50% breakthrough is 7.8 mg Cs/g AMP-PAN.

Larger-scale (60 cm$^3$) columns were tested in series with simulated waste (4). Stable cesium (greater than 10 times the amount expected in the actual waste) was added to the waste simulant to facilitate analytical detection. Each column was purposefully run to complete breakthrough. Cesium breakthrough results are shown in Figure 3, where the ratio of cesium concentration in the column effluent (C) divided by the cesium concentration in the feed (Co) is plotted versus bed volumes of solution processed. A second order kinetic equation (22) was used to predict cesium effluent concentration as a function of the volume of feed processed (at a given feed concentration). Using the mass transfer coefficient derived from AMP-PAN testing in 1.5 cm$^3$ columns, breakthrough
curves for the two 60 cm$^3$ columns were predicted. The predicted breakthrough curves are also shown in Figure 3 and indicate excellent agreement with the experimental data. Scale-up of the AMP-PAN ion exchange process from 1.5 cm$^3$ columns to 60 cm$^3$ columns was accurately predicted using the kinetic model, even though cesium feed concentrations varied by greater than an order of magnitude between the different column tests.

Fig. 3. Cesium breakthrough curves for the AMP-PAN IX columns A and B. (Feed 130 mg/L Cs, 60 mL bed volume per column, 1.32 L/hr flowrate).

Fifty-percent cesium breakthrough was observed at approximately 280 bed volumes for column A and 525 bed volumes for column B. It is important to note that complete cesium breakthrough of column A occurred before 1% cesium breakthrough occurred in column B. This is significant since it indicates complete loading of the first column, in a two column series arrangement, can be realized while maintaining the desired Cs removal, thus minimizing the total amount of sorbent that is required.

Ionsiv IE-911

The commercial engineered form of crystalline silicotitanate, manufactured by UOP LLC, is marketed under the name Ionsiv IE-911. This sorbent was originally developed for alkaline radioactive wastes, but has been shown to be effective at removing cesium under alkaline, neutral and acidic conditions, as well as removing strontium under certain alkaline and neutral conditions. The binding matrix for Ionsiv IE-911 is proprietary, however, it is known that the matrix is inorganic.

In small-scale (1.5 cm$^3$) column tests performed at the INEEL with simulated and actual tank waste, Ionsiv IE-911 demonstrated moderate selectivity for cesium over the other
waste matrix components and cesium sorption capacity was about an order of magnitude less than for the AMP-PAN (23). Cesium breakthrough was 50% after processing 450 bed volumes of simulated tank. Dynamic sorption capacity at 50% breakthrough was 0.46 mg Cs/g Ionsiv IE-911. Ionsiv IE-911 performance is more dependent on the composition of the waste stream, and is significantly affected by increases in potassium, acid, and sodium concentrations.

As mentioned previously, Ionsiv IE-911 is effective at removing cesium and strontium from neutral solutions. Over 1100 bed volumes of contaminated injection well water from the Ground Water Treatment Facility at the INEEL were processed through a 120 cm³ column containing Ionsiv IE-911 (24). Cesium and strontium feed concentrations were approximately 500-1100 pCi/L and 240 pCi/L, respectively. No cesium was detected in the column effluent for the duration of the test (detection limit 15 pCi/L), and strontium breakthrough was approximately 4% at 1100 bed volumes of water processed.

SUMMARY

Chemical separations processes have been demonstrated to be effective for the treatment of INEEL tank waste and dissolved calcines. The INEEL has played a major role in the progression of newly developed technologies to the demonstration stage with actual highly-radioactive wastes. These technologies represent viable treatment options for the INEEL EM High-Level Waste program, however, current INEEL direction is to proceed with development and demonstration of direct immobilization technologies for tank waste. Regardless of the primary choice of waste treatment technology, separations technologies may be utilized to treat secondary waste from melter off-gas streams and provide technically-viable alternatives if technical or cost issues preclude the use of the selected technology. The INEEL separations capabilities also support non-EM funded programs.

REFERENCES


