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Development of Cesium and Strontium Separation and Immobilization Technologies in Support of an Advanced Nuclear Fuel Cycle

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ABSTRACT

As part of the Advanced Fuel Cycle Initiative, two solvent extraction technologies are being developed at the Idaho National Laboratory to simultaneously separate cesium and strontium from dissolved spent nuclear fuel. The chlorinated cobalt dicarbollide/polyethylene glycol (CCD/PEG) process utilizes a solvent consisting of chlorinated cobalt dicarbollide for the extraction of Cs and polyethylene glycol for the synergistic extraction of Sr in a phenyltrifluoromethyl sulfone diluent. Countercurrent flowsheets have been designed and tested on simulated and actual spent nuclear fuel feed streams with both cesium and strontium removal efficiencies of greater than 99%. The Fission Product Extraction (FPEX) process is based on two highly-specific extractants: 4,4',(5')-Di-(t-butyl)dicyclo-hexano)-18-crown-6 (DtBuCH18C6) for the extraction of Sr and Calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) for the extraction of Cs. Laboratory test results of the FPEX process, using simulated feed solution spiked with radiotracers, indicate good Cs and Sr extraction and stripping performance. A preliminary solvent extraction flowsheet for the treatment of spent nuclear fuel with the FPEX process has been developed, and testing of the flowsheet with simulated spent nuclear fuel solutions is planned in the near future.

Steam reforming is currently being developed for stabilization of the Cs/Sr product stream because it can produce a solid waste form while retaining the Cs and Sr in the solid, destroy the nitrates and organics present in these aqueous solutions, and convert the Cs and Sr into leach resistant aluminosilicate minerals. A bench-scale steam reforming pilot plant has been operated with several potential feed compositions and steam reformed product has been generated and analyzed.

INTRODUCTION

The United States Department of Energy's Advanced Fuel Cycle Initiative (AFCI) is developing advanced separation technologies to process spent light water reactor fuel [1]. The purpose of these separation processes is to remove the bulk of the mass of spent nuclear fuel (uranium) and the primary heat generating elements, which limit the amount of material that can be placed in the repository. The thermal load to the repository is a function of both short-term heat-generating elements, such as the fission products cesium and strontium, and long-term heat generating elements, such as plutonium and americium. Calculations indicate that removal of these four elements would allow a substantial increase in drift loading in the repository, as much as 50 times greater than for direct disposal of fuel [2]. The current AFCI program includes strategies for the separation of uranium for low-level waste disposal or eventual recycle into MOX fuel. Cesium and strontium would be separated for decay storage (approximately 300 years) then

disposed as low-level waste. Separation of actinides (neptunium, plutonium, americium, curium) and the lanthanides would also be performed and the resulting materials would be burned in thermal or fast reactors.

Included in the AFCI program is development of technologies for the separation of Cs and Sr from spent LWR fuel. Simultaneous separation of the primary short-term heat generators, cesium and strontium, can be achieved utilizing solvent extraction technologies. Simultaneous extraction of cesium and strontium reduces overall process complexity and allows for a single waste form to be produced. Two new solvent extraction technologies have been recently developed to simultaneously separate cesium and strontium from spent nuclear fuel, following dissolution in nitric acid.

The first Cs/Sr separation process utilizes chlorinated cobalt dicarbollide (CCD) and polyethylene glycol (PEG) in a phenyltrifluoromethyl sulfone diluent [3]. The CCD/PEG process is most efficient when the feed is $\leq 1 \text{ M}$ nitric acid; therefore, it can be used directly on the Uranium Extraction (UREX) process raffinate or on the UREX co-decontamination process raffinate, after an acid recovery process. Cesium and strontium, along with any barium or rubidium present, are extracted into the solvent. A nitric acid scrub is used to remove any trace actinides present in the solvent. Cesium and strontium are effectively stripped using a guanidine carbonate/ diethylenetriamine pentaacetic acid (DTPA) strip solution. Recent results indicate that a new, regenerable, strip reagent, based on methylamine carbonate, would significantly reduce the amount of organics in the cesium/strontium strip product and greatly simplify subsequent solidification operations [4]. The cesium and strontium strip product may be solidified in a number of ways, namely sorption onto a zeolite-type matrix, mineralization by steam reforming, calcination, etc.

The second technology for the separation of cesium and strontium, referred to as the fission product extraction (FPEX) process, is based on a combined solvent containing two extractants - 4,4',5'-Di-(t-butyl)dicyclohexano-18-crown-6 (DtBu18C6) and Calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) combined with a phase modifier- 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB) in a branched aliphatic hydrocarbon diluent (Isopar[®] L). This solvent composition was based on the Strontium Extraction (SREX) process developed at Argonne National Laboratory and the Caustic Side Solvent Extraction (CSSX) process developed at Oak Ridge National Laboratory (for alkaline waste) [5,6]. A simple combination of the two solvents produced unacceptable extraction results; however, it was found that the Cs-7SB modifier used in the CSSX process had a synergistic effect on the extraction of strontium. Therefore, the modifier used in the SREX process (TBP) was not needed in the new combined solvent. Preliminary batch contact testing of the combined Cs/Sr extraction process has been completed and results indicate that the process is effective at selectively removing cesium and strontium from simulated feed solutions and that the cesium and strontium can be stripped from the solvent using dilute nitric acid.

It is anticipated that the separated Cs/Sr product stream will be immobilized and enter decay-storage, for approximately 300 years, at which time the activity of the Cs and Sr will be below the limits for low-level waste. Steam reforming is currently being developed for stabilization of this stream because it can produce a solid waste form while retaining the Cs and Sr in the solid, destroy the nitrates and organics present in these aqueous solutions, and convert the Cs and Sr into leach resistant aluminosilicate minerals. A bench-scale steam reforming pilot plant has been

operated with several potential feed compositions and steam reformed product has been generated and analyzed.

Development of the Cs/Sr separation processes and the steam reforming process for the immobilization of the Cs/Sr product stream are detailed in this paper.

EXPERIMENTAL EQUIPMENT AND CHEMISTRY

Solvent Extraction Testing

All chemicals were of at least reagent grade and were used as received. Deionized water was used to prepare all aqueous acid solutions. The CCD/PEG solvent consists of 0.08 to 0.13 M CCD for the extraction of Cs, 0.016 to 0.027 M PEG-400 for the extraction of Sr, and a phenyltrifluoromethyl sulfone (FS-13) diluent. The FPEX process solvent was a mixture of 0.15 M DtBuCH18C6, 0.007 to 0.01 M BOBCalixC6 and 0.75 M Cs-7SB modifier in Isopar[®] L.

Nitric acid dependency tests for Cs and Sr were performed in varying concentrations of HNO₃ contacted with the appropriate solvent in equal volume proportions. All batch contacts were shaken by hand for 1 minute, centrifuged for 1 minute, the organic and aqueous fractions were separated and the two phases analyzed.

Flowsheet testing of a chlorinated cobalt dicarbollide (CCD)/polyethylene glycol (PEG-400) based solvent extraction process for the separation of Cs and Sr from dissolved LWR fuel was performed using 24 stages of 3.3-cm diameter centrifugal contactors and simulated feed solution representing leached spent LWR fuel after uranium separation. The CCD/PEG solvent composition for the flowsheet testing was 0.13 M CCD and 0.027 M PEG-400 in phenyltrifluoromethyl sulfone (FS-13), which was developed to minimize loading of the PEG-400 extractant with Sr and Ba. The composition of the feed simulant used for this testing and FPEX batch contact testing is given in Table I and is based upon a U separation process, UREX, preceding the CCD/PEG process.

Table I. Feed simulant composition

Component	Conc. (M)	Component	Conc. (M)
HNO ₃	0.6-1.0	Nd	5.20E-03
Sr	1.60E-03	Sm	1.00E-03
Cs	2.33E-03	Gd	9.33E-03
Zr	1.27E-03	Eu	1.27E-04
Ba	5.53E-03	Y	8.67E-04
La	1.53E-03	Pr	1.53E-03
Ce	2.60E-03	Rb	6.67E-04

Steam Reforming Testing

There are two potential strip feed compositions for the CCD/PEG process which will result in two very different compositions going to a Cs/Sr solidification process; 1) guanidine carbonate/diethylenetriaminepentaacetic acid (DTPA) and 2) methylamine carbonate (MAC)/DTPA. The FPEX process uses dilute nitric acid (0.01 M) to strip the extracted Cs and Sr from the solvent. The estimated composition of the solidification process feeds are summarized in Table II.

A small, 7.5 cm diameter, bench-scale fluidized-bed enclosed vessel was used to conduct the steam reforming tests (Figure 1). The test system can achieve the thermal and temporal conditions required to produce a mineralized granular product. The system can match the solid-liquid-gas reaction time scales and governing mechanisms and phenomena of larger pilot scale systems.

Table II. Estimated composition of Cs/Sr solidification feed streams.

Component	CCD/PEG Feed 1	CCD/PEG Feed 2	FPEX Feed 3
Guanidine carbonate (g/L)	100	---	---
DTPA (g/L)	20	60	---
Methylamine carbonate (<u>M</u>)	---	0.5	---
Nitric acid (<u>M</u>)	---	---	0.04
Cesium (g/L)	0.30	1.2	0.60
Strontium (g/L)	0.10	0.4	0.20

RESULTS

CCD/PEG Solvent Extraction Process

Nitric acid dependency tests were performed with the CCD/PEG process. Results of these tests for cesium and strontium are presented in Fig. 2. The distribution coefficient of Cs decreases with increasing nitric acid concentration, ranging from 380 in 0.1 M HNO₃ to 0.24 in 10 M HNO₃. The Sr distribution coefficient decreases with increasing nitric acid concentration,

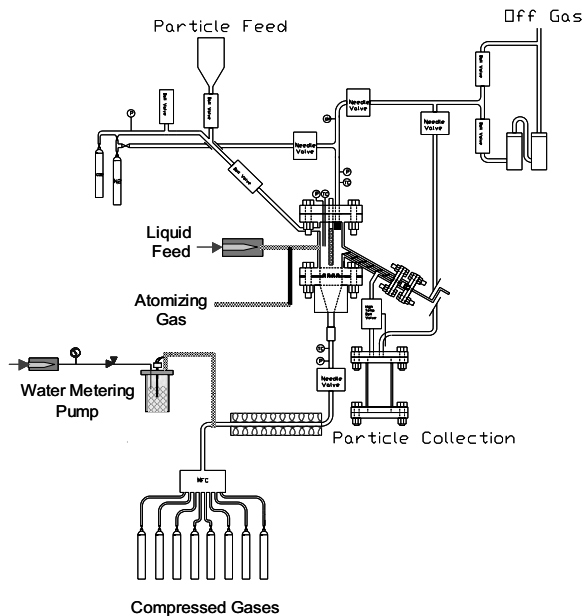


Fig. 1. Schematic of Steam Reforming Experimental Equipment

ranging from 5,100 in 0.1 M HNO₃ to 6.5 in 10 M HNO₃. These data indicate that the simultaneous extraction of Cs and Sr, using the CCD/PEG solvent, is viable from aqueous solutions with acid concentrations below approximately 5 M HNO₃, with the optimum nitric acid concentration below approximately 1.0 M.

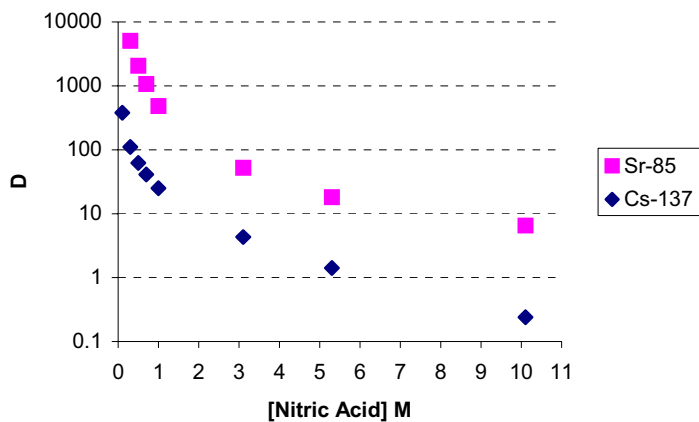


Fig. 2. Nitric Acid Dependency of Cs and Sr in CCD/PEG solvent at 25 °C

Flowsheet Testing of CCD/PEG Process

Nitric acid dependencies are important to determine process feasibility, but significantly more work is needed to develop a process flowsheet. Significant amounts of research have been performed on the CCD/PEG process, which is not reported here [3]. Based upon the results of this laboratory testing, a countercurrent flowsheet was developed and tested with simulated and actual spent LWR feed. The flowsheet for the CCD/PEG process is shown in Fig. 3

For the flowsheet testing with spent LWR fuel stimulant, the percentages of Cs, Sr, and the lanthanides in the effluent streams at the time of shutdown are show in Table III. The removal efficiencies for Cs and Sr were 99.6% and >99.995%, respectively. Also, an average decontamination factor of 2.6E+05 was obtained for the lanthanides.

Several other components of the spent fuel were also studied, including Ba, Rb, Y, and Zr. As expected, Ba and Rb were nearly completely extracted with the Cs and Sr. Only 0.02% of the Y and 0.14% of the Zr were extracted and exited with the strip product.

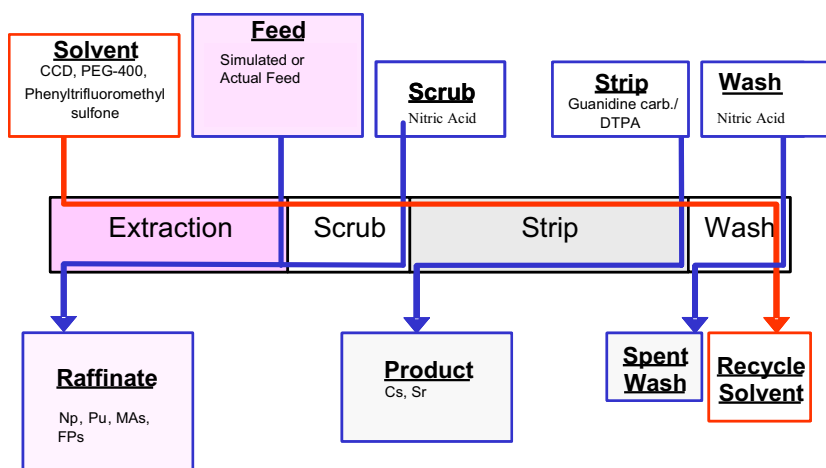


Fig. 3. Schematic of flowsheet used for testing of CCD/PEG process

Table III. Percentage of each component in each of the effluent streams for CCD/PEG flowsheet test with simulated spent LWR feed solution

Effluent Stream	Cs	Sr	Ba	La	Ce	Nd	Rb
Raffinate	0.42%	< 0.005%	< 0.025%	110%	90.6%	97.8%	0.02%
Strip Product	113%	106.6%	109.4%	0.004%	7E-4%	4E-4%	113%
Wash Effluent	0.04%	< 0.30%	<2E-4%	<2E-4%	4E-4%	<6E-4%	<4E-3%

Testing of a similar flowsheet was also performed using actual dissolved spent LWR fuel. Results from this testing also met process goals, with removal efficiencies of 99.99% and 99.8% for Cs and Sr, respectively. Additionally, the activity of Am in the Cs/Sr product indicate that the solidified product would contain <100nCi/g, therefore remaining a non-TRU waste. This will allow disposal of the Cs/Sr product stream as a LLW after allowing the Cs and Sr to decay (200-300 years).

FPEX Solvent Extraction Process

Nitric acid dependency tests were performed with the FPEX process solvent. Results of these tests for cesium and strontium are shown in Table IV. The increasing distribution coefficient with increasing nitric acid concentration trend was observed, as expected from previous work with the individual extractants. The FPEX solvent requires nitric acid concentrations of about 0.5 M or higher to effectively separate cesium and strontium. At nitric acid concentrations above 2.0 M, coloration of the solvent and third phase formation were observed; therefore, use of this process is not recommended in this nitric acid regime.

Nitric acid dependencies are important to determine process feasibility, but significantly more work is needed to develop a process flowsheet. Significant amounts of research have been performed on the FPEX process which is not reported here [7]. Based upon the results of this research, a countercurrent flowsheet was developed for future testing with simulated and actual spent LWR feed. The flowsheet for the FPEX process is shown in Fig. 4. This flowsheet has been designed to achieve 99.9% separation of Cs and Sr from the spent fuel.

Stability of the BOBCalixC6 in the FPEX solvent is an issue in the presence of nitric acid solutions. Additionally, the solubility of the BOBCalixC6 is limited in the FPEX solvent. Research has been initiated to evaluate an alternative calixarene, 1,3-alt-bis-*n*-octyloxycalix[4]arene-benzo-crown-6, for the FPEX process which is expected to be more stable in the presence of nitric acid and have increased solubility in the aliphatic diluent [8].

Table IV. Cs and Sr distribution coefficients as a function of nitric acid with the FPEX solvent

Nitric Acid Conc. (<u>M</u>)	D _{Sr-85}	D _{Cs-137}
0.01	0.01	0.19
0.10	0.23	1.1
0.50	2.0	3.4
1.0	7.4	5.7
2.0	22.7	9.2

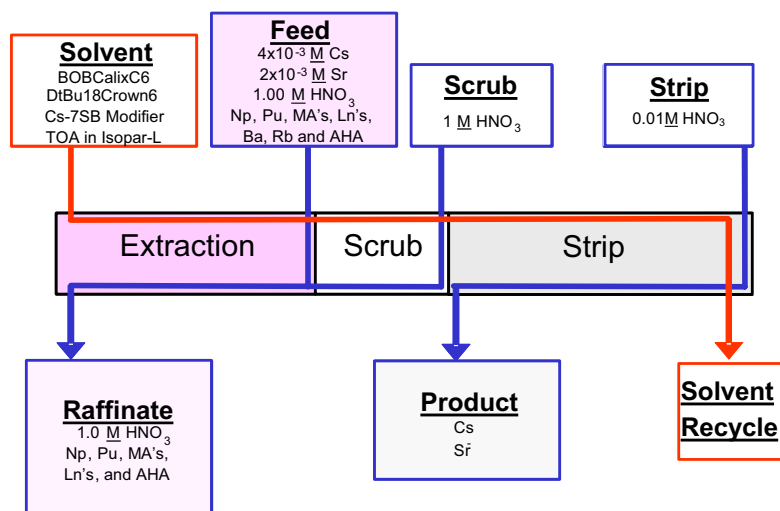


Fig. 4. Nitric acid dependencies of Cs and Sr in the FPEX solvent

Steam Reforming of the Cs/Sr Product

The steam reforming technology was tested with each of the three potential feed streams detailed in Table 2. One basic test condition was focused on for the three different feeds. For these feeds, the average reactor operating temperature target of 700°C was achieved, which is well into the “intermediate” to “hot” combustion gas reaction temperature regime. The fluidizing gas composition (dry) was held on the lean limit of flammability for the present studies (3.75% H_2 , 4.98% CO , balance CO_2). Hence, the bulk gas composition is representative of a dilute steam reformat gas, but contains sufficient reducing species (CO and H_2) to destroy the nitrates, while producing sufficient radicals. Steam was mixed with the fluidizing gas to produce a gas stream that is around 25 vol% H_2O . A starting bed of 100-300 micron aluminum oxide particles was used for the initial tests. Sagger clay was slurried with the feed to produce pollucite and other alumino-silicate minerals. Due to mass transfer and solid diffusion limits on the clay particles, excess clay is required to mineralize the cationic feed constituents. The amount of clay added for these tests was generally 200% of stoichiometric to attempt complete mineralization of the cations. The clay particles are less than $10 \mu\text{m}$ to achieve a high surface area for reaction and are suspended in the liquid feed.

A total of six tests were performed under these conditions with the three feed solutions. The main solid products from these experiments were the bed material, deposits that formed in the reactor on or across from the nozzle, and fines from the off-gas/blowback filters. The final bed material in each run was generally a granular material much like the initial aluminum oxide starting bed with some additional smaller diameter solids. Each run had some amount of nozzle

deposits indicating buildup of the dried feed material on the nozzle, the cartridge heater, and the opposite vessel wall. These deposits ranged from 5 grams to several hundred grams. The sizes of the deposits appear to be greater in the runs where there was more difficulty in keeping the bed fluidized. SEM analyses of the deposits show particles stacked together which are even smaller than the size of the 10 micron clay particles used. Fines were recovered from the off-gas filter and blowback filter on several of the runs. The fines generally consisted of very small (< 1 micron) particles.

The x-ray diffraction and SEM analyses were not conclusive in determining the form of the Cs and Sr in the solids formed due to the low concentrations present. To determine what percent of the total Cs and Sr in the bed and deposits was present as a water-soluble compound (i.e., most likely an oxide), a two gram sample of the bed and deposit material was contacted with 10 mL water at room temperature. The supernate from this process was analyzed for Cs and Sr by inductively coupled plasma-mass spectroscopy (ICP-MS). The remaining solids were subjected to aqua regia digestion or fusion and the resulting solution analyzed by ICP-MS. These results indicate the Sr is essentially all in a mineralized form for the guanidine carbonate and nitric acid feeds and is 90% mineralized for the MAC/DTPA feed. The Cs is 86% mineralized for the guanidine carbonate feed, 78% for the MAC/DTPA feed and 97% for the nitric acid feed. These results are promising as optimization of the steam reforming operations has not yet been completed. It is anticipated that 100% mineralization of all feeds will be possible as the operating parameters (temperature, clay concentration, feed rates, gas composition, etc) are optimized.

The off-gas was routed through a condenser to remove the moisture prior to discharge into the hood. The resulting solution was collected for each run and analyzed for pH, Cs content and Sr content. These results indicate that very little of the Cs (<0.05%) and Sr (<0.001%) are volatilized.

CONCLUSION

The CCD/PEG process is viable for the separation of Cs and Sr from leached spent LWR fuel. The CCD/PEG process has been successfully demonstrated with actual spent LWR fuel. Results of testing of the FPEX process to date indicate this process is also potentially viable. A flowsheet has been designed for testing of the FPEX process with simulated and actual spent LWR fuel. Also, testing of a potentially more stable calixarene for the extraction of Cs has been initiated.

The bench-scale steam reformer successfully converted all three Cs/Sr strip products to a solid form without volatilizing the Cs. Results also indicate that, with optimization of the steam reforming operating parameters, 100% mineralization is possible.

Optimization of these operating parameters will continue including varying temperatures, feed rates, and clay concentrations, etc. The off-gas will also be analyzed for nitrous oxides and total unburned hydrocarbons, and the solids analyzed for unburned hydrocarbons to determine the completeness of the reactions.

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