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Steam Reforming Solidification of Cesium and Strontium Separations Product from Advanced Aqueous Processing of Spent Nuclear Fuel

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ABSTRACT

The Advanced Fuel Cycle Initiative program is conducting research on aqueous separations processes for the nuclear fuel cycle. This research includes development of solvent extraction processes for the separation of cesium and strontium from dissolved spent nuclear fuel solutions to reduce the short-term decay heat load. The cesium/strontium strip solution from candidate separation processes will require treatment and solidification for managed storage. Steam reforming is currently being investigated for stabilization of these streams because it can potentially destroy the nitrates and organics present in these aqueous, nitrate-bearing solutions, while converting the cesium and strontium into leach-resistant aluminosilicate minerals, such as pollucite. These ongoing experimental studies are being conducted to evaluate the effectiveness of steam reforming for this application.

INTRODUCTION

The Advanced Fuel Cycle Initiative (AFCI) program is conducting research on aqueous separations processes for the nuclear fuel cycle. This research includes development of solvent extraction processes for the separation of cesium (Cs) and strontium (Sr) from dissolved spent nuclear fuel solutions to reduce the short-term decay heat load. The Cs/Sr strip solution from candidate separation processes will require treatment and solidification for managed storage. In fiscal year 2004, an Engineered Product Activity Team was formed from a subset of the members of the AFCI Separations Working Group. This team identified the preferred storage forms and vehicles for the Cs/Sr waste stream arising from the treatment of spent fuel. For the Cs/Sr stream, encapsulation in borosilicate glass, similar to that used for high level waste, was considered a baseline against which other storage forms are judged. Steam reforming was a Cs/Sr solidification processes recommended for further study.

Investigation into the use of steam reforming for this application was initiated in FY-05. The objectives of this testing includes:

- Convert the Cs/Sr strip product solutions to a solid form
- Destroy the organics and nitrates present in the strip solutions
- Retain the Cs and Sr in the solid waste form (i.e., do not volatilize Cs)

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- Form a leach resistant aluminosilicate product.

Formation of a mineralized product is a target, but may not be required, since the storage requirements for this waste are uncertain at this time. This waste will be contained in a canister and stored for 200-300 years during which time the Cs/Sr will decay to levels which will allow the waste to be classified as low-level. A leach resistant waste form will not necessarily be required for this decay storage since the waste form is contained in the sealed canister. If a leach resistant product is required and a mineralized aluminosilicate product is not completely formed the solid Cs/Sr product can be incorporated into a leach resistant grout.

EXPERIMENTAL EQUIPMENT AND CHEMISTRY

Steam reforming was developed over the past 20 years for reforming nitrate and organic constituents that often occur in radioactive waste solutions. In an oxygen-deficient environment, nitrates can be reduced to nitrogen by a reducing agent, such as carbon or hydrogen. Similarly, organic solvents can be reformed and oxidized by nitrates and radicals produced by chain reactions involving hydrogen, and hydroxyl radicals produced from dissociation of super-critical steam and subsequent oxy-reduction chain reactions.

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. The choice of process unit selected for steam reforming can have a significant impact on the final product due to mixing, mass-transfer, and heat-transfer effects. In a batch (i.e., crucible container) or rotary process, solid-state reactions are impacted by solids mixing, gas diffusion through the solid matrix and pore space, and heat-transfer limitations. Heat transfer is impeded by the solid mass, which can result in incomplete mineralization of the dry solid salts. Additionally, rotary and fixed-bed processes are not amenable to highly radioactive wastes due to mechanical reliability and solid phase plugging.

A fluidized-bed process is preferred when; 1) the feed solution can be atomized and sprayed into the hot bed of particles, 2) the bed temperature can be held below the solids fusion and melting point of solid oxides, but above the critical decomposition temperature of alkali nitrates and hydroxide compounds. Fluidized-beds exhibit high particle-particle and particle-gas heat transfer. Gas mixing and diffusion to the particle surface effectively promotes volatilization and the heterogeneous gas-solid reactions that are key to waste reforming destruction of organics and nitrates in the final product. The main limitation to fluidized-bed steam reforming is preventing flash evaporation and surface film boiling due to the high temperatures required to mineralize the solids.

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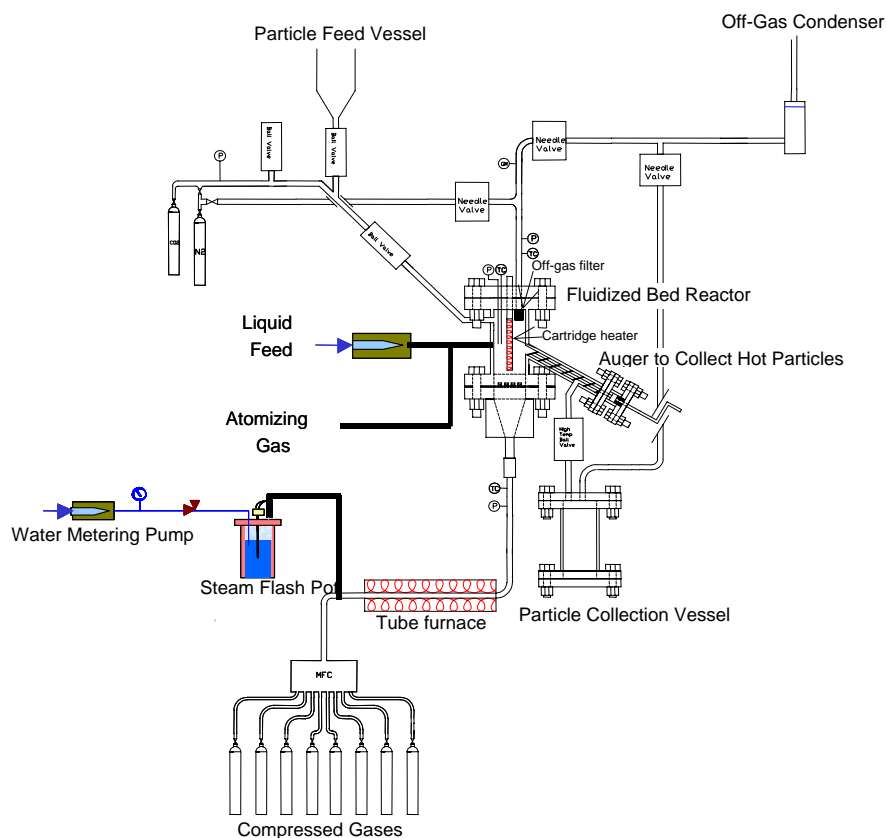


Fig. 1. Schematic of steam reforming experimental equipment

EXPERIMENTAL CONDITIONS

Two processes are being developed for the separation of Cs and Sr from spent nuclear fuel: the chlorinated cobalt dicarbollide and polyethylene glycol (CCD/PEG) process and the Fission Product Extraction (FPEX) process. There are two potential strip feed compositions for the CCD/PEG process which will result in two very different feed compositions 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 I.

Table I. 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 (M)	---	0.5	---
Nitric acid (M)	---	---	0.04
Cesium (g/L)	0.30	1.2	0.60
Strontium (g/L)	0.10	0.4	0.20

The most important parameters in the steam reforming tests include:

- Bed Temperature
- Concentration of the clay mineralizing additive in the Feed
- Starting bed material
- Feed Rates
- Composition of reforming gas
- Need for other additives

For the tests conducted in FY-05, one basic test condition (bed temperature, clay concentration, starting bed, and reforming gas composition) was focused on for the three different feeds.

For these tests, the average reactor operating temperature target of 700°C was achieved, which is well into the “intermediate” to “hot” combustion gas reaction temperature regime.

To produce pollucite and other aluminosilicate minerals, sagger clay was slurried with the feed. 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 200% of stoichiometric to attempt complete mineralization of the feed. The clay particles are less than 10 µm to achieve a high surface area for reaction and are suspended in the liquid feed.

A starting bed of 100-300 micron aluminum oxide particles and feed rates of 6-8 ml/min were used. No other bed or feed additives were used.

The fluidizing gas composition (dry) was held on the lean limit of flammability for the present studies (3.75% H₂, 4.98% CO, balance CO₂). Hence, the bulk gas composition is representative of a dilute steam reformat gas, but contains sufficient reducing species (CO and H₂) 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% H₂O.

In some steam reforming applications, carbon is added to the bed to produce a reductant for nitrates. Carbon was not required in these tests since the reducing conditions were achieved with

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the fluidizing gas mixture. In addition, Feed 1 and Feed 2 already contain significant levels of hydrocarbons and amine-type groups that will serve as reductants for the nitrates in the feed, viz

Guanidine Carbonate— $(\text{H}_2\text{NC}(=\text{NH})\text{NH}_2)_2 \cdot \text{H}_2\text{CO}_3$

DTPA— $((\text{HOOCCH}_2)_2\text{NCH}_2\text{CH}_2)_2\text{NCH}_2\text{COOH}$

MAC— $(\text{CH}_3\text{NH}_3)\text{CO}_3$ and similar carbonate and bi-carbonate ion pairs.

The operating conditions for the various tests completed are summarized in Table II. This table shows some variation in the fluidizing gas rate due to operational problems. The same basic test conditions were used twice on Feed #1 and once on Feed #2. Three runs were completed on Feed #3 using the same basic conditions to make more product material for analysis.

Table II. Operating Conditions for the FY-05 Cs and Sr Strip Product Steam Reforming Test

Parameter		Feed #1, Run #1	Feed #1, Run #2	Feed #2, Run #1	Feed #3, Run #1	Feed #3, Run #2	Feed #3, Run #3
Fluidizing Gas	Flowrate Target (slm)	9	16	16	12	16	16
	Actual Flowrate (slm)	0-9	8-15	10-16	0-12	11-16	8-18
	Approximate Composition	68.4 % CO ₂ , 3.8% CO, 2.8% H ₂ , 25.0% H ₂ O					
	Water Addition (mL/min)	2.25	3	4	3	3.7	3.7
Feed, Additives	Target Slurry Feed Rate (mL/min)	8	6	6	8	6	6
	Clay Addition (g/l)	4.3	4.3	11.43	8.6	8.6	8.6
	Total Feed Added (ml)	200	1440	750	1820	500	2000
Bed Parameters	Bed temperature (°C)	550-600	670-716	700-723	675-728	650-710	670-719
	Starting bed volume (ml)	350	350	350	350	350*	**
Atomizing Gas	Slurry Nozzle Atomizing Ratio (NAR)	500	600	700	500	1000***	1000***
	Atomizing N ₂ rate target (slm)	4	3.6	4.2	4	6	6
	Composition	91.25 % CO ₂ , 5.0% CO, 3.75% H ₂					
*270 ml from F3R1 plus 80 ml new aluminum oxide.							
** Continued with same bed left after F3R2.							
***Different nozzle/aircap resulted in higher NAR needed.							

RESULTS TO DATE

Condensate Analysis

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 (Table III). These results indicate that very little of the Cs and Sr are volatilized as the concentration in the condensate is very low when compared to that of the feed solution. Thus, steam reforming achieved one of the major goals of making a solid product with no significant volatilization of Cs.

Table III. Concentration of Cs and Sr in the Condensate

Run	Condensate			Feed	
	pH	Cs (ppm)	Sr (ppm)	Cs (ppm)	Sr (ppm)
F1R1	8	0.004	0.008	299.2	101.5
F1R2	8	0.113	0.001	299.2	101.5
F2R1	8-9	0.012	0.001	1277.3	403.3
F3R1	7	0.030	0.001	550.6	198.4
F3R3	7	0.011	0.000	550.6	198.4

Product Appearance

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 (Figure 2). 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 (right side of Figure 2). The 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. Scanning Electron Microscope (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.

SEM analyses of the bed material indicate the similarity to the starting bed and show that the feed solutions are not satisfactorily building on the aluminum oxide bed. The short droplet life in the reactor and the high temperature of the particles attributes to the excessive formation of fines instead of the desired mineral growth on the surface of the bed particles. The theoretical extinction time for a droplet of water in a humid nitrogen gas stream at 600°C and 700°C, respectively is only about 18 msec. The calculated droplet life accounts for particle heating by conduction to the droplet, assuming that the velocity of the droplet is equivalent to the velocity of the surrounding gas. This assumption is a reasonable approximation for droplets that are atomized by the co-flowing atomizing gas. Deposition of the spray droplets on the bed particles is influenced by the Leidenfrost phenomenon in which the droplet does not spread over the particle surface before evaporating but is supported above the particle surface by a layer of vapor

caused by the high evaporation rate of the droplet. Future work will attempt to reduce this affect by increasing feed droplet size, changing bed materials to one with a lower heat capacity and possibly lowering the bed temperature while feeding.



Fig. 2. Bed material and nozzle deposit formed during operation with the MAC/DTPA feed

Product Analysis

The bed, nozzle deposit and fines were analyzed by several methods. 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. Results from the analysis on the nozzle products are shown in Figures 3 and 4. The analyses from the nozzle deposits are used as the most representative due to the lack of deposition of the feed material on the aluminum oxide bed. However, for Feed 2 the bed analysis results are used because very little nozzle deposit was formed. 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.

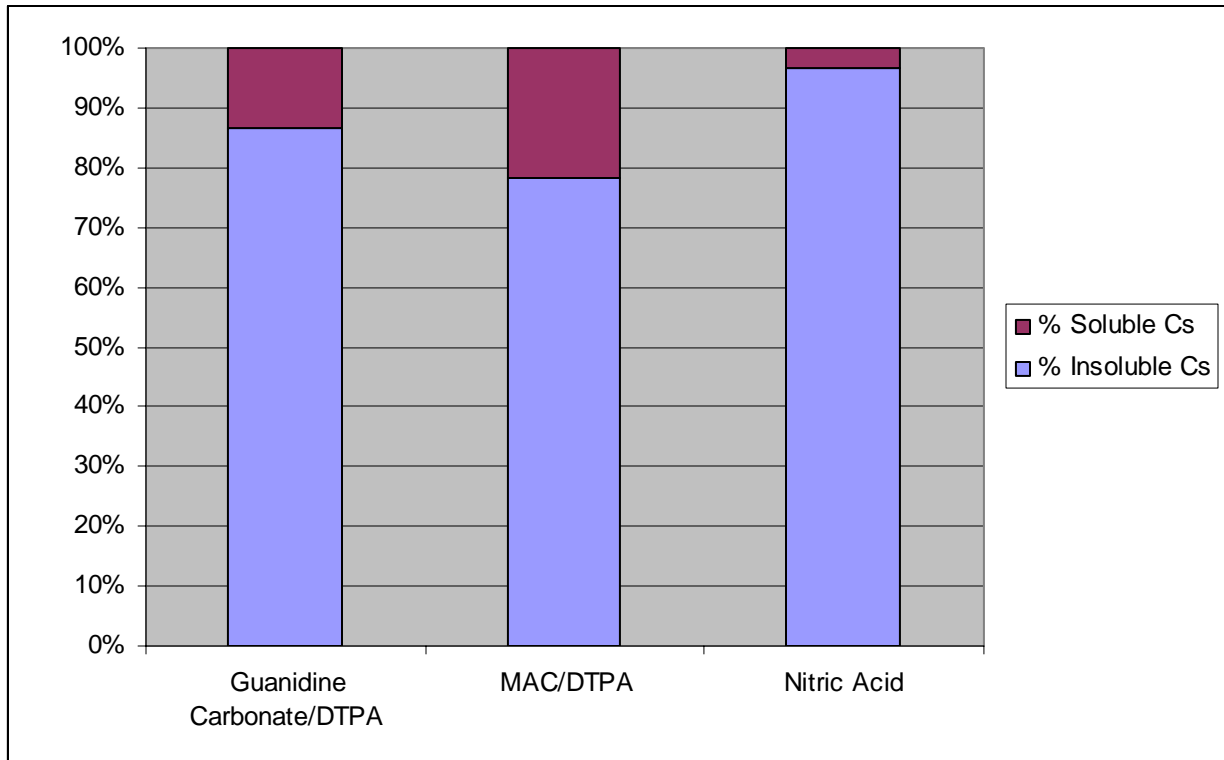


Fig. 3. Percent of Cs present as a mineralized product versus a soluble product

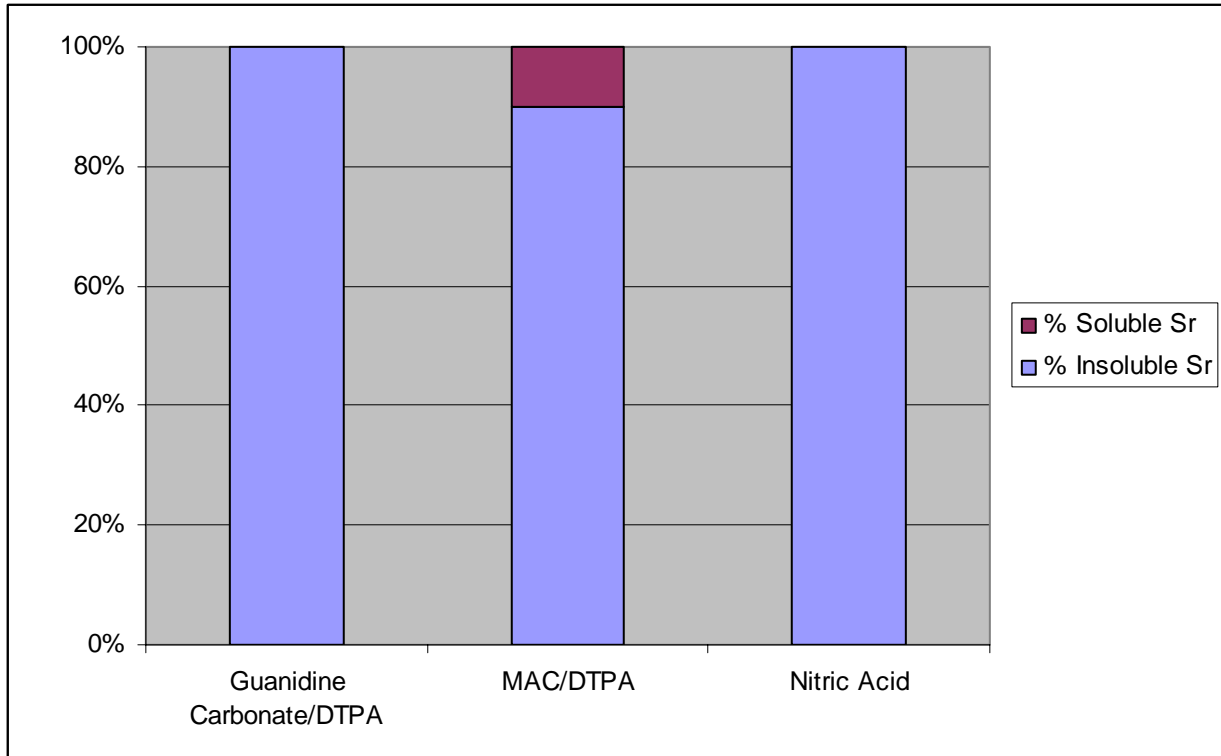


Fig. 4. Percent of Sr present as a mineralized product versus a soluble product

CONCLUSION

Investigation into the use of steam reforming for this application was initiated in FY-05. The objectives of this testing includes:

- Convert the Cs/Sr strip product solutions to a solid form
- Destroy the organics and nitrates present in the strip solutions
- Retain the Cs and Sr in the solid waste form (i.e., do not volatilize Cs)
- Form a leach resistant aluminosilicate product.

The FY-05 testing 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 that 100% mineralization is possible.

In FY-06, 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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