Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Tripp, Julia , Garn, Troy , Boardman, Richard and Law, Jack(2006) 'Development of Steam Reforming for the Solidification of the Cesium and Strontium Separations Product from Advanced Aqueous Reprocessing of Spent Nuclear Fuel', Separation Science and Technology, 41: 10, 2147 — 2162

To link to this Article: DOI: 10.1080/01496390600742914

URL: http://dx.doi.org/10.1080/01496390600742914

Separation Science and Technology, 41: 2147–2162, 2006
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ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600742914

Development of Steam Reforming for the Solidification of the Cesium and Strontium Separations Product from Advanced Aqueous Reprocessing of Spent Nuclear Fuel

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Abstract: Steam reforming is one option currently being investigated for stabilization of the cesium/strontium strip products from spent fuel reprocessing solvent extraction processes 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. To produce pollucite and other mineral analogs of the alkaline metals, the feeds must be mixed with aluminosilicate compounds and thermally sintered or calcined to activate solid-state crystal formation. Scoping tests completed indicated that the cesium/strontium in these organic and acid solutions can be converted into aluminosilicate materials using steam reforming.

Keywords: Solvent extraction, solidification, steam reforming

INTRODUCTION

The Advanced Fuel Cycle Initiative (AFCI) 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 spent nuclear fuel to reduce the short-term decay heat load. The Cs/Sr strip solution from candidate separation processes will

Received 28 October 2005, Accepted 20 March 2006

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require treatment and solidification for managed storage. Steam reforming was one strip solution solidification option that was investigated in fiscal year 2005 (FY-05) by the Idaho National Laboratory (INL).

The thermal load on the repository is greatly reduced if the emplacement of Cs/Sr waste is delayed until these relatively short-lived (half-lives of ~30 yrs) materials decay. Separation of Cs and Sr along with plutonium and americium would allow a substantial increase in the repository drift loading, up to a factor of 40–50. The storage of Cs and Sr for the life cycle of the waste processing plant can be accomplished using existing casks and requiring a relatively small area (one to two football fields in size for the life of the plant). Safe interim storage will require a waste form that is stable, does not produce dangerous radiolysis products (e.g., buildup of potentially explosive gases like H_2), has relatively high product density (to minimize storage volume), and has properties that enhance heat management (e.g., high thermal conductivity).

STEAM REFORMING FEED COMPOSITIONS

The baseline process for separation of Cs and Sr from dissolved spent light water reactor fuel, as part of the Uranium Extraction Plus (UREX +) process, is a solvent extraction process utilizing chlorinated cobalt dicarbollide and polyethylene glycol (CCD/PEG) in a phenyltrifluormethyl sulfone (FS-13) diluent. Cs and Sr are stripped from the CCD/PEG organic stream with an aqueous solution of guanidine carbonate and diethylenetriaminepentaacetic acid (DTPA) yielding a metal carbonate product solution.

Alternative extraction processing methods are also under investigation. The first alternative is a variation of the baseline CCD/PEG process but uses a methylamine carbonate (MAC)/DTPA solution to strip the organic extractant. This yields a product containing the metal and DTPA (with small amounts of MAC) and allows the MAC to be recovered and recycled. A second alternative is the Fission Product Extraction (FPEX) process which extracts the Cs/Sr with a calixarene-crown ether extractant consisting of 4,4′,(5′)-Di-(t-butyldicyclohexano)-18-crown-6 (DtBuCH18C6), Calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6), and 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB modifier) in a branched aliphatic kerosene (Isopar® L). With this process, the organic extractant is stripped with dilute nitric acid. The estimated compositions of the solidification process feed resulting from the CCD/PEG process are summarized in Table 1.

EXPERIMENTAL OBJECTIVES

The primary steam reforming objective for FY-05 was to determine if the Cs and Sr in the solutions could be converted into leach resistant aluminosilicate

Table 1. 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

minerals, such as pollucite ($Cs_2Al_2Si_4O_{12} \cdot H_2O$) without the volatilization of Cs. In order to produce pollucite and other mineral analogs of the alkaline metals, the feeds must be mixed with aluminosilicate compounds such as natural clays and subsequently thermally sintered or calcined to activate solid-state crystal formation. The fluidized-bed steam reforming tests by Olson et al. (1) and associated product characterization tests by Jantzen et al. (2) for low-activity, sodium-bearing, aqueous wastes served as a guide for the present experimental scoping tests. If the Cs/Sr waste streams can be converted into a mineralized solid product, then they may be suitable for direct long-term disposal in a radioactive waste disposal facility.

STEAM REFORMING EQUIPMENT & CHEMISTRY

The steam reforming experiments were carried out in a small (7.5 cm diameter) high temperature/high pressure fluidized-bed vessel, which was retrofitted with a spray nozzle on the side wall. A schematic of the test system is shown in Fig. 1. A photographic view of the reactor system is shown in Fig. 2.

A spray-fed, laboratory fluidized vessel was used to simulate the temporal conditions that would exist in the most practical process for steam reforming. 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. The competitive, parallel, and sequential physical transformation and chemical reactions relevant to the present work are summarized in Table 2.

The choice of process unit selected for steam reforming can have significant impact on the final product due to mixing, mass-transfer, and

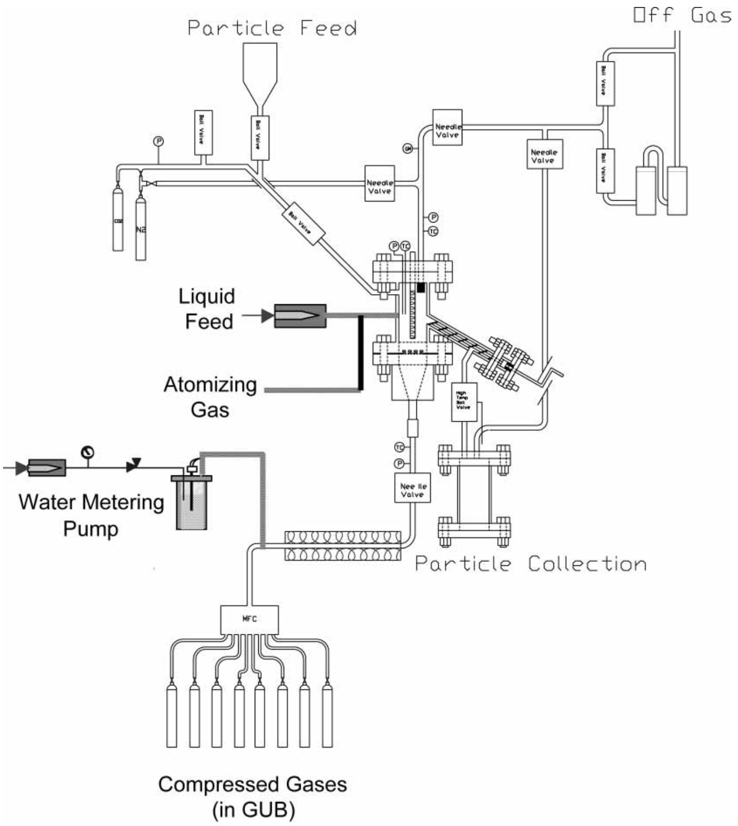

Figure 1. Fluidized-bed steam reformer test system schematic.

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 process are not amenable to highly radioactive wastes due to mechanical reliability and solid phase plugging.

The INL has a 50+ year history of investigating waste denitration and calcination process technology. A fluidized-bed process is preferred when;

1. the feed solution can be atomized and sprayed onto 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.

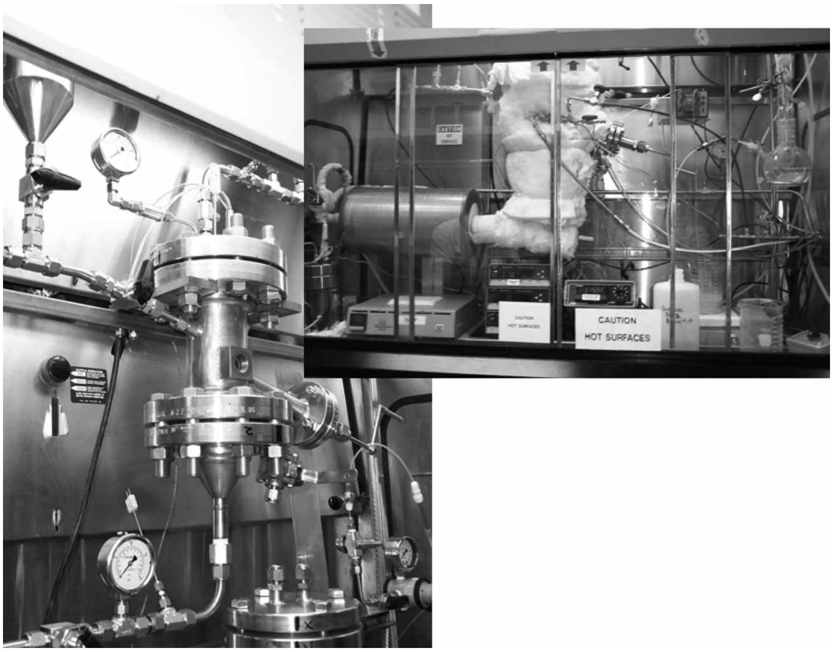

Figure 2. Steam reforming system equipment.

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 dried waste. 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.

In order to determine the effectiveness of steam reforming in a fluidized-bed reactor, it is important to simulate practical conditions. The laboratory fluidized-bed used for the present studies meets this criterion while limiting the amount of fluidizing gas and the complexity the test apparatus to a manageable scale.

The fluidized bed consists of a 3-inch schedule 40, 304 stainless steel (SST) pipe, with an inner diameter of 7.8 cm, and a length of approximately 15.7 cm (measured from the inside edges of the flanged ends). The pipe is situated in an upright position with the top opening sealed by a 3-inch, 300 lb rated, 304 SST blind flange. The bottom opening is flanged to a 3.5-inch diameter schedule 80, 304 SST pipe reducer with 3-inch, 300 lb rated, 304 SST socket weld flanges. A 316 SST metal fluidizing media plate is positioned in a race between the lower flanges to serve as the fluidizing gas distributor. This bed has a total void volume of about 1.0 L. Approximately 350 mL

Table 2. Key waste reforming physical and chemical reactions

Process step	General reaction examples
Solution evaporation/ particles drying	Waste solution (liquid) $\longrightarrow H_2O$ (gas) + solid salts ($CsNO_3$, $Sr(NO_3)_2$, etc.) @ spray droplets [or] @ liquid film on particle surface
Solid salt thermal dissociation/ decomposition	$2CsNO_3\ (s) \longrightarrow Cs_2O\ (s) + 2NO_2\ (g) + 1/2\ O_2\ (g)$ $2CsNO_2\ (s) \longrightarrow Cs_2O\ (s) + NO_2\ (g) + NO\ (g)$ $Cs_2CO_3\ (s) \longrightarrow Cs_2O\ (s) + CO_2\ (g)$
Solid state inorganic reactions	$2CsNO_3\ (s) + Al_2O_3\ (s) \longrightarrow 2CsAlO_2\ (s) + 2NO_2,\ 1/2\ O\ (g)$ $2Cs_2O\ (s) + SiO_2\ (s) \longrightarrow Cs_4SiO_4\ (s)$
Heterogeneous inorganic reactions	$Cs_2O\ (s) + 2NO_2\ (g) + 1/2\ O_2 \longrightarrow 2CsNO_3\ (s)$ $SrO\ (s) + NO_2\ (g) + 1/2\ O_2 \longrightarrow SrNO_3\ (s)$ $Cs_2O\ (s) + CO_2\ (g) \longrightarrow Cs_2CO_3\ (s)$ $SrO\ (s) + CO_2\ (g) \longrightarrow SrCO_3\ (s)$ $Cs_2O\ (s) + H_2O\ (g) + 1/2\ O_2 \longrightarrow 2CsOH\ (s)$ $SrO\ (s) + H_2O\ (g) \longrightarrow Sr(OH)_2\ (s)$ $Cs_2O\ (s) + 2HCl\ (g) \longrightarrow 2CsCl\ (s) + H_2O$ $SrO\ (s) + 2HCl\ (g) \longrightarrow SrCl_2\ (s) + H_2O$
Reducing zone: Gaseous hydrocarbon chemistry	$CO + H_2O \longleftrightarrow CO_2 + H_2$ $CO + 4H_2 \longleftrightarrow CH_4 + 4OH$ $H_2O \longleftrightarrow H + OH$ $H + H_2O \longleftrightarrow H_2 + OH$ $CO + OH \longrightarrow CO_2 + H$ $CO + O \longleftrightarrow CO_2$
Reducing zone: Gaseous nitrogen chemistry	$CH_4 + 4NO_2 \longrightarrow 4NO + CO_2 + 2H_2O$ $CH_i + NO \longrightarrow HCN + H_{i-1}O$ $HCN + OH \longrightarrow HNCO + H$ $HCNO + H \longrightarrow \ldots NH_i\ (i = 1,2,3)$ $NH_2 + NO \longrightarrow N_2 + H_2O$ $2CO + 2NO \longrightarrow N_2 + 2CO_2$ $NO + H_2 \longrightarrow NH + OH$ $NH_{i=0,1,2} + H \longrightarrow NH_{j=1,2,3}$

of 100–300 micron aluminum oxide particles were loaded into the reactor as the starting bed for each feed. A Spraying Systems liquid siphoning atomization nozzle has been tapped into the side wall to inject the feed on the particulate bed. Compressed gas cylinders were used to supply the test gas (3.75% H_2, 4.98% CO, balance CO_2) which was mixed at the manufacturer. The dry gas mixture was humidified by superheated steam supplied by a water flash pot. A two micron sintered metal filter was threaded on the inside discharge line to filter the exiting gas.

TARGET TEST CONDITIONS

The average reactor operating temperature target was 700°C, which is well into the "intermediate" to "hot" combustion gas reaction temperature regime. At this temperature, the steam partially dissociates to produce reactive hydroxyl radicals that abstract hydrogen from the organic molecules introduced with the feed. Hydrocarbon scissioning (which follows hydrogen abstraction) generates intermediate radicals that react with the nitrates, NO_x, and other radicals in the reactor. Chain propagation is terminated by the high surface area and moisture in the system.

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 was representative of a dilute steam reformate gas, but contained sufficient reducing species (CO and H_2) to destroy the nitrates, while producing sufficient radicals. The organics in the feed are all thermally unstable at the reactor test conditions. Steam was mixed with the fluidizing gas to produce a gas stream that is approximately 25 vol% H_2O. Table 3 lists the target operating variables for the current tests.

A starting bed of 100–300 micron aluminum oxide particles was used. 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 the fluidizing gas mixture. Reacting nitrates with reducing agents is a direct and efficient route to produce N_2 rather than NO_x as a final decomposition product of the nitrates in the feed. A large number of chemical reducing agents have been examined for the denitrification of aqueous solutions. These chemicals include iron metal, Fe^{2+}, N_2H_2, glucose, CO, formaldehyde, formic acid, sugar, glycolic acid, starch, and urea. Feed 1 and Feed 2 already contain significant levels of hydrocarbons, and cyano and amine-type groups that will serve as reductants for the nitrates in the feed, viz

Guanidine Carbonate—$(H_2NC(=NH)NH_2)_2 \cdot H_2CO_3$

DTPA—$((HOOCCH_2)_2NCH_2CH_2)_2NCH_2COOH$

MAC—$(CH_3NH_3)CO_3$ and similar carbonate and bi-carbonate ion pairs.

At 700°C, evaporation of the liquid feed on the particles, and subsequent decomposition and equilibration of the organic, amine, and nitrate groups is rapid and attains a quasi-equilibrium state in the steam reformer reactor. Atomic nitrogen tends to form NH_3 and N_2 under the reducing conditions, while the hydrocarbons equilibrate according to the water-gas shift reaction:

$$CO + H_2O \longleftrightarrow CO_2 + H_2$$

In order to produce pollucite and other alumino-silicate minerals, sagger clay was slurried with the feed. The desired product for Cs mineralization is

Table 3. Target operating conditions for the Cs and Sr strip solution steam reforming test

Parameter	Prescribed test condition
Fluidizing gas	0.15 m/s
Gas velocity at the distributor	
Composition	68.4% CO_2, 3.8% CO, 2.8% H_2, 25.0% H_2O
Feed additives	
Feed type	Feed 1, feed 2, feed 3
Slurry feed rate (total)	360–480 mL/hr
Slurry specific gravity	1.5
Clay mineralizing additive	K-T Sagger ball clay
Clay addition	Feed 1: 4.3 g/L Feed 2: 17.2 g/L Feed 3: 8.6 g/L
Atomizing gas	
Slurry NAR	500–1000
Composition	91.25 % CO_2, 5.0% CO, 3.75% H_2
Bed parameters	
Bed temperature	700°C
Starting bed mass	350–500 mL (unfluidized/packed)
Starting alumina Particle size	0.01–0.03 cm
Reactor pressure	Approximately atmospheric (or 12.35 psia at reactor elevation)
Starting alumina Particle true Density	3.79 g/ml

NAR = Nozzle atomizing ratio, the volumetric ratio of the atomizing gas and the liquid flow rates.

pollucite, with chemical formula $Cs_2Al_2Si_4O_{12} \cdot H_2O$. 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% stoichiometric to attempt complete mineralization of the feed. The clay particles were less than 10 μm to achieve a high surface area for reaction and are suspended in the liquid feed.

RESULTS

Nozzle Testing

Clay-feed admixture suspension and spray atomization studies were completed to confirm homogeneous clay-feed mixtures can be fed to the reactor at the design rates of the system. The optimum nozzle atomizing ratio (NAR) was determined through subjective liquid feed mixture spray visualization tests. A liquid droplet size of 25–50 microns was desired to avoid droplet flash evaporation prior to contact with the bed, while achieving rapid droplet evaporation and reaction on the surface of the bed particles without quenching individual particles.

Initial testing indicated that settling of the clay in the feed lines was going to be a problem at the low flowrates being used. A peristaltic micropump with 1.02 mm ID tubing was obtained to allow pumping at the low feed rates while maintaining a liquid velocity in the line that prevented the clay from settling out during pumping. The nozzle testing was completed using clay concentrations of 4.3, 8.6 and 17.2 grams of clay per liter of water. No settling of solids was observed in the line using this small diameter tubing.

To achieve the desired spray patterns at the 6 ml/min feed rate, a NAR of at least 650 is needed (i.e. atomizing gas flowrate of 3.9 slm) when using a 28/50 (28 mm ID and 50 mm OD) liquid nozzle with a 70 mm ID aircap. At a liquid flowrate of 8 ml/min a NAR of 500 (i.e., atomizing gas flowrate of 4.0 slm) seems to be a good minimum point for operation. Increasing sagger clay concentrations from 4.3 to 17.2 g/l does not seem to have a negative impact on the spray patterns obtained at NARs of 450–600. Testing results using a regular nozzle vs an antibearding nozzle were very similar. To achieve the desired spray patterns at the 6 ml/min feed rate a NAR of at least 1000 is needed (i.e. atomizing gas flowrate of 6 slm) when using a 28/100 (28 mm ID and 100 mm OD) liquid nozzle with a 120 mm aircap.

Test System Shakedown

System shakedown and component functionality testing were completed to verify system operability while obtaining essential experimental operating practice. Major system functions tested included bed fluidization, thermocouple accuracy, nozzle performance, and reactor heatup.

Several methods of determining fluidization characteristics of the bed were attempted including adding a viewport at the nozzle location and plotting the heatup temperatures with respect to time to observe heat spikes represented by thermocouple readouts. However, the bed material fluidizes much differently at room temperature versus operating temperature (700°C) and it is quite difficult in this small reactor to determine when the actual bed fluidization is taking place. A test was completed where a thermocouple was inserted into the nozzle port to compare with the “bed” thermocouple, which is in a thermowell extended into the vessel. It was determined that the thermowell thermocouple provides an accurate bed temperature if the bed is fluidized. If the bed is not fluidized the “bed” thermocouple can read 100°C lower than actual bed temperature.

The nozzle port was positioned as close as possible to the inside of the vessel wall to avoid buildup up material in the nozzle port. In addition, it was determined that the atomizing air and a nitrogen purge to the liquid side of the nozzle must be on at all times when fluidizing the bed or blowing back the off-gas filter to avoid nozzle plugging. To prevent vaporization of the feed inside the nozzle, the nozzle body was cooled by winding copper tubing around the nozzle body and recirculating a 50% ethylene glycol solution with a cooling bath.

Obtaining the required experimental temperatures was difficult with this set-up partly due to the large heat sink created by the flange assemblies. The current configuration includes heat tapes and a tube furnace on the inlet fluidization gas which will heat the entering gas to between 650–750°C. In addition, there is a 1000 W cartridge heater inside the vessel and a 1000 W ceramic bead heater wound around the outside of the reaction vessel. Heat up times of 3–4 hours were required to bring the bed to 700°C. Temperature control during operation was typically 700°C ± 30°C.

The fluidization plate originally consisted of a 316 SST Dynapore© porous plate which consists of 8 layers of SST mesh with a proprietary design. It had a 20 micron screen across the top and the media is designed to allow air flow of 2 scfm/sf at 3 inches water column. At room temperature it was possible to deliver the 16–18 slm of fluidization gas needed to fluidize the bed. However, as the vessel heats up it became more and more difficult to maintain this flowrate. At 700°C, the flowrate was only about 10 slm using a 70 psi supply pressure. When the plate cooled back down the permeability increased again, which indicates it is not just solids restricting the flow. A SST fluidizing plate with approximately twice the permeability was used for the last half of the tests but this plate also caused some restrictions. Further research is needed to develop a better distributor plate for this experimental setup.

Steam Reforming Test Conditions

The operating conditions for the various tests completed are summarized in Table 4. This table shows some variation in the fluidizing gas rate due to operational problems. The same basic test conditions (bed temperature of 700°C, clay concentration 200% stoichiometric, starting bed of 100–300 micron aluminum oxide, and reforming gas composition) were used twice on Feed #1, once on Feed #2, and three times on Feed #3.

STEAM REFORMING RESULTS

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

Table 4. 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_2O					
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[a]	[b]
Atomizing gas						
Slurry NAR	500	600	700	500	1000[c]	1000[c]
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					

[a] 270 ml from F3R1 plus 80 ml new aluminum oxide.

[b] Continued with same bed left after F3R2.

[c] Different nozzle/aircap resulted in higher NAR needed.

from the off-gas/blowback filters. The other product was the liquid condensate. The major focus of the experiments was to form mineralized Cs and Sr in the reactor vessel. A mass balance on the Cs and Sr was not completed due to the scoping nature of these tests and because of high uncertainties from equipment malfunctions and sample analyses.

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. After the third nitric acid feed run, the bed also included large diameter spherical particles that appear to be pieces of deposits that have broken off and been ground into spheres by the action of the bed (Fig. 3). Scanning Electron Microscope (SEM) analyses of the bed material indicate the similarity to the starting bed (Fig. 4) and show that the feed solutions are not building on the aluminum oxide bed to a high degree.

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. The Feed #1 and Feed #2 deposits were darker in color and more friable than the Feed #3 deposits (Fig. 5). 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. SEM analyses of the deposits show very small micron particles stacked together which are even smaller than the size of the 10 micron clay particles used (Fig. 6).

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

Figure 3. Bed material from Feed #3 Run #3 contained large diameter spherical particles that appear to be pieces of deposits that have broken off and been ground into spheres.

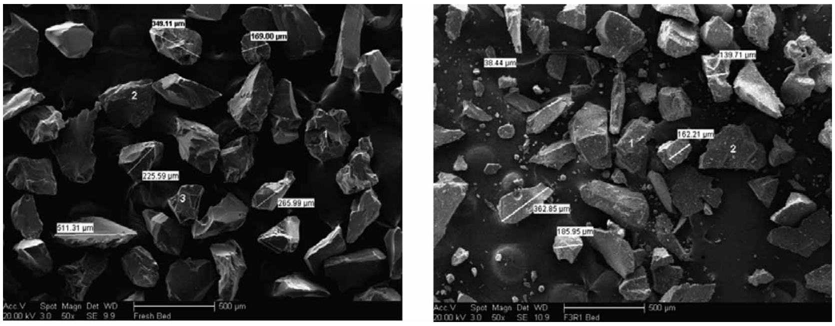

Figure 4. Starting aluminum oxide bed (left) is similar to bed after Feed #3 Run #3.

(Fig. 7). The short droplet life in the reactor and the high temperature of the particles attributes to the excessive formation of fines, as opposed to mineral growth on the surface of the 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 (Fig. 8). 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.

Cs Volatility

The off-gas was routed through a condenser to remove most of the moisture prior to gas discharge into the hood. The resulting solution was collected for each run and analyzed for pH, and Cs/Sr content (Table 5). These

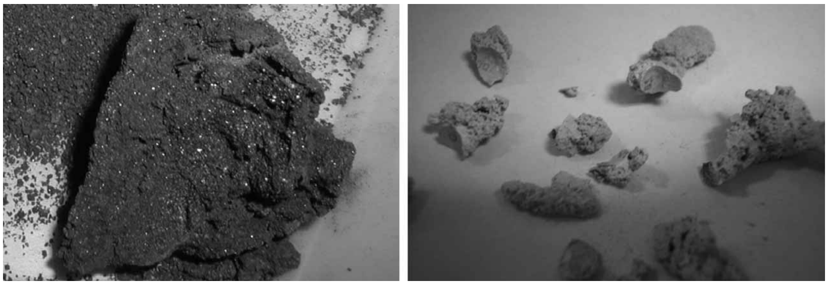

Figure 5. Nozzle deposits from Feed #1 Run #2 (left) and Feed #3 Run #1 (right).

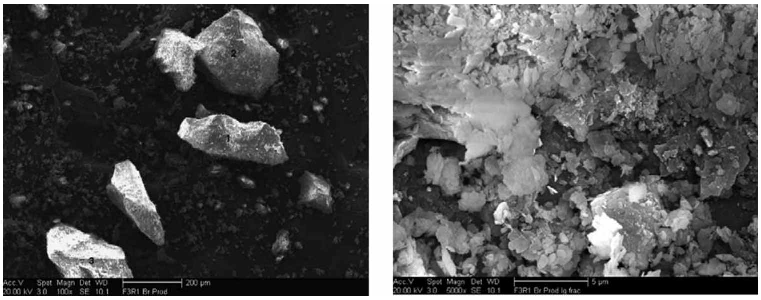

Figure 6. Nozzle deposits typically exhibited a "platelet" formation as shown from this Feed #3 Run #1 deposit.

results indicate that very little of the semi-volatile Cs and Sr was collecting in the condensate when compared to the feed solution concentrations. Thus, steam reforming achieved one of the major goals of making a solid product with no significant volatilization of Cs.

Product Form

The main objective of the FY-05 steam reforming tests was to solidify the Cs/Sr preferably into a mineralized (i.e., insoluble) form. The x-ray diffraction

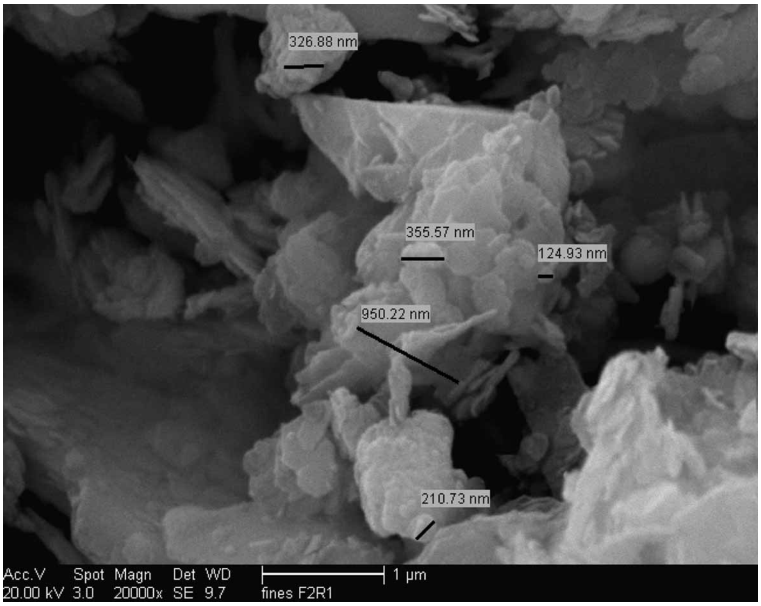

Figure 7. Fines from the off-gas filter after Feed #2 Run #1.

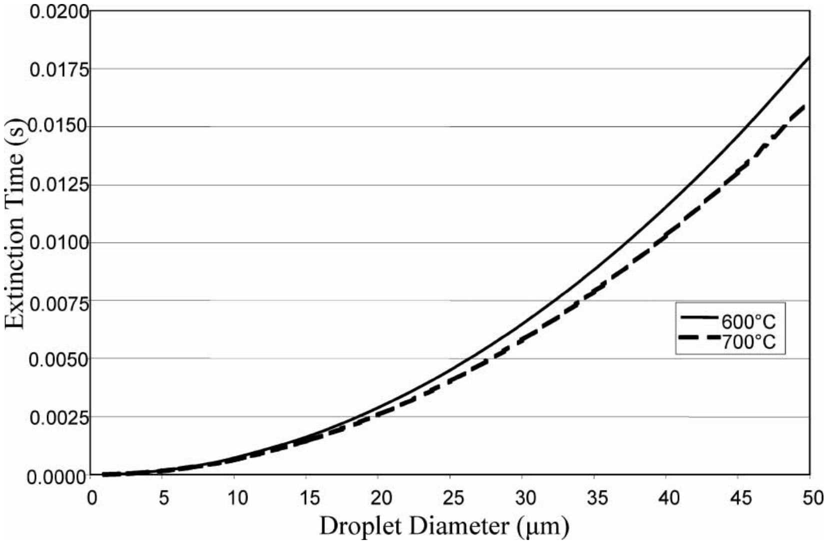

Figure 8. Comparison of 50 μm diameter droplet extinction time in 600°C and 700°C gas mixture containing 35% H_2O and 65% N_2.

and SEM analyses were inconclusive for determining the form of the Cs and Sr in the solids 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 mLs of nano-pure water at room temperature. The supernate from this process was analyzed for Cs and Sr by inductively coupled plasma-mass spectroscopy (ICPMS). The remaining solids were subjected to aqua regia digestion and the resulting solution analyzed by ICP-MS.

The results of these analyses indicated only a fraction of the Cs and Sr is present as an oxide. The currently available results indicate that 70–95 wt% of the Cs and 82–100 wt% of the Sr are present as insoluble minerals. These

Table 5. Concentration of Cs and Sr in the condensate

	Condensate			Feed	
Run	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

results are promising as optimization of the steam reforming operation has not been completed. Alternative methods of more accurate solids analysis are being investigated. Future reports will detail the results of these ongoing analyses.

STEAM REFORMING CONCLUSIONS

The primary steam reforming objective was to determine if the Cs and Sr in the solutions can be converted into leach resistant aluminosilicate minerals, such as pollucite ($H_2Cs_4Al_4(SiO_3)_9$) without the volatilization of Cs. The FY-05 testing successfully converted all three Cs/Sr strip products to a solid form without volatilizing the Cs. The results from the steam reforming scoping tests conducted in FY-05 indicate that 70 to 95 wt% of the Cs and 82 to 100 wt% of the Sr in the bed and deposit materials is an insoluble mineral. Results indicate that with optimization of the steam reforming operating parameters that 100% mineralization is possible. This optimization will include varying temperatures, feed rates, clay concentrations, bed dynamics, and nozzle spray patterns as well as alternative bed materials.

ACKNOWLEDGMENTS

This work was carried out under the auspices and financial support of the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology through contract DE-AC07-05ID14517.

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