

MINERALIZING, STEAM REFORMING TREATMENT OF HANFORD LOW-ACTIVITY WASTE

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ABSTRACT

The U.S. Department of Energy (DOE) documented, in 2002, a plan for accelerating cleanup of the Hanford Site, located in southeastern Washington State, by at least 35 years. A key element of the plan was acceleration of the tank waste program and completion of "tank waste treatment by 2028 by increasing the capacity of the planned Waste Treatment Plant (WTP) and using supplemental technologies for waste treatment and immobilization." The plan identified steam reforming as a candidate for treating as much as 70% of the low-activity waste (LAW).

Mineralizing steam reforming technology, offered by THORsm Treatment Technologies, LLC, (TTT), produces a denitrated, granular mineral waste form using a moderate-temperature fluidized bed process. A pilot scale demonstration of the technology was completed in a 15-cm diameter vessel. The pilot scale facility was equipped with a cyclone separator and heated sintered metal filters for particulate removal, a thermal oxidizer for destroying reduced gas species, and a packed activated carbon bed for residual volatile species capture. The pilot scale equipment is owned by the DOE, and located at the Science and Technology Applications Research (STAR) Center in Idaho Falls, Idaho. Pilot scale testing was performed August 2–5, 2004. Flowsheet chemistry and operational parameters were defined through a collaborative effort involving Idaho National Engineering and Environmental Laboratory (INEEL), Savannah River National Laboratory (SRNL), and TTT personnel. Personnel of Science Application International Corporation (SAIC), owners of the STAR Center, performed actual pilot scale operation.

The pilot scale test achieved a total of 68.4 hours of continuous processing operation before termination in response to a bed de-fluidization condition. 178 kg of LAW simulant were processed, resulting in 123 kg of solid sodium aluminosilicate product (including both bed product and elutriated fines, but excluding the alumina starting bed and unreacted solid carbon reductant), a mass reduction of about 31%. The process achieved essentially complete bed turnover within 40 hours. Samples of mineralized solid product materials were analyzed for chemical/physical properties. SRNL will report separately the results of product performance testing that were accomplished.

INTRODUCTION

The U.S. DOE documented, in 2002, a plan for accelerating cleanup of the Hanford Site, located in southeastern Washington State, by at least 35 years. A key element of the plan was acceleration of the tank waste program and completion of "tank waste treatment by 2028 by increasing the capacity of the planned Waste Treatment Plant (WTP) and using supplemental technologies for waste treatment and immobilization." The plan identified specific technologies to be evaluated for supplemental treatment of as much as 70% of the low-activity waste (LAW). In concert with this acceleration plan, DOE, the U.S. Environmental Protection Agency (EPA), and the Washington State Department of Ecology proposed to accelerate – from 2014 to 2006 – the Hanford Federal Facility Agreement and Consent Order milestone (M-62-11) associated with a final decision on the balance of tank waste that is beyond the capacity of the WTP.

The DOE Office of River Protection tank farm contractor, CH2M HILL Hanford Group, Inc. (CH2M HILL), was tasked with testing and evaluating selected supplemental technologies to support final decisions on tank waste treatment. DOE identified the need in January 2004 for further experimental data, with regard to steam reforming technology, to make informed decisions concerning selection of supplemental treatment technology and to support the 2006 decision date. Experimental data from tests using actual radioactive waste were desired to provide the most beneficial information to DOE. An experimental fluidized bed test system/facility was not available to

generate experimental data using actual radioactive waste in the desired time frame. Therefore, a plan was conceived that would provide the information in the required time frame. The basis for the plan was correlations hypothesized between laboratory and pilot scale results, validation of which would enable laboratory experiments performed in hot cells using actual radioactive waste to provide the desired information. A collaboration involving laboratory work at Savannah River National Laboratory (SRNL) and pilot scale work at INEEL was initiated to validate the correlations.

Background

Several demonstrations of fluidized bed steam reforming (FBSR) technology as applied to simulated radioactive liquid waste streams have been performed in the last four years. Three tests that are specifically related to the work reported here. The first, conducted at the Hazen Research facility in Colorado, initially demonstrated using FBSR to generate a sodium aluminosilicate (mineralized) product from Hanford low-activity waste (LAW). The results of this experiment were considered promising and characteristics of the product have been published and evaluated [Jantzen, 2002, McGrail, 2003, Mann, 2003].

The second demonstration, performed at the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) Center in Idaho Falls, Idaho, under the oversight of INEEL personnel, generated a sodium aluminosilicate product from INEEL's simulated sodium-bearing waste (SBW). The results of this experimental demonstration were also considered promising and have been published [Soelberg, 2004].

A third demonstration was recently performed between July 8-16, 2004 at the STAR Center and again on September 27 through October 1, 2004. This SBW FBSR demonstration used selected additive materials and enhanced equipment configuration. Sufficient product was generated for characterization, and the results have been documented and published [Olson, 2004b].

Other FBSR demonstrations have been performed, producing alkali carbonate or alkali silicate solids that are potentially disposable at the Waste Isolation Pilot Plant or that can be fed to a melter for vitrification. These products, which can be considered for the alternate applications given above, were not the aluminosilicate mineralized waste form examined in the current study.

Scope of Work

The scope of the collaborative work performed by the SRNL and INEEL includes:

- Laboratory scale experiments at SRNL to optimize steam reforming raw materials selection and mineralization chemistry
- Pilot scale FBSR experiments at INEEL to independently demonstrate Hanford LAW steam reforming and to produce a mineralized product, to which the products of the laboratory scale tests could be compared
- Product characterization via chemical assays, x-ray diffraction, and scanning electron microscopy
- Product durability tests including Toxic Characteristic Leach Procedure (TCLP), and Product Consistency Test (PCT) measurements; product performance tests including single pass flow through (SPFT) testing and pressurized unsaturated flow (PUF) testing
- Determination, based on comparisons to the products of the pilot-scale tests, if the laboratory tests produce steam reforming conditions and mineralized products that are representative of actual fluidized bed steam reforming.

This paper summarizes the INEEL pilot scale FBSR tests [Olson, 2004a]. Assessment of the product performance with regard to leach resistance and durability are to be reported by SRNL separately.

Experimental Approach

Mineralizing fluidized bed steam reforming technology, offered by THORsm Treatment Technologies (TTT), LLC, under U.S. Patent No. 6280694, provided the basis for process materials and conditions utilized in this demonstration program. Classical steam reforming is a versatile process that decomposes organic materials through reaction with steam. Steam reforming has been used on a large scale by the petrochemical industry to produce hydrogen for at least 65 years. In the THORsm process, an aqueous, hazardous, radioactive feed material like Hanford LAW is converted into a denitrated, granular mineral waste form designed to immobilize hazardous metals and radionuclides in a leach-resistant mineral form.

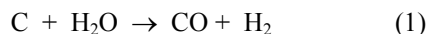
Mineral Waste Forms

Previous development work has shown that sodium (Na) aluminosilicate (NAS) minerals provide host phases that can immobilize radionuclide species in a leach-resistant waste form. Waste forms of aluminosilicate crystalline assemblages of mutually compatible, refractory, and leach-resistant solid solution phases have been proposed for the incorporation of radionuclide species [Rusin, 1979]. An assemblage of silicate mineral phases (supercalcine ceramics) such as apatite (host for lanthanides), pollucite (host for Cs), and other oxide host phases for Sr, Ba, U, Zr, etc. seem appropriate [McCarthy, 1976 and Rusin, 1979]. If the waste contains considerable Na and Si, then phases such as nepheline may form, while wastes enriched in Al may form high temperature phases such as Al₂O₃ and magnetoplumbite aluminate species [Morgan, 1981 and Jantzen, 1982]. The feldspathoid, sodalite, is a mineral phase found to incorporate Cs and Sr and Mo into the cage-like structure, e.g. Mo as (NaAlSiO₄)₆(NaMoO₄) [Brookins, 1984]. A more detailed discussion of this subject can be found in Jantzen, 2002.

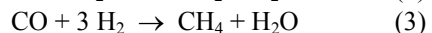
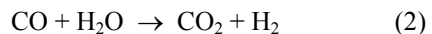
The objective of this work was to create the types of minerals that would provide leach resistant (durable) waste forms for immobilizing Hanford's low-activity waste (LAW). This has been approached by selecting an aluminosilicate clay with the appropriate Al:Si mole ratio that would suitably react with the Na and other constituents in the LAW. There may be significant substitution of different alkali and alkaline earths, and some Fe for Al, in the feldspathoid mineral products.

Steam Reforming Chemistry

Fluidized bed steam reforming for treating liquid radioactive wastes involves (a) a bed of particles fluidized by an upward flowing gas (steam in the THORsm steam reforming process) into which the liquid waste is sprayed, and (b) a reductant that is reformed by reactions with steam to produce reformed products and intermediate products that create a reactive, chemically reducing environment to destroy nitrates and nitrites in the feed to produce environmentally benign N₂, H₂O, and CO₂. A reductant, such as carbon, is steam reformed at elevated temperatures, exemplified by the following simple reaction:



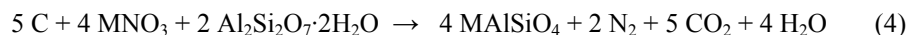
CO reacts further with both steam and H₂:



Consumption of CO and H₂ (such as through reactions with NO_x) in a steam reformer, in addition to reactions (2) and (3), drives reaction (1) to produce more CO and H₂. Reaction (1) is endothermic, so added heat is required to enable this reaction to proceed. If air or oxygen is included in the reaction mixture, the process can be autothermal. That is, exothermic reactions of carbon and the reduced gas species CO, H₂, and CH₄ with oxygen to produce CO₂ and H₂O can provide sufficient thermal energy to heat the steam reforming process. A tendency for steam reforming reactions to form more complex hydrocarbon species is suppressed by operating with a moderate excess of steam.

Ultimately, the final mix of gaseous products from the thermal decomposition of nitrate, i.e., the ratio of NO_x to N₂ in the product stream, depends on a number of chemical and physical factors, such as catalyzing metals, residence times, reductant types, reductant:oxidant stoichiometry, temperature, and flow patterns in the reaction vessel. Reacting nitrates with reducing agents is a more direct and efficient route to produce N₂ rather than NO_x as a final

decomposition product. 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 [Gunderloy, 1968, 1970], formic acid [Bradley, 1972], sugar [Bray, 1963], glycolic acid [Seymour, 1995], starch [Ryan, 1995], and urea [Cox, 1994]. Nitrate ions can be reduced to ammonia (and sometimes N_2) with aluminum [Murphy, 1991; Mattus, 1993] or iron [Cheng, 1997] powder, depending on the pH of the solution. Coke (carbon) has also been successfully used to directly reduce nitrates to N_2 although higher temperatures were required [Meile, 1984]. The overall denitration/mineralization reactions that occur in the FBSR are exemplified as follows:



The M represents primarily Na but can also represent other alkali metals, especially K. The most efficient C: MNO_3 and C: MNO_2 reactions produce N_2 and no CO, H_2 , or C char. The most efficient C: NO_3 mole ratio is 1.25 to 1. The most efficient C: NO_2 mole ratio is 0.75 to 1. Numerous reactions can be written that produce various proportions of reduced or incompletely oxidized products including NO, N_2O , HCN, NH_3 , H_2 , CO, or C. These are all less efficient or summed with water-gas reactions. When incompletely reduced or oxidized species are included in the reaction products, the C: NO_3 mole ratio is higher than 1.25 to 1 and the C: NO_2 ratio is higher than 0.75:1, because the carbon is less efficiently utilized to convert NO_x to N_2 .

Fluidized Bed Dynamics

When the liquid slurry feed is sprayed into the bed, slurry droplets rapidly heat up and begin evaporation, denitration, and mineralizing reactions. Droplets might evaporate leaving a new solid particle containing the solid products, or it might impact on and coat an existing particle, and then evaporate, leaving a coating of solid residue on the existing particle. New or existing particles might agglomerate to form larger particles, or some particles might become fractured into smaller separate particles.

Excessive particle growth (and other conditions such as growth of feed nozzle accretions) can lead to agglomerations large enough to cause the bed to become defluidized, and need to be avoided for long-term operation. The production of particles small enough to be elutriated with the upward moving gases must also be minimized while producing a sufficient amount of small "seed" particles to provide nuclei for particle growth. A steady mean particle diameter must be achieved while the bed is withdrawn at the same rate as it is generated to maintain steady bed particle fluidization and dynamics.

Several operating parameters can affect particle size in the FBSR process. These include 1) feed rate and properties of the slurry feed, 2) FBSR operating temperature, 3) atomizing gas flow rate and nozzle atomizing ratio (NAR, the ratio of the volumetric flow rates of the atomizing gas and the atomized slurry), and 4) bed particle properties such as melting point, chemistry, and resistance to attrition. If operating conditions result in the formation of new solid particles from the feed, then these particles might be small enough to easily elutriate from the bed. In this case, elutriated fines, collected in downstream equipment, would comprise the majority of the solid product. If operating conditions tend to result in new coatings on existing bed particles, then solid particles drained from the bed would comprise the majority of the solid product, and bed draining could be necessary to control bed particle size.

Stable fluidized bed particle dynamics requires a balance between the production of fines and control of particle growth in the fluidized bed. The particle size distribution (PSD) and average particle size are a good indicators of the fluidized bed operational health. Two common methods of determining the "average" particle size are the mass-mean particle diameter (MMPD) and the harmonic mass mean diameter (HMPD). The MMPD is the diameter at which half of the mass is attributed to particles of lesser diameters and the other half to particles of larger diameters. The HMPD is the size of the particle that has the same surface-area to volume ratio as the average of the entire bed. The HMPD is used when calculating pressure drop through the bed and the minimum fluidizing gas velocity. Close agreement between the MMPD and HMPD indicates a narrow particle size distribution. Divergence between the MMPD and HMPD indicates a wide particle size distribution or the presence of extreme particle sizes (e.g., significant quantities of coarse agglomerates or fine "flour") that differ from the particle sizes in the bulk media. Ideally, particle growth will be balanced by particle attrition, resulting in a steady state MMPD and HMPD.

Experimental Setup

The DOE FBSR test system (Figure 1) at the STAR Center occupies a space approximately 40 feet by 40 feet in area and 20 feet in height. The FBSR test system includes several primary subsystems: 1) feed systems for gases, liquids/slurries, and small solids, 2) the fluidized bed vessel, 3) the solid product collection and management systems, 4) the off-gas control system, and 5) the process monitoring and control system. All wetted components are constructed from corrosion resistant materials. Equipment and piping are fabricated from 300-series stainless steel except for the reformer vessel, which is fabricated from Inconel 800H.

The system can be manually controlled or automatically controlled using a Process Logic Controller (PLC) system with multiple human-machine interface (HMI) stations. The STAR Center provides all necessary test system utilities and support services including electrical power, water, compressed air, nitrogen, oxygen, various specialty calibration gases for continuous emissions monitoring systems, test system operations, permits, and materials/wastes management.

The Inconel 800H fluidized bed vessel has a nominal 15-cm inside diameter and is designed for temperatures up to 800°C, oxidizing or reducing conditions, and corrosive or hazardous materials. The main features of the fluidized bed vessel are the fluidized bed section and the freeboard (particle disengaging) section. The fluidizing gas distributor section mounted below the bed vessel provides entry and distribution for the fluidizing gas. Various fluidizing gas distributor types are possible; however, the fluidizing gas distributor utilized for this test was a TTT proprietary design. The vessel bottom receiver below the fluidizing gas distributor is temperature-instrumented and enables removal of bed media during operation while maintaining atmospheric isolation. The fluidized bed vessel is externally heated for bed temperature control using electric resistance heaters.

Gases and elutriated solid particles (fines) exit the top fluidized bed vessel freeboard section and flow through a 15-cm diameter cyclone separator designed to remove 70% of 3-5 μm solid particles when operating at a pressure drop of 13 cm of water column. Fines collected in the cyclone are continuously recycled back to the fluidized bed using an auger and shuttle valve system. The off-gas exiting the cyclone is subsequently filtered for remaining very small entrained particulate in a heated filter. This filter consists of a stainless vessel containing seven 6.4 cm diameter, 61 cm long, sintered-metal filters with a nominal pore size of 2 μm . Fines that pass through the cyclone and are captured by the heated filter are not recycled to the bed.

The liquid feed system consists of three tanks equipped with variable speed agitators and a recirculation/transfer pump to ensure that solutions are fully mixed and that insoluble solids remain suspended and uniformly blended. The liquid waste simulant from a simulant makeup tank is slurried with the powdered clay additive in the feed mixing tanks and is continually recirculated through the feed/mix tanks with recirculation pumps. A slipstream of the recirculated slurry is delivered to the fluidized bed by a peristaltic pump that is automatically controlled by a coriolis mass flow meter that measures the slurry feed rate. The simulant feed slurry is atomized into the fluidized bed through a gas-atomizing nozzle. A variation of a SprayCo® nozzle design was selected for use during this Hanford LAW demonstration. This nozzle was uniquely modified based on prior nozzle evaluation and testing activities to minimize the formation of solid deposits on the nozzle surfaces exposed to the fluidized bed.

Solid carbon reductant is metered into the process by a vibratory feeder. The hopper of the vibratory feeder is manually charged with a batch of carbon that is then fed via a controlled vibratory ramp to a small weigh hopper/funnel mounted on a load cell. The carbon reductant feed rate is automatically controlled by a signal from the load cell to the vibratory feeder. The carbon reductant is fed gravimetrically from the vibratory feeder to a lock hopper. Nitrogen gas purges the lock hopper, keeping atmospheric air from entering the process with the carbon feed, and providing a motive force to loosen and inject the low density carbon granules into the bed. This system is calibrated for the specific carbon that is used, and the PLC controls the carbon feed rate near the desired value.

Process gases include the bed fluidizing gas, the atomizing nozzle gas, instrument purge gas, oxidizer air, jet eductor air, and oxidizer fuel (natural gas). The fluidizing gas used for this test was superheated steam blended with a small amount of oxygen. The fluidizing steam is generated for the test system in a small steam generator/boiler and superheated in electrical resistance Inconel tube heaters, which include customized 303 stainless steel mesh internals for improved heat transfer to the fluidizing gas at low flow rates. Nitrogen was used as the atomizing nozzle gas and also for a variety of small instrument and feed line purges, hot filter pulse gas, etc. A diesel-powered compressor

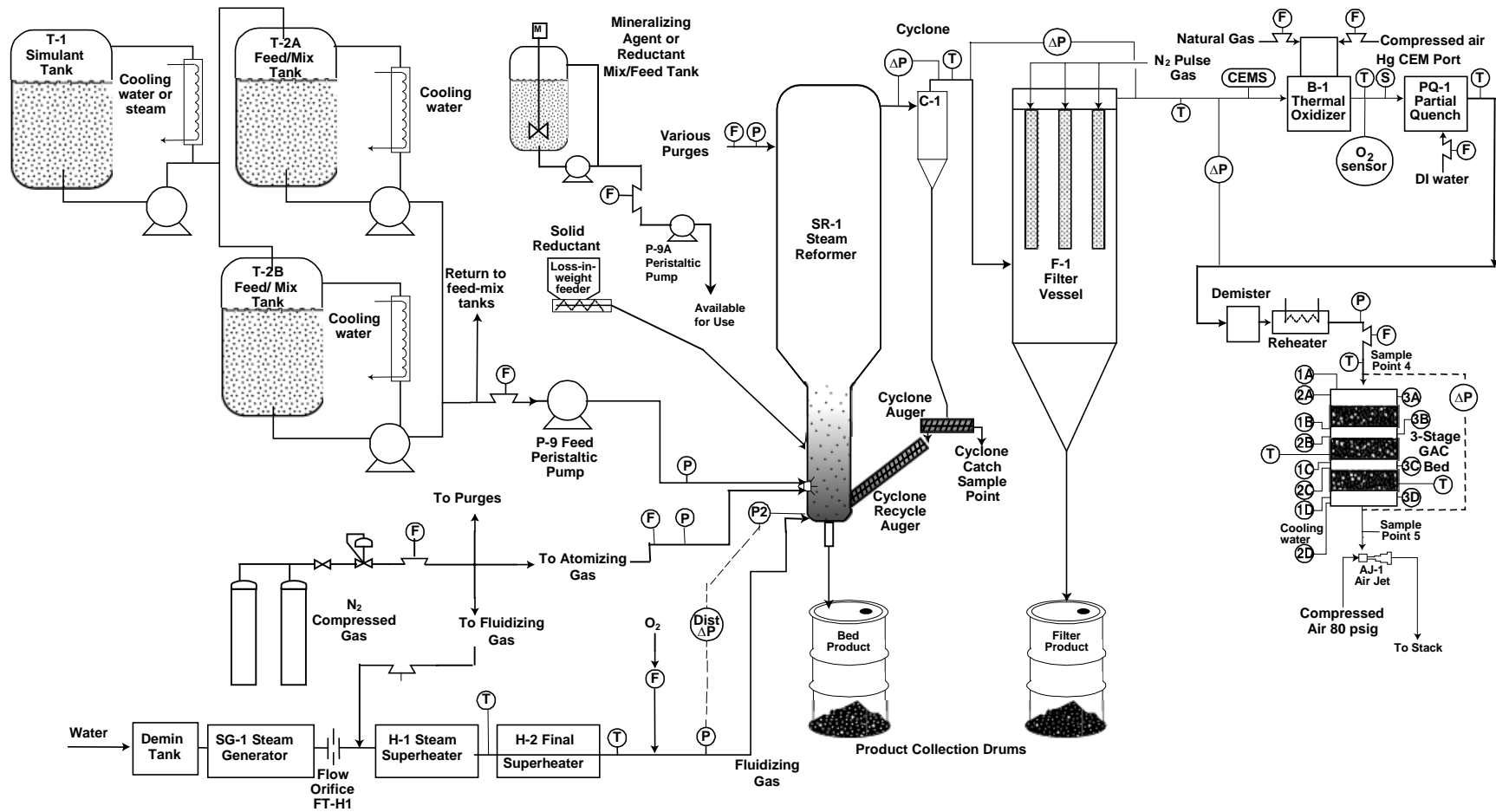


Fig. 1. Process flow diagram for the fluidized bed mineralizing steam reforming demonstration with Hanford LAW simulant

provides oxidizing air for the thermal oxidizer and air as the motive force in an air jet eductor for maintaining system vacuum.

The off-gas treatment system, down-stream of the cyclone and hot filter, consists of a natural gas-fired thermal oxidizer, partial quench vessel, demister, re-heater, and a three-stage granular activated carbon filter bed. The off-gas exiting the hot filter flows into the natural gas-fired thermal oxidizer (typically operated at 1,000°C), where any residual reduced gas species (H₂, CO, CH₄, etc) from the FBSR are fully oxidized. The oxidized off-gas is then partially quenched with water spray to a temperature of 130°C. The partial quench temperature control maintains the off-gas well above the dew-point temperature (no entrained mist), but the off-gas is still passed through a demister and a re-heater to assure desired gas conditions entering the granular activated carbon bed. The carbon bed captures trace concentrations of halogen gases, SO₂, NO_x, and trace hydrocarbons.

A continuous emissions monitoring system (CEMS) provides continuous off-gas composition measurements for process control, safety, air emissions measurements, and determining the fate of feed constituents that were converted to gaseous compounds. The off-gas composition was measured at two locations in the off-gas system. CEMS 1 was used to measure the off-gas composition at the outlet of the heated filter (upstream of the thermal oxidizer), to characterize the composition of the FBSR off-gas. CEMS 2 was used to measure the off-gas composition at operator-selectable locations at the inlet of the carbon bed or the outlet of any of the three stages of the carbon bed. Gas species measured were O₂, CO₂, H₂, CO, CH₄, NO, NO_x, THC, HCl, SO₂.

Test Results

The test operation was continuous, 24 hours per day, starting at 0900 on August 2 and continuing nonstop until the test was terminated at 0526 on August 5. The total continuous operating time (COT) was 68 hours 26 minutes (68.4 hours). Operating conditions are shown in Table I. The overall operations and performance of the fluidized bed processing test system equipment were good. Several minor incidents required operator actions/interventions, but they were corrected rapidly and had no significant discernible impacts upon the mineralized steam reforming process. Some operating condition changes were made to maximize the process throughput and achieve high bed turnover (conversion of the fluidized bed from the starting aluminum oxide particles to particles of mineralized steam reformer product), respond to process changes, and maintain stable fluidized bed operation. The test was terminated due to bed agglomerations causing defluidization of the bed.

Fluidized Bed Performance

An objective of this test was to demonstrate a stable fluidized bed within the steam reforming vessel. The bed particle size, bulk density, and particle (true) density are key operating parameters and characteristics of the bed product. Table II shows these properties of the bed media and product as the test progressed. The fluidized bed density leveled out at about 0.4 g/cc, while the bulk density stabilized at about 0.7 g/cc, and the particle (true) density stabilized at about 2.0 g/cc. The bed particle size gradually decreased from an initial HMPD of about 0.21 mm to a relatively stable value of about 0.11 mm after the bed turnover reached 95%. The bed particle MMPD increased from 0.22 mm to an average of 0.26 mm during the same time period. The bed density and particle size (HMPD) values were lower than desired for this test. Several test condition changes during the test (increasing the slurry feed rate, lowering fluidizing gas rate, lowering the atomizing gas rate, and removing fines that would have been recycled by the cyclone) were made to try to increase both the bed particle size and density. In addition, some of the fines recycled back to the bed by the cyclone were harvested at two different times, thereby increasing the average bed particle size.

Product Characterization

The bed was almost entirely sodium aluminosilicate product after the bed turnover exceeded about 99 wt% (after about COT 43), as evidenced in Figure 2. The starting alumina bed media (left portion of Figure 2) looks like broken pieces of glass, all of fairly uniform size. These pieces have sharp edges and angular surfaces, and are nearly transparent. Carbon reductant particles in the bed are very dark, angular particles that range in size up to several mm. The starting alumina bed was replaced over time with product bed (right portion of Figure 2). Individual bed product particles have a popcorn-like appearance. The scale graduations shown in Figure 2 are 1 mm.

Table I. Key Operating Conditions for the August 2004 Hanford LAW FBSR Demonstration.

Parameter		Value	
		Range	Average
Fluidizing gas	Ratio (U/U_{mf}) ^a	8 – 30	---
	Gas velocity at the distributor	0.12 – 0.21 m/s	0.17 m/s
	Composition	12-24 wt% O ₂ , and 76-88 wt% steam.	18 wt% O ₂ , 82 wt% steam
	Fluidizing gas temp.	Superheated to 560 – 740°C, depending on flow rate	670
	Distributor differential pressure	2.4 – 14 cm (6 – 30 inches) water, 50 – 160% of the total bed differential pressure	ND ^b
Feed, additives, and cyclone recycle rate	Slurry feed rate (total)	3.0 kg/hr at continuous operating time (COT) 0. Increased to 4.0 kg/hr as stable conditions were observed at about COT 8; increased to 5 kg/hr at COT 24, and to 5.5 kg/hr at COT 54, to maximize bed turnover.	4.7 kg/hr, 3.2 L/hr
	Slurry specific gravity	1.43 – 1.49	1.46
	carbon reductant	2 kg/hr for 30 minutes before slurry feed initiation, then adjusted between 0.59 – 0.85 kg/hr, to maintain reducing conditions for NO _x destruction	0.63 kg/hr
	clay mineralizing additive	635 gm/L LAW	
	Cyclone recycle rate	1.6 – 5.7 kg/hr	3.4 kg/hr
Atomizing nitrogen	LAW slurry NAR ^c	Varied between 670 – 1,300 to control fines generation	800
	Atomizing N ₂ rate	2.6 – 3.5 kg/hr	2.9 kg/hr
Bed Parameters	Bed temperature	721 – 724°C	722°C
	Starting bed mass	20 kg white alumina	
	Fluidized bed depth	63.5 – 71 cm (25 – 28 inches)].	ND
	Reformer pressure at distributor	Atmospheric	
	Starting alumina particle size (HMPD)	0.0211 cm	
	Starting alumina particle density	3.79 g/ml	
Off-gas Parameters	Cyclone diff. pressure	1.0 – 1.8 cm (0.4 – 0.7 in.) water	1.3 cm (0.5 in.) water
	Off-gas filter temperature	470 – 515°C	488°C
	Off-gas filter outlet gas flow rate	7.0 – 9.2 kg/hr	8.3 kg/hr
	Oxidizer chamber temperature	1,000°C	1,000°C
	Carbon bed temp. ^d	117 – 120°C	119°C

^a U_{mf} = Minimum fluidizing velocity, as calculated by the Wen and Yu correlation [Kunii and Levenspiel, 1991].
^bNot determined.
^cNAR = Nozzle atomizing ratio, the volumetric ratio of the atomizing gas and the atomized liquid flow rates.
^dCarbon bed consists of 30.5 cm of Barneby Sutcliffe 208C, 4x8 mesh, to capture any halogen gas species in the off gas for analysis and mass balance closure calculations.

Bed product, cyclone fines, and filter fines were analyzed by X-ray diffraction to determine the primary mineral phases (Table III). Carnegieite was determined to be the major phase of all of the samples. Carnegieite is a metastable alkali aluminosilicate that converts to nepheline with sufficient time and temperature. Increasing the residence time of the product in the bed should increase the nepheline yield, which is a more favorable host phase

because of its thermodynamic stability. Nosean was also an expected and desired product phase to retain anions, radionuclides and hazardous metals. Nosean was only found in the coarse bed product and not in the cyclone samples or the fines. Its formation may be kinetically limited to longer residence times than the fines encounter.

Table II. Fluidized Bed and Product Properties as the Test Progressed.

COT	Bed turnover, wt%	Bed product				Fluidized bed density, g/cc	Recycled cyclone fines particle size, mm		Filter fines		
		Particle size, mm		Bulk density, g/cc	Particle (true) density, g/cc		Particle size, mm		Bulk density, g/cc		
		HMPD	MMPD				HMPD	MMPD		HMPD	MMPD
0.0	0.0	0.211	0.216		3.79	1.37	---	---	---	---	---
7.0	6.0	0.204	0.244	1.90	3.70	1.23	---	---	---	---	---
9.5	13.6	0.185	0.233	1.66	3.30	1.12	---	---	---	---	---
10.0	---	---	---	---	---	---	---	---	0.006	0.009	0.48
11.0	---	---	---	---	---	---	0.021	0.035	---	---	---
12.4	22.4	0.178	0.261	1.57	2.96	0.93	---	---	---	---	---
14.4	29.8	0.153	0.236	1.45	3.06	0.78	---	---	---	---	---
16.7	43.6	0.156	0.223	1.21	2.70	0.72	---	---	---	---	---
20.3	57.9	0.148	0.227	1.10	3.02	0.61	---	---	---	---	---
23.0	69.4	0.130	0.243	1.03	2.66	0.54	---	---	---	---	---
25.5	78.7	0.136	0.297	0.92	2.27	0.49	---	---	---	---	---
27.0	82.2	0.126	0.279	0.88	2.16	0.46	---	---	---	---	---
31.0	89.6	0.129	0.298	0.88	2.20	0.45	---	---	---	---	---
35.0	94.7	0.111	0.241	0.80	2.00	0.42	---	---	---	---	---
39.3	97.4	0.112	0.249	0.79	2.68	0.41	---	---	---	---	---
43.0	98.9	0.116	0.261	0.72	2.06	0.40	---	---	---	---	---
47.0	99.4	0.112	0.252	0.74	1.87	0.38	---	---	---	---	---
51.0	99.6	0.117	0.292	0.81	1.89	0.38	---	---	---	---	---
55.5	99.7	0.116	0.292	0.74	1.59	0.38	---	---	0.007	0.013	0.52
62.3	99.95	0.164	0.433	0.71	2.19	0.40	---	---	---	---	---
64.3	99.96	---	---	---	---	---	0.021	0.039	---	---	---
65.8	99.97	0.166	0.459	0.68	1.87	0.38	---	---	---	---	---

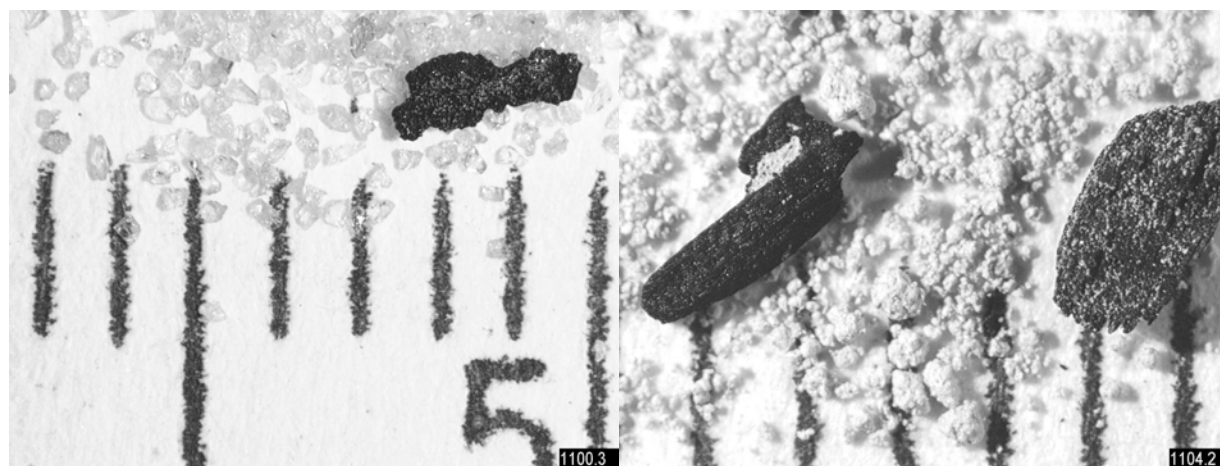


Fig. 2. Starting alumina bed (left) compared to the mineralized bed product at COT 55:30 (right)

Table III. Summary of FBSR Solid Product Mineral Phases.

Sample	Na _{7.15} (Al _{7.2} Si _{8.8} O ₃₂) [Nepheline (Si rich)] PDF# 79-0993	NaAlSiO ₄ (Carnegieite) PDF #11-0220	Na ₆ [Al ₆ Si ₆ O ₂₄](Na ₂ SO ₄) (Nosean) PDF# 73-1734	TiO ₂ (Anatase) PDF# 21-1272
Bed Product COT 39:15	Some	Major	Minor	Trace
Bed Product COT 55:30	Some	Major	Minor	Trace
Final Bed	Some	Major	Minor	Trace
Cyclone fines COT 11:00	Minor	Major	None	Trace
Cyclone fines COT 64:20	Minor	Major	None	Trace
Filter fines COT 10:00	Trace	Major	None	Trace
Filter fines COT 55:30	Trace	Major	None	Trace
PDF – Powder Diffraction File				

Process Mass Balance

The total input solid masses were the starting bed media, nonvolatile solid forming constituents from the feed slurry, and the carbon reductant. The output solid masses were the bed product, the mass of the cyclone recycle material that was sampled or harvested for bed particle size control (and not returned to the bed), and fines removed from the off-gas by the heated filter. The output bed product was the bed removed at the end of the test and the bed media removed at discrete times during the test. Bed media was removed during the test to control the bed height as new product from the feed added to the bed mass, to obtain samples for analyses, to inspect the bed media for appearance and agglomerations, and to provide a pathway for agglomerations to be removed from the bed. The total mass of the bed product includes the product formed from the feed slurry, the starting alumina bed, and smaller amounts of unreacted carbon additive and inorganic ash from the carbon additive that was reacted. The cyclone fines and filter fines include elutriated particles of product from the feed slurry and smaller amounts of unreacted carbon additive, inorganic ash from the carbon additive that was reacted, and any particles of elutriated starting alumina bed. Analyses show that the amount of elutriated starting alumina bed in the cyclone fines and filter fines was very small.

Table IV summarizes the total mass balance closure. At the end of the test the cumulative total output, including the starting alumina bed and the final bed mass after the test, reached 145 kg, which was essentially the same as the total input solid mass of 148 kg (including the starting alumina bed mass), resulting in a mass balance closure of 98%. This mass balance closure is well within reasonable error bounds for the various measurements used to provide data for the mass balance calculations.

The distribution of FBSR product between the bed product and the filter fines was calculated after excluding the mass of the starting alumina bed and the mass of unreacted carbon additive. The product to fines ratio (mass of net product divided by mass of net filter fines) was 1.08, indicating that about ½ of the net input reformer product stayed in the bed, and the other half of the net input reformer product formed fines sufficiently small to pass through the cyclone into the heated filter.

Table V shows the weighted average elemental concentrations in the bed product and fines and the elemental mass distribution between the bed product and the filter fines. The product distributions for Al and for elements present at trace levels in the starting bed were adjusted to be on a starting bed-free (product only) basis. The ratios of the weighted average elemental concentrations in the fines and the bed product (including cyclone samples) indicate if any elements preferentially partitioned to either the filter fines or the bed product. Ratios >1 indicate preferential partitioning to the filter fines. Ratios near 1 indicate that the elements partitioned equally, and ratios <1 indicate that the element partitioned preferentially to the bed product.

The mass balance closure (total output elemental mass as a percentage of input mass for that element) was within reasonable experimental error of 80-120% for the elements present in the highest concentrations in the feed (Al, Na, and Si), and also for some other elements present at lower concentrations (K, P, and Ti). The mass balance closure for most other elements [Cr, Fe, Mg, Re (a radionuclide surrogate), S, and Cl) was within about 70-130%, also considered reasonable for these lower-concentration elements.

Table IV. Total Mass Balance for the Hanford LAW FBSR Demonstration.

Solid Input Masses	Mass, kg	Solid Output Masses	Mass, kg	Wt% of Total Input Mass
Starting alumina bed	17.7	Bed product	74.5	50.2%
Total solid product (from total slurry fed and the % solids in slurry)	123.8	Cyclone samples	9.6	6.5%
Ash from reacted carbon additive	1.9	Total bed product and cyclone samples	84.1	56.7%
Unreacted carbon additive	5.0	Filter fines catch	61.4	41.7%
		Total output solid mass	145.4	98%
		Total output product (excluding starting bed and unreacted carbon)	122.7	---
Total input mass	148.4			
Input solids from the feed slurry (excluding unreacted carbon and starting bed)	125.7			

Product to Fines Ratio	
Total net bed product and cyclone samples, kg	63.7
Net filter fines less unreacted carbon, kg	59.1
Product to fines ratio (net product mass/net fines mass)	1.08

Table V. Elemental Partitioning Between Bed And Filter Products For The Hanford LAW FBSR

	Total product		Re			Cs			Re/Cs
	Mass	%Mass	Mass	%Mass	Conc.	Mass	%Mass	Conc.	w/w
Bed + cyclone product	84.1 kg	58%	3.7E-3 kg	54%	0.004%	1.5E-4 kg	12%	0.0002%	24.6
Filter fines	61.4 kg	42%	3.2E-3 kg	46%	0.005%	1.1E-3 kg	88%	0.0018%	2.8
Fines-Product ratios	0.73	---	0.87	---	1.2	7.5	---	10.3	---

	Al		Na			Si			
	Mass	%Mass	Conc.	Mass	%Mass	Conc.	Mass	%Mass	
Bed + cyclone product	18.4 kg	62%	21.9%	11.9 kg	54%	14.2%	13.2 kg	52%	15.8%
Filter fines	11.2 kg	38%	18.3%	10.0 kg	46%	16.3%	12.4 kg	48%	20.2%
Fines-Product ratios	0.61	---	0.83	0.84	---	1.1	0.94	---	1.3

	Ca		Cl			Cr			
	Mass	%Mass	Conc.	Mass	%Mass	Conc.	Mass	%Mass	
Bed + cyclone product	1.1 kg	56%	1.27%	0.11 kg	59%	0.134%	7.0E-2 kg	62%	0.084%
Filter fines	0.8 kg	44%	1.37%	7.8E-2 kg	41%	0.127%	4.3E-2 kg	38%	0.070%
Fines-Product ratios	0.79	---	1.1	0.70	---	1.0	0.61	---	0.84

	K		P			S			
	Mass	%Mass	Conc.	Mass	%Mass	Conc.	Mass	%Mass	
Bed + cyclone product	0.25 kg	54%	0.298%	0.17 kg	59%	0.203%	0.19 kg	49%	0.229%
Filter fines	0.22 kg	46%	0.354%	0.12 kg	41%	0.195%	0.20 kg	51%	0.322%
Fines-Product ratios	0.87	---	1.2	0.70	---	0.96	1.03	---	1.4

[LAW test summary and mass balances Nov 16.xls]Chemical mass balance table

Demonstration

About 76% of the total input sulfur and 68% of the total input chlorine were accounted for in the solid mineralized products. Neither SO₂ nor HCl was detected in the FBSR off-gas. If these species were present in the off-gas at concentrations up to the CEMS and CEMS condensate minimum detection limits, then up to 12% of the input S and up to 24% of the input Cl could have evolved to the off-gas. At least 88% of the input S and at least 76% of the input Cl were retained in the solid FBSR mineralized products.

The data indicate that Al and Cr partitioned somewhat preferentially to the bed product. Na, Ca, Cl, and P partitioned almost evenly between the bed product and filter fines. Re, Si, K, and S partitioned somewhat to the fines, but not as significantly as did Cs, which more strongly partitioned to the fines. The degree of partitioning determined for these elements based on the product elemental analyses could be impacted by the degree of mass balance closure, if a high or low mass balance closure is a result of either a high or low analysis for either the bed (and cyclone) samples or the filter fines samples.

Off-gas Characterization and NO_x Destruction

Table VI shows the off-gas composition and NO_x destruction at the outlet of the fluidized bed heated filter and also downstream of the oxidizer, partial quench, and electric reheater. The wet basis compositions were calculated from the dry, as-measured composition by 1) correcting for zero and span calibration error/drift, and 2) normalizing the dry composition to a wet basis using the off-gas moisture content.

The primary components of the FBSR off-gas were H₂O (from the fluidizing steam, and evaporated water, NaOH, and oxidation of hydrogen-bearing sodium acetate in the feed simulant) and N₂ (from various instrument gas purges and conversion of NO_x to N₂). Essentially no O₂ was detected in the FBSR off-gas, as expected considering the reducing conditions used for NO_x destruction. Percent-level ranges of CO₂ and H₂ were present. Other measured gas species [CO, total hydrocarbon (THC), CH₄, NO, and NO_x] were present at concentrations below 1 volume % (wet basis). Measured NO_x levels ranged similar to or slightly less than the measured NO levels, indicating that there was essentially no NO₂ present in the off-gas.

Table VI. Off-Gas Compositions and NO_x Destruction for Hanford LAW FBSR Demonstration.

Off-gas Composition (wet volumetric basis)				
Component	FBSR Heated Filter Outlet		Oxidizer Outlet	
	Range of averages for each of 11 test conditions	Test overall average	Range of averages for each of 11 test conditions	Test overall average
O ₂ , %	0.01 - 0.08	0.04	3.0	3.0
CO ₂ , %	3.5 - 4.1	3.8	4.8 - 5.0	5.0
CO, %	0.19 - 0.55	0.28	0-1.7	0
H ₂ , %	0.65 - 3.0	1.2	Not measured at this location	
THC, ppm	750 - 2,200	1,000	Not measured at this location	
CH ₄ , ppm	510 - 1,600	770	Not measured at this location	
NO, ppm	340 - 1,400	900	48 - 120	81
NO _x , ppm	340 - 1,400	900	51 - 110	80
SO ₂ , ppm	Not measured at this location		0 - 4.3	0
HCl, ppm	Not measured at this location		0	0
H ₂ O, %	61.1 - 67.7	65.3	40.4 - 44.2	41.9
N ₂ , %	27.8 - 32.5	29.7	48.7 - 52.2	50.8
Total, %	100.2 - 100.6	100.3	100.6 - 100.7	100.7

NO _x destruction, % (Based on total NO _x measurements compared to NO _x Maximum Theoretical Emission Concentrations)				
	86.6 - 98.0	92.4	93.1 - 97.3	94.8
	NO _x destruction, %, in the oxidizer (based on oxidizer inlet and outlet NO _x concentrations)			
	-52 to +55			22.3

NO_x destruction easily met the test objective of at least 80%, averaging 92% for the FBSR, and 95% for the entire system including the oxidizer. The FBSR NO_x destruction exceeded 90% whenever 1) the wet basis FBSR H₂

concentration exceeded 1% (dry basis $H_2 > 2.5\%$), or 2) the C:oxidant stoichiometry exceeded 375% and the carbon inventory in the fluidized bed was at a relatively steady state for that stoichiometry.

Defluidizing Agglomeration

Bed particle agglomerations, which bridged across the inside diameter of the fluidized bed vessel and caused the bed to become defluidized, resulted in test termination at COT 68.4 hours, prior to planned 100-hour continuous operating time, were caused by a combination of several possible contributing factors. The slurry waste feed rate at the time (5.5 kg/hr) may have been too high for the operating conditions, resulting in excessive cooling and eventually agglomerating the bed media in the feed spray zone. The atomizing gas rate (<3 kg/hr), maintained as low as considered possible to minimize bed grinding and control fines generation, may have been too low to adequately atomize the liquid feed slurry. Growth of agglomerations attached to or near the nozzle could have further interfered with feed atomization. The fluidized bed density, which started at about 1.4 g/cc but decreased to about 0.4 g/cc as the aluminosilicate product replaced the starting bed media, may have been too low to provide the needed thermal inertia in the bed to prevent excessive bed particle cooling in the spray zone. The fluidizing gas velocity, decreased from a starting velocity of 0.21 m/s to 0.12 m/s to control fines generation, was still up to 30 times higher than the minimum value needed to maintain fluidization, but may have been low enough that heat and mass transfer in the spray zone was insufficient to prevent excessive bed particle cooling. A low distributor differential pressure and presence of several plugged distributor orifices may have led to poor distribution of the fluidizing gases and uneven fluidization in the lower portion of the bed, including the feed zone.

CONCLUSIONS

A THORsm mineralizing steam reforming demonstration on simulated Hanford LAW was successfully performed at the INEEL's pilot scale fluidized bed processing test system. The FBSR process successfully converted the Hanford LAW simulant from the caustic aqueous form to a mineralized solid form by evaporating the liquid, destroying nitrates, nitrites, and organics, and producing a mineralized solid sodium aluminosilicate product material.

The majority of the bed product material consists of granular particles with a rough "popcorn like" appearance. The granules appear to be collections of much smaller micron-size particles, which have been successively deposited onto the surface of existing larger particles. The major phase found in the bed product was carnegieite, with lesser amounts of nepheline and minor amounts of nosean. The fines consisted of the major phase carnegieite with lesser amounts of nepheline and TiO_2 (a trace component in the clay). Leach resistance of the mineralized product is being evaluated and will be reported by SRNL.

A large amount of operating and product data was obtained. Bed turnover (replacement of the starting bed with mineralized product solids) was essentially complete (>98%) within approximately 40 hrs. Test operation continued until the test was ended at 68.4 hours due to a defluidizing bed agglomeration. 178 kg of LAW simulant were processed, resulting in 123 kg of solid sodium aluminosilicate product (including both bed product and elutriated fines, but excluding the alumina starting bed and unreacted solid carbon reductant), a mass reduction of about 31%. The bed product to fines mass ratio was about 1 to 1. This value did not achieve the desired value of 3.5 to 1, and further optimization and/or development is needed to achieve this objective.

Extensive measurements were made to characterize the FBSR off-gas. The FBSR NO_x destruction averaged 92%, and the overall system NO_x destruction averaged 95%, effectively meeting the test objective of greater than 80% destruction. The off-gas NO_x and H_2 levels were used for controlling the FBSR NO_x reducing stoichiometry. The carbon reductant feed rate was less than that utilized in previous tests, leading to less unreacted carbon in the solid products. Cyclone recycle captured and returned larger carbon fines to the bed for more efficient use.

Several different, important FBSR process mechanisms and complex interactive situations cannot be well understood from the currently available data and analyses alone. Considerable additional controlled testing and model-based evaluations of both the local and global heat transfer, fluid dynamics, and reaction rate driven chemistry conditions are needed to better understand controlling mechanisms and parameters and provide for predictive means for scaling and optimizing process parameters. It is recommended that these efforts be pursued to provide a more effective design bases for a potential future production process.

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