

## **FLUIDIZED BED STEAM REFORMING FOR MIXED AND RADIOACTIVE WASTES**

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### **ABSTRACT**

Various proof-of-concept and demonstration tests using laboratory scale and demonstration-scale fluidized bed steam reforming test facilities have been performed at the Idaho National Engineering and Environmental Laboratory (INEEL) and at a subcontractor facility, the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) Center in Idaho Falls, Idaho. These tests were performed using non-radioactive simulants of radioactive and mixed wastes. Steam reforming tests have been conducted for various mixed and radioactive waste streams including the INEEL's sodium bearing waste (SBW), waste stored in Tank 48H at the Savannah River Site (SRS), and for other mixed or radioactive wastes.

These tests have demonstrated viability of the steam reforming vendor technologies. Conditions have been demonstrated under which various types of radioactive and mixed wastes can be steam-reformed to produce a dry solid granular product that retains essentially all of the hazardous metals and radionuclides, but is a fraction of the original waste volume. The solid product is essentially 100% denitrated. The products demonstrated to date are primarily carbonates or aluminosilicates of the metal cations in the feed.

The steam reformer offgas composition has been rigorously measured. The steam reformer offgas contains the fluidizing gas, evaporated water, and gasified reaction products of the nitrates and organic constituents in the feed streams. When a single reformer is operated under reducing conditions to convert the nitrates in the feed to  $N_2$ , the offgas also contains incompletely oxidized organic species including  $CO$ ,  $CH_4$ , and  $H_2$ . Oxidation of the offgas would be required if the process is regulated under EPA's hazardous waste combustor (HWC) maximum achievable control technology (MACT) standards, under which mixed waste thermal treatment is being regulated. The most recent steam reforming tests have demonstrated MACT compliance.

### **INTRODUCTION**

Approximately one million gallons of acidic, hazardous and radioactive, sodium-bearing waste (SBW) is stored in stainless steel tanks at the Idaho Nuclear Technology and Engineering Center (INTEC), which is a major operating facility of the Idaho National Engineering and Environmental Laboratory (INEEL). This mixed waste was produced during nuclear fuel reprocessing activities that were halted in the 1990's, and remains after cessation of fluidized bed calcination that has already converted raffinate waste (also from nuclear fuel reprocessing) and much of the SBW into a more safely stored solid calcine powder. Further treatment of the remaining SBW inventory is on hold pending a review and determination of the most appropriate treatment method. Traditional calcination and steam reforming are two of the candidate technologies being investigated for treatment of the SBW into a "road ready" waste form that can be shipped to the Waste Isolation Pilot Plant in New Mexico for internment.

Various proof-of-concept and demonstration tests using laboratory-scale and demonstration-scale steam reforming test facilities have been performed at the Idaho National Engineering and Environmental Laboratory (INEEL) and at a subcontractor facility, the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) Center in Idaho Falls, Idaho. These tests were performed using non-radioactive simulants of radioactive and mixed wastes.

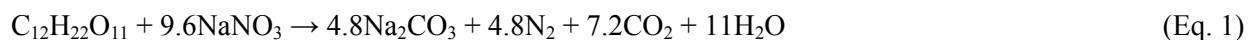
Both of the test systems include fluidized beds in which a liquid feed is sprayed through a nozzle into a bed of fluidized particles. The fluidized bed is heated to a temperature of 550-750°C so that water and other volatile components in the liquid feed very rapidly evaporate. Steam reforming tests have been conducted for various mixed and radioactive waste streams including the INEEL's sodium bearing waste (SBW), which is a highly acidic (1 mol/L nitric acid) aqueous waste that contains dissolved nitrates (5 mol/L), sodium (2 mol/L), aluminum, heavy metals, and radionuclides. Steam reforming tests have also been performed for a basic (1.8 mol/L sodium hydroxide) waste stored in Tank 48 at the Savannah River Site (SRS), and for other mixed or radioactive wastes.

## FLUIDIZED BED STEAM REFORMING PROCESS THEORY

Steam reforming is a process wherein a material or mix of materials is reacted at elevated temperatures to achieve desired reactions and produce desired products. Steam reforming mixed and radioactive wastes can (a) destroy complex, hazardous, organic materials, reforming the organic molecules into simpler, less hazardous or more reusable molecules (hence the label "steam reforming"), (b) evaporate water in high-water-content streams, (c) denitrate nitrated materials, and (d) produce a dried, nitrate and organic-free solid product for disposal or further processing.

In fluidized bed steam reforming, a liquid feed is sprayed into a vessel that contains a bed of particles that is fluidized by a gas stream that flows up through the bed. When the gas stream velocity exceeds the stagnation velocity of the particles then the particles are fluidized and float in the gas stream. When the entire bed mass of particles is fluidized, gas/particle mixing, mass transfer, and heat transfer rates are very high, so chemical reactions can proceed quickly based on chemical kinetics and thermodynamics. With high particle surface areas, fluidized beds are an excellent method to perform catalytically enhanced reactions when the particles are catalytically active. Fluidized bed technology has many uses, including several decades of successful treatment of INEEL high level waste (HLW) and SBW.

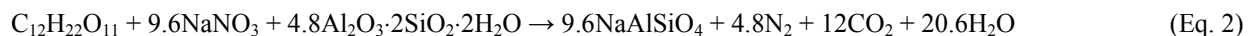
A reductant such as sugar (which can be dissolved in aqueous feeds) or activated carbon (fed separately as a solid additive) provides the reducing potential to cause nitrates (common in many liquid mixed wastes) to be reduced to N<sub>2</sub>. Equation 1 shows an example reaction between sugar and sodium nitrate:



This reaction, as shown, is 100% efficient for producing a sodium carbonate product, converting the NO<sub>3</sub> to N<sub>2</sub>, and producing residual, fully oxidized CO<sub>2</sub> and H<sub>2</sub>O. In reality, an excess of organic reductant is required to achieve high (>90%) conversion of NO<sub>3</sub> to N<sub>2</sub>, and other metals in the feed may or may not tend to react like Na does to form carbonates. Excess reductant results in residual amounts of reduced gas species such as CO, C<sub>n</sub>H<sub>m</sub>, and H<sub>2</sub>. Depending on operating conditions, some residual condensable organic species or solid char may also remain.

All but one of the tests performed at the INEEL have produced a carbonate solid product. A carbonate product is a natural and relatively easy-to-achieve product for such mixed wastes as INEEL SBW, which contains high levels of Na. However, the carbonate product is highly water-soluble and can leach radionuclides and heavy metals. A carbonate product is a potential road-ready final waste form for INEEL SBW if the SBW is destined for the Waste Isolation Pilot Plant in New Mexico. A carbonate is presently not an approved waste form for the Yucca Mountain high-level waste repository.

An alternative to sodium carbonate is a mineralized sodium aluminosilicate product, produced by adding a clay additive:



Like Equation 1, this equation represents perfect reactions of the reductant, the feed species, and the clay additive. In practice, both excess reductant and excess clay are required for efficient conversion of  $\text{NO}_3$  to  $\text{N}_2$  and complete conversion of Na (and other metals) to aluminosilicate mineral forms. An aluminosilicate product may be preferred over a carbonate product because it is leach-resistant, and may be as leach resistant or more leach resistant than borosilicate glass, which is presently the only approved high level waste form for disposal.

The scope of this paper is limited to test results that show the operating conditions and results of steam reforming tests for SBW treatment, and does not include evaluations of the solid products with respect to disposal site waste acceptance criteria.

## **FLUIDIZED BED TEST SYSTEM DESCRIPTIONS**

Two fluidized bed test systems have been used for proof-of-concept and demonstration testing. A smaller, 8-cm (3.25-inch) inside diameter (ID) lab-scale fluidized bed test system located at the INEEL Engineering and Demonstration Facility (IEDF) is used for feasibility-type tests, but the size is too small to model larger fluidized beds. At such a small diameter, the gas flow through the bed tends to slug rather than bubble, and particle attrition and growth dynamics may not adequately scale to larger beds.

A larger bed diameter of at least 15 cm (6 inches) is the smallest size at which slugging is minimized (but not eliminated) to better model particle attrition and growth. The 15-cm demonstration scale bed is a reasonable compromise between a bed large enough to provide representative test data and a system small enough to control testing and waste disposal costs. The 15 cm demonstration scale fluidized bed test system is Department of Energy-owned equipment located at the Science Applications International Corporation (SAIC) Science and Technology Applications Research Center located in Idaho Falls, Idaho.

### **8 cm Fluidized Bed Test System**

The fluidized bed vessel is an 8 cm (3.25-inch) inside diameter vessel that is 46 cm (18 inches) high from the distribution plate to the 15 cm (6-inch) diameter disengaging section. The bed media is fluidized in the fluidized bed vessel. When the fluidizing gas expands to the 15 cm inside diameter of the disengaging section, the gas flowrate decreases by a factor of about 4 times. At the lower gas velocity in the disengaging section, entrained bed particles tend to defluidize and fall back into the fluidized bed vessel. The disengagement section includes a baffle to deflect bed particles entrained in the offgas away from the offgas outlet.

The fluidized bed vessel is externally heated with an electric "clam-shell" heater. Fluidizing steam is superheated in excess of the reactor operating temperature. The reactor is filled to a depth of about 41 cm (16 inches) with bed media and operates in slugging mode. Several thermocouples are mounted through the side of the fluidized bed zone to monitor bed temperatures. The system is designed for a liquid feed rate of about 1 L/hr.

### **15 cm Fluidized Bed Demonstration Test System**

The 15 cm diameter fluidized bed demonstration test system (Figure 1) was designed and built in 2002 to provide a test bed for evaluating steam reforming for SBW treatment. The test system was designed to facilitate testing, with extensive process monitoring and controls, and electronic data collection and reporting features. Some specific features such as the capability to add solid reductants were provided to emulate vendor-specific technologies. Since that time, the test platform has been expanded to add off-gas treatment equipment and instrumentation to increase the understanding of the various thermal treatment options tested in the fluidized bed system.



The primary components of the 15 cm test system include the reformer vessel, the product collection systems, the feed systems, the off-gas control system, and the process logic controller (PLC) system. The test system covers a footprint of about 12 m by 12 m. 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 PLC system with multiple human-machine interface (HMI) stations.

The main features of the fluidized bed vessel are the fluidized bed section, the freeboard (particle disengaging) section, and the gas distributor through which the fluidizing gas enters the vessel. The bed and freeboard sections are externally heated with electrical resistance heaters for temperature control. The fluidized bed section is 15 cm in diameter and 76 cm (30 inches) tall. The freeboard section is 30 cm (12 inches) in diameter and 1.5 m (60 inches) high. Numerous ports in the bed and freeboard sections enable access for various liquid and solid input streams and process instrumentation. Interchangeable distributor and bottom receiver designs and the numerous ports make the test platform very versatile and more easily reconfigured to meet the needs and demands of each technology.

The off-gas exits the fluidized bed reactor and passes through a cyclone to remove the larger of the entrained particulates. The cyclone catch can be routed to a product collection drum or returned to the reactor via the solids auger. The off-gas is subsequently filtered in a vessel with seven 6.3-cm (2.5-inch) diameter, 61cm (24-inch) long, sintered-metal filters with a nominal pore size of 2  $\mu\text{m}$ . Filter dust falls from the filter vessel into a purged product drum.

Filtered off-gas passes into a natural gas-fired thermal oxidizer, operated at 800-1,000°C, where the offgas is combined with air to oxidize the hydrogen, carbon monoxide, methane, and other hydrocarbons resulting from the decomposition and reformation of the liquid and solid reductants. Alternatively, the thermal oxidizer can be reconfigured to function as a staged combustor unit to perform both NO<sub>x</sub> destruction and organic oxidation. The oxidized off-gas is quenched with a water spray and scrubbed in a venturi scrubber. The quench exit temperature and the scrub solution temperatures are controlled using a scrub water heat exchanger to maintain a "water neutral" scrubber, where neither water makeup or water discharge is required. This simplifies the operation of the test system and evaluation of test results, although a full-scale operating system would require some scrub solution discharge that would require treatment and disposal, or recycle back to the steam reformer. The scrubbed off-gas is reheated and passed through a 3-stage carbon bed for mercury control performance testing.

The 15 cm test system is equipped with an automated PLC system. The PLC uses Rockwell hardware and software to monitor and control operation of the process from two or more human-machine interface (HMI) personal computer workstations. The process control functions include automated control of valve and pump sequences for the feed system, automated control of all gas flow rates, selectable input temperature control for the fluidized bed vessel, vacuum control of the system based on the pressure in the reformer, and limited control of the CEMS. The graphical user interface for the system shows the status of the components, provides a control interface for the operator and displays readings from all the instrumentation in numeric and trend form. The PLC electronically archives data as it is monitored in a Sequel database. Analog values from the system are archived once per second, and discrete values are archived on change of state. The database is accessible from multiple computers via a web interface. A web interface provides data access from any web-accessible computer, and averages the data at user defined intervals in Microsoft Excel spreadsheets.

## **OVERVIEW OF TESTS CONDUCTED TO DATE**

Several fluidized bed steam reforming tests have been performed during the past four years at the INEEL using two different fluidized bed test systems. These tests are summarized in Table I.

Table I Operating experience for two INEEL fluidized bed test systems.

Test system	Test	Test date	Reference	Key results
8 cm test system	Proof-of-concept tests for steam reforming INEEL sodium bearing waste (SBW) using THOR <sup>sm</sup> technology	July-August 2000	Marshall 2000	Showed process viability; liquid, high nitrate acidic feed converted to solid, free-flowing alkali carbonate product; ~90% NO <sub>x</sub> reduction.
	Calcination tests for an international customer to treat a liquid mixed waste	July-October 2003	---	Demonstrated a viable calcination process for a unique mixed waste.
15 cm test system	Phase 1 demonstration test for SBW steam reforming based on ThermoChem Waste Remediation (TWR) technology	December 2002	Marshall 2003a	Showed TWR process viability; free-flowing alkali carbonate product; 6:1 mass reduction, 3:1 volume reduction compared to liquid feed; 86% average NO <sub>x</sub> destruction.
	Phase 1 demonstration test for SBW steam reforming based on THOR <sup>sm</sup> process technology	January 2003	Marshall 2003b	Showed THOR <sup>sm</sup> process viability; free-flowing alkali carbonate product; 4:1 mass reduction, 30% volume reduction compared to liquid feed; 99% average NO <sub>x</sub> destruction.
	Proof-of-concept tests for steam reforming Savannah River Site (SRS) Tank 48H mixed waste	July 2003	Soelberg 2003	Demonstrated steam reforming simulated Tank 48H waste using sucrose as a reductant; produced a free-flowing sodium carbonate product; product denitration up to 99.9%; tetraphenyl borate destruction >99.98%.
	Phase 2 demonstration test for SBW steam reforming based on TWR process technology	October 2003	Soelberg 2004a	Demonstrated higher feedrate up to 10 kg/hr and a single reductant; free-flowing alkali carbonate bed product; >90% NO <sub>x</sub> destruction; demonstrated a MACT-compliant offgas system.
	Phase 2 demonstration test for SBW steam reforming based on THOR <sup>sm</sup> process technology	November 2003	Soelberg 2004b	Demonstrated total feedrate up to 11 kg/hr; evaluated several reductants; 2 different test campaigns produced an alkali carbonate product and a more leach-resistant NaAlSiO <sub>4</sub> product; >90% NO <sub>x</sub> destruction; demonstrated a MACT-compliant offgas system; achieved 99.9% Hg control.
	High temperature SBW calcination tests	January 2004	Boardman 2004	Demonstrated ability to operate with higher efficiency cyclone and lower amounts of calcination additives; demonstrated staged combustor to achieve >98% NO <sub>x</sub> destruction.

Initial proof-of-concept tests for steam reforming INEEL sodium bearing waste (SBW) were performed in 2000 using the 8 cm test system (Marshall 2000). The test was designed to demonstrate key aspects of the THOR<sup>sm</sup> steam reforming technology, patented by Studsvik, Incorporated and subsequently licensed to THOR Treatment Technologies. The same test system was also used for proof-of-concept calcination tests in 2003 for an international customer that had a unique mixed waste that requires treatment.

The 15 cm test system has been used for initial demonstration (Phase 1) tests for two vendor steam reforming technologies (THOR Treatment Technologies and ThermoChem Waste Remediation (TWR)) in the winter of 2002-2003, a test series to evaluate the feasibility of steam reforming Savannah River Site Tank 48H mixed waste in July 2003, and Phase 2 tests for the same two vendor technologies late in 2003. The same test system, with minor reconfiguration to emulate the INEEL New Waste Calcining Facility (NWCF), was used for an SBW calcination test series in January 2004.

## SIMULANT COMPOSITIONS

Simulant compositions tested to date (Table II) have been prepared from commercially available, nonradioactive reagents. Several tests have been performed using a simulant of INEEL SBW. SBW varies somewhat in composition from tank to tank and in the quantity of undissolved solids that have accumulated on the bottom of the tanks. The simulant blends used to date were formulated based on the Tank WM-180 SBW composition, with and without simulated heel solids. Another simulant that has been tested was formulated based on the SRS Tank 48H composition. This simulant contained tetraphenylborate, which is an organic constituent of the waste.

Table II Ranges of simulant compositions used in steam reforming tests to date

Analyte	SBW molarity	SRS Tank 48H molarity	Analyte	SBW molarity	SRS Tank 48H molarity
Acid	1.0	---	Manganese	0.014	---
Base	---	1.8	Mercury	1.35 E-3 to 2.02 E-3	---
Aluminum	0.66	0.11	Nickel	0.00	---
Boron	0.012	0.073	Nitrate	5.3	0.36
Calcium	0.047	---	Nitrite	---	0.47
Carbonate	---	0.13	Phenyl	---	0.29
Cesium	0.0025 to 0.0064	0.0088	Phosphate	0.014 to 0.029	0.0077
Chloride	0.030	0.0088	Potassium	0.20	0.078
Chromium	0.0033	---	Rhenium	0.00089 to 0.0023	---
Fluoride	0.047	0.0059	Silicon	---	---
Iron	0.022	0.00090	Sodium	2.1	3.1
Lead	0.0013	---	Sulfate	0.070	0.0071
Magnesium	0.012	---	Tetraphenyl borate	---	0.073
			Zinc	0.0010	---

simulant composition

## OPERATING CONDITIONS

A variety of test conditions (shown in Table III) have been evaluated during several tests using the 15 cm test system. The bed operating temperature must be high enough, nearly 600°C, to encourage denitration and other reactions, but not so high as to risk bed agglomeration from molten species. For a carbonate-based product, the highest safe temperature is under 700°C. For a mineralized product, the operating temperature can be increased somewhat above 700°C.

Table III Operating conditions for various steam reforming tests to date

Parameter	THOR	TWR	SRS Tank 48H
Temperature	670 – 725°C	570 – 610°C	650°C
Simulant	SBW	SBW	SRS Tank 48
Reductant phases	Dissolved, liquid, & solid	Liquid & solid	Dissolved
Total liquid feed rate	5.5 – 11 L/hr	2 – 10 L/hr	2 – 5.5 L/hr
Maximum undissolved solids (UDS)	≤ 335 gm/L SBW	< 5 gm/L	≤ 65 gm/L
Product types	Carbonate and mineral	Carbonate	Carbonate and silicate

## PRODUCT COMPOSITIONS AND PROPERTIES

The feed solution, when sprayed into the bed, dries and undergoes evaporation, thermal decomposition, and other reactions that denitrate and devolatilize the feed constituents. The solid residual products of the steam reforming process either stay in the bed or elutriate from the bed with the off-gas, depending on operating conditions and properties of the bed media and solid products. If the solid products form relatively durable coatings on existing bed particles, then the products tend to stay in the bed. During continued operation, the bed mass would grow and would need to be removed. Most of the steam-reformed product would be in the form of solid product drained from the bed.

If the solid products tend to form new, small particles, or fragile coatings on bed particles that readily break off, they would be easily entrained in the fluidizing gas and would tend to elutriate from the bed. This mode of operation would tend to leave the bed particles intact and result in a primary elutriated product captured in the cyclone and filter.

The solid product distribution for selected tests is shown in Figure 2. The measured product distributions show that solid product distributed to both the bed and elutriated fines for these tests. The amount of solid product that distributed to the bed ranged from as low as 30% to as high as 90%, depending on operating conditions. When the cyclone fines are recycled, there is no cyclone product, and the distribution of product to the filter fines and the bed product increases. The heated filter used in the tests was about 99.9% efficient, so only around 0.1% of the solid mass passed through the filter and was collected in the wet scrubber. These results show that the solid product distribution can be controlled by fluidized bed design and operation. Feed atomization or bed attrition could be increased to produce more elutriated product. Alternatively, feed atomization or bed attrition could be decreased, or fines recycling could be increased, to maximize the bed product distribution.



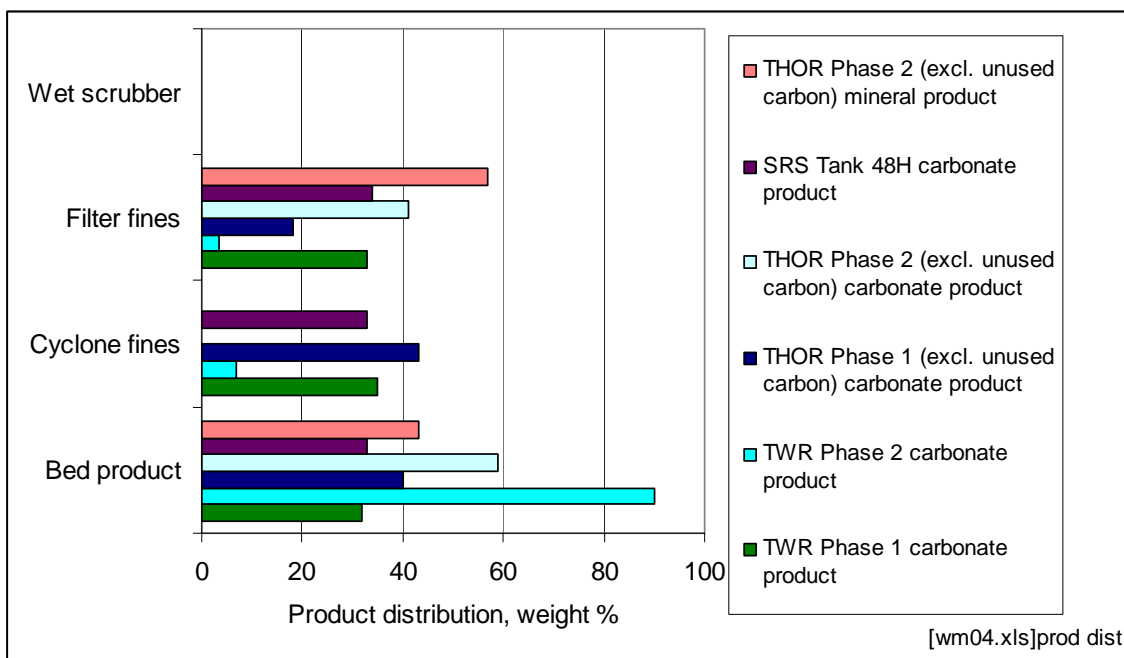


Fig. 2 Solid Product Distributions Measured for Different Tests.

Figures 3 and 4 show optical micrographs of sodium carbonate and sodium aluminosilicate bed product particles from the Phase 2 THOR<sup>sm</sup> technology steam reforming tests. The bed particles consist of surface layers of solid product that coat an inner core of seed material. During all carbonate tests to date, few new seed particles have been formed, and the inner core of the bed particles has been a particle of starting bed media, which has been alumina. The average bed particle size typically doubled during the carbonate tests from the average particle size of the initial starting bed media (around 200 to 500  $\mu\text{m}$ , depending on test series) to around 350 to 1,000  $\mu\text{m}$ . The bed particle size growth was not controlled during the tests to date, but several options for bed particle size control are available.

Bed particle size was more easily controlled for the THOR<sup>sm</sup> mineralized test series, because new seed particles of product were formed. The inner cores of many of the mineralized bed particles did not contain starting alumina bed, and the particle size distribution included many particles that were smaller than the starting bed media.

Figure 5 shows higher magnifications using a scanning electron microscope of sodium carbonate bed particles from the latest TWR technology steam reforming tests. The surface coating of these bed particles consisted largely of submicron solid particles agglomerated onto the particle surface.

Many of the elutriated particles were very small because they consist of individual or agglomerated submicron particles. The average particle sizes for elutriated fines ranged from about 1  $\mu\text{m}$  to over 10  $\mu\text{m}$ , depending on the degree of particle agglomeration in the fluidized bed.

Bed particle and bulk densities decreased during each test from the densities of the starting alumina bed media. As solid product replaced the starting bed media, the bed density asymptotically approached that of the granular carbonate or mineralized product. End-of-test bed product bulk densities ranged between 1.2 and 1.4 gm/mL for the carbonate product. The end-of-test bed product bulk density for the THOR<sup>sm</sup>

mineral test was lower at about 0.7 gm/mL. Elutriated fines from both carbonate and mineral tests were less dense, typically ranging between 0.3 and 0.5 gm/mL.



Fig. 3 Optical Micrograph of Sodium Carbonate Bed Product Particles. Blue Marks at the Left Indicate Scale (1 mm Between Marks). Some particles are crushed to show the Inner Core of Starting Bed Media.

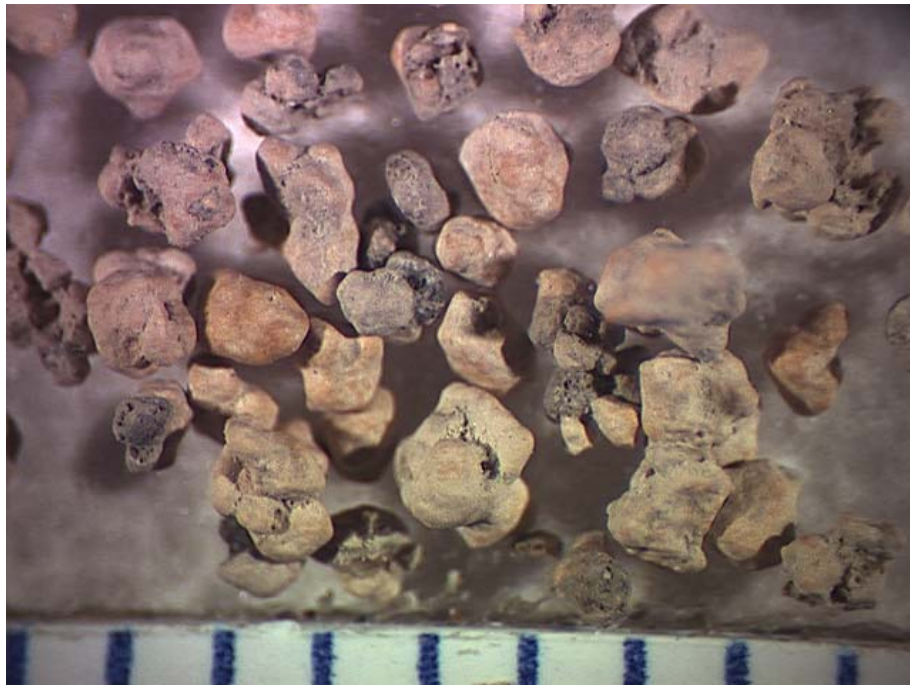


Fig. 4 Optical micrograph of Sodium Aluminosilicate Bed Product particles. Blue Marks at Bottom Indicate Scale (1 mm between marks).

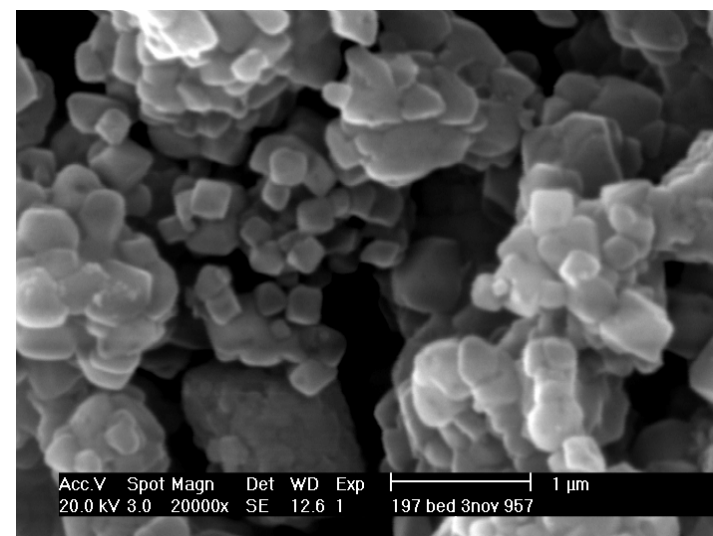
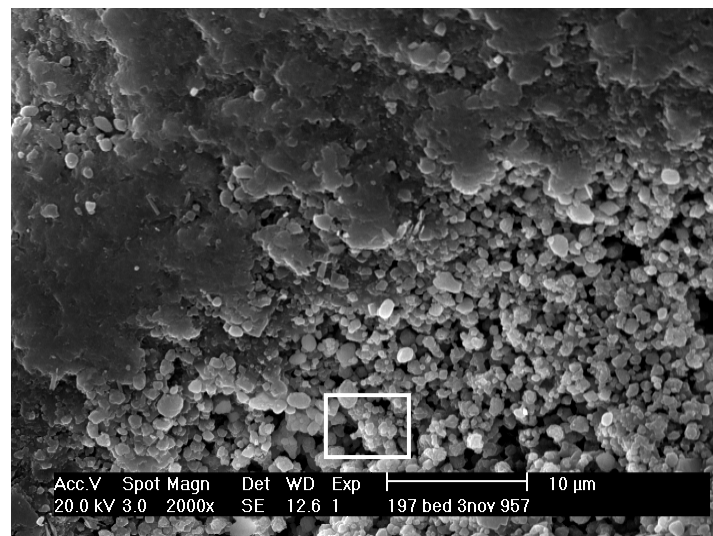
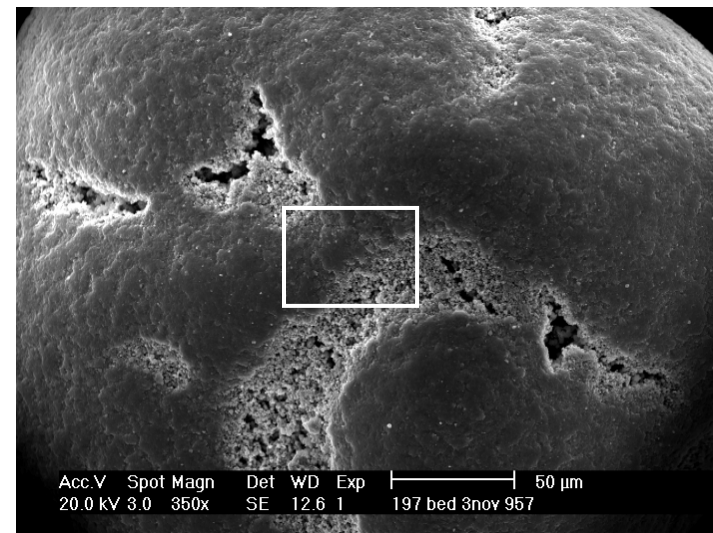
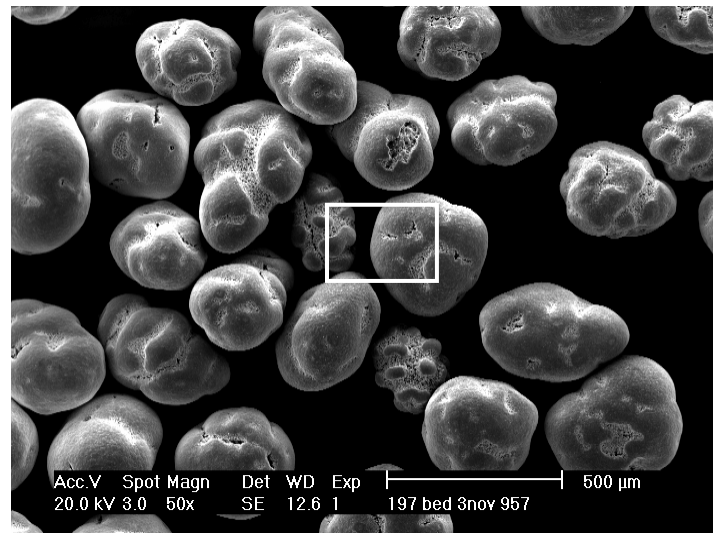


Fig. 5 SEMS of a Carbonate Bed Product. Magnification Increases From Left to Right and Top to Bottom. Insets Show Field Illustrated at Next Lower Scale to Right or Below. The 20,000x Magnification Illustrates that Individual Product Particles are Less Than 1  $\mu\text{m}$  In Size and Appear Cubic.

Table IV shows a typical composition of carbonate bed product produced from steam reforming tests. Even when a starting bed material is something chemically different from the carbonate product, the chemical composition of the bed material will asymptotically approach the carbonate product composition. The primary constituents of the carbonate product are carbonates of sodium and potassium and aluminum species, presumably alumina and sodium aluminate. The primary constituents of the mineral product are sodium and potassium aluminosilicates.

Elutriated fines are generally similar in composition to the bed product composition, except for some species that tend to partition more to the fines than to the bed product. As shown in Table V, species including anions  $\text{SO}_4$ , Cl, F, and elements Cs, K, Ni, Pb, and Re disproportionately partition to the elutriated fines. Even though these species have partitioned more to the elutriated fines than to the bed product, every one of these is nearly quantitatively retained in the combined bed and elutriated fines products. These species do not significantly partition to the offgas or the scrub water. The essentially quantitative retention of Cl, radionuclide surrogates (Cs and Re) and hazardous metals (Cr, Ni, and Pb) is a very favorable feature of steam reforming for mixed waste treatment applications.

Test results confirm that mercury, common in some mixed waste streams, is not retained in the solid products. Mercury is volatilized from the feed and passes through any dry particulate control equipment into the offgas system. Table VI shows the fate of mercury and capture efficiency for mercury in a 3-stage carbon bed located at the end of the offgas system. The carbon bed contains sulfur-impregnated Mersorb carbon from NUCON, International, and was designed according to design criteria developed at the INEEL in collaboration with NUCON. Total mercury in the offgas at the outlet of the carbon bed was typically 1-10  $\mu\text{g/dscm}$ , about  $1/10^{\text{th}}$  of the Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) standard for total mercury emissions.

#### **OFFGAS COMPOSITION, $\text{NO}_x$ DESTRUCTION, ORGANIC DESTRUCTION, AND HWC MACT COMPLIANCE**

Continuous monitoring provided off-gas composition measurements for process control, air emissions measurements, and determination of the fate of feed constituents that are converted to gaseous compounds. Steam reformer offgas composition measurements were made at the outlet of the heated filter, and also downstream of the thermal oxidizer and wet scrubber after the thermal oxidizer was installed. Ranges of measured offgas compositions are shown in Table VII. This table also shows that the oxidized offgas complies with the HWC MACT standards for all measured species (HCl, CO, and total hydrocarbons (THC)).

Table VIII shows that steam reforming efficiently destroys nitrates and organic species in the simulant feeds. Product denitration typically exceeded 99.9%, and  $\text{NO}_x$  destruction typically exceeded 90%. Tetraphenyl borate destruction (measured during the SRS Tank 48H test) exceeded 99.98%.

Table IV Carbonate bed product composition for the Phase 2 steam reforming technology tests

	Highest species concentration in bed product samples, weight %													
	TOC	CO <sub>3</sub>	NO <sub>3</sub>	SO <sub>4</sub>	Cl	Al	Ca	Cr	Cu	Fe	Mn	Na	Re	Si
TWR Phase 2	0.05	19	0.003	3.0	0.33	6.4	0.65	0.08	0	0.52	0.22	21	0.03	0.03
THOR Phase 2	5	22	0.024	2.2	0.30	9.8	1.00	0.05	0.02	1.00	0.36	24	0.09	0.11
Calculated from feed	---	29	0	2.3	0.74	12	1.3	0.12	0.03	0.8	0.53	30	0.14	0.10

Notes:

1. TOC = total organic carbon.
2. The concentrations of feed constituents gradually increase in the bed product as the mass of starting bed in the fluidized bed is replaced by feed products.
3. The concentrations of some species in the mineral product have been normalized for incomplete dissolution of solid samples during sample analysis.

[wm04 feb 27.xls]prod comp

Table V Elemental distribution to bed, recycled cyclone fines, and filter fines for the recent Phase 2 THOR steam reforming technology test

	Elemental mass distribution, % of mass in the output stream divided by total mass in the total of all output streams															
	NO <sub>3</sub>	SO <sub>4</sub>	Cl	F	Al	Ca	Cr	Cs	Cu	Fe	K	Na	Ni	Pb	Re	Si
Bed product	35.5	50.1	25.7	10.3	70.7	68.7	66.6	6.5	58.8	80.4	46.7	66.4	59.0	4.3	45.1	76.4
Cyclone samples	2.0	1.4	3.8	2.9	1.5	1.5	1.3	7.3	2.8	0.8	3.5	1.5	1.8	1.7	1.9	3.5
Filter fines	44.2	45.2	70.0	80.9	27.7	29.8	31.9	86.2	38.0	18.7	49.8	32.1	38.3	94.0	52.9	16.3
Scrub solution	18.3	3.2	0.5	5.9	0.0	0.0	0.2	0.0	0.4	0.0	0.0	0.0	0.9	0.0	0.0	3.9
Total outputs	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total elemental mass balance closure, sum of total output mass divided by sum of total input mass																
Total outputs	0.0004	1.52	1.12	0.95	1.0	0.91	0.54	1.06	0.89	1.59	0.96	0.94	1.02	0.98	0.90	1.22
Nitrate destruction efficiency, %:	99.96		Note: The mass balance closure for Al is normalized to the Al in the simulant feed, excluding Al in the starting alumina bed.													
Heated filter PM capture efficiency, %:	99.7															

[thor carb elemental mass mb.xls]thor carb table for wm04

Table VI Hg speciation, concentrations, mass balance closure, and carbon bed sorption efficiency for the Phase 2 THOR carbonate test series.

Test	Simulant feedrate, l/hr	Hg conc. g/L	Off-gas flow rate at the GAC bed, wscfm	Cooling water mass flow to PQ-1 partial quench		Off-gas flow rate at the quench inlet, wscfm	MTEC at quench inlet, ug/wscm	MTEC at GAC inlet, ug/wscm	Concentration, ug/m <sup>3</sup> , wet basis															
				kg/hr	scfm				Quench inlet			Scrubber outlet			Stage 1 outlet			Stage 2 outlet			Stage 3 outlet			
									Hg el	Hg tot	Hg ox	Hg el	Hg tot	Hg ox	Hg el	Hg tot	Hg ox	Hg el	Hg tot	Hg ox	Hg el	Hg tot	Hg ox	
									corr	corr	corr	corr	corr	corr	corr	corr	corr	corr	corr	corr	corr	corr	corr	
Average	4.82	0.27	121	41	32	89	8,665	6,326	13,534	13,844	309	5,930	6,181	250	949	959	9	4	10	6	3	4	1	
Std dev	1.22	0.00	7	6	5	4	2,108	1,484	3,080	3,417	1,790	1,272	1,432	644	326	321	166	41	57	43	7	8	4	
Mass balance closure, mass out/mass in						1.60			Total Hg concentration, ug/dscm corrected to dry, 7% O <sub>2</sub> basis															6
Wet scrubber removal efficiency, %						2.3			HWC MACT limit for total Hg, ug/dscm (dry, 7% O <sub>2</sub> )															45
Carbon bed stage 1 removal efficiency, %						84.5			Hg measurements as a % of the HWC MACT limit															13
Carbon bed stage 2 removal efficiency, %						98.9																		
Carbon bed stage 3 removal efficiency, %						60.5																		
Carbon bed total removal efficiency, %						99.93																		
Notes:																								
1. The Hg concentration in the simulant feed is 0.27 gm/L.																								
2. The Hg mass balance closure exceeds 100%. The scrub solution sample analyses show that very little (0.18%) of the total mercury fed to the system was captured in the wet scrubber. Therefore, the quench inlet MTEC is used instead of the measured quench inlet values to calculate the scrubber efficiencies. The quench inlet MTEC concentrations have been normalized to the GAC inlet offgas flowrate in the scrubber efficiency calculation.																								
3. The correction factors to dry, 7% O <sub>2</sub> basis are the average CEMS 2 O <sub>2</sub> and H <sub>2</sub> O values.																								

Table VII Steam reformer offgas measurements during demonstration tests

Species	Typical values during stable system operation (as-measured wet basis unless otherwise indicated)	
	Steam reformer outlet	Downstream of thermal oxidizer and scrubber
O <sub>2</sub>	0-0.2 volume %	2-3%
CO <sub>2</sub>	>7%	5-10%
CO	0.2-2% (when NO <sub>x</sub> destruction >90%)	~10 ppm (dry, 7% O <sub>2</sub> , 1/10 <sup>th</sup> of the MACT standard)
NO	<2,000 ppm (when NO <sub>x</sub> destruction >90%)	100-500 ppm
NO <sub>2</sub>	<100 ppm (when NO <sub>x</sub> destruction >90%)	0-10 ppm
NO <sub>x</sub>	<2,100 ppm (when NO <sub>x</sub> destruction >90%)	100-500 ppm
CH <sub>4</sub>	0.2-2%	Not measured
THC	0.1-1%	0-5 ppm (dry, 7% O <sub>2</sub> , ½ or less of the MACT standard)
HCl	Not measured	~1 ppm (dry, 7% O <sub>2</sub> , 1/20 <sup>th</sup> of the MACT standard)
SO <sub>2</sub>	Not measured	0-10 ppm

Table VIII Product denitration, no<sub>x</sub> destruction, and tetraphenyl borate destruction

Measurement	Typical values during stable system operation
Product denitration	>99.9%
Steam reformer NO <sub>x</sub> destruction	90-99% (only 60% NO <sub>x</sub> destruction was accomplished during the Tank 48H proof-of-concept tests, when conditions were not optimized for NO <sub>x</sub> destruction)
Total system NO <sub>x</sub> destruction	90-99% (additional NO <sub>x</sub> destruction was often achieved in the thermal oxidizer if the steam reformer NO <sub>x</sub> destruction did not exceed 90-95%)
Tetraphenyl borate destruction	>99.98% (only measured during the SRS Tank 48H proof-of-concept test)

## SUMMARY AND CONCLUSIONS

Several different steam reforming test series, for a cumulative duration of about 1,000 hours, have been completed using two different fluidized test systems. Demonstration testing has been completed for two different commercial steam reforming vendor technologies, and for two different types of liquid, nitrated mixed wastes. Some key conclusions and test results include:

- Both highly acidic and highly basic waste stream simulants were successfully converted from the liquid form into a more stable granular solid form.
- Several different reducing and product quality additives have been evaluated.
- Process operability, including process chemistry, temperature, flowrate, and other conditions that are required for stable process operation were identified and demonstrated.
- The compositions, amounts, and physical properties of the solid and gaseous products have been characterized.

- The fate of key feed constituents, and distribution between the solid and gaseous products, have been determined. Halides, radionuclide surrogates, and heavy metals are nearly quantitatively retained in the solid products.
- Product denitration, organic destruction, NO<sub>x</sub> destruction, and HWC MACT compliance were demonstrated.

Several areas of continued process optimization, demonstration, or research and development are recommended based on the test results. These areas are:

- Control of the carbonate bed particle size growth. Several available options include the use of in-bed attrition, elutriated fines recycle, addition of starting bed media, or recycling crushed bed product.
- Increase the mineralized product density. Several options are available including modifications in how the liquid feed and the mineralizing additives are injected into the fluidized bed.
- Methods to avoid, and recover from, bed agglomerations that cause bed defluidization. Agglomerations were not common when the process was run during operational run periods when the system operation was not being varied for the test program. Several conditions related to bed defluidizing agglomerations were found during tests. Identifying, avoiding, and recovering from bed defluidizing agglomerations is necessary for long-term stable operation.
- Better retention of product and reductant utilization in the denser bed product by recycling more fines than were captured and recycled by the cyclone used during the test series.
- Better demonstration or improved performance of key system components, including the gas distributor, the bed drain, and the feed nozzle.
- Operation for longer times to demonstrate long-term performance.

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