**Steam Reforming Technology Demonstration for the Destruction of Organics on Actual DOE Savannah River Site Tank 48H Waste – 9138**

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## ABSTRACT

This paper describes the design of the Bench-scale Steam Reformer (BSR); a processing unit for demonstrating steam reforming technology on actual radioactive waste [1]. It describes the operating conditions of the unit used for processing a sample of Savannah River Site (SRS) Tank 48H waste. Finally, it compares the results from processing the actual waste in the BSR to processing simulant waste in the BSR to processing simulant waste in a large pilot scale unit, the Fluidized Bed Steam Reformer (FBSR), operated at Hazen Research Inc. in Golden, CO. The purpose of this work was to prove that the actual waste reacted in the same manner as the simulant waste in order to validate the work performed in the pilot scale unit which could only use simulant waste.

## INTRODUCTION

Steam reforming technology has the potential to be of great value in the processing of various waste streams throughout the DOE complex. The process removes organics from a waste stream by pyrolysis, converting them to $CO_2$. The process also de-nitrates the solutions, producing $N_2$ and $CO_2$. If carbon is the only additive to the waste stream, then a solid carbonate product will be formed. This product is water soluble making it easy for further processing such as to a slurry fed glass melter. If sodium-alumina-silicates are added as well, then a final waste form can be produced for storage in drums. This form can also be captured in a cementatious monolith.

The SRS Tank 48H waste contains about 240,000 gallons of salt solution with 2 wt% tetraphenylborate (TPB) which is an organic solid that is formed when NaTPB exchanges its Na for K and more importantly Cs. Steam reforming will destroy all of the TPB and de-nitrate the liquid to form a Cs rich carbonate product. The product can then be dissolved in water, adjusted, and processed through the Defense Waste Processing Facility (DWPF) slurry fed glass melter.

Fluidized Bed Steam Reforming (FBSR) has been demonstrated to be a viable technology to remove >99% of the organics from Tank 48H simulant, to remove >99% of the nitrate/nitrite from Tank 48H simulant, and to form a solid product that is primarily carbonate based. The technology was demonstrated in October of 2006 in the Engineering Scale Test Demonstration Fluidized Bed Steam Reformer (ESTD FBSR) at the Hazen Research Inc. (HRI) facility in Golden, CO. [2] The purpose of the BSR testing was to demonstrate that the same reactions occur and the same product is formed when steam reforming actual radioactive Tank 48H waste.

The approach was to test the BSR with the same Tank 48H simulant and same GC coal as was used at the ESTD FBSR under the same operating conditions. This comparison would allow verification that the same chemical reactions occur in both the BSR and ESTD FBSR. Then, actual radioactive Tank 48H material would be steam reformed in the BSR to verify that the actual tank 48H sample reacts the same way chemically as the simulant Tank 48H material.

The actual Tank 48H waste demonstration had to be performed in the Savannah River National Laboratory (SRNL) Shielded Cells Facility (SCF) due to its radioactivity, mostly Cs-137. There was no known FBSR system that was small enough to fit inside the shielded cells or that could be operated
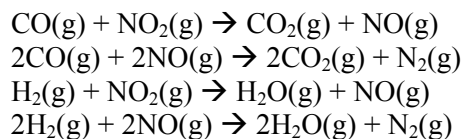
remotely using cell manipulators.  Thus the SRNL developed the BSR to mimic the reactor conditions of the FBSR in order to demonstrate that the chemical reactions of the actual waste were comparable to the chemical reactions of the simulant in the FBSR.

**The Chemistry of Steam Reforming**

Steam reforming destroys organics by the water gas shift reactions at temperatures above $600^oC$.  Any carbon bearing species is converted to CO and $CO_2$ as $H_2O$ becomes $H_2$.

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
$H_2O(g) + CO(g) \rightarrow H_2(g) + CO_2(g)$
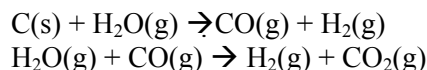
In addition to destroying the organics, the CO and $H_2$ rich atmosphere then promote the de-nitration of the salt solution.

$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$
$2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$
$H_2(g) + NO_2(g) \rightarrow H_2O(g) + NO(g)$
$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$

Typically, the $H_2$ concentration was controlled to about 2% on a dry basis in order to completely reduce the $NO_x$ gases to steam and $N_2$.  It was controlled by adding air to create more steam and heat.

$2H_2 (g) + O_2(g) \rightarrow 2H_2O(g) + heat$
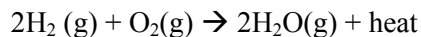
Off-gases from the steam reformer still included some organics so a second reformer operated at $925^oC$ with excess air to oxidize the remaining organics fully to $CO_2$ and to convert the remaining $H_2$ to steam ($H_2O$ gas).

The steam reformer creates a solid carbonate product which is readily soluble in water for further processing.

$5C(s) + 4NaNO_3 \rightarrow 3CO_2(g) + 2Na_2CO_3(s) + 2 N_2(g)$
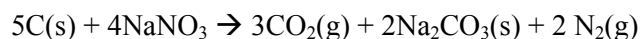
Thermonatrite, [ $Na_2CO_3H_2O$ ], Sodium Carbonate, [ $Na_2CO_3$ ], and Trona, [ $Na_3H(CO_3)_2 2H_2O$ ] are the major carbonate products formed from an alkali rich waste and the $CO-CO_2$ reactions in the FBSR.

Note that these reactions represent the overall chemistry, but are not all inclusive.

An FBSR can be electrically heated externally if the diameter of the reaction chamber is small enough. For larger diameter FBSR units, heat must be generated in an auto-thermal mode.  For auto-thermal operation the energy needs are supplied by the incoming superheated steam and by the oxidation of organics from the waste and carbon reductants.

In the ESTD FBSR, General Carbon (GC) coal was added to the DMR as fuel to provide the necessary auto-thermal heat.  The BSR did not require the coal for heat since it was small; however excess coal was added to the BSR to provide some of the heat to closer mimic the FBSR chemistry.

GC coal is a mineral based coal chosen by THOR® Treatment Technologies (TTT) because it is very reactive at low temperatures.  Also, the GC coal was heat treated to remove volatiles, sulfur, and nitrogen so that it burned cleaner in the FBSR.

The GC coal also reacted with the nitrate salts in the feed to form a carbonate product and $NO_x$ gases.  Finally, the coal reacted with the superheated steam to produce the water gas shift reactions which produced $H_2$, CO, and $CO_2$.   The $H_2$ and CO reacted with the $NO_x$ gases to form $H_2O$, $CO_2$, and $N_2$.  Oxygen was added to the DMR to control the hydrogen concentration in the DMR process outlet gas to between 2% to 3% on a dry basis which was an adequate concentration to ensure that all the $NO_x$ gases were consumed [2].

## EXPERIMENTS

### Description of the Bench-scale Steam Reformer

The BSR designed at SRNL is a two-stage unit used to produce the same mineralized products and gases as the ESTD FBSR. A schematic of the unit designed is shown in Figure 1.
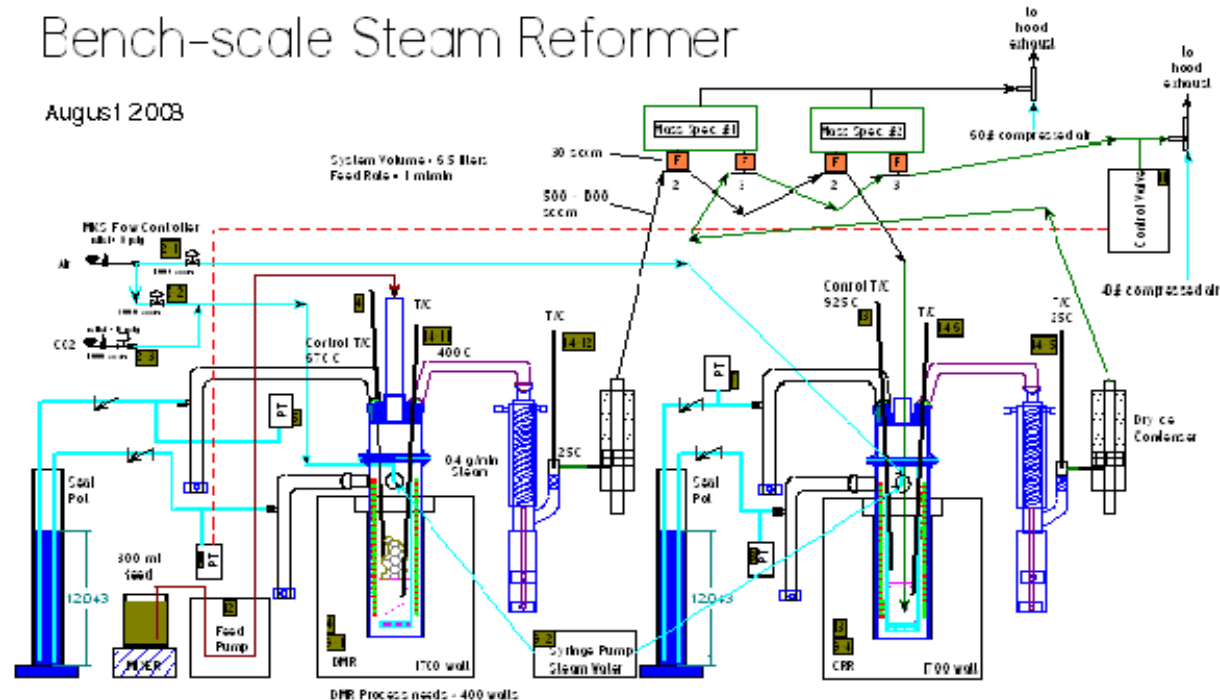


Figure 1.  Schematic of the Bench-Scale Steam Reformer

The nomenclature for the two reformers came directly from the ESTD FBSR unit.  Approximately 300 ml of feed slurry was kept agitated with a stir bar mixer while a peristaltic pump fed the slurry through the center feed port in the lid of the Denitration Mineralization Reformer (DMR) at about 1 ml/min.  A solid carbonate product formed in the DMR in the presence of superheated steam and carbon and the off-gases flowed toward the DMR condenser.  The condenser cooled the off-gas stream down to about 25°C and removed the steam.  A bubbler in the trap section of the condenser removed particulate carry-over which

mainly consisted of the fine coal additive.  The off-gas was further cooled by a dry ice condenser prior to being measured by a Mass Spectrometer (MS) for $H_2$, $O_2$, $CO_2$, $N_2$, $C_6H_6$, and argon.  The off-gas then flowed into the Carbon Reduction Reformer (CRR) where any CO, $H_2$, $C_6H_6$, or other oxidizable species would be converted to $H_2O$ and $CO_2$.  The off-gas leaving the CRR received the same treatment as the off-gas leaving the DMR before being measured by a MS for the same gases.  An eductor drew the gases through the system and expelled them into the cell along with the motive air used to operate it.  A control valve bled air into the suction side of the eductor to control the pressure of the DMR outer chamber to -2 inches of water column (inwc).

The DMR inner reaction chamber was 70mm ID x 385mm tall with a porous bottom.  The bottom 75mm was filled with zirconia beads (not shown).  The zirconia beads were heavy enough not to be suspended by the gases and steam flowing up past them.  They acted as a base for the product to form on, allowed easy removal of the product from the reaction chamber, allowed easy separation of the product from the beads for analytic purposes, and provided a heat transfer medium for the gases that flowed up through them.  Zirconia beads are inert at the temperatures and oxygen fugacity at which the DMR operated and did not affect the steam reforming chemistry.

The DMR outer chamber was 120mm ID x 400mm and provided connections for the outer chamber pressure relief and measurement line, and each of the two 20 foot coils which were housed between the DMR inner reaction chamber and the outer chamber.  The outer chamber was sealed by the top flange of the inner chamber and thus had a pressure relief line going to a seal pot which relieved at about 15 inwc.  Water, $CO_2$, and air entered the DMR via the coils which were between the inner and outer walls of the DMR and were converted to superheated steam and hot gases with heat provided by the furnace that the DMR sat in.  The steam and gases left the coils and flowed through the bottom of the DMR inner reaction chamber, the zirconia beads, the product, and out through the top of the DMR to the DMR condenser.  The $CO_2$ flow rate was a constant based on the HRI PROD-4 [2] conditions.  The air flow rate was varied in order to control the $H_2$ concentration leaving the reactor from 1.5% to 4% on a dry basis which was close to the Hazen PROD-4 [2] run condition of 2% - 3%.  The DMR inner reaction chamber could hold about 70 grams of product which was converted from about 300 ml of Tank 48H waste with 60 grams of GC coal added.

The maximum height requirement in the shielded cells prevented having a fluidized bed steam reformer.  There was not enough height to allow for proper disengagement of the product from the off-gas stream.  Therefore the BSR was not fluidized, so the product formed a porous stalagmite on the top of the zirconia beads at the bottom of the DMR reaction chamber as the feed was dripped onto them from the top, center of the reactor.

The same GC coal was added as was used by the ESTD FBSR as a reducing agent.  However, for the BSR, the coal was ground, then sifted through an 80 mesh sieve (177 microns) and mixed with the feed slurry prior to being pumped into the DMR versus the ESTD coal which was much larger and was added as a separate stream in the FBSR.  In addition, a 1.3 gram amount of $Fe(NO_3)_3 9H_2O$ was added to the BSR runs to act as an analytical indicator for the REDuction/OXidation (REDOX) potential in the product. The REDOX measurement was used to verify that pyrolysis was occurring under highly deoxygenated conditions.

The DMR lid was 120mm ID x 80mm and was sealed to the top of the inner chamber.  The lid held two type K thermocouples, the centered feed line that was cooled with standing water, the inner chamber pressure relief and measurement line, and the off-gas line going to the DMR condenser.  In the event that the off-gas line plugged, the inner chamber and lid had a pressure relief line going to a seal pot which relieved at about 15 inwc.  One thermocouple was positioned at 1.5 inches into the zirconia bead bed and the control thermocouple was positioned 2 inches above the surface of the bead bed.  The control

temperature was $670^{\circ}C$ in the DMR. The first four inches of the stalagmite are formed in a region where the temperature is between $676^{\circ}C$ and $645^{\circ}C$ which is within the temperature range for making good product. Samples were taken from this region and analyzed separately from the upper samples.

The condenser/bubbler/dry ice condenser units were necessary for pretreatment of the off-gas to prevent filter pluggage or damage to the mass spectrometers.

The condenser was cooled by a chiller bath flowing approximately 1 gpm of $5^{\circ}C$ water through its inner coils and outer jacket. The off-gases and steam entered at the top of the condenser and flowed and condensed down through the center tube which ended at the bottom of a 75mm deep water reservoir filled with zirconia beads. The water would overflow into a sealed reservoir (not shown), the particulate would accumulate in the water and on the walls, and the gases would bubble up through the water and exit past the thermocouple and into the dry ice condenser.

The dry ice condenser was a 3 inch ID x 9 inch tall pipe with a 1 inch ID tube for off-gas flow inside. Dry ice was added in the annular space between the 1" tube and the 3" pipe. The dry ice condenser typically froze about 7 ml of liquid per run which was drained out of the bottom after each run.

The BSR used dual Monitor Instruments LAB 3000 Cycloidal mass spectrometers (MS's) for the dual reformers. Both spectrometers were set up identically to measure $H_2$, $O_2$, $N_2$, $CO_2$, benzene, and argon. One MS would measure the DMR off-gas on channel 2 while the other MS measured CRR off-gas on channel 3. Channel 1 was used for the calibration gas for both MS's. Both channels 2 and 3 had 7 micron sintered metal filters in the 1/8" lines going to the instruments to prevent plugging the lines inside the MS's.

Since the line pressure near the MS's would be down to -25 inwc, it was necessary to run a second eductor and vacuum regulator to draw the sample gases through the MS's. The vacuum was controlled to -30 inwc while the flow rate of gases pulled by an MS sample line was kept at 30 sccm. The flow rate of the gases coming from the DMR dry ice condenser varied between 500 to 1000 sccm while the flow rate of the gases coming from the CRR dry ice condenser were 400 sccm greater because of the oxidizing air added to the CRR.

Both MS's were controlled by a single Personal Computer (PC) with Monitor Instruments proprietary software loaded. Data from the MS computer was transferred to the control computer in real time via serial connections. The DMR $H_2$ values were continuously trended on the control computer and operating personnel would manually vary the air flow into the DMR to control the DMR $H_2$ value between 1.5% and 4%. As an operator aid, the computer would automatically shut off the feed pump if the DMR $H_2$ reached 12%.

The MS's would determine and transmit the gas concentration data about once every 8 seconds. However, the lag time between the measurement and the conditions in the DMR ranged between 1 to 2 minutes depending on flow rates. The system was controlled within the limits about 80% of the time manually, but might have been improved with an automatic controller.

The CRR was essentially the same as the DMR except instead of having a feed line in the lid, it had a down-comer for the DMR off-gases to enter. The down-comer was a 13mm diameter tube which ended 10 mm off the bottom of the inner basket. The inner basket was filled to 75mm with zirconia beads as in the DMR. Air and water flowed in through the two 20 foot heating coils to become hot air and superheated steam which flowed up through the inner basket and out through the lid to the CRR condenser.

The thermocouples had the same placement as the DMR and the control temperature was set to $925^{\circ}$C. The sole purpose of this unit was to fully oxidize the gases which came from the DMR as done in the HRI/TTT dual reformer flowsheet. The steam does not enter into the reactions, but was added so that this unit mimicked the conditions in the ESTD FBSR CRR.

The BSR was assembled in the cells mockup shop on a 3' x 4' stainless steel pan. Bolts were welded to the pan and the equipment was strapped to the pan using heavy duty wire ties. All the connections were made and the system was leak checked prior to placement into the High Level Cells. A special lifting yoke was fabricated and the BSR was lowered into the cell as a single unit using a crane. The estimated total weight of the BSR was 220 pounds and the weight distribution was fairly even as the pan canted less than $5^{\circ}$ to the CRR side.

The BSR was controlled by a single PC running Windows XP with 16 serial port connections. Omniserver software was used as the server software to communicate through the serial ports. Intouch software was used as the client software and man machine interface. Data acquisition was continuous and trended in real time on screen as the process ran. Real time data were also saved to a file on a frequency of once per minute. Control logic was programmed into Intouch to provide operator aid (including a PID pressure controller).

Figure 2 shows the computers for the MS and process control along with the steam water pumps, MKS gas flow controllers, furnace controllers, furnace safety relays, and input/output box were on or below a 30" x 45" table situated just to the right of the cell 4 window. The MS's were in a radio-hood behind cell 5. The actual BSR was in cell 4. Connections between process and control systems required the use of 9 inner wall connection tubes (known at SRNL as KAPL plugs which were first developed at Knolls Atomic Power Laboratory).

Cell 3 (not shown) was available for use in performing sample preparatory work and providing space for sample residues until the runs were completed.
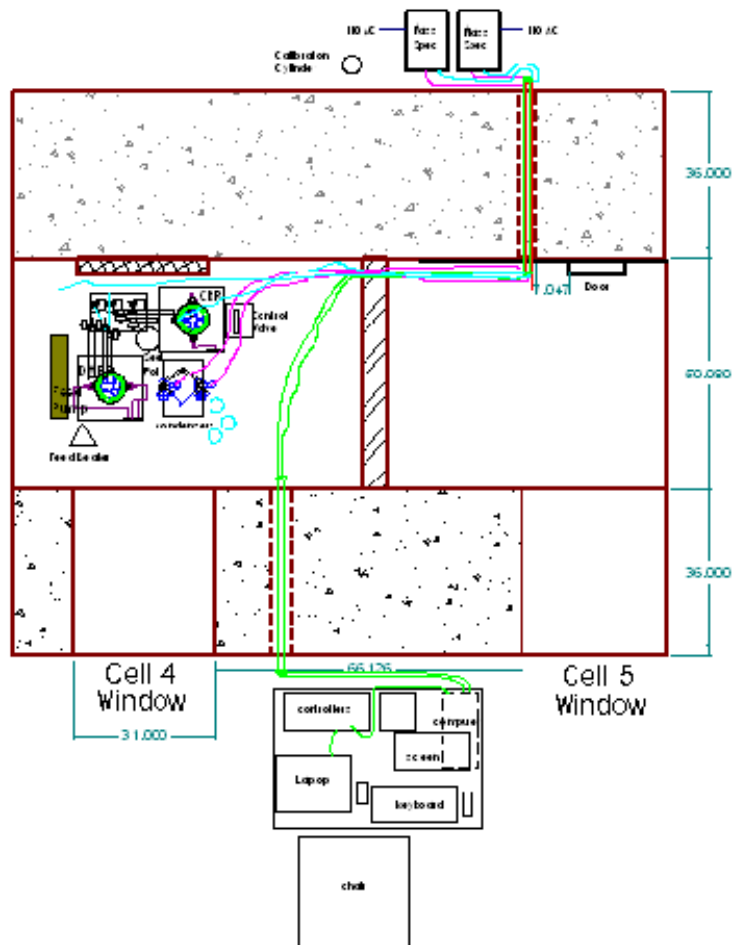
Figure 2.  Total System Layout at Cell 4 (Simplified)


**BSR Operating Conditions for Tank 48H Waste**

Table I shows the flows for the 2006 THOR Hazen Tank 48H ESTD FBSR Production Run 4 values from Table 6-1, Table 8-1, and Table 8-2 from the TTT report [2], the scaled BSR equivalent flows, and the actual flows for both the BSR simulant runs and the BSR Tank48H radioactive runs.  The BSR feed rate is the primary parameter for scaling this process to the ESTD FBSR process.  After the ESTD FBSR values are scaled down based on the BSR feed rate, the actual operating BSR values were then adjusted due to configuration differences between the ESTD FBSR and BSR.

Table I.  BSR Process Operation Conditions compared to Pilot-Scale FBSR Conditions for Prod-4 [2]

| DMR Feed Stream | FBSR Value | Scaled Simulant BSR DMR Value | Actual Simulant BSR DMR Operating Value | Actual Radioactive Tank48H BSR DMR Operating Value |
|---|---|---|---|---|
| **Waste Slurry** | 0.21 gpm (795 ml/min) | 1 ml/min | 1 ml/min | 1 ml/min |
| **Waste Slurry** | 930 g/min[a] | 1.17 g/min[a] | 1.17 g/min[a] | 1.17 g/min[a] |
| **Carbon[b]** | 12.6 kg/hr (210 | 0.26 g/min | 0.20 g/min[b] | 0.20 g/min[b] |

| | g/min) | | | |
|---|---|---|---|---|
| **Atomizing Air** | 9.85 SCFM (2.79E5 sccm) | 0.0127 SCFM (360 sccm) | 0-0.035 SCFM (0-1000 sccm)[c] Avg. 0.011 SCFM (312 sccm) | 0-0.035 SCFM (0-1000 sccm)[c] Avg. 0.009 SCFM (245 sccm) |
| **Fluidizing Steam** | 18.6 kg/hr (310 g/min) | 0.40 g/min | 0.40 g/min | 0.40 g/min |
| **Oxygen[c]** | 7.7 SCFM (2.18E5 sccm) | 0.0099 SCFM (281 sccm) | [c] | [c] |
| **$CO_2$** | 8 SCFM (2.26E5 sccm) | 0.01 SCFM (292 sccm) | 0.011 SCFM (320 sccm)[b] | 0.011 SCFM (320 sccm)[b] |
| **$N_2$ Purges[c]** | 25.9 SCFM 7.34E5 sccm) | 0.034 SCFM (946 sccm) | [c] | [c] |

[a]Approximate rates;
[b]Adjusted BSR Operating Value during Simulant Runs based on system performance;
[c]Oxygen and $N_2$ purges set by DMR Air supply (78%$N_2$/21%$O_2$) which is adjusted in specified range to maintain $H_2$ vol% between 1.5-4 vol %

In the ESTD FBSR, coal was added separately from the feed. For the BSR, the coal was premixed with the feed and both were fed through the top of the unit as a single stream. The same GC coal used in the ESTD FBSR, was ground and sieved to 80 mesh (177 microns), then mixed into the Tank 48H feed for the BSR. A mixture of 60 grams coal to 300 ml of feed produced enough hydrogen in the BSR DMR to allow off-gas control similar to the ESTD FBSR DMR [2]. The BSR feed rate was set at 1 ml/min to reduce the amount of carry-over of carbon and other particulates from the DMR. Since the non-radioactive and radioactive BSR systems were identical, the operating parameters determined for the non-radioactive runs were used in the radioactive runs.

In the ESTD FBSR, oxygen was bled in to provide the heat necessary by consuming $H_2$ and carbon. In the BSR, the heat was added by chemical reaction with oxygen and by an electric furnace to control the temperature to 670$^o$C at the control thermocouple point.

The temperature control for all three runs was within +/- 10$^o$C of set-point. The pressure control was expected to maintain the DMR outer pressure to -2 inwc. The decrease in the CRR outer pressure over time was due to ice forming in the DMR dry ice condenser as expected. The unit would be shut down if the CRR outer pressure decreased to < -25 inwc to prevent measurement problems with the MS which ran at -30 inwc. Figure 3 shows the run 2 data which was typical.
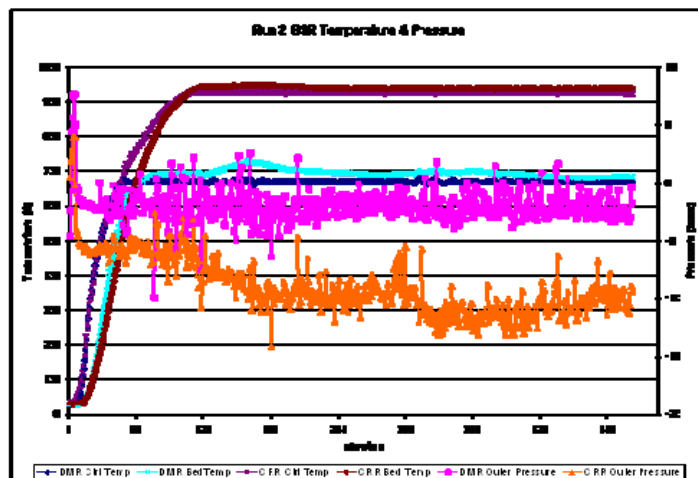
Figure 3. Run 2 BSR Temperature & Pressure

The BSR used a DMR air supply (78%$N_2$/21%$O_2$) to control the DMR $H_2$ concentration so the $N_2$ and $O_2$ flows were determined by the air flow rate. The BSR air flow rate was varied from 0 to 1000 sccm (standard cubic centimeters per minute) with an average air flow of 245 sccm to control the volume % of $H_2$ between 1.5% and 4.0%. Table II shows the DMR $H_2$ vol% goes through ranges from about 1.0 vol% to 9 vol%. This variance is due to the fact that the $H_2$ vol% is being manually controlled by the amount of air fed into the DMR and the mass spectrometer reading lags 1-2 minutes behind. Overall these variances have minimal impact as evidenced by the average DMR hydrogen rates from 2.06% to 2.64%. (Also see Figure 4.)

Comparing Table II to Table III shows that the destruction of $H_2$ and benzene in the CRR was virtually completed. For the $H_2$, the concentration entering the CRR averaged up to 2.64 vol% where the highest average concentration leaving the CRR was 0.03 vol%. For benzene, the concentration entering the CRR averaged up to 900 ppm where the highest average concentration leaving the CRR was 0 ppm. These off-gas measurements compare well with those from the HRI testing [2] in 2006 where the stack gas after the CRR had on average 0.00% of total hydrocarbons (keeping in mind that they used a flame total hydrocarbon analyzer).

Table II. DMR Mass Spectrometer Off-gas Measurement Summary Data (vol%)

| Rad Run | DMR $H_2$ | | | DMR $O_2$ | | | DMR $N_2$ | | | DMR $CO_2$ | | | DMR Benzene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Max | Avg | Min | Max | Avg | Min | Max | Avg | Min | Max | Avg | Min | Max | Avg |
| 1 | 1.5 | 8.96 | 2.06 | 0.33 | 20.66 | 4.45 | 12.29 | 76.40 | 40.12 | 0.43 | 75.75 | 48.18 | 0.00 | 0.30 | 0.04 |
| 2 | 1.0 | 7.13 | 2.64 | 0.43 | 9.78 | 5.40 | 3.72 | 53.20 | 45.39 | 21.06 | 83.06 | 32.82 | 0.03 | 0.50 | 0.09 |
| 3 | 1.0 | 8.98 | 2.59 | 0.60 | 10.68 | 5.51 | 3.01 | 56.71 | 46.91 | 20.31 | 90.94 | 34.04 | 0.02 | 0.37 | 0.08 |

Table III. CRR Mass Spectrometer Off-gas Measurement Summary Data (vol%)

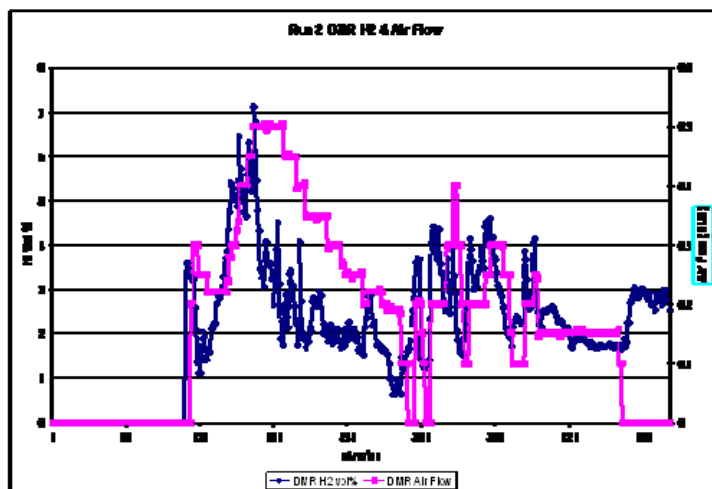| Rad Run | CRR $H_2$ | | | CRR $O_2$ | | | CRR $N_2$ | | | CRR $CO_2$ | | | CRR Benzene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Max | Avg | Min | Max | Avg | Min | Max | Avg | Min | Max | Avg | Min | Max | Avg |
| 1 | 0.02 | 0.04 | 0.03 | 9.37 | 19.94 | 14.38 | 44.17 | 75.53 | 62.66 | 0.12 | 40.44 | 14.66 | 0.00 | 0.01 | 0.00 |
| 2 | 0.02 | 0.04 | 0.02 | 4.63 | 12.41 | 9.76 | 43.52 | 62.11 | 58.35 | 13.67 | 38.33 | 20.64 | 0.00 | 0.00 | 0.00 |
| 3 | 0.02 | 0.04 | 0.02 | 4.35 | 14.00 | 10.25 | 39.68 | 65.28 | 60.02 | 11.48 | 44.34 | 20.95 | 0.00 | 0.00 | 0.00 |

Figure 4.  Run 2 DMR Off-gas $H_2$ & Air Flow

## ANALYSIS & OBSERVATIONS

### Analysis of Solid DMR Product

The feed TPB anion concentration showed 21000 mg/L.  300ml of feed were fed per run.  All runs showed less than the detection limit of 5 mg/kg TPB in the estimated 70 grams of product.  Therefore the TPB destruction calculated to > 99.99% destruction.

Table IV showed the DMR product was primarily made up of soluble carbonates.  The three most abundant species were thermonatrite, $[Na_2CO_3H_2O]$, sodium carbonate, $[Na_2CO_3]$, and trona, $[Na_3H(CO_3)_2 2H_2O]$.  It is thought that the minor amount of silicates and aluminosilicates $(Na_8(AlSiO_4)_6(OH)_2 \bullet 2H_2O$ which is hydroxysodalite, nepheline, muscovite and $SiO_2$) may have come from the coal ash and/or the Si and Al in the waste.

Table IV.  DMR and Insoluble Phase Analysis by X-Ray Diffraction (XRD)

| XRD DMR | | | |
|---|---|---|---|
| | Run 1 | Run 2 | Run 3 |
| | $Na_2CO_3 \bullet H_2O$ | $Na_2CO_3 \bullet H_2O$ | $Na_2CO_3 \bullet H_2O$ |
| | $Na_2CO_3$ | $Na_2CO_3$ | $Na_2CO_3$ |
| | $Na_3H(CO_3)_2 \bullet 2H_2O$ | | $Na_3H(CO_3)_2 \bullet 2H_2O$ |
| | $Na_8(AlSiO_4)_6(OH)_2 \bullet 2H_2O$ | $Na_8(AlSiO_4)_6(OH)_2 \bullet 2H_2O$ | $Na_8(AlSiO_4)_6(OH)_2 \bullet 2H_2O$ |
| | $Na_2Al_2SiO_6$ | | $Na_2Al_2SiO_6$ |
| XRD INSOLUBLES | | | |
| | $Na_8(AlSiO_4)_6(OH)_2 \bullet 2H_2O$ | $Na_8(AlSiO_4)_6(OH)_2 \bullet 2H_2O$ | $Na_8(AlSiO_4)_6(OH)_2 \bullet 2H_2O$ |
| | $Na_{0.75}K_{0.24}Al_{0.95}Fe_{0.13}Si_{0.77}O_4$ | $Na_{0.75}K_{1.5}Al_{0.89}Si_{1.11}O_4$ | $Na_{0.75}K_{1.5}Al_{0.89}Si_{1.11}O_4$ |
| | $NaFeTiO_4$ | $NaFeTiO_4$ | $NaFeTiO_4$ |
| | Muscovite aluminosilicate | | $SiO_2$ |

The REDOX or $Fe^{2+}/Fe_{total}$ ratio was determined for the BSR DMR products to determine if a reducing pyrolysis environment was maintained in the BSR DMR.  Note that a ratio close to 0 is highly oxidizing

and a ratio of 1 is highly reducing.  The desired REDOX is > 0.5.  The REDOX analyses in Table V showed the reactions occurred in a reducing atmosphere as was required for pyrolysis.

Table V.  DMR REDuction/OXidation (REDOX) of Product

|  | Run 1 | Run 2 | Run 3 |
|---|---|---|---|
| REDOX Fe+2/Fe(tot) | 0.58 | 0.98 | 1 |
| REDOX Fe+2/Fe+3 | 1.4 | Fully reduced | Fully reduced |

Table VI shows that the Tank 48H radioactive runs in the BSR met all the validation results [3].

Table VI.  Validation Results

| Performance Criteria | BSR Results Converted to Performance Criteria | Validation Criteria Met | Analytic Methods | BSR Analytic Result | | |
|---|---|---|---|---|---|---|
| Show >99% removal of feed phenylborates (TPB) | 99.99% destruction of TPB | Yes | HPLC Analyses on feed sample & DMR Solid Product | . 0.35 mg TPB (detection limit) in DMR solid product vs 6300 mg TPB fed | | |
| Show that product is primarily carbonate | Product is primarily carbonate.  The silicates and aluminosilicate are minor constituents coming from the coal ash. | Yes | XRD on DMR Solid Product | $Na_2CO_3$  $H_2O$ | | |
| | | | | $Na_2CO_3$ | | |
| | | | | $Na_3H(CO_3)_2$  $2H_2O$ | | |
| | | | | $Na_8(AlSiO_4)_6(OH)_2$  $2H_2O$ | | |
| | | | | $Na_2Al_2SiO_6$ | | |
| Verify reducing environment (pyrolysis) in DMR | DMR reactions are pyrolitic as evidenced by $H_2$ generation monitored by mass spectrometers during the experiments and the measured REDOX of the solid product being > 0.5. | Yes | REDOX on DMR Solid Product | In DMR solid product the REDOX ratio $Fe^{2+}/Fe_{total}$REDOX ranged from 0.58 to 1. | | |

| | | | | |
|---|---|---|---|---|
| Show >99% destruction of feed nitrates | Destruction of the feed nitrates and nitrites was >99%. | Yes | IC Anions/ICP-ES cations on Soluble Solid Product; wt% solids and IC Anions of feed slurry | <17.5 mg vs. 4275 mg $NO_3$ fed <br> <17.5 mg vs 7125 mg $NO_2$ fed <br> (based on detection limits) |
| Check if DMR product has insoluble carbonate | There was no detectable insoluble carbonates down to the detection limit of 2% for XRD analysis. | Yes | XRD on dissolved/filtered insoluble solids from DMR solid product | $Na_8(AlSiO_4)_6(OH)_2$ 2 $H_2O$ <br> $Na_{0.75}K_{0.24}Al_{0.95}Fe_{0.13}Si_{0.77}O_4$ <br> $NaFeTiO_4$ <br> Muscovite aluminosilicate <br> $SiO_2$ |
| Offgas Measurement of $H_2$, $O_2$, $N_2$, $CO_2$, Benzene | The DMR and CRR offgas had expected levels of $H_2$, $O_2$, $N_2$, $CO_2$, and Benzene, ie. the DMR offgas showed evidence of $H_2$ and benzene evolution while the CRR values were equivalent to zero. | Yes | Online Monitor Instrument Mass Spectrometer Series 3000 | DMR Offgas Average Ranges 2.06-2.64 vol% $H_2$ <br> 4.45-5.51 vol% $O_2$ <br> 40.1-45.4 vol% $N_2$ <br> 32.8-48.2 vol% $CO_2$ <br> 0.04-0.09 vol% Benzene <br> CRR Offgas Averages: <br> 0.02-0.03 vol% $H_2$ <br> 9.8-14.4 vol% $O_2$ <br> 58.4-62.7 vol% $N_2$ <br> 14.7-21 vol% $CO_2$ <br> 0.00 vol% Benzene* |

**Analysis of Condensates**

The d/m/ml (disintegrations/minute/milliliter) of the DMR bubbler condensate and CRR bubbler condensate were measured for each run.  The DMR bubbler holds 650ml per run and the CRR bubbler holds 350ml per run.  The d/m/ml of the feed was analyzed in 2005 [4].  Each run used 300ml of feed.  As shown in Table VII, the majority of the radioactivity ended up in the product (based on calculation).  The actual FBSR is expected to capture >99% of the radioactive material due to its sophisticated particle and off-gas controls that were not part of the BSR design.

**Table VII.  Radioactivity Distribution of Feed to Product**

| | Feed | DMR Bubbler | CRR Bubbler | Product |
|---|---|---|---|---|
| Run | % rad. | % rad. | % rad. | % rad. |
| 1 | 100 | 8.172 | 0.002 | 91.827 |
| 2 | 100 | 4.633 | 0.015 | 95.352 |
| 3 | 100 | 3.453 | 0.032 | 96.515 |

**Analysis of the Off-Gas**

Analysis of the off-gas was performed in real time and was shown earlier in this paper. However, two species of gas that were not measured due to measurement difficulty were NO and $NO_2$. Fortunately, $NO_2$ is a strongly colored gas which appears yellowish-brown even at very low concentrations. During the simulant runs, close observation of the gases while holding white paper behind the off-gas line leaving the DMR revealed only clear off-gas indicating that all of the $NO_2$ was destroyed. This same observation was made during the radioactive runs but may not be as accurate due to the poorer visibility in the cells. The $H_2$ concentration leaving the DMR, i.e. excess hydrogen, was also a good indication that all the $NO_x$ was destroyed in the vapor phase.

**Analysis of Tank 48H Waste**

Radioactive Tank 48H samples were obtained from a 3.0 L composite located in the shielded cells facility. The characterization data for the radioactive sample that was obtained and analyzed in 2005 is given in "Analysis of Tank 48H Sample – HTF-E-05-021", WSRC-TR-2005-00358 [4].

**Analysis of the Simulant**

Simulants of the Tank 48H slurries were obtained from excess feed from the 2006 pilot-scale testing from Hazen Research, Inc. (HRI) facility in Golden, CO. By normalizing the component data it becomes clear that both the actual waste and the simulant contain nearly the same ratios of the major components Al, B, K, Na, Ti, $NO_2$, $NO_3$, and $PO_4$. The solids, pH, and density data also showed fairly good agreement. The detailed report on the simulant development is SRNL-LWP-2004-0042 [5] and a detailed report of the simulant validation is WSRC-LWP-2004-00009 [6].

**Comparison of BSR to FBSR and Comparison of Simulant Product to Actual Waste Product**

Table VIII shows that both the ESTD FBSR and BSR successfully operated at the right temperatures with superheated steam and reducing conditions to destroy >99% of the TPB, destroy >99% of the nitrates and nitrites, and produce a primarily carbonate product. Insoluble species were found in the product from all tests, however no insoluble carbonates were detected using XRD which has a detection sensitivity down to ~2 wt%. These insoluble species are thought to form from the GC coal impurities and/or Si and Al species in the waste except for the $NaFeTiO_4$ and $ZrO_2$. The $NaFeTiO_4$ was formed from the monosodium titanate and sludge impurities found in the waste and simulant. The $ZrO_2$ can be attributed to the bed material used in the BSR. The products formed from running the simulant are very nearly the same as the products formed from running the actual Tank 48H waste.

Table VIII. FBSR Simulant vs BSR Simulant vs BSR Tk48H Waste Product Comparison

| Performance Criteria | FBSR Simulant [2] | BSR Simulant [7] | BSR Actual Tk48H |
|---|---|---|---|
| Show >99% removal of feed phenylborates (TPB) | 99.9% destruction of TPB | 99.9% destruction of TPB | 99.99% destruction of TPB |
| Show that product is primarily carbonate | $Na_2CO_3$  $H_2O$<br>$Na_2CO_3$<br>$Na_3H(CO_3)_2$  $2H_2O$<br>Nepheline | $Na_2CO_3$  $H_2O$<br>$Na_2CO_3$<br>$Na_3H(CO_3)_2$  $2H_2O$<br>$Na_2Al_2SiO_6$ | $Na_2CO_3$  $H_2O$<br>$Na_2CO_3$<br>$Na_3H(CO_3)_2$  $2H_2O$<br>$Na_8(AlSiO_4)_6(OH)_2$   2H |

| | | | |
|---|---|---|---|
| | Cristobalite | Nepheline | $_2$O |
| | | Cristobalite | $Na_2Al_2SiO_6$ |
| Verify reducing environment (pyrolysis) in DMR | $Fe^{2+}/Fe_{total}$ of around 0.60 for DMR product. | $Fe^{2+}/Fe_{total}$ REDOX was 1 for DMR products.* | $Fe^{2+}/Fe_{total}$ REDOX ranged from 0.58 to 1 for DMR product. |
| Show >99% destruction of feed nitrates | 99.9% Destruction of the Feed Nitrates and nitrites | 99.9% Destruction of the Feed Nitrates and nitrites | >99.6% destruction of $NO_3$<br><br>> 99.8% destruction of $NO_2$ |
| Check if DMR product has insoluble carbonate | Nepheline<br>NaFeTiO4<br>Quartz<br><br><br>No insoluble carbonate detected. | Nepheline*<br>Na8(AlSiO4)6(NO3)2<br>NaFeTiO4<br>Quartz<br>ZrO2<br><br>No insoluble carbonate detected. | Na SiAl oxide hydrate<br>Hydrosodalite<br>nepheline<br>NaFeTiO4<br>Muscovite - 3T<br>Quartz<br>No insoluble carbonate detected. |
| Offgas Measurement of $H_2$, $O_2$, $N_2$, $CO_2$, Benzene | Average DMR offgas on dry basis:<br>1.1-2.5 vol% $H_2$<br>0.07-3.54 vol% $O_2$<br>22.8-45.1 vol% $CO_2$<br>0.5-1.7 vol% Benzene<br><br><br>CRR Offgas Averages:<br>10.1-11.6 vol% $O_2$<br>15.7-21.6 vol% $CO_2$<br>0.00-2.3 ppm THC | Average DMR offgas on dry basis:<br>1.76-1.90 vol% $H_2$<br>0.38-3.96 vol% $O_2$<br>47.8-61.2 vol% $N_2$<br>45.7-51.9 vol% $CO_2$<br>0.04 vol% Benzene<br><br>CRR Offgas Averages:<br>0.05 vol% $H_2$<br>3.43-11.7 vol% $O_2$<br>60.2-70.4 vol% $N_2$<br>21.0-22.4 vol% $CO_2$<br>0.00 vol% Benzene* | Average DMR offgas on dry basis:<br>2.06-2.64 vol% $H_2$<br>4.45-5.51 vol% $O_2$<br>40.1-45.4 vol% $N_2$<br>32.8-48.2 vol% $CO_2$<br>0.04-0.09 vol% Benzene<br><br>CRR Offgas Averages:<br>0.02-0.03 vol% $H_2$<br>9.8-14.4 vol% $O_2$<br>58.4-62.7 vol% $N_2$<br>14.7-21 vol% $CO_2$<br>0.00 vol% Benzene* |

**CONCLUSIONS**

The conclusions from the BSR study and comparison to the ESTD FBSR are the following:

► A Bench-scale Steam Reforming (BSR) unit was successfully designed and built that:
- Emulated the chemistry of the Hazen ESTD FBSR Denitration Mineralization Reformer (DMR) and Carbon Reduction Reformer (CRR) known collectively as the dual reformer flowsheet.
- Measured and controlled the off-gas stream.
- Processed real (radioactive) Tank 48H waste.
- Met the standards and specifications for radiological testing in the Savannah River National Laboratory (SRNL) Shielded Cells Facility (SCF).

► Three runs with radioactive Tank 48H material were performed.

► The TPB was destroyed to > 99% for all radioactive Bench-scale tests.

► The feed nitrate/nitrite was destroyed to >99% for all radioactive BSR tests the same as the ESTD FBSR.

► The radioactive Tank 48H DMR product was primarily made up of soluble carbonates.  The three most abundant species were thermonatrite, [ $Na_2CO_3H_2O$ ], sodium carbonate, [ $Na_2CO_3$ ], and trona, [ $Na_3H(CO_3)_2 2H_2O$ ] the same as the ESTD FBSR.

► Insoluble solids analyzed by X-Ray Diffraction (XRD) did not detect insoluble carbonate species.  However, they still may be present at levels below 2 wt%, the sensitivity of the XRD methodology.  Insoluble solids XRD characterization indicated that various Fe/Ni/Cr/Mn phases are present.  These crystalline phases are associated with the insoluble sludge components of Tank 48H slurry and impurities in the GC coal ash.

► The $Fe^{+2}/Fe_{total}$ REDOX measurements ranged from 0.58 to 1 for the three radioactive Bench-scale tests.  REDOX measurements > 0.5 showed a reducing atmosphere was maintained in the DMR indicating that pyrolysis was occurring.

► Greater than 90% of the radioactivity was captured in the solid product with the balance being captured in the off-gas condenser / bubblers for all three runs in the BSR.

► The collective results from the FBSR simulant tests and the BSR simulant tests indicate that the same chemistry occurs in the two reactors.

► The collective results from the BSR simulant runs and the BSR radioactive waste runs indicates that the same chemistry occurs in the simulant as in the real waste.

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