

BENCH-SCALE STEAM REFORMING OF ACTUAL TANK 48H WASTE

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September 2008

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EXECUTIVE SUMMARY

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 Reformer¹ (ESTD FBSR) at the Hazen Research Inc. (HRI) facility in Golden, CO. The purpose of the Bench-scale Steam Reformer (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 used in the current study was to test the BSR with the same Tank 48H simulant and same Erwin 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 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 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 Tetraphenylborate (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, [$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$], sodium carbonate, [Na_2CO_3], and trona, [$\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$] 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 Erwin coal ash. The percent insoluble

solids, which mainly consist of un-burnt coal and coal ash, in the products were 4 to 11 wt% for the radioactive runs.

- ▶ The $\text{Fe}^{+2}/\text{Fe}_{\text{total}}$ 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 product for all three runs.
- ▶ 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.

The FBSR technology has been proven to destroy the organics and nitrates in the Tank 48H waste and form the anticipated solid carbonate phases as expected.

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LIST OF ACRONYMS

ADD	Analytic Development Directorate
BSR	Bench-scale Steam Reformer
CHAP	Consolidated Hazard Analysis Package
CRR	Carbon Reduction Reformer
Cs-TPB	Cesium Tetrphenylborate
d/m/ml	disintegrations/minute/milliliter
DMR	Denitration Mineralization Reformer
DOE	Department of Energy
DSA	Design Safety Analysis
DWPF	Defense Waste Processing Facility
ESTD FBSR	Engineering Scale Test Demonstration Fluidized Bed Steam Reforming
FBSR	Fluidized Bed Steam Reformer or Reforming
GC	Gas Chromatograph
HAP	Hazards Analysis Package
HLW	High Level Waste
HPLC	High Pressure Liquid Chromotography
HRI	Hazen Research Inc.
IC	Ion Chromotography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
inwc	INches Water Column
ITP	In-Tank Precipitation
KAPL	Knolles Atomic Power Laboratory
LFL	Lower Flammability Limit
LWO	Liquid Waste Operations
MS	Mass Spectrometer
Na-TPB	Sodium Tetrphenylborate
PC	Personal Computer
REDOX	REDuction/OXidation
sccm	standard cubic centimeters per minute
SCF	Shielded Cells Facility
SLM	Standard Liters per Minute
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SVOA	Semi-Volatile Organic Analyses
THOR [®]	THermal Organic Reduction
TPB	TetraPhenylBorates
TTR	Task Technical Request
TTT	THOR [®] Treatment Technologies
TT&QAP	Task Technical and Quality Assurance Plan
VOA	Volatile Organic Analyses
XRD	X-Ray Diffraction

1.0 INTRODUCTION

Fluidized Bed Steam Reforming (FBSR) is being considered as a potential technology for the removal of Tetraphenylborate, (TPB) and other organics due to the breakdown of TPB from the Tank 48H waste. The desired plan was to develop a laboratory scale system that provides the same gas reactions and atmosphere and solid phase chemistry as in the Engineering Scale Test Demonstration Fluidized Bed Steam Reforming (ESTD FBSR) test¹ performed in 2006. The laboratory scale system would then be operated with the same simulant as was used in the ESTD FBSR, and then repeat the operation using the actual radioactive Tank 48H waste. In this way, the simulant run data between the ESTD FBSR and the laboratory scale system could be compared to determine if both reactors provide the same chemistry, then the actual waste run data and the simulant run data from the laboratory scale system could be compared to determine if the actual waste behaves the same as the simulant.

The actual Tank 48H waste demonstration had to be performed in the 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 Savannah River National Laboratory (SRNL) developed the Bench-scale Steam Reformer (BSR) to fulfill this need.

Liquid Waste Operations (LWO) personnel at the Savannah River Site (SRS) issued a Task Technical Request (TTR) for the bench-scale steam reforming of radioactive Tank 48H samples related to FBSR technology using the carbonate flowsheet.²

Engineering Process Development personnel at the SRNL issued a Task Technical and Quality Assurance Plan (TT&QAP)³ and a validation plan⁴ to address the testing criteria and objectives for the radioactive bench-scale steam reforming work. The purposes of the study were to demonstrate the following objectives with actual radioactive Tank 48H material:

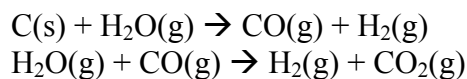
- ▶ Design and fabricate a Bench scale Steam Reforming (BSR) unit that:
 - Emulates the chemistry of the ESTD FBSR Denitration Mineralization Reformer (DMR) and Carbon Reduction Reformer (CRR) known collectively as the dual reformer flowsheet.
 - Characterizes the Off-Gas product stream.
 - Can process real (radioactive) Tank 48H waste.
 - Meets standards and specifications for radiological testing.
- ▶ Perform three runs with radioactive Tank 48H material.
- ▶ Characterize product chemistries to show 1) > 99% destruction of feed TPB, 2) >99% destruction of feed nitrates and nitrites, 3) the majority of solid product is in the carbonate form, and 4) the chemistry in the DMR was reducing.
- ▶ Measure and control BSR off-gas on a real time basis.

2.0 BACKGROUND

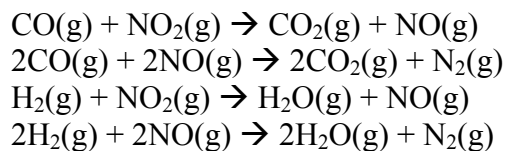
Tank 48H currently holds approximately 240,000 gallons of legacy waste from the In-Tank Precipitation (ITP) project, containing organic tetraphenylborate (TPB) solids, and is incompatible with other waste treatment processes at Savannah River Site (SRS). Consequently, Tank 48H remains isolated from Tank Farm operations. Returning Tank 48H to service on a schedule is critical to meet the Tank Farm mission and the tank space management program.

After several well-documented evaluations, the Fluidized Bed Steam Reforming (FBSR) technology was selected as the primary technology capable of safely and cost-effectively dispositioning the Tank 48 waste in a manner compatible with current tank farm operations.

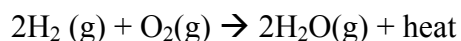
Steam reforming destroys organics by the water gas shift reactions at temperatures above 600°C. Any carbon bearing species is converted to CO and CO₂ as H₂O becomes H₂.



In addition to destroying the organics, the CO and H₂ rich atmosphere then promote the denitration of the salt solution.

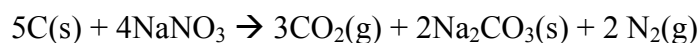


Typically, the H₂ concentration was controlled to about 2% on a dry basis in order to completely reduce the NO_x gases to steam and N₂. It was controlled by adding air to create more steam and heat.



Off-gases from the steam reformer still included some organics so a second reformer operated at 925°C with excess air to oxidize the remaining organics fully to CO₂ and to convert the remaining H₂ to steam (H₂O gas).

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



Thermonatrite, [Na₂CO₃•H₂O], Sodium Carbonate, [Na₂CO₃], and Trona, [Na₃H(CO₃)₂•2H₂O] are the major carbonate products formed from an alkali rich waste and the CO-CO₂ 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, Erwin 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.

The Erwin 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 consumed¹.

Erwin coal was chosen by THOR[®] Treatment Technologies (TTT) because it is very reactive at low temperatures. Also, the Erwin coal was calcined to remove volatiles, sulfur, and nitrogen so that it burned cleaner in the FBSR.

3.0 APPROACH

Initially, the SRS LWO customer requested TTT to perform pilot scale tests on Tank 48H simulant at the Hazen Research Institute (HRI) in Golden, Colorado. These tests were performed during October 2006. The conditions for the PROD-4 run¹ were chosen for the BSR tests because these conditions were the most reactive at 670°C, produced the least amount of residual coal, and did not degrade the carbonate product.

Thus the first runs performed with the BSR were with the same process conditions, the same Tank 48H simulant, and the same Erwin coal as was used during the PROD-4 runs at HRI. Once two successful runs were completed using the simulant, three runs were performed in the radioactive BSR using actual Tank 48H waste. In the radioactive runs, the same process conditions and the same Erwin coal were used as was used during the BSR simulant runs.

4.0 EXPERIMENTS

4.1 BENCH-SCALE STEAM REFORMER DESCRIPTION

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.

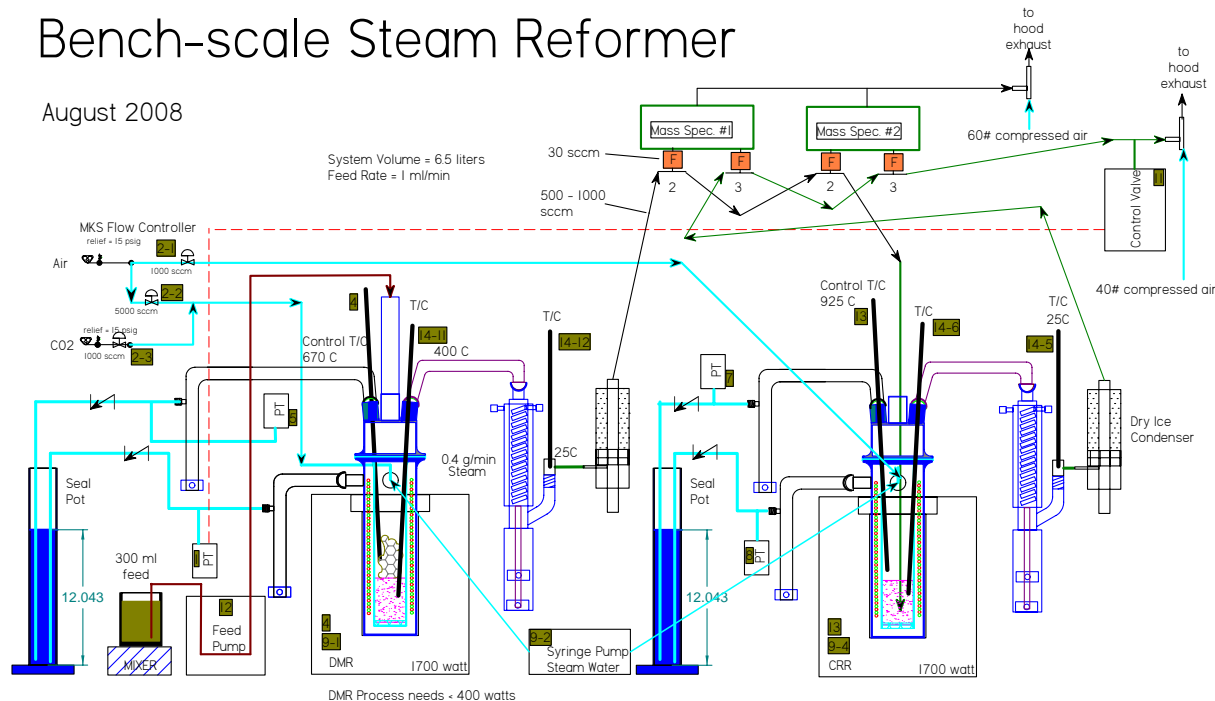


Figure 1. Schematic of the Bench-Scale Steam Reformer

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 H₂, O₂, CO₂, N₂, C₆H₆, and argon. The off-gas then flowed into the Carbon Reduction Reformer (CRR) where any CO, H₂, C₆H₆, or other oxidizable species would be converted to H₂O and CO₂. 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).

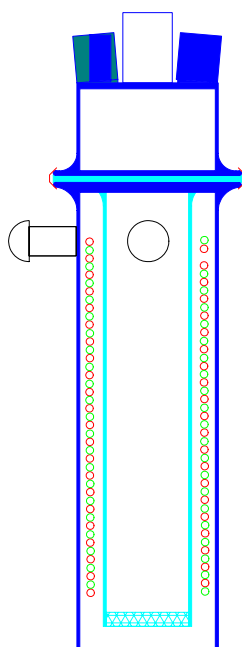


Figure 2. The Denitration Mineralization Reformer

The Denitration Mineralization Reformer (DMR) received the Tank 48H waste stream (or simulant) as feed and converted it to a solid carbonate product in the presence of superheated steam and carbon. 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, 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, CO₂, 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 CO₂ flow rate was a constant based on the HRI PROD-4¹ conditions. The air flow rate was varied in order to control the H₂ concentration leaving the reactor from 1.5% to 4% on a dry basis which was close to the Hazen PROD-4¹ 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 Erwin 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 Erwin 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 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 determine the oxygen fugacity inside the DMR and ensure that pyrolysis was occurring under highly deoxygenated conditions, e.g. $-\log f\text{O}_2 \sim -20$.

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°C in the DMR. Figure 3 shows that the first four inches of the stalagmite are formed in a region where the temperature is between 676°C and 645°C which is within the temperature range for making good product. Samples were taken from this region and analyzed separately from the upper samples.

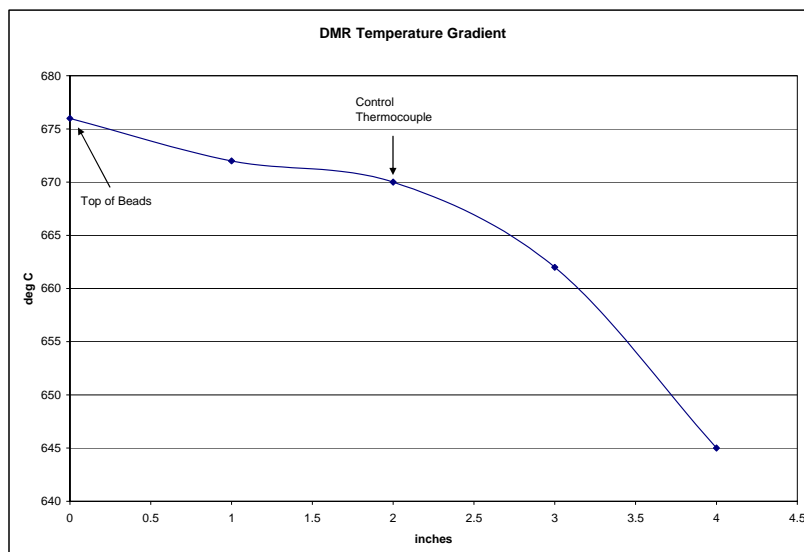


Figure 3. DMR Temperature Gradient Around Control Thermocouple

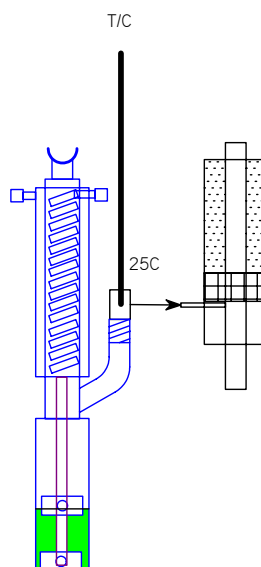


Figure 4. The Condenser / Bubbler / Dry Ice Condenser

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°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. If not sized correctly or if a large leak occurred in the system prior to the dry ice condenser, a plug could form.

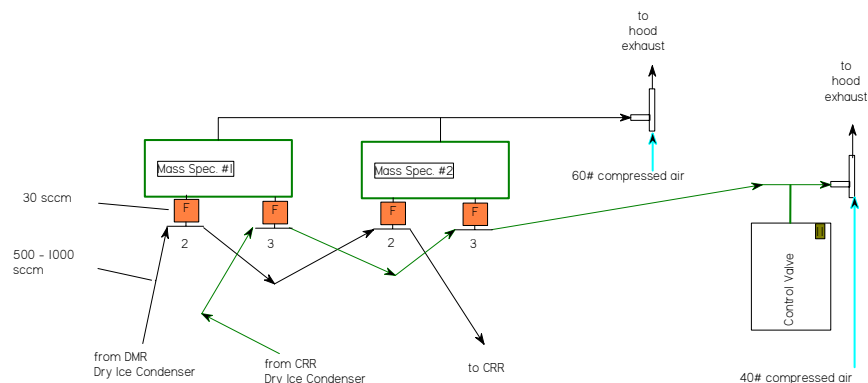


Figure 5. The Mass Spectrometers

The BSR used dual Monitor Instruments LAB 3000 Cycloidal mass spectrometers (MSs) 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 MSs. 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 MSs.

Since the line pressure near the MSs would be down to -25 inwc, it was necessary to run a second eductor and vacuum regulator to draw the sample gases through the MSs. 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 MSs 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 MSs 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.

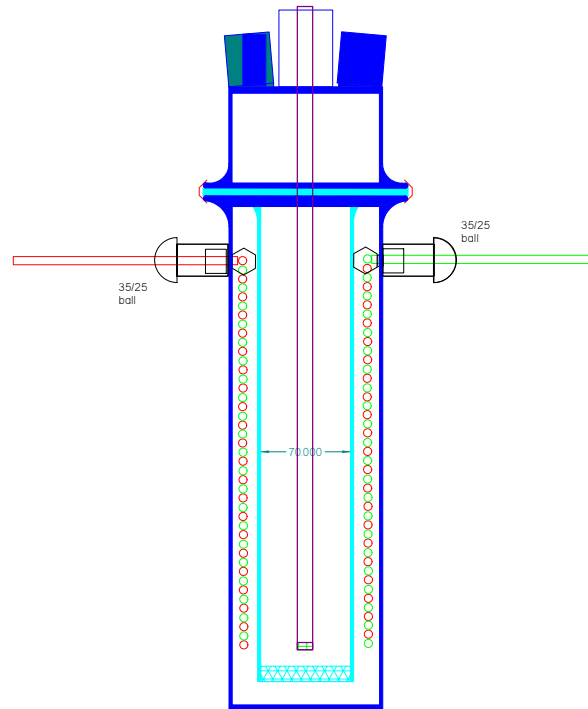


Figure 6. The Carbon Reduction Reformer

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 (not shown) 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°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.

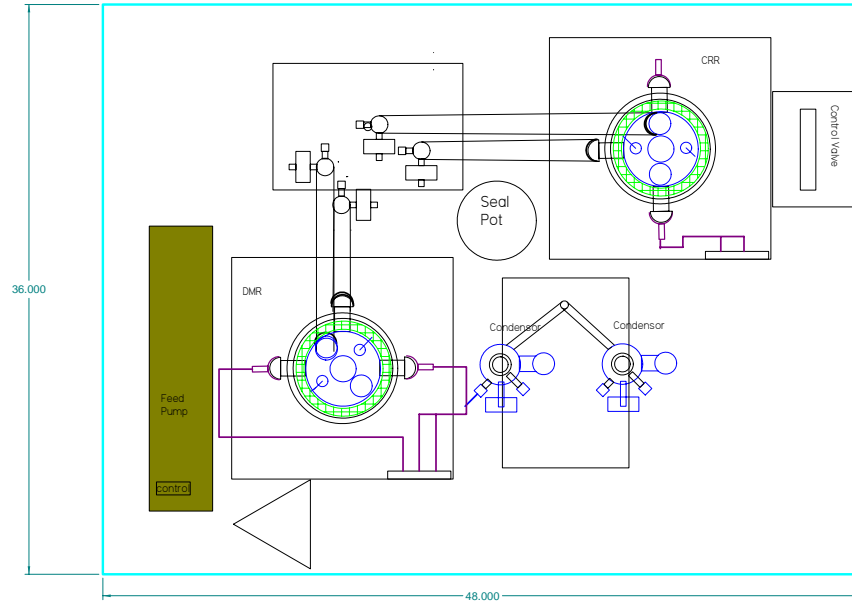


Figure 7. BSR Pan Layout for Cell (Simplified)

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 cell. 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° to the CRR side.

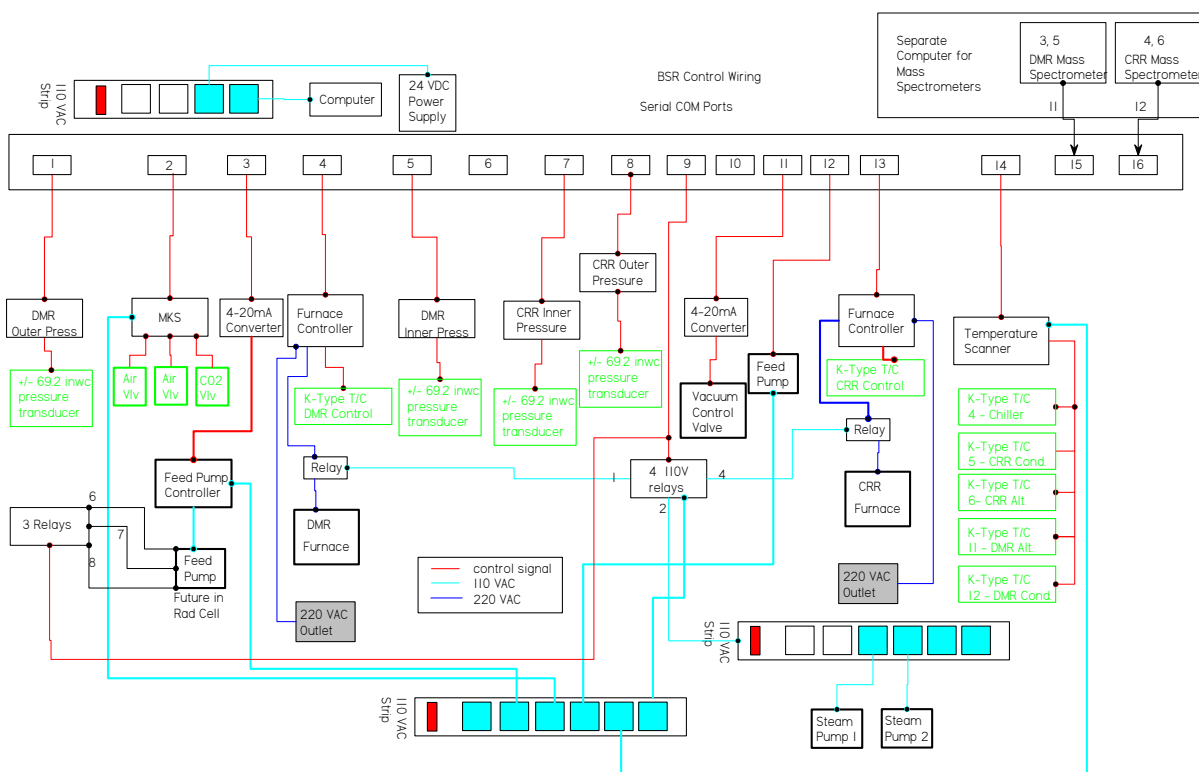


Figure 8. BSR Process Control Diagram

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 was 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).

Table 1. M&TE Associated Equipment

Name:	P1	F2a	F2b	F2c	T4
Description:	DMR Outer Pressure	CRR Air	DMR Air	DMR CO ₂	DMR Ctrl Temp
M&TE #	GT4-PB13	FC1K-02	FC5K-15	FC1K-03	GT4-PB20
Range	+/- 50 inwc	1000 sccm	5000 sccm	1000 sccm	0 -1000 C
Error	+0.1/-0.4	+6 / -5	+0 / -39	+0 / -8	+ 0.6 / -3.0
Name:	P5	T14-11	P7	P8	T13
Description:	DMR Inner Pressure	DMR Alt. Temp	CRR Inner Pressure	CRR Outer Pressure	CRR Ctrl Temp
M&TE #	GT4-PB12	GT4-PB24	GT4-PB10	GT4-PB11	GT4-PB26
Range	+/- 50 inwc	0 -1000 C	+/- 50 inwc	+/- 50 inwc	0 -1000 C
Error	+/- 0.2	+0.4 / -3.0	+ 0.5 / - 0.9	+ 0.1 / -0.4	+0 / -3.4
Name:	T14-12	T14-6	T14-5		
Description:	Condenser Exit Temp	CRR Alt. Temp	CRR Cond. Exit Temp.		
M&TE #	GT4-PB22	GT4-PB25	GT4-PB33		
Range	0-200 C	0-1000 C	0-200 C		
Error	+0.6/-1.6	+0 / -3.6	+0.2 / -1.7		

Table 1 shows the measuring equipment that was calibrated at the Standards Laboratory for the BSR.

Process parameters measured were:

DMR outer pressure, DMR Inner Pressure, DMR Bed Temperature, DMR Control Temperature, DMR Condenser Temperature, DMR H₂, DMR O₂, DMR N₂, DMR CO₂, DMR benzene, DMR argon, CRR outer pressure, CRR Inner Pressure, CRR Bed Temperature, CRR Control Temperature, CRR Condenser Temperature, CRR H₂, CRR O₂, CRR N₂, CRR CO₂, CRR benzene, CRR argon, and chiller bath temperature.

Process parameters controlled were:

Slurry Feed Rate, DMR Control Temperature, DMR outer pressure, DMR H₂, DMR CO₂ flow-rate, DMR Air flow-rate, CRR Control Temperature, CRR Air flow-rate.

Each MS was calibrated before and after each run with the certified calibration gas standard. The certification of analysis for the gases can be found on page 97 in the Laboratory Notebook⁵.

Table 2. Mass Spectrometer Calibration Checks

Run	Standard	Pre -1	Post-1	Pre -2	Post-2	Post-3
Mass Spec #1					Pre-3	
Date		8/5/2008	8/6/2008	8/7/2008	8/11/2008	8/12/2008
Hydrogen	1.01	1.0178	0.998	1.0131	1.025	1.023
Oxygen	4.12	4.2514	4.0931	4.1886	4.308	4.256
Nitrogen	60.8644	61.8957	60.3563	61.4151	63.038	62.645
Carbon Dioxide	29.94	30.052	29.3349	30.2803	30.561	30.694
Benzene	0.0256	0.0251	0.0247	0.0252	0.0257	0.0262
Argon	4.04	4.0833	3.9807	4.1003	4.186	4.169
Mass Spec #2						
Hydrogen	1.01	1.008	0.9635	0.9791	0.9875	0.9589
Oxygen	4.12	4.119	3.9044	4.0293	4.183	4.004
Nitrogen	60.8644	61.797	58.9369	60.6851	62.812	60.238
Carbon Dioxide	29.94	30.16	28.6782	29.8116	30.81	29.659
Benzene	0.0256	0.0277	0.0221	0.0224	0.0226	0.0224
Argon	4.04	4.079	3.8639	4.0141	4.17	4
Mass Spec #1		%Error	%Error	%Error	%Error	%Error
Hydrogen		0.77	-1.19	0.31	1.49	1.29
Oxygen		3.19	-0.65	1.67	4.56	3.30
Nitrogen		1.69	-0.83	0.90	3.57	2.93
Carbon Dioxide		0.37	-2.02	1.14	2.07	2.52
Benzene		-1.95	-3.52	-1.56	0.39	2.34
Argon		1.07	-1.47	1.49	3.61	3.19
Mass Spec #2						
Hydrogen		-0.20	-4.60	-3.06	-2.23	-5.06
Oxygen		-0.02	-5.23	-2.20	1.53	-2.82
Nitrogen		1.53	-3.17	-0.29	3.20	-1.03
Carbon Dioxide		0.73	-4.21	-0.43	2.91	-0.94
Benzene		8.20	-13.67	-12.50	-11.72	-12.50
Argon		0.97	-4.36	-0.64	3.22	-0.99

The raw calibration data is shown in the upper part of Table 2 and the %Error off the standard is shown in the lower portion. The %Error was calculated as:

$$\%Error = \frac{(Reading - Std)}{Std} \times 100$$

All values were well within the +/-10% error range except for the benzene readings on MS#2. We were unable to correct this within the expected timeframe allowed and accepted that the MS#2 benzene was within +/-15%.

Based on the results with the calibration gases, MS#2 was used for the DMR analyses and MS#1 was used for the CRR analyses to allow a more accurate reading of benzene leaving the CRR.

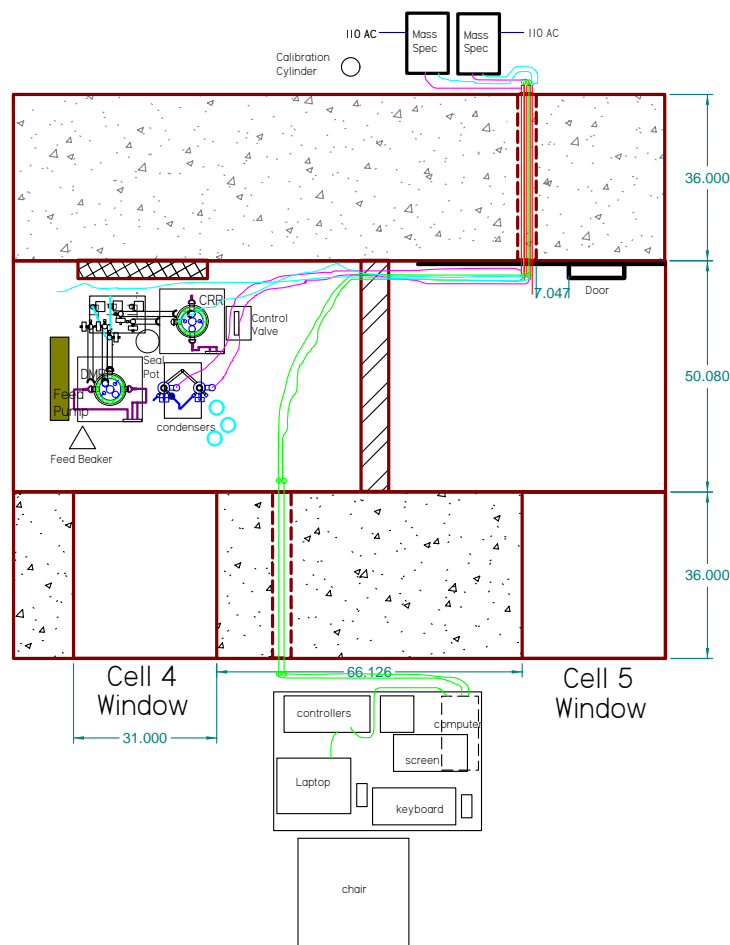


Figure 9. Total System Layout at Cell 4 (Simplified)

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 MSs 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 Knolles 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.

4.2 BSR OPERATING CONDITIONS FOR ACTUAL TANK 48H WASTE

Table 3 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 report¹, 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 3. BSR Process Operation Conditions compared to Pilot-Scale FBSR Conditions for Prod-4¹

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 [#]	1.17 g/min [#]	1.17 g/min [#]	1.17 g/min [#]
Carbon*	12.6 kg/hr (210 g/min)	0.26 g/min	0.20 g/min*	0.20 g/min*
Atomizing Air	9.85 SCFM (2.79E5 sccm)	0.0127 SCFM (360 sccm)	0-0.035 SCFM (0-1000 sccm) ^{&} Avg. 0.011 SCFM (312 sccm)	0-0.035 SCFM (0-1000 sccm) ^{&} 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 ^{&}	7.7 SCFM (2.18E5 sccm)	0.0099 SCFM (281 sccm)	&	&
CO ₂	8 SCFM (2.26E5 sccm)	0.01 SCFM (292 sccm)	0.011 SCFM (320 sccm)*	0.011 SCFM (320 sccm)*
N ₂ Purges ^{&}	25.9 SCFM 7.34E5 sccm)	0.034 SCFM (946 sccm)	&	&

*Adjusted BSR Operating Value during Simulant Runs based on system performance; [#]Approximate rates; [&]Oxygen and N₂ purges set by DMR Air supply (78%N₂/21%O₂) which is adjusted in specified range to maintain H₂ 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 Erwin 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 DMR¹. 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 $670^\circ C$ at the control thermocouple point.

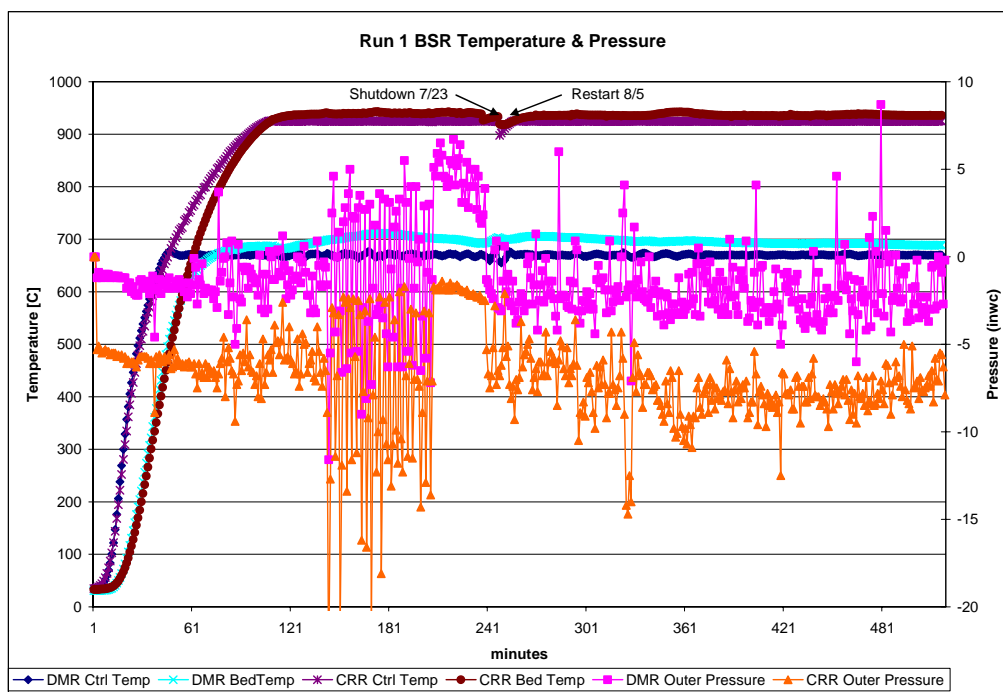


Figure 10. Run 1 BSR Temperature & Pressure

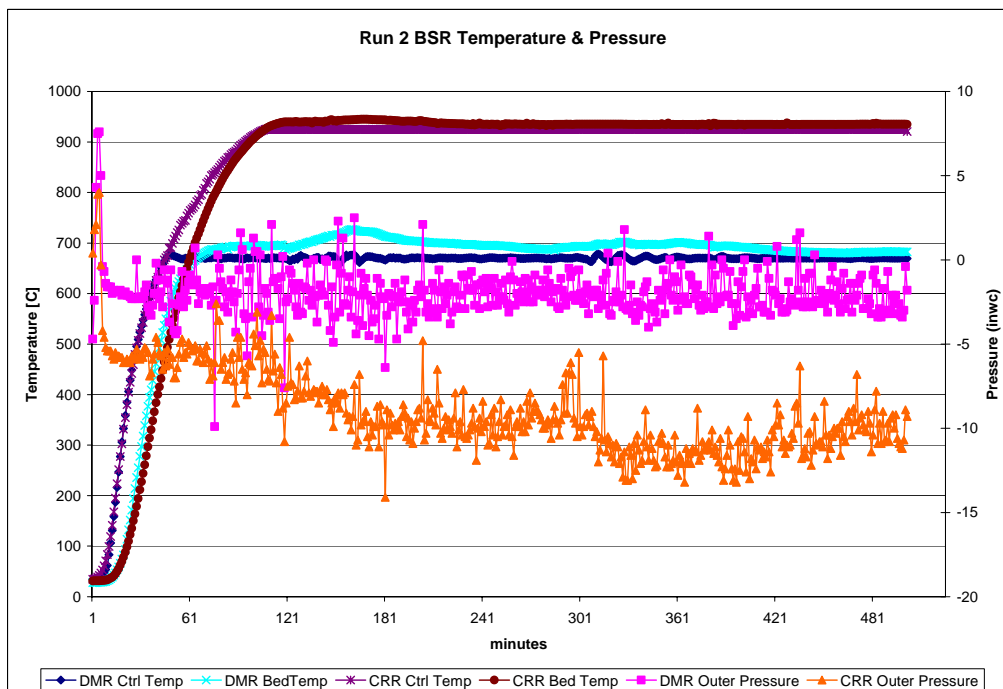


Figure 11. Run 2 BSR Temperature & Pressure

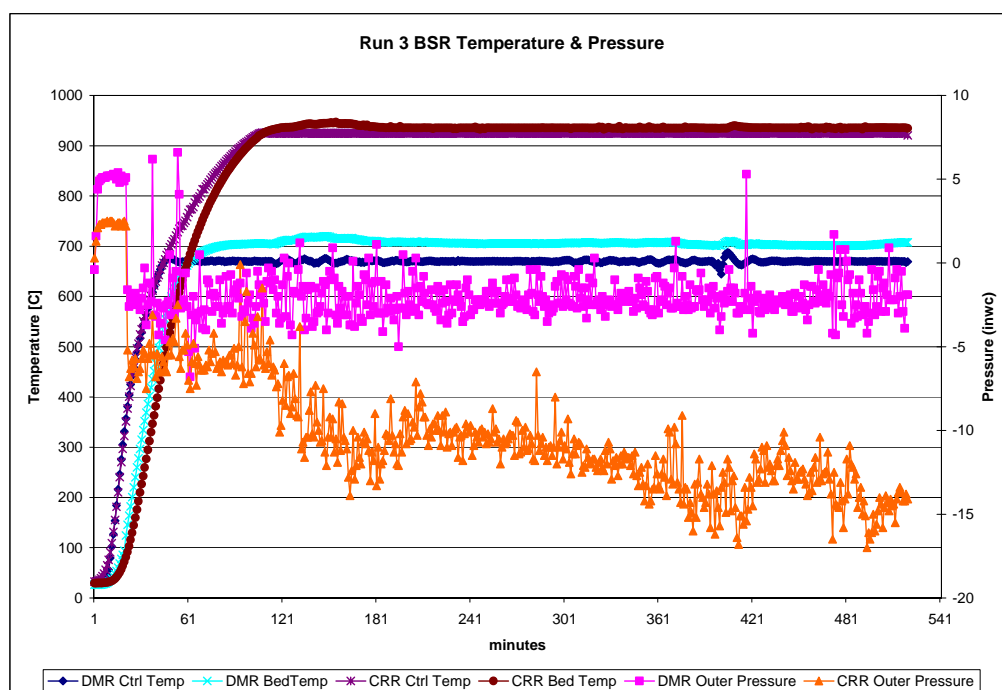


Figure 12. Run 3 BSR Temperature & Pressure

Temperature control for all runs was within $\pm 10^{\circ}\text{C}$ of set-point.

Run 1 had to be shutdown about 240 minutes after startup as seen in the trend in Figure 10. Though the BSR was leak checked prior to placement in the cell, a leak had developed in a CRR side joint where either the water or air enter due to handling while moving it to the cell. The leak caused an excessive amount of air and moisture to flow through the CRR dry ice condenser. The excessive moisture froze to create an excessively small restricting orifice in the dry ice condenser rendering the pressure control system ineffective.

It was remediated by doubling the capacity of the CRR dry ice condenser by adding a second condenser in parallel. However, upon restarting the unit, the leak in the CRR had self sealed itself due to the heat-up and cool-down cycle of the initial run so run 2 and run 3 ran flawlessly as seen in Figure 11 and Figure 12. The reason the joint self sealed was because the metal tubing expands and contracts much more than the quartz so the movement of the tubing pulled the seal back in upon cool down. A small amount of movement was allowed in the design such that the metal tube has some freedom to move through a graphite ferrule within the joint.

During a normal run, the pressure control was expected to maintain the DMR outer pressure to -2 inwc. Runs 2 and 3 met this expectation. 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.

Table 4. 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			DMR Argon		
	Min	Max	Avg	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	0.13	0.90	0.47
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	0.05	0.60	0.51
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	0.04	0.64	0.53

Table 5. 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			CRR Argon		
	Min	Max	Avg	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	0.52	0.89	0.72
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	0.50	0.71	0.67
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	0.45	0.73	0.69

The BSR used a DMR air supply (78%N₂/21%O₂) to control the DMR H₂ concentration so the N₂ and O₂ 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 H₂ between 1.5% and 4.0%. Table 4 shows the DMR H₂ vol% goes through ranges from about 1.0 vol% to 9 vol%. This variance is due to the fact that the H₂ 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 14, Figure 16, and Figure 18)

Comparing Table 4 to Table 5 shows that the destruction of H₂ and benzene in the CRR was virtually completed. For the H₂, 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 testing¹ 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).

Figure 13 through Figure 21 show the trends of the MS off-gas measurements for the DMR and CRR for the three consecutive radioactive BSR runs.

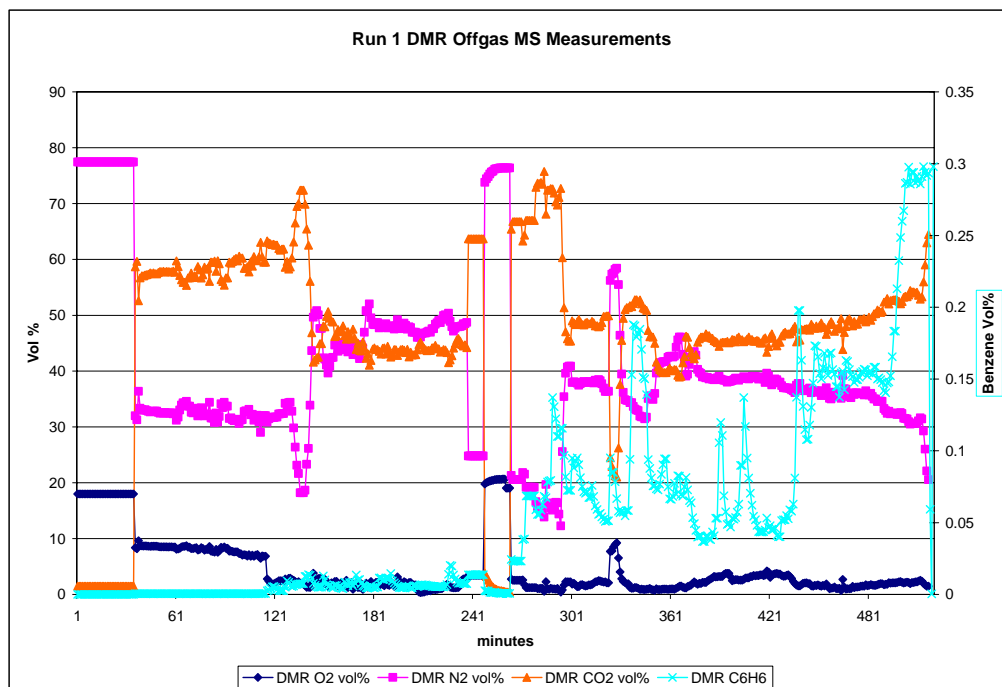


Figure 13. Run 1 DMR Off-gas Measurements

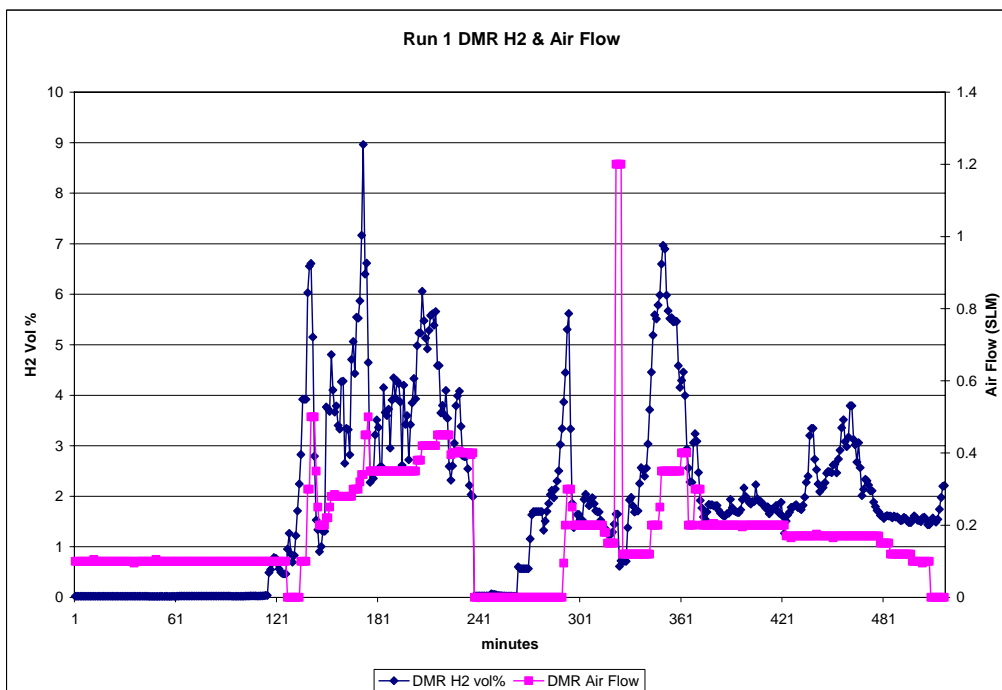


Figure 14. Run 1 DMR Off-gas H₂ & Air Flow

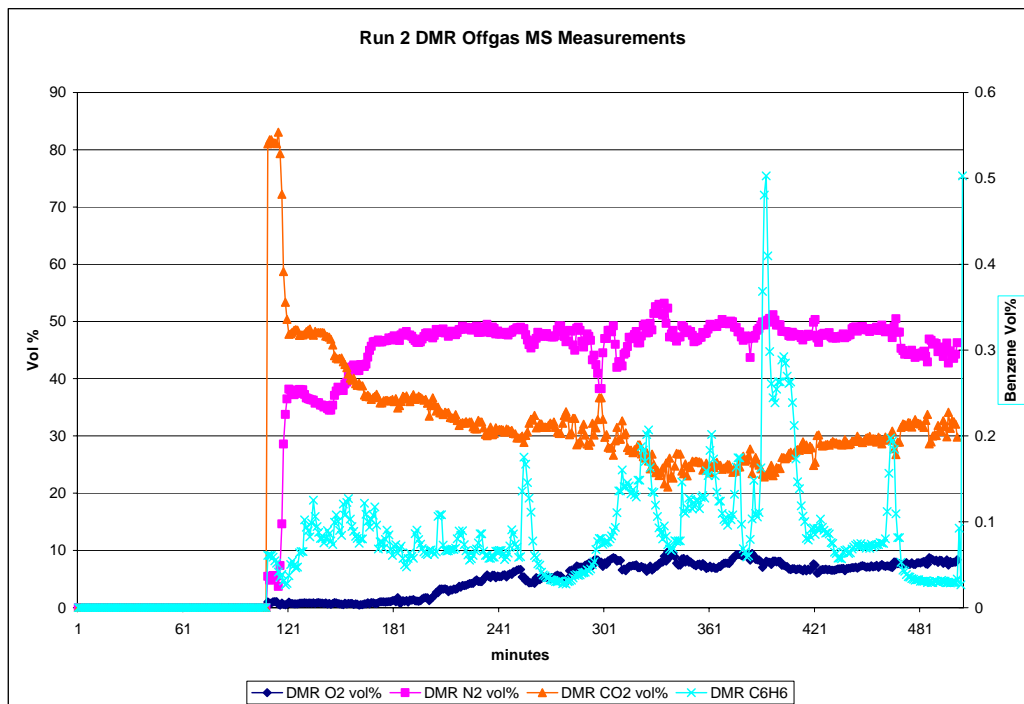


Figure 15. Run 2 DMR Off-gas Measurements

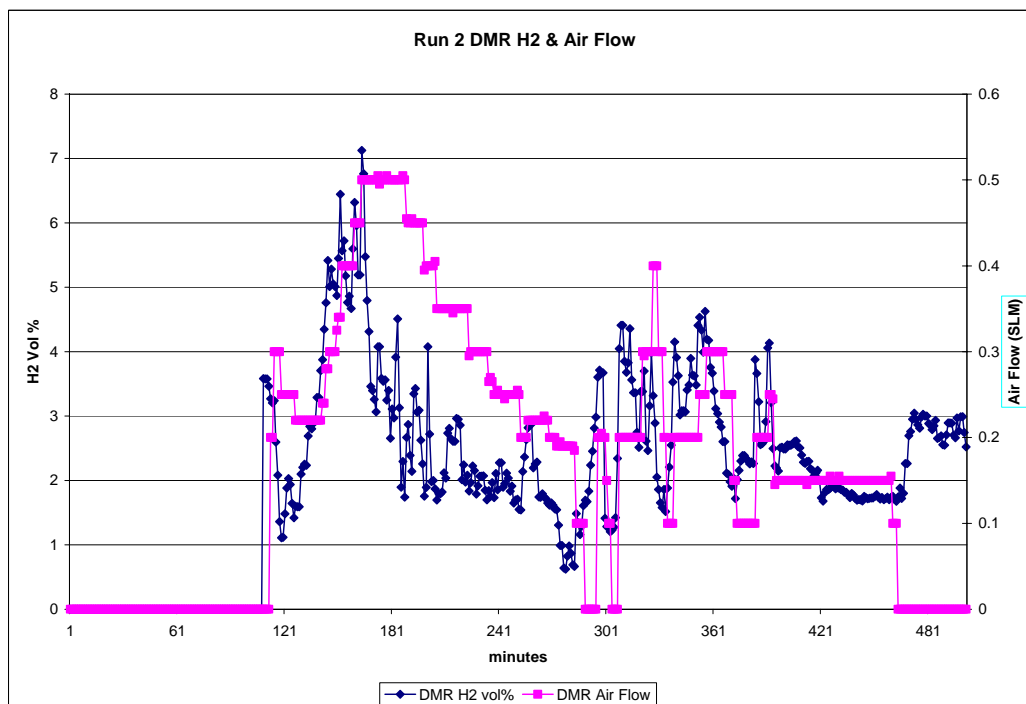


Figure 16. Run 2 DMR Off-gas H₂ & Air Flow

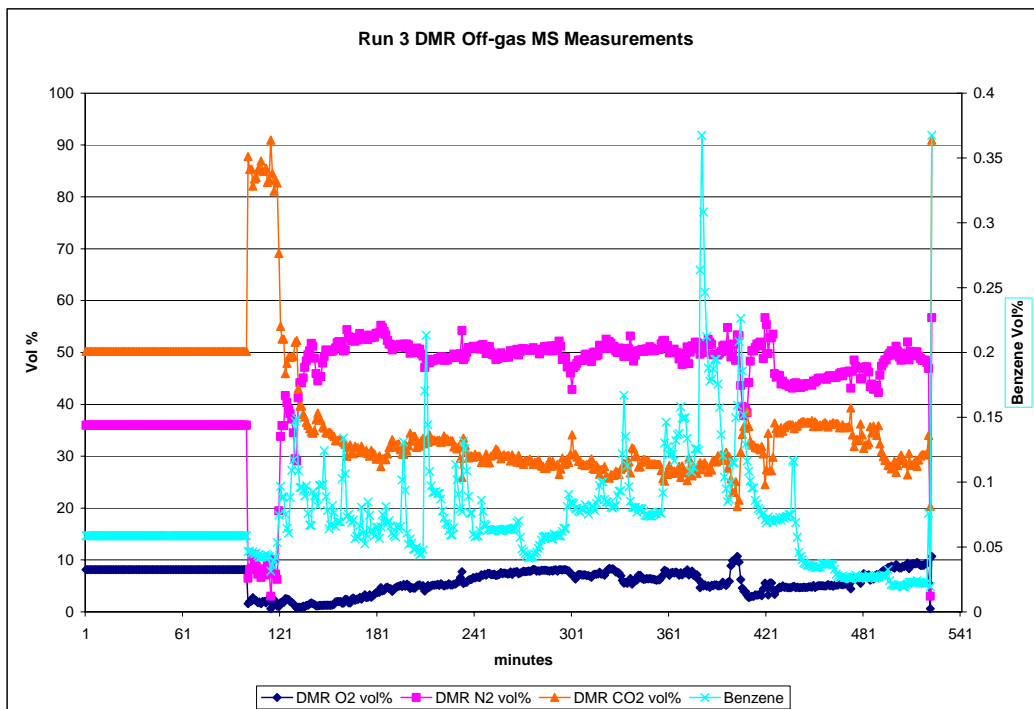


Figure 17. Run 3 DMR Off-gas Measurements

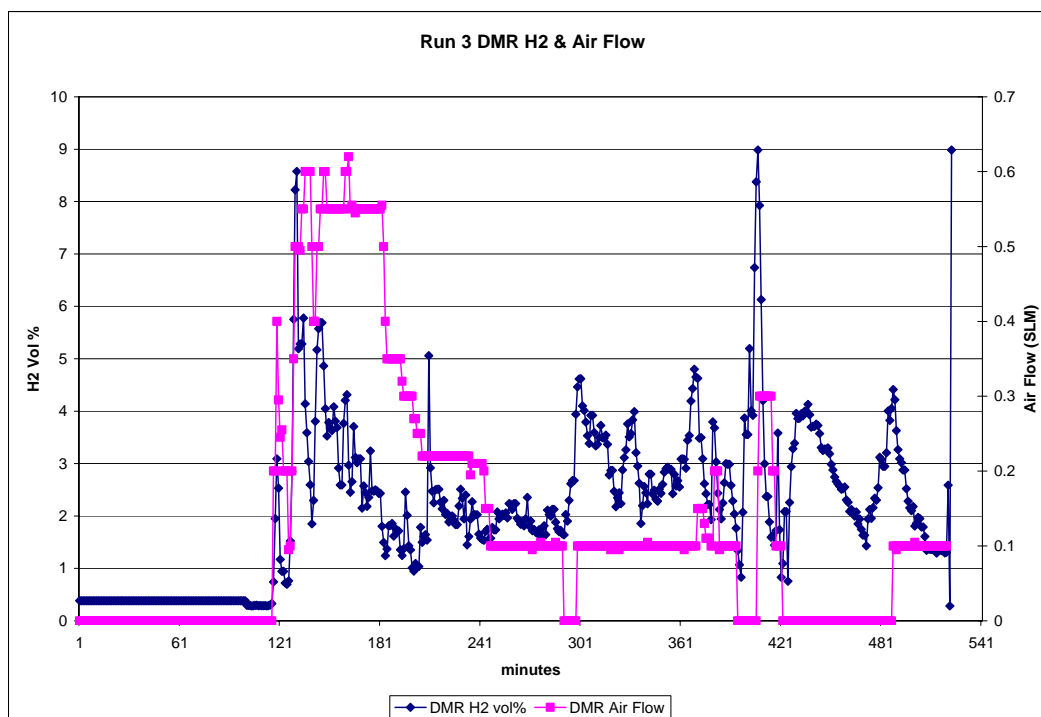


Figure 18. Run 3 DMR Off-gas H₂ & Air Flow

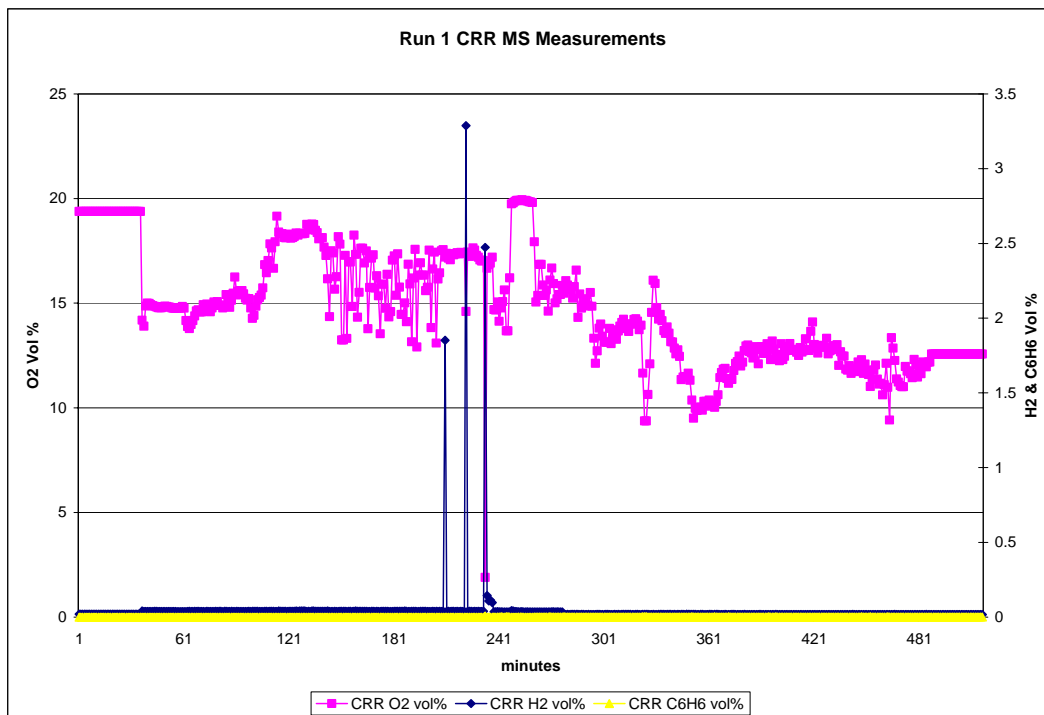


Figure 19. Run 1 CRR Off-gas MS Measurements

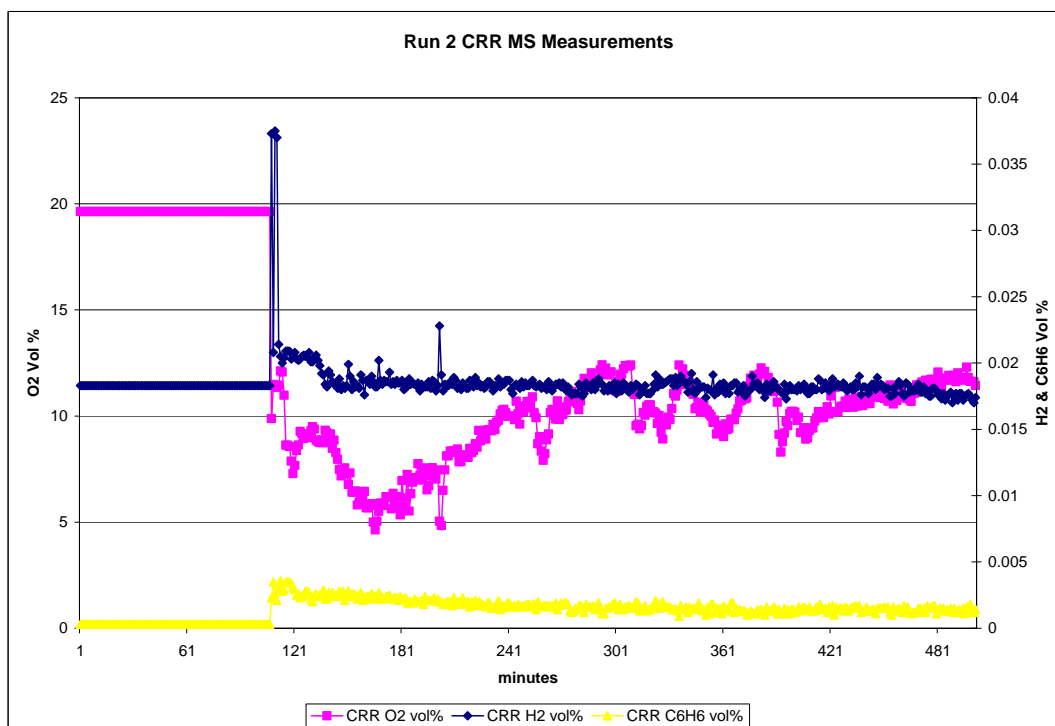


Figure 20. Run 2 CRR Offgas MS Measurements

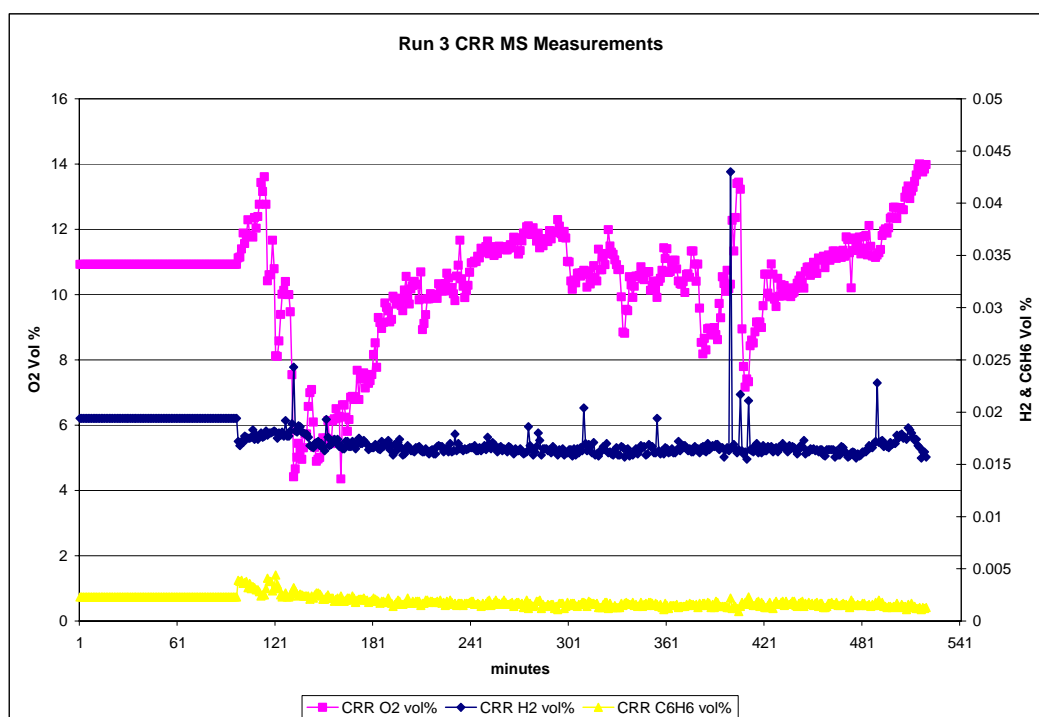


Figure 21. Run 3 CRR Offgas MS Measurements

Not shown on Figure 13 through Figure 21 above are the DMR CO₂ flow rate which flowed at a constant 321 sccm, the CRR air flow rate which flowed at a constant 400 sccm, and the vol% argon since it was no longer used as a blanket gas.

The DMR off-gas showed evidence of benzene with average values from 0.04% to 0.09% on a dry basis. A certain amount of benzene is expected in the DMR off-gas as the HRI testing¹ in 2006 showed an average about 0.18 vol% benzene on a wet basis.

Sufficient air (O₂) was added to the CRR to destroy any oxidizable species as evidenced by the lack of H₂ and benzene; and since the O₂ level never dropped below 4%. However, it would be prudent to raise the air flow rate to the CRR in future tests such that the O₂ concentration never drops below 10%.

5.0 ANALYSIS & OBSERVATIONS

5.1 ANALYSIS OF TANK 48H WASTE

Radioactive Tank 48H samples were obtained from a 3.0 L composite located in the shielded cells facility. Table 6 and Table 7 show characterization data for the radioactive sample that was obtained and analyzed in 2005.⁶

Table 6. Radioactive Tank 48H Data of HTF-E-05-021 Slurry Sample⁶

Tank 48H Radioactive			
Component	(mg/L)	Component	(mg/L)
Al	2014	Sn	<0.11
B	867	Sr	9
Ba	<0.008	Ti	826
Ca	43	U	7
Cd	<0.017	V	<0.007
Ce	5	Zn	5
Cr	70	Zr	1.47
Cu	4	F	14
Fe	169	Cl	172
K	5155	NO ₂	23750
La	<0.032	NO ₃	14250
Mg	19	SO ₄	323
Mn	6	PO ₄	428
Mo	<0.053	wt% Total solids	20.19
Na	87899	wt% Insoluble solids	3.05
Ni	<0.015	wt% Soluble solids	17.14
P	129	pH	14
Pb	<0.283	Density (g/mL)	1.14
S	378		
Si	125		

Table 7. The High Pressure Liquid Chromotography (HPLC) results of HTF-E-05-021 T48 Slurry Sample⁶

Analyte	Concentration, (mg/L slurry)	St. Dev, (mg/L)
TPB Anion	21,000	970
Calculated KTPB	23796	-
3PB	74	16.5
2PB	142	19
1PB	151	7.6
Phenol	771	22
Biphenyl	420	54.3

5.2 ANALYSIS OF SOLID DMR PRODUCT

5.2.1 Sample Preparation

The bottom 4 inches of product in the DMR basket were separated from the remainder of the DMR product and analyzed separately since this portion of the product was in the proper reactor heat zone as shown in Figure 3. The upper portions of the product were analyzed as well, but are not discussed since the process conditions for this portion of the product are unknown.

Each sample of solid product was first ground and sieved. A mortar and pestle was used for grinding, and all sample material outside of the zirconium dioxide beads was ground to pass a #20 sieve. The beads were manually removed from the sample material as soon as they were free of the product that was clinging to them.

The ground solid product was put in sample jars, capped, and agitated to homogenize the powder. Samples of each DMR product were taken out and sent for XRD, REDOX, and HPLC analyses. A separate sample of solids was weighed out for water dissolution. This sample was added to a bottle of deionized water in the ratio of 1 gram of solids per 100 mL of water. A magnetic stir bar was added to the bottle and stirring was provided for at least 2 hours at ambient temperature.

All of the slurry resulting from the water dissolution was passed through a 0.45 micron filter pad using laboratory vacuum. All insoluble solids were collected and air dried. Weight of the insoluble sample was recorded and the sample was sent to the Analytical Development Dept. (ADD) for XRD. The weight of the insoluble solids could then be subtracted from the input weight to indicate the amount of soluble material in the DMR product. Filtrate was submitted for cation analyses by Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES) and for anion analysis by Ion-Chromotography (IC) anions.

5.2.2 Sample Analyses

Table 8. Mass of DMR Products

	Run 1	Run 2	Run 3
DMR Mass Total, g	67.85	88.84	70.73
Wt% Insoluble	4.0	5.5	10.9

The mass reported is of the total product in the DMR. The wt% insoluble solid was largely due to un-burnt coal and coal ash. Run 1 had less coal because it was run longer and in two parts due to unrelated process problems with the CRR dry ice condenser. Run 3 had more coal because the unit was off center which caused the product to form along the wall. The lack of air diffusion to the product along the wall probably contributed to the slower burning of coal. The actual mass of carbonate product was less than 70 grams per run, but that value will be used conservatively to show various criteria were met.

Table 9. DMR Product HPLC Analyses for Organics

DMR HPLC (mg/kg)	Run 1	Run 2	Run 3
TPB Anion	<5.	<5.	<5.
3PB	<5.	<5.	<5.
2PB	<5.	<5.	<5.
PBA	<5.	<5.	<5.
Phenol	<5.	<5.	<5.
Biphenyl	<5.	<5.	<5.

The feed TPB anion concentration showed 21000 mg/L in Table 7. 300ml of feed were fed per run. All runs show less than the detection limit of 5 mg/kg TPB in the estimated 70 grams of product. Therefore the TPB destruction calculates to:

$$300ml_{\text{ feed }} \times \frac{21000mg_{\text{ TPB }}}{1000ml} = 6300mg_{\text{ TPB Fed }}$$

$$70g_{\text{ Pr oduct }} \times \frac{5mg_{\text{ TPB }}}{kg_{\text{ product }}} \times \frac{kg}{1000g} \leq 0.35mg_{\text{ TPB Pr oduct }}$$

$$\frac{6300 - 0.35}{6300} \times 100 \geq 99.99\% \text{ destruction of TPB.}$$

99.99% is greater than the required minimum of 99.9%. Since the Tank 48 feed is subjected to the DMR operating temperature above 600°C, no organic, including TPB salts and its by-products in the feed are expected to remain with the FBSR product that may contribute to the Tank Farm receipt tank CLFL at 100°C.

Table 10. DMR and Insoluble Phase Analysis by X-Ray Diffraction (XRD)

	Run 1	Run 2	Run 3
XRD DMR			
	Na ₂ CO ₃ •H ₂ O	Na ₂ CO ₃ •H ₂ O	Na ₂ CO ₃ •H ₂ O
	Na ₂ CO ₃	Na ₂ CO ₃	Na ₂ CO ₃
	Na ₃ H(CO ₃) ₂ •2H ₂ O		Na ₃ H(CO ₃) ₂ •2H ₂ O
	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O
	Na ₂ Al ₂ SiO ₆		Na ₂ Al ₂ SiO ₆
XRD INSOLUBLES			
	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O
	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 DMR product was primarily made up of soluble carbonates. The three most abundant species were thermonatrite, [Na₂CO₃•H₂O], sodium carbonate, [Na₂CO₃], and trona, [Na₃H(CO₃)₂•2H₂O]. It is thought that the minor amount of silicates and aluminosilicates (Na₈(AlSiO₄)₆(OH)₂•2H₂O which is hydroxysodalite, nepheline, muscovite and SiO₂) may have come from the coal ash and/or the Si and Al in the waste (Table 6). See APPENDIX 1 for XRD graphs of products and the insoluble portion of the products.

Table 11. DMR REDuction/OXidation (REDOX) of Product

	Run 1	Run 2	Run 3
REDOX- Fe²⁺/Fe(tot)	0.58	0.98	1
REDOX - Fe²⁺/Fe³⁺	1.4	Fully reduced	Fully reduced

The REDOX or Fe²⁺/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 showed the reactions occurred in a reducing atmosphere as was required for pyrolysis.

Table 12. DMR Anions in mg/L of Dissolved Product

Soluble	Run 1	Run 2	Run 3
FLUORIDE	<2.5	<2.5	<2.5
FORMATE	<2.5	<2.5	<2.5
CHLORIDE	32	25	21
NITRITE	<2.5	<2.5	<2.5
NITRATE	<2.5	<2.5	<2.5
PHOSPHATE	33	29	14
SULFATE	80	55	38
OXALATE	<2.5	<2.5	18
BROMIDE	<2.5	<2.5	<2.5

To determine the destruction of NO_2 and NO_3 , 4 grams of DMR product were dissolved into 400 ml of DI water. Thus:

$$\frac{2.5\text{mg}}{1000\text{ml}} \times \frac{400\text{ml}}{4\text{g}_{\text{product}}} \leq 0.25 \frac{\text{mg}}{\text{g}_{\text{product}}} \text{ of } \text{NO}_2 \text{ and of } \text{NO}_3 \text{ in the product based on lower detection limit in Table 12.}$$

$$70\text{g}_{\text{product}} \times \frac{0.25\text{mgNO}_x}{\text{g}_{\text{product}}} \leq 17.5\text{mgNO}_x$$

With 70g product, 17.5 mg of NO_2 and of NO_3 is the lower limit of the measurement.

The Tank 48H waste contained 14250 mg/L nitrate and 23750 mg/L nitrite as shown in Table 6. Each run fed 300 ml of waste to the DMR. Thus:

$$300\text{ml} \times \frac{14250\text{mgNO}_3}{1000\text{ml}} = 4275\text{mgNO}_3$$

$$300\text{ml} \times \frac{23750\text{mgNO}_2}{1000\text{ml}} = 7125\text{mgNO}_2$$

Converting to % destruction:

$$\frac{4275 - 17.5}{4275} \times 100 \geq 99.6\% \text{ destruction of nitrates (shown) and}$$

$$\frac{7125 - 17.5}{7125} \times 100 \geq 99.8\% \text{ destruction of nitrites (shown).}$$

The process met the criteria of showing greater than 99% destruction of NO_2 and NO_3 .

Table 13. Soluble Cations from DMR Product vs Feed

	Run 1	Run 2	Run 3	Feed
Soluble ICP-ES	wt%	wt%	wt%	wt%
Al	1.000	0.751	0.715	1.039
B	0.561	0.392	0.417	0.447
Ca	0.062	0.051	0.048	0.022
Cr	0.021	0.003	0.008	0.036
Fe	0.002	0.003	0.003	0.087
K	1.180	0.926	0.851	2.661
Mg	0.004	0.006	0.005	0.010
Na	47.800	38.900	36.600	45.366
P	0.139	0.111	0.110	0.067
S	0.254	0.196	0.222	0.195
Si	0.077	0.077	0.122	0.065
Sr	0.004	0.005	0.003	0.005

The soluble cations in the DMR products are present at similar ratios as they are in the starting Tank 48H slurry. Sodium is present in the range of 36 to 46 wt% and potassium and aluminum are present in the range of 0.7 to 1.1 wt%. These are the main soluble cations present in the DMR products along with lower levels of B, Ca, P, S and Si.

Table 14. Validation Results⁴

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	<table><tr><td>Na₂CO₃•H₂O</td></tr><tr><td>Na₂CO₃</td></tr><tr><td>Na₃H(CO₃)₂•2H₂O</td></tr><tr><td>Na₈(AlSiO₄)₆(OH)₂•2H₂O</td></tr><tr><td>Na₂Al₂SiO₆</td></tr></table>	Na ₂ CO ₃ •H ₂ O	Na ₂ CO ₃	Na ₃ H(CO ₃) ₂ •2H ₂ O	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O	Na ₂ Al ₂ SiO ₆
Na ₂ CO ₃ •H ₂ O									
Na ₂ CO ₃									
Na ₃ H(CO ₃) ₂ •2H ₂ O									
Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O									
Na ₂ Al ₂ SiO ₆									
Verify reducing environment (pyrolysis) in DMR	DMR reactions are pyrolytic 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 <17.5 mg vs 7125 mg NO ₂ fed (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	<table><tr><td>Na₈(AlSiO₄)₆(OH)₂•2H₂O</td></tr><tr><td>Na_{0.75}K_{0.24}Al_{0.95}Fe_{0.13}Si_{0.77}O₄</td></tr><tr><td>NaFeTiO₄</td></tr><tr><td>Muscovite aluminosilicate</td></tr><tr><td>SiO₂</td></tr></table>	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O	Na _{0.75} K _{0.24} Al _{0.95} Fe _{0.13} Si _{0.77} O ₄	NaFeTiO ₄	Muscovite aluminosilicate	SiO ₂
Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O									
Na _{0.75} K _{0.24} Al _{0.95} Fe _{0.13} Si _{0.77} O ₄									
NaFeTiO ₄									
Muscovite aluminosilicate									
SiO ₂									
Offgas Measurement of H ₂ , O ₂ , N ₂ , CO ₂ , Benzene	The DMR and CRR offgas had expected levels (*see Table 4 and Table 5) 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 4.45-5.51 vol% O ₂ 40.1-45.4 vol% N ₂ 32.8-48.2 vol% CO ₂ 0.04-0.09 vol% Benzene CRR Offgas Averages: 0.02-0.03 vol% H ₂ 9.8-14.4 vol% O ₂ 58.4-62.7 vol% N ₂ 14.7-21 vol% CO ₂ 0.00 vol% Benzene*					

The Tank 48H radioactive runs in the BSR met all the validation results⁴ as shown in Table 14.

Though not associated with a validation requirement, the LWO customer requested analysis of the DMR products for mercury. Results showed no detectable mercury from the three runs with a detection limit of 0.497 micrograms of mercury per gram of solid DMR product. As expected, the steam stripped the mercury away from the product at high pH conditions. Though the feed sample results for HTF-E-05-021⁶ showed no mercury because the method probably drove it off, 20.4 mg/L mercury was measured in sample HTF-E-04-049⁷ which also came from Tank 48H.

5.3 ANALYSIS OF CONDENSATES

Table 15 shows the Volatile Organic Analyses (VOA) and the Semi-Volatile Organic Analyses (SVOA) of the off-gas condensates. VOA is the quantitative analysis of solids/liquids/gases for most organic compounds which boil $\leq 200^{\circ}\text{C}$ and partition favorably into the gas phase. SVOA is the quantitative organics analysis for radioactive and non-radioactive samples containing high boiling analytes.

At the start of the 3 runs, there is about 100ml of process water in the DMR bubbler and 200 ml of process water in the CRR bubbler. All steam that is condensed from the DMR and CRR condenses into the DMR bubbler and CRR bubbler respectively. As liquid accumulates in either bubbler, it reaches an overflow where it flows into a sealed collection container. At the end of each run, the DMR collection container and the CRR collection container are emptied, but the fluid left over in each bubbler remains for the beginning of the next run. So the expectation is that each run will have more organics in the DMR bubbler than the last. Since that was not the case, the sampling technique for the DMR bubbler data may have been an issue. Benzene and biphenyl were expected in the DMR bubbler due to the partial destruction of TPB.

The DMR dry ice condensers were in series and the first condenser was expected to have more benzene than the second as was the case. Though these condensers did remove benzene, they did not remove it all as can be seen in the off-gas data in Table 4.

The CRR destroys organics by design. The off-gas data in Table 5 confirmed the destruction of benzene, but Table 15 shows a large amount of benzene left the CRR in run 2 as well as some benzene in run 3. This data contradicts itself since the run 2 benzene is much greater than the run 3 benzene ($7500 \gg 4.3$) and does not represent the process.

The DMR collection container typically ends up with about 650ml of aqueous per run while the CRR collection container ends up with about 350ml per run.

Table 15. Organic Analyses of Condensates

VOA / SVOA	Run 1 VOA, mg/L	Run 1 SVOA, mg/L	Run 2 VOA, mg/L	Run 2 SVOA, mg/L	Run 3 VOA, mg/L	Run 3 SVOA, mg/L
DMR Bubbler	Benzene = 50.	Phenol = 28.	Benzene = 60.	no analytes detected	no analytes detected	Phenol = 100
	Toluene = 5.7	Biphenyl = 18.				Benzonitrile = 7.6
						2-methylphenol = 2.0
						4-methylphenol = 2.2
						Acetophenone = 2.1
						Biphenyl = 17.
						Phthalates = 26.
CRR Dry Ice Cond.	no analytes detected	no analytes detected	Benzene = 130.	no analytes detected	no analytes detected	Phthalates = 94.
			Biphenyl = 53.			
CRR Bubbler	no analytes detected	Phenol = 30.	Benzene = 7500.	Phenol = 48.	Benzene = 4.3	no analytes detected
		Biphenyl = 16.	Toluene = 340.	Biphenyl = 63.		
		Benzonitrile = 4.1				
DMR Dry Ice #1	Benzene = 7300.	Biphenyl = 500.	Benzene = 5100.	Phenol = 8.8	Benzene = 2300.	Benzaldehyde = 7.1
		Naphthalene = 140.		Benzonitrile = 5.8		Benzonitrile = 2.3
		Xylenes = 46.		Hexanal = 5.4		Napthalene = 33.
		Benzonitrile = 35.				Biphenyl = 260.
		o-Terphenyl = 29.				Dibenzofuran = 5.8
		Benzofuran = 16.				o-Terphenyl = 14.
		Hexanal = 14.				m-terphenyl = 6.1
		m-Terphenyl = 12.				p-Terphenyl = 6.9
		Ethylbenzene = 10.				
		Benzaldehyde = 9.9				
		Dibenzofuran = 8.5				
		2-Methylbenzofuran = 8.0				
		Methoxybenzene = 3.1				
DMR Dry Ice #2	Benzene = 360.	Benzonitrile = 18.	Benzene = 940.	Benzonitrile = 12.	Benzene = 1400.	Biphenyl = 190.
	Biphenyl = 6.7	Phenol = 16.	Toluene = 190.	Phenol = 12.		Phthalates = 180.
		Biphenyl = 6.8	Naphthalene = 110.	Hexanal = 6.1		Phenol = 33.
		Acetophenone = 1.8		Biphenyl = 6.0		Napthalene = 32.
		Benzofuran = 1.1				Benzonitrile = 15.
						Hexanal = 14.
						o-Terphenyl = 8.5
						Benzofuran = 8.0
						Dibenzofuran = 3.4
						Heptanal = 3.0
						m-terphenyl = 3.0
						Ethylbenzene = 2.5
						p-Xylene = 2.3
						2-Nonaone = 2.3
						Nonane = 1.9
						Decyl trifluoroacetate 1.9
						Tridecane = 1.9
						2-Phenylpyridine = 1.9
						2-Heptanone = 1.7

Table 16. Radioactivity Distribution of Feed to Product

Run	Feed % rad.	DMR Bubbler % rad.	CRR Bubbler % rad.	Product % 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

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 2005.⁶ Each run used 300ml of feed. As shown in Table 16, the majority of the radioactivity ended up in the product (based on calculation). The calculations are shown in APPENDIX 2.

5.4 OBSERVATION OF OFF-GAS

Analysis of the off-gas was performed in real time and was shown in section 4.2 of this report. However, two species of gas that were not measured due to measurement difficulty were NO and NO₂. Fortunately, NO₂ 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 NO₂ 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 H₂ concentration leaving the DMR, i.e. excess hydrogen, was also a good indication that all the NO_x was destroyed in the vapor phase.

5.5 COMPARISON OF SIMULANT WASTE WITH ACTUAL WASTE

Table 17. Simulant Characterization Data

Tank 48H Simulant			
Component	(mg/L)	Component	(mg/L)
Al	1918	Ru	<1
B	573	S	122
Ba	0.68	Si	116
Ca	90.3	Sn	16.8
Cd	<1	Sr	16.6
Ce	3.47	Ti	650
Cr	37.1	Zn	4.84
Cu	4.48	Zr	<1
Fe	144	F	<92
K	2983	Cl	136
La	1.06	NO ₂	19877
Mg	1.07	NO ₃	11637
Mn	30.5	SO ₄	185
Mo	7.33	PO ₄	357
Na	73182	wt% Total solids	17.45
Ni	10.4	wt% Insoluble solids	1.68
P	170	wt% Soluble solids	15.8
Pb	17.9	pH	14
Pd	2.11	Density (g/mL)	1.09
Rh	6.68		

Table 4-8 and 4-9 from Ref.1.

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. Table 17 shows the characterization data (obtained from Analysis Results Tables 4-8 and 4-9 from Ref.1)

Table 18. Tank 48H Simulant vs Actual Tank 48H Waste Comparison

	Simulant	Actual		Simulant	Actual
Component	mg/L	mg/L		Normalized	Normalized
Al	1918	2014		5.96	5.06
B	573	867		1.78	2.18
Ba	0.68	0		0.00	0.00
Ca	90.3	43		0.28	0.11
Cd	<1	0		0.00	0.00
Ce	3.47	5		0.01	0.01
Cr	37.1	70		0.12	0.18
Cu	4.48	4		0.01	0.01
Fe	144	169		0.45	0.42
K	2983	5155		9.27	12.96
La	1.06	<0.032		0.00	0.00
Mg	1.07	19		0.00	0.05
Mn	30.5	6		0.09	0.02
Mo	7.33	<0.053		0.02	0.00
Na	73182	87899		227.33	220.93
Ni	10.4	<0.015		0.03	0.00
P	170	129		0.53	0.32
Pb	17.9	<0.283		0.06	0.00
Pd	2.11			0.01	0.00
Rh	6.68			0.02	0.00
S	122	378		0.38	0.95
Si	116	125		0.36	0.31
Sn	16.8	<0.11		0.05	0.00
Sr	16.6	9		0.05	0.02
Ti	650	826		2.02	2.08
U		7		0.00	0.02
Zn	4.84	5		0.02	0.01
Zr	<1	1.47		0.00	0.00
F	<92	14		0.00	0.04
Cl	136	172		0.42	0.43
NO ₂	19877	23750		61.75	59.70
NO ₃	11637	14250		36.15	35.82
SO ₄	185	323		0.57	0.81
PO ₄	357	428		1.11	1.08
wt% Total solids	17.45	20.19			
wt% Insoluble solids	1.68	3.05			
wt% Soluble solids	15.8	17.14			
pH	14	14			
Density (g/mL)	1.09	1.14			

Data from Table 6, “Radioactive Tank 48H Data of HTF-E-05-021 Slurry Sample” and from Table 17, “Simulant Characterization Data”, were combined into Table 18. By normalizing the component data it becomes clear that both liquids contain nearly the same ratios of the major components Al, B, K, Na, Ti, NO₂, NO₃, and PO₄. The solids, pH, and density data also showed fairly good agreement. The detailed report on the simulant development is SRNL-LWP-2004-0042⁸ and a detailed report of the simulant validation is WSRC-LWP-2004-00009⁹.

5.6 COMPARISON OF DMR PRODUCTS AND KEY PROCESS CONDITIONS

Table 19. FBSR Simulant vs BSR Simulant vs BSR Tk48H Waste Comparison

Performance Criteria	FBSR Simulant ¹	BSR Simulant ¹⁰	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 ₂ CO ₃ •H ₂ O	Na ₂ CO ₃ •H ₂ O	Na ₂ CO ₃ •H ₂ O
	Na ₂ CO ₃	Na ₂ CO ₃	Na ₂ CO ₃
	Na ₃ H(CO ₃) ₂ •2H ₂ O	Na ₃ H(CO ₃) ₂ •2H ₂ O	Na ₃ H(CO ₃) ₂ •2H ₂ O
	Nepheline	Na ₂ Al ₂ SiO ₆	Na ₈ (AlSiO ₄) ₆ (OH) ₂ •2H ₂ O
	Cristobalite	Nepheline	Na ₂ Al ₂ SiO ₆
	Cristobalite		
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 1for 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 > 99.8% destruction of NO ₂
Check if DMR product has insoluble carbonate	Nepheline	Nepheline*	Na SiAl oxide hydrate
	NaFeTiO4	Na8(AlSiO4)6(NO3)2	Hydrosodalite
	Quartz	NaFeTiO4	nepheline
		Quartz	NaFeTiO4
		ZrO2	Muscovite - 3T
	No insoluble carbonate detected.	No insoluble carbonate detected.	Quartz No insoluble carbonate detected.
Offgas Measurement of H ₂ , O ₂ , N ₂ , CO ₂ , Benzene	Average DMR offgas on dry basis: 1.1-2.5 vol% H ₂ 0.07-3.54 vol% O ₂ 22.8-45.1 vol% CO ₂ 0.5-1.7 vol% Benzene	Average DMR offgas on dry basis: 1.76-1.90 vol% H ₂ 0.38-3.96 vol% O ₂ 47.8-61.2 vol% N ₂ 45.7-51.9 vol% CO ₂ 0.04 vol% Benzene	Average DMR offgas on dry basis: 2.06-2.64 vol% H ₂ 4.45-5.51 vol% O ₂ 40.1-45.4 vol% N ₂ 32.8-48.2 vol% CO ₂ 0.04-0.09 vol% Benzene
	CRR Offgas Averages: 10.1-11.6 vol% O ₂ 15.7-21.6 vol% CO ₂ 0.00-2.3 ppm THC	CRR Offgas Averages: 0.05 vol% H ₂ 3.43-11.7 vol% O ₂ 60.2-70.4 vol% N ₂ 21.0-22.4 vol% CO ₂ 0.00 vol% Benzene*	CRR Offgas Averages: 0.02-0.03 vol% H ₂ 9.8-14.4 vol% O ₂ 58.4-62.7 vol% N ₂ 14.7-21 vol% CO ₂ 0.00 vol% Benzene*

FBSR Data taken from Table 4-8 in the Hazen Report¹.
BSR Simulant data taken from SRNL-PSE-2008-00162¹⁰.
*BSR simulant data from last two runs only.

Table 19 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 Erwin 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.

Table 19 also shows that the products formed from running the simulant are very nearly the same as the products formed from running the actual Tank 48H waste.

6.0 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, $[\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}]$, sodium carbonate, $[\text{Na}_2\text{CO}_3]$, and trona, $[\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}]$ 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 Erwin coal ash. The percent insoluble solids in the products were 4 to 11 wt% for the radioactive runs.
- ▶ The $\text{Fe}^{+2}/\text{Fe}_{\text{total}}$ 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 product for all three runs.
- ▶ 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.

7.0 RECOMMENDATIONS

Determine the source of the toluene and naphthalene found in the DMR bubbler and dry ice condenser samples.

8.0 QUALITY ASSURANCE & SAFETY

All the data reported in this study were developed under the quality assurance given in the Technical Task and Quality Assurance Plan SRNL-PSE-2007-00022, Rev. 1³. The research program and task plan were developed to address the Technical Task Request SP-TTR-2006-00006, Rev. 1, Mar. 12, 2007.² The data are recorded in laboratory notebook WSRC-NB-2007-00175.⁵

The Hazards Analysis Package¹¹ (HAP) which details all the risks and mitigations was saved as SRNL-PSE-2008-00153. Since the H₂ gas generation from steam reforming exceeded the past limit in the 773-A Design Safety Analysis (DSA), a Consolidated Hazard Analysis Package¹² (CHAP) was written as WSRC-TR-2007-00457, Rev. 3 to address this issue. A change was made in the H₂ gas generation limit, however, this change did not affect the ultimate safety limit of ensuring that the concentration of flammable gases in the cell remain less than 25% of the Lower Flammability Limit (LFL).

APPENDIX 1. XRD GRAPHS OF DMR PRODUCTS

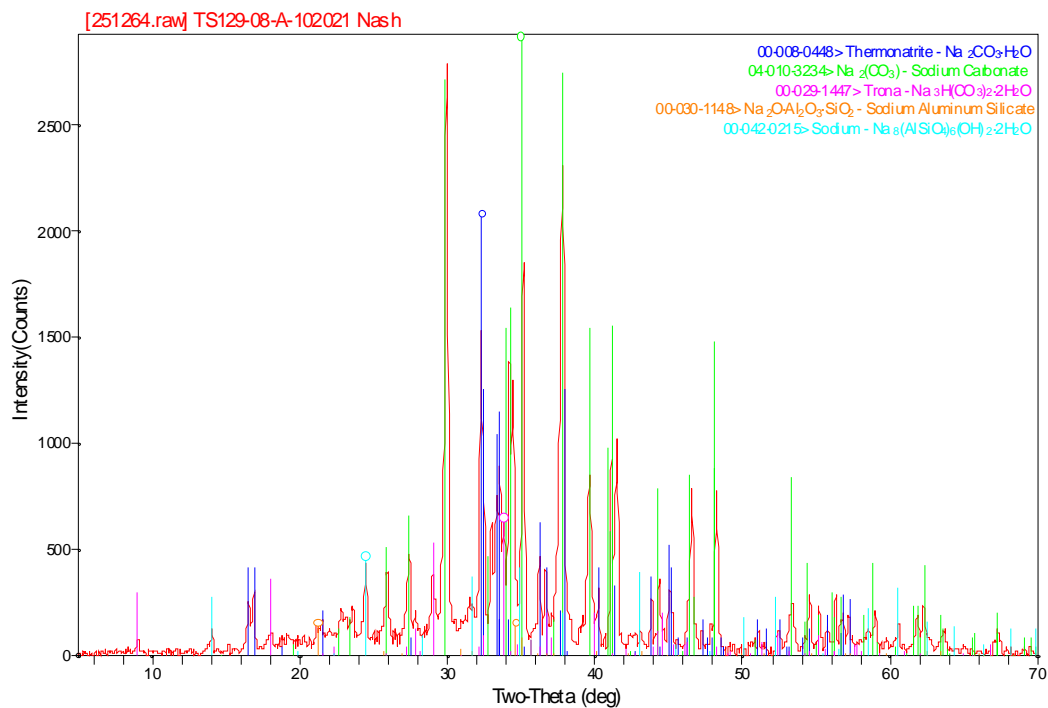


Figure A-1. Run 1 Bottom Product XRD

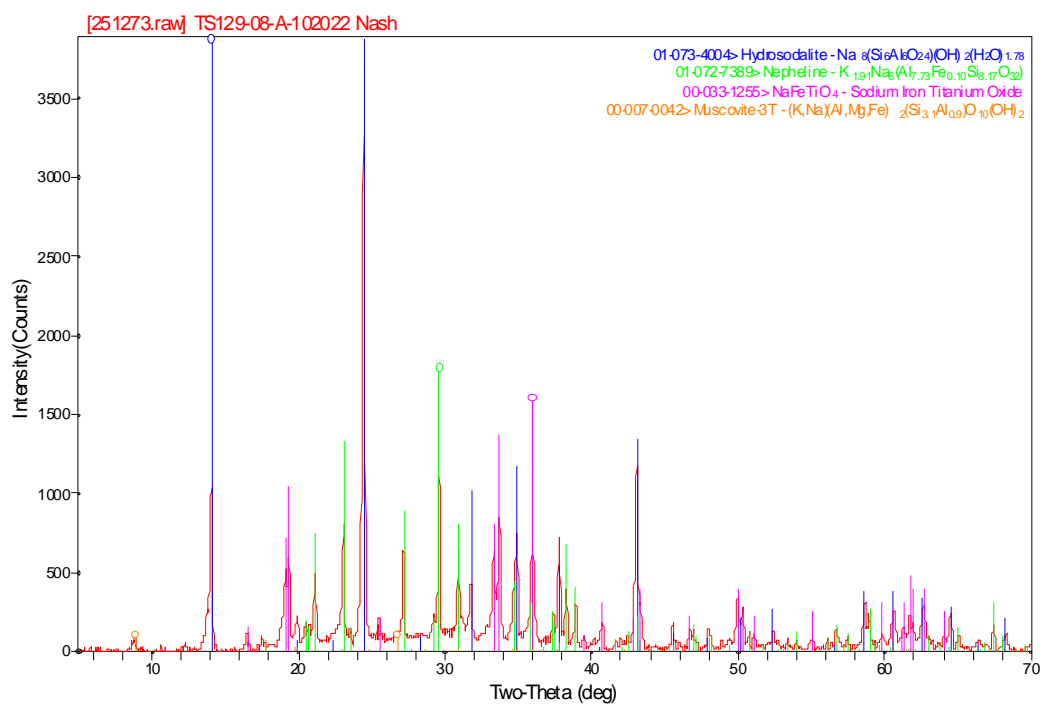


Figure A-2. Run 1 Bottom Insoluble Solids XRD

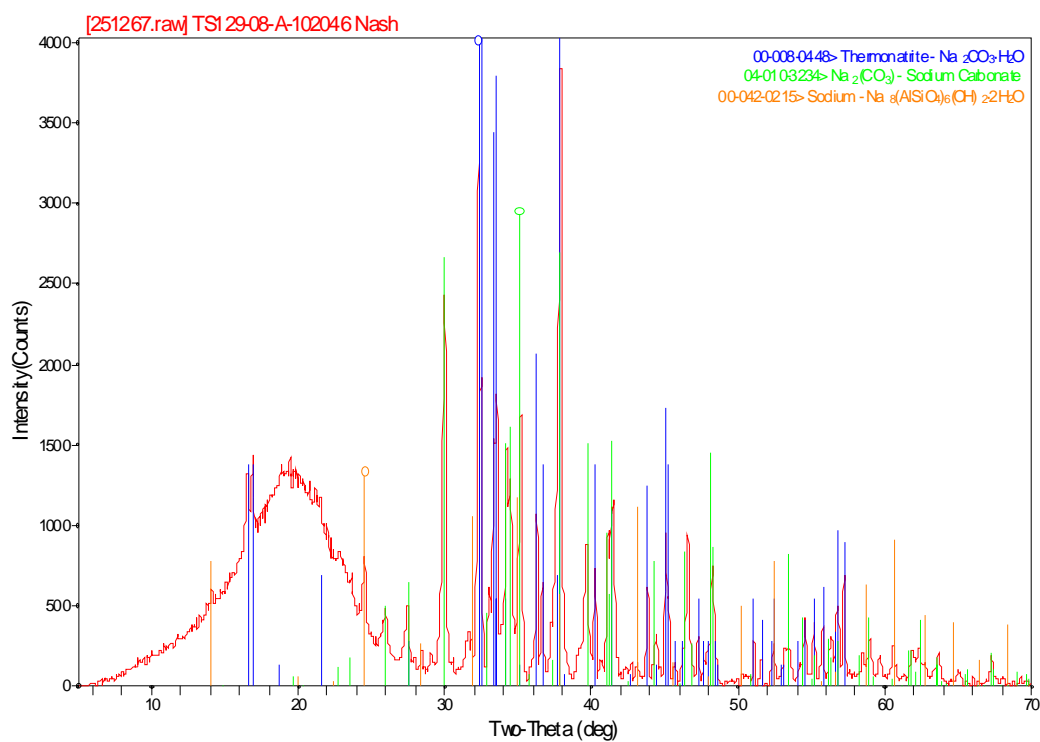


Figure A-3. Run 2 Bottom Product XRD

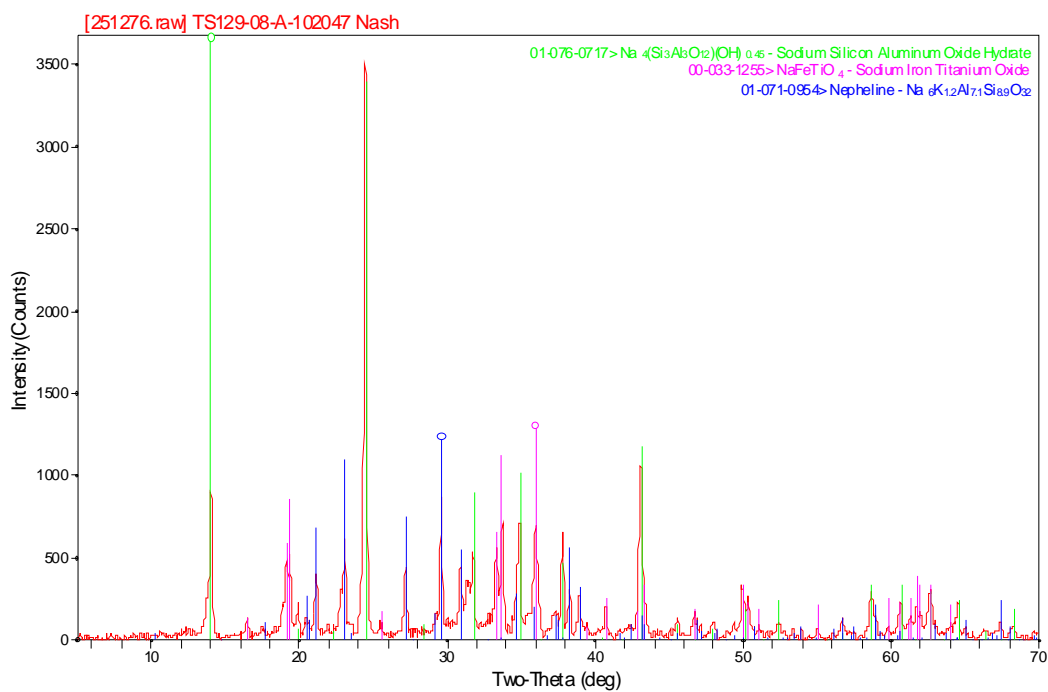


Figure A-4. Run 2 Bottom Insoluble Solids XRD

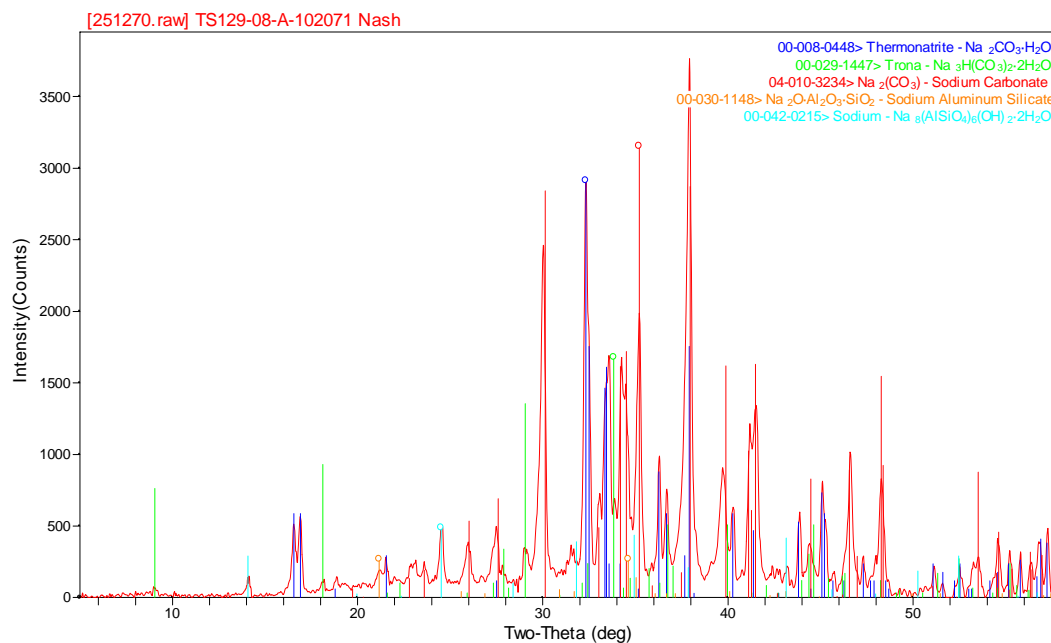


Figure A-5. Run 3 Bottom Product XRD

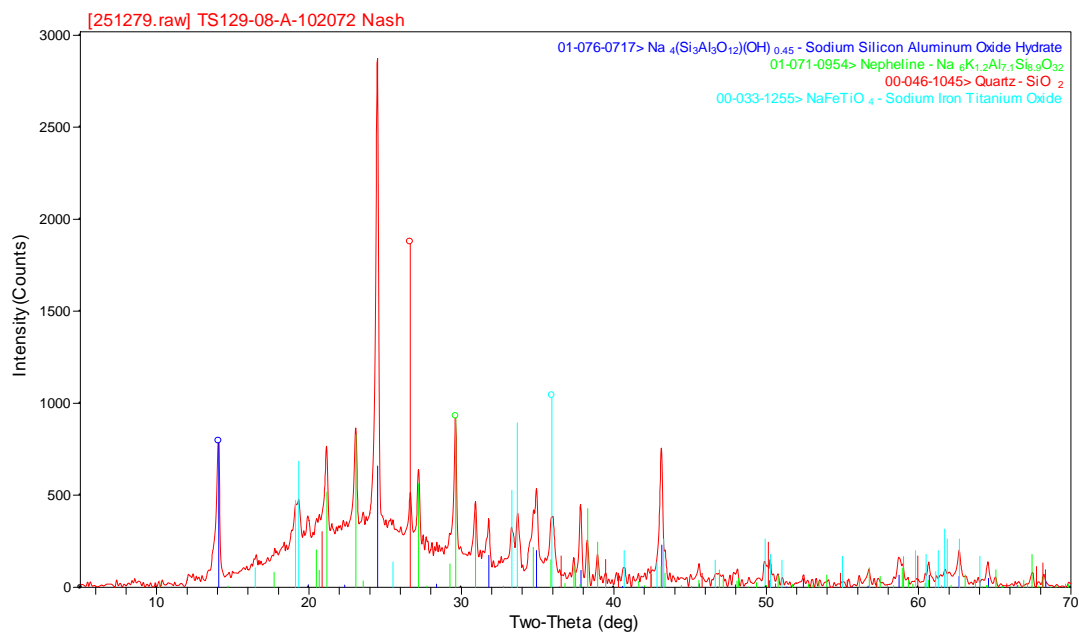


Figure A-6. Run 3 Bottom Insoluble Solids XRD

APPENDIX 2. Calculation of Radioactive Distribution

Run	Feed ml	Feed d/m/ml	Feed d/m	percentage rad.	DMR Bubbler ml	DMR Bubbler d/m/ml	DMR Bubbler d/m	percentage rad.	CRR Bubbler ml	CRR Bubbler d/m/ml	CRR Bubbler d/m	percentage rad.	Product Percent
1	300	7.53E+08	2.26E+11	100	650	2.84E+07	1.85E+10	8.17	350	1.11E+04	3.89E+06	0.00	91.83
2	300	7.53E+08	2.26E+11	100	650	1.61E+07	1.05E+10	4.63	350	9.63E+04	3.37E+07	0.01	95.35
3	300	7.53E+08	2.26E+11	100	650	1.20E+07	7.80E+09	3.45	350	2.06E+05	7.21E+07	0.03	96.52

$$bubbler_d / m = bubbler_ml \times bubbler_d / m / ml$$

$$bubbler_rad\% = \frac{bubbler_d / m}{feed_d / m} \times 100$$

9.0 REFERENCES

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