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High-Temperature MACT Calcination Test

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Bechtel BWXT Idaho, LLC

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Idaho National Engineering and Environmental Laboratory
Environmental Technology and Engineering
Idaho Falls, Idaho 83415

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ABSTRACT

About one million gallons of acidic, hazardous, and radioactive sodium-bearing waste are stored in stainless steel tanks at the Idaho Nuclear Technology and Engineering Center (INTEC), which is a major operating facility of the Idaho National Engineering and Environmental Laboratory. Calcination at high-temperature conditions (600°C, with alumina nitrate and calcium nitrate chemical addition to the feed) is one of four options currently being considered by the Department of Energy for treatment of the remaining tank wastes. If calcination is selected for future processing of the sodium-bearing waste, it will be necessary to install new off-gas control equipment in the New Waste Calcining Facility (NWCF) to comply with the Maximum Achievable Control Technology (MACT) standards for hazardous waste combustors and incinerators. This will require, as a minimum, installing a carbon bed to reduce mercury emissions from their current level of up to 7,500 to <45 μg/dscm, and a staged combustor to reduce unburned kerosene fuel in the off-gas discharge to <100 ppm CO and <10 ppm hydrocarbons. The staged combustor will also reduce NO_x concentrations of about 35,000 ppm by 90–95%.

A pilot-plant calcination test was completed in a newly constructed 15-cm-diameter calciner vessel. The pilot-plant facility was equipped with a prototype MACT off-gas control system, including a highly efficient cyclone separator and off-gas quench/venturi scrubber for particulate removal, a staged combustor for unburned hydrocarbon and NO_x destruction, and a packed activated carbon bed for mercury removal and residual chloride capture. Pilot-plant testing was performed during a 50-hour system operability test January 14–16, followed by a 100-hour high-temperature calcination pilot-plant calcination run January 19–23. Two flowsheet blends were tested: a 50-hour test with an aluminum-to-alkali metal molar ratio (AAR) of 2.25, and a 50-hour test with an AAR of 1.75.

Results of the testing indicate that sodium-bearing waste can be successfully calcined at 600°C with an AAR of 1.75. Unburned hydrocarbons are reduced to less than 10 ppm (7% O_2, dry basis), with >90% reduction of NO_x emissions. Mercury removal by the carbon bed reached 99.99%, surpassing the control efficiency needed to meet MACT emissions standards. No deleterious impacts on the carbon bed were observed during the tests. The test results imply that upgrading the NWCF calciner with a more efficient cyclone separator and the proposed MACT equipment can process the remaining tanks wastes in 3 years or less, and comply with the MACT standards.

EXECUTIVE SUMMARY

Liquid radioactive waste, most of which contains a high concentration of alkali-metal salts, is currently stored at the Idaho Nuclear Technology and Engineering Center (INTEC). This waste was generated from solvent recovery and decontamination activities associated with spent nuclear reactor fuel reprocessing. The waste is acidic and contains high concentrations of sodium, potassium, and nitrates, and is commonly referred to as sodium-bearing waste (SBW). If calcination using the existing New Waste Calcining Facility (NWCF) is selected for future SBW processing, new off-gas control equipment will be required to meet the Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) standards. This will require, as a minimum, installing off-gas control equipment to reduce mercury emissions from their current level of up to 7,500 µg/dscm to <45 µg/dscm, and to reduce unburned kerosene fuel in the off-gas discharge to <100 ppm CO and <10 ppm hydrocarbons. Several engineering design files (EDFs) have been completed that address the technical requirements, facility modifications, and schedule required to upgrade the NWCF to achieve these emissions limits.

The primary objective of the high-temperature flowsheet is an increase in the net waste processing rate. The elevated temperature accelerates nitrate decomposition and reduces bed agglomeration, but it potentially increases the amount of fines generated. The higher operating temperature results in accelerated feed spray drying and possibly droplet-film boiling on the surface of the individual particles; both phenomena can generate more fines that are elutriated into the off-gas system. The problem of fines generation is exacerbated by the fact that the NWCF cyclone is not optimally designed, and therefore does not achieve a high efficiency of fine particles removal. As the rate of fines generation increases, so too does the load on the cyclone separator, as well as on the venturi scrubber. Higher solids loading in the scrubber solution necessitates more frequent scrub solution recycle to the feed makeup tanks, and occasionally blowdown (deep recycle) back to the tank. Hence, the generation of fines and their behavior in the off-gas system is critical to understanding the relative benefits of operating at higher temperature.

The reality is that several significant design and operating risks are associated with the Calciner MACT upgrade. It was therefore incumbent on the program to identify the most significant data gaps and to reduce the design risks by operating a pilot-plant calciner with a prototypical MACT-compliant off-gas system, commensurate with the design basis.

In summary, the data gaps and design risks for the Calciner MACT upgrade option for SBW treatment can be mapped to two overarching needs:

1. Data that support calciner throughput projections and calciner production rates

2. Data that support the evaluation and design of a MACT-compliant off-gas cleaning system.

Limited pilot-plant testing was authorized by DOE in Fiscal Year 2004 to help close the data gaps associated with the Calciner MACT SBW process alternative. The Department of Energy (DOE)-owned fluidized bed steam reforming test system located at the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) Center in Idaho Falls, Idaho was modified to operate as a fluidized bed calciner with a prototypical MACT-compliant off-gas system. The off-gas system, including a cyclone separator and off-gas quench/venturi scrubber for particulate removal, a staged combustor for unburned hydrocarbon and NO_x destruction, and a packed activated carbon bed for mercury and residual chloride capture were designed and installed for testing. Construction and setup was completed in November and December 2003. A 50-hour system operability test was performed during January 14–16, followed immediately with a 100-hour high-temperature calcination run January 19–23. This report discusses the test objectives, approach, and results of the system operability test and the 100-hour run.

The purpose of the 100-hour pilot-plant calcination tests was to simultaneously address as many of the calciner throughput data gaps as possible and to verify that the conceptual design for the off-gas cleaning system upgrade will meet the MACT standards. The scope of the tests was designed to provide the following information, in accordance with the *Sodium-Bearing Waste Treatment Applied Technology Plan* (INEEL/EXT-03-00477, June 2003):

Calciner Process Throughput Data Needs:

- Verify that the recommended AAR of 2.25 is acceptable for a representative SBW feed, and if successful, determine whether an additional step reduction to an AAR of 1.75 is feasible
- Verify that the fines generation rate for the high-temperature tests (a) is acceptable for the NWCF process and (b) exhibits a particle size distribution that can be efficiently captured by the NWCF cyclone
- Determine whether the NWCF quench/scrubber system will capture the fine particulate that passes through the cyclone separator and determine the solubility of fines in the scrubber
- Determine fate of volatile elements and compounds (namely, alkali species, chloride species, and mercury) in the calciner, cyclone, quench/scrubber, and off-gas system
- Project the NWCF net waste processing rate, considering fines generation, particle and chloride capture in the scrub system, and scrub recycle rates.

Calciner MACT Technology Implementation Needs:

- Quantify THC/CO, NO/NO_2, and HCl/Cl emissions rates in the product
- Verify retention of semi-volatile and low-volatile metals
- Verify the design-basis performance of the multi-stage combustor for NO_x and THC/CO destruction
- Determine optimum operating conditions and control logic of the multi-stage combustor with respect to (a) destroying THC/CO and NO_x and (b) minimizing the amount of natural gas, combustion air, and quench vapor required in the respective stages
- Examine the performance of the combustor refractory, water spray quench, and burner equipment
- Determine the speciation of mercury leaving the staged combustor and entering the carbon bed
- Verify the design-basis of the carbon bed for mercury removal, including packing diameter and depth, operating temperature, and capacity
- Determine the mass transfer zone of mercury (i.e., axial profile) in the carbon bed.

A simplified process flow diagram is shown in Figure ES-1. Table ES-1 describes the various subcomponents of the system. Before the 100-run, a 50-hour shakedown of the facility was performed, during which system operability (SO) testing of the new test facility components was performed. The SO test produced a suitable starting bed for the 100-hour waste simulant calcination test. The bed was sieved and sampled before the 100-run. The scrub solution was replenished with fresh 4-molar (4-mol/L HNO_3) before test startup. Non-radioactive Tank 180 feed simulant, left over from the recent steam reforming tests, was used as the feed simulant. Aluminum nitrate solution (ANN) was supplied by BBWI in two 55-gal drums. Chemical analysis of the surrogate waste feed and ANN solutions was completed by INEEL Analytical Laboratory Department to confirm feed composition specifications. The surrogate waste was blended with the ANN to achieve target feed solutions. Summary test conditions were as follows:

- Starting bed: Amorphous aluminum oxide-borate bed produced by SO test
- Feed rate: 4-6 L/hr feed blend
- 0-50 COT: Target aluminum-to-alkali-metal ratio (AAR) of 2.25
- 50-100 COT: Target aluminum-to-alkali-metal ratio (AAR) of 1.75.

Through the use of the wall heaters in the SAIC facility, it was possible to control heat losses and to trim the kerosene/oxygen flow rate to more closely match the pilot-plant calciner bed conditions to the NWCF. Additional heat tracing on the off-gas line and cyclone separator made it possible to match the off-gas temperature in the cyclone and entrance to the off-gas quench. The overall effect is a system that represents the chemistry in the NWCF calciner and off-gas system. This is especially important to evaluate the performance of the scrubber system and NO_x reduction and unburned hydrocarbon destruction in the staged-combustor.

Concurrently with the SO test and 100-run, the off-gas staged combustor was investigated. Variations of operating conditions included the amount of reducing natural gas used to "reburn" the calciner off-gas, stage temperatures, and combustion air injection. The carbon bed was tested during the 100-hr run. Mercury concentrations in the Tank 180 simulant feed were increased by a factor of four (from 1.4 to 5.6 mmol/L) in order to match and bound the higher mercury concentrations in other SBW storage tanks (i.e., Tank WM-189).

On-line off-gas monitoring was performed by SAIC using two continuous emissions monitors (CEMS) for major species and criteria pollutants (O_2, CO_2, CO, CH_4, total unburned hydrocarbons, H_2, NO, NO_2, and HCl). Two mercury CEM systems (CEMS) were used to monitor and speciate elemental (Hg^o) and oxidized mercury ($HgCl_2$) concentrations. Solid and liquid samples were collected throughout the test to perform mass balances and to help qualify the product. At the conclusion of the tests, the carbon bed was sampled at various axial and radial positions to establish a map of mercury concentrations throughout the bed. The carbon bed was also analyzed for sulfur, halides, and ammonium to determine the co-adsorption of species and any possible affects of the gas matrix on the carbon bed.

Data collection was performed primarily by a data acquisition and control system (DACS). Approximately 200 separate process control parameters and process conditions are tracked by the DACS, including flow rates, pressure, differential pressure, temperature, gas compositions, bed level, and liquid levels. Data sheets were also used to manually collect key information and data throughout the tests. Additionally, mass and scrub solution accountability log sheets were maintained to record product and fines production rates, scrub solution blowdown and makeup additions, and condensate collection volumes.

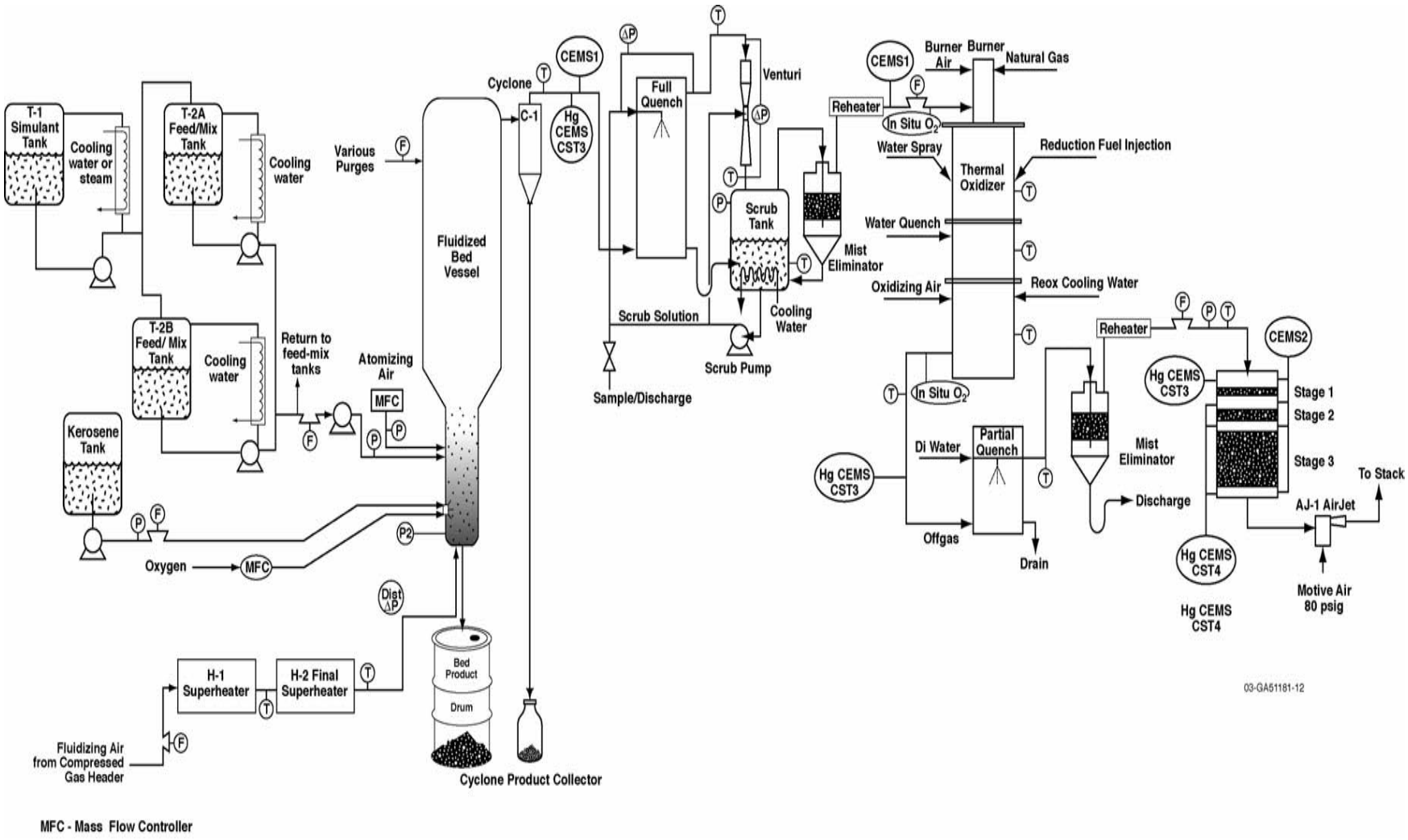

Figure ES-1. Fluidized bed test system process flow diagram.

Table ES-1. Fluidized bed test system components.

Fluidized Bed Reactor		
• Bed material feed subsystem, product recovery line, bed drains, product containers	• Fluidizing air compressor, pre-heater, and gas distributor ring	• Kerosene fuel tanks, pumps, delivery line, spray nozzle
• Compressed oxygen cylinders, burner nozzle feed line	• SBW simulant feed makeup, feed metering, and feed injection subsystems	• Liquid feed atomizing air supply line and metering system
• Thermocouple and pressure taps, pressure transducers	• Instrument line purge air supply and metering gauges	
Off-gas Control System		
• Off-gas cyclone separator, fines collection line, fines container	• Full wet quench, venturi scrubber, scrub tank, recirculation pumps, scrub water sample collection location	• Off-gas mist eliminators, and reheaters, condensate traps
• Multi-stage combustor, natural gas supply line, gas flow meters and controllers, water quench, combustion air supply, thermocouples, pressure indicators, oxygen analyzers	• Granular activated charcoal bed, external wall heaters, thermocouples, off-gas sample lines	• Air eductor and stack discharge
Programmable Logic Control System and Process Monitoring Equipment		
• Human-machine Interface computers for automatic process monitoring and process control	• Data collection and data management computers	• Continuous emissions monitors, sample collection probes, sample delivery lines, instrument calibration gases, data collection computers
• Off-gas mercury monitors, sample collection probes, and sample delivery lines	• Particle sieve trays, and shaker	• Balances, solid and liquid sample containers

Solid and liquid samples included bed product, fines, scrub and condensate solutions, and carbon bed pellets. Samples were collected throughout the run to establish key trends. The activated carbon bed was mapped to establish radial and axial composition profiles for mercury, chloride, fluoride, ammonium, and nitrate.

The 100-hr high-temperature trial was completed without any significant operating difficulties. Bed growth was consistent throughout the run. The mean particle size of the bed was stabilized at 400–450 μm with NAR levels of 600–800. Some nozzle plugging occurred during the tests; however, the plugs were readily cleared with the liquid orifice plunger or by short nozzle flushes with nitric acid. The nozzle plugs likely contributed to some agglomeration of the feed; the amount of agglomeration was considered minor and was not attributed to the high-temperature chemistry.

Fines generation was minimal; however, the particle size distribution of the fines exhibited a lower mean diameter than has been typically measured in previous 15-cm Enclosed Pilot Plant tests and high-temperature trials at the NWCF (namely, 12 μm versus ~45 μm). The high-efficiency cyclone installed at the SAIC STAR Center pilot plant achieved higher fines removal efficiency with minimal plugging.

Both the AAR 2.25 and AAR 1.75 flowsheets were successfully tested. A bed turnover of 97.9% was achieved for the first test. Bed turnover for the second test was 98.5%. For the entire 100-hour run, a bed turnover of 99.9% was achieved. The high bed turnover is an indication that the bed chemistry of

both flowsheets is acceptable. Nitrate decomposition was acceptable, with only 3.2 wt% and 2.7 wt% in the ending bed product of the 2.25 AAR and 1.75 AAR tests, respectively. Nitrate levels in the fines were slightly higher at 4.7 wt% for the AAR 2.25 flowsheet, and 3.8 wt% for the AAR 1.75 flowsheet. None of the levels are high enough to cause particle agglomeration in the bed or off-gas line. Bed composition and scrub solution concentration trends match bed turnover progression.

The product-to-fines ratio (P/F) for the two cases was 5.1 and 2.8, respectively. This exceeds all previous SBW high-temperature pilot-plant calcination tests in the 10-cm and 15-cm Enclosed Pilot Plant Calciners. During the previous NWCF H4 high-temperature trial, a P/F of 1.0 was observed. Therefore, the P/F ratio for the current tests in comparably excellent. The scrubber undissolved solids (UDS) concentration approached 700 mg/L, which is well under the accepted limit of 10,000 mg/L. Chloride in the scrub solution leveled off at 690 mg/L, again under the accepted limit of 3,000 mg/L. The mercury concentration in the scrub climbed to 170 mg/L.

The WM-180/ANN flowsheet performed acceptably at an AAR of 1.75, and therefore an AAR of 1.75 should be assumed for future NWCF throughput projections. No boron addition was necessary for calcination of the blend. No calcium nitrate above that which is already in the WM-180 waste (at only 36% of stoichiometric) was necessary to control chloride and fluoride volatility. However, additional calcium nitrate may still be required for calcination of the other SBW wastes that have higher sulfate contents that may reduce the effect of calcium to suppress chloride and fluoride volatility. In addition, the use of ANN with a concentration of 2.3 to 2.4 instead of 2.2 molar aluminum improves blend performance.

With these improvements in blend AAR and scrub recycle, and with modifications to the NWCF cyclone, the existing SBW waste can be calcined in 3 years, assuming a calciner on-stream efficiency of 73.1% and total turnaround time of 273 days. The Calcination with MACT Upgrade treatment alternative therefore could meet the requirement to remove all the waste from the Tank Farm by 2012.

Future testing should be performed using simulated WM-187 or other waste containing a high amount of simulated heel solids—preferably including zirconium sulfate as a solid simulant. This would show whether the high amount of zirconium sulfate in the heel solids will detrimentally affect calcination chemistry, or whether the solids will pass through the calciner as inert solids. Future tests need not include calcium nitrate addition unless chloride and fluoride volatility becomes poor during the early tests. Testing at AARs lower than 1.75 should be attempted in the future to determine whether further improvements in NWCF throughput can be achieved.

Performance of the pilot-plant MACT off-gas system demonstrated that CO, THC, Hg, and HCl emissions can comply with the HWC MACT standards. Less than 1 ppmv HCl was measured in the off-gas at the staged combustor outlet. A large portion of the chloride was also retained by the calcine product and fines as chloride salts. The acidic scrubber solution effectively scrubbed most of the HCl that evolved from the calciner.

The staged combustor consistently reduced CO to <10 ppmv (dry, 7% O_2). This is well below the limit of 100 ppmv (dry, 7% O_2) required by MACT. THC emissions were reduced to <5 ppmv (dry, 7% O_2) on average, meeting the standard of 10 ppmv. Overall, the staged combustor achieved a NO_x reduction of 90–98% when the reducing stage equivalence ratio (φ) was about 1.2. These results are consistent with previous NO_Xidizer technology tests performed in Butte, Montana in 2000/2001.

Overall, the pilot-plant system and activated carbon bed achieved over 99.99% removal of mercury. Outlet mercury concentrations from the carbon bed were <0.7 $\mu g/m^3$ (dry, 7% O_2), complying with the MACT standard of 45 $\mu g/m^3$. Due to the short length of operating time, mercury loading on the

carbon only reached a maximum of 1.6 wt%, significantly less than the theoretical capacity of about 20 wt%. Halogen compounds and nitrate loading on the bed was nearly negligible, due to the relatively low concentrations of acid gases in the off-gas downstream of the off-gas scrubber. There was no apparent interference by NO_x, chloride, or other off-gas constituents. No ammonia was detected in the carbon.

Although additional testing will be necessary to determine long-term effects of matrix components on the carbon bed, the current tests are encouraging and greatly reduce the design risks. A mass transfer zone (MTZ) of 3–4 in. in the bed was observed for the test conditions with a gas velocity of 1.6 ft/s. Further testing will also help confirm the Calciner MACT design life for the carbon bed.

Further testing of the staged combustor may help to optimize conditions, with one objective being the minimization of the effluent volume. This would necessitate a parametric testing of stage temperatures in conjunction with variations in the reducing zone equivalence ratio and quench water spray. The pilot-plant system should be insulated to reduce heat loss.

Electrical heating of the carbon bed vessel prompted ignition and burning of the carbon bed during the startup before the tests. Additional testing of adsorption isotherms during bed startup conditions will help determine an acceptable method for bringing the carbon bed on line. Although there is reasonable assurance that the bed can be safely started, additional testing will alleviate the concern that any possible excursion in off-gas concentrations, resulting in exothermic vapor adsorption, may cause a local temperature excursion.

ACKNOWLEDGEMENTS

Many persons from several organizations contributed to the success of this research and testing activity. Under direction from the Idaho National Engineering and Environmental Laboratory (INEEL), Science Applications International Corporation (SAIC) modified and operated the (DOE)-owned fluidized bed test facility at the SAIC Science and Technology Research (STAR) Center. The INEEL Technical Project Manager and Engineer over pilot-plant setup and testing was Gary Anderson. Arlin Olson was the INEEL Sodium-Bearing Waste Technology Development Manager.

Significant modifications were made to convert the existing steam reforming test system into a calciner pilot plant with a prototype MACT off-gas control system. Mechanical and process design changes were supported by INEEL research engineers, Richard Boardman, Barry O'Brien, Nick Soelberg, and Brian Raivo. Significant changes were also made to the process logic controller interfaces, software, and data acquisition/data archive system, lead by Curtis St Michel with the support of Trent Taylor, John Yadon (Havlovick Engineering), Desiree Reagan, and Von Scholes.

Richard Boardman and Barry O'Brien developed the test plan and sample analysis plan (with advice from Nick Soelberg), and directing the pilot-plant tests. Steve Bates also provided technical oversight during the pilot-plant runs. Brad Ward coordinated sample collection and analysis, which were completed by several INEEL analytical groups, but most significantly by Byron White with technical support of Bill Bauer. Cal Johnson and Tony Watson supported feed makeup, liquid feed sampling and analysis, and off-gas measurements.

SAIC was responsible for modifying and operating the calciner bed pilot plant and continuous off-gas monitors. Bart Packer was the SAIC project manager. James Atkinson, Director of STAR Center, completed system modifications and supported test operations, along with Troy Thomson (senior shift lead), Roy Woodvine, Bryan Bird, Paul Perez, and Brent Haines as system operators. Tim Hertzler and Chad Ross set up and operated the continuous emissions monitors and supported data reduction.

The authors and editors of this report have achieved the metaphoric equivalent of using nine persons to produce a baby in one month. In addition to the seven report authors, INEEL report editors David Pack and Debra Iverson are credited with the timely delivery of the report. All of the authors contributed equally to data reduction, tabulation, plotting, and interpretation. The authors also shared report writing responsibilities. Brian Raivo is credited with the creation of the facility figures and description.

CONTENTS

FIGURES

TABLES

ACRONYMS

AAR	aluminum-to-alkali metal ratio
AE	analysis element
AJ	air eductor jet
AL	Analytical Laboratories
ANN	aluminum nitrate solution
CEM(S)	continuous emission monitor(ing) (system)
COD	chemical oxygen demand
COT	continuous operating time (time on line with feed injection)
CST	CEMS Sampling Train
D/F	dioxins and furans
DACS	data acquisition and control system
DUV	dispersive ultraviolet
EDF	engineering design file
FID	flame ionization detection
GFC	gas filter correlation
HLW	high-level waste
HMI	human-machine interface
HWC	hazardous waste combustion (or combustor)
IC	ion chromatography
INTEC	Idaho Nuclear Technology and Engineering Center
KNAR	kerosene-oxygen nozzle atomizing volumetric ratio
MACT	Maximum Achievable Control Technology
NAR	nozzle atomizing gas flow ratio
NAR	nozzle atomizing ratio
NDIR	nondispersive infrared
NDUV	nondispersive ultraviolet
NESHAP	National Emission Standards for Hazardous Air Pollutants
NSNCR	non-selective, non-catalytic NO_x reduction
NWCF	New Waste Calciner Facility (or Calciner)
PCB	polychlorinated biphenyl compound
PE	polyethylene
P/F	product-to-fines ratio
PLC	programmable logic controller

PQ	partial quench
PSD	particle size distribution
RCRA	Resource Conservation and Recovery Act
SAIC	Science Applications International Corporation
SBW	sodium-bearing waste
SEM	scanning electron microscope
SO	system operability
SpG	specific gravity
STAR	Science and Technology Applications Research
SVOC	semi-volatile organic compounds
TFF	Tank Farm Facility
THC	total hydrocarbon
TIC	total inorganic carbon
TOC	total organic carbon
UDS	undissolved solids
UV	ultraviolet
VOC	volatile organic compounds
w.c.	water column
WCF	Waste Calcining Facility
WIPP	Waste Isolation Pilot Plant

High-Temperature MACT Calcination Test

1. INTRODUCTION

Liquid radioactive waste, most of which contains a high concentration of alkali-metal salts, is currently stored at the Idaho Nuclear Technology and Engineering Center (INTEC). This waste was generated as a result of solvent recovery and decontamination activities associated with spent nuclear reactor fuel reprocessing. The wastes are acidic and contain high concentrations of sodium, potassium, and nitrates and are commonly referred to as sodium-bearing wastes (SBW). A 1995 Court-Order Settlement Agreement requires that the SBW, along with any additional waste generated and stored in the INTEC Tank Farm Facility (TFF), be treated by 2012. Historically, calcination has been used to convert the Tank Farm wastes into a solid, granular, pneumatically transportable calcine. Approximately 4,500 m^3 of granular calcine has been produced that is currently stored in stainless steel, shielded bin sets. The Settlement Agreement requires that the calcine be made road-ready for transport to a suitable long-term disposal area by 2035. In 2000, the New Waste Calciner Facility (NWCF or Calciner) was shut down, mainly because the Calciner is currently not compliant with the Maximum Achievable Control Technology (MACT) rule for hazardous waste combustors and incinerators.

If calcination is selected for future processing of the SBW, it will be necessary to install new off-gas control equipment to achieve the MACT standards. This will require, as a minimum, installation of NWCF off-gas control equipment to reduce mercury emissions from their current level of up to 7,500 µg/dscm to <45 µg/dscm, and to reduce unburned kerosene fuel in the off-gas discharge to <100 ppm CO and <10 ppm hydrocarbons. Several engineering design files (EDFs) have been completed that address the technical requirements, facility modifications, and schedule required to upgrade the NWFC to achieve these emissions limits. Pilot-plant testing was recommended to reduce key design risks and to provide additional necessary data for process design, permitting, and operation.

Limited pilot-plant testing was authorized by DOE in Fiscal Year 2004 to help close the data gaps associated with the Calciner MACT SBW process alternative. The steam reforming pilot-plant facility constructed by Science Applications International Corporation (SAIC, Idaho Falls office) was converted into a pilot-plant calciner. A prototype MACT off-gas control train, including a cyclone separator and off-gas quench/venturi scrubber for particulate removal, a staged combustor for unburned hydrocarbon and NO_x destruction, and a packed activated carbon bed for mercury removal and residual chloride capture was designed and installed for testing. Pilot-plant construction and setup was completed in November and December 2003. Pilot-plant testing was performed during a 50-hr system shakedown test January 14–16, followed immediately with a 100-hr high-temperature calcination pilot-plant calcination run January 19–23. This report discusses the test objectives, test approach, and test results of the system shakedown and the 100-hr run.

1.1 Background

Fluidized bed calcination has been used at the Idaho Nuclear Technology and Engineering Center (INTEC), formerly called the Idaho Chemical Processing Plant, since the early 1960s to solidify acidic metal nitrate wastes generated in fuel reprocessing operations. The Waste Calcining Facility (WCF) was operated from 1961 to 1981, and the NWCF from 1981 to 2000. During waste processing at the NWCF, SBW was typically blended with high-level waste (HLW) in order to minimize sodium and potassium concentrations in the calciner feed solution. This was necessary due to the propensity of sodium and potassium nitrates to form molten liquids in the calciner, resulting in bed agglomeration. However, near the end of HLW processing, work was initiated to modify the calcination process to treat SBW directly without blending it to lower the alkali content of the product. The result of this development effort was to

increase the operating temperature of the calciner from 500 to 600°C. The 600°C SBW flowsheet was successfully demonstrated at the NWCF during two separate trials during 1999 and 2000. The conclusion from these demonstrations was that operation of the existing NWCF at 600°C is a viable long-term method for processing SBW. Calcination at 600° is now referred to as high-temperature calcination.

The primary objective of the high-temperature flowsheet is an increase in the net waste processing rate. However, although elevated temperature helps accelerate nitrate decomposition and reduces bed agglomeration, it potentially increases the amount of fines generated. Higher operating temperature results in accelerated feed spray drying and possibly droplet-film boiling on the exterior or the individual particles; both phenomenon lead to the generation of fines that are carried over into the off-gas system. The problem of fines generation is exacerbated by the fact that the NWCF cyclone is not optimally designed, and therefore does not achieve a high efficiency of fine particles removal. As the rate of fines generation increases, so too does the load on the cyclone separator, as well as on the venturi scrubber. Higher solids loading in the scrubber solution necessitates more frequent scrub solution recycle to the feed makeup tanks, and occasionally blowdown (deep recycle) back to the tank. Hence, the generation of fines and their behavior in the off-gas system is critical to understanding the relative benefits of operating at higher temperature.

In addition to higher fines generation, the volatility of alkali compounds (including radioactive cesium), and chloride species may increase. Therefore, it is imperative to understand the behavior of chemical constituents as a function of high-temperature flowsheet conditions, both in the hot bed as well as the off-gas scrubber system. The volatility of chloride compounds is especially significant, since the scrub system has a limit on the level of chloride in the solution to avoid accelerated corrosion of the stainless steel tanks, piping, and pumps.

Finally, although the high-temperature flowsheet helps to reduce unburned hydrocarbons and CO emissions, it is still not adequate to achieve the MACT standards of 10 ppm THC and 100 ppm CO. However, it appears to have relative little impact on mercury, which is essentially all volatilized at all practical calcination temperatures.

The NWCF was operated under a State of Idaho Permit to Construct and under interim Resource Conservation and Recovery Act (RCRA) status. In the early and mid-1990s, DOE initiated an effort to better determine the calciner off-gas composition to support a RCRA permitting emissions inventory process for the calciner. At the same general time (1996), the EPA proposed the Hazardous Waste Combustion (HWC) National Emission Standards for Hazardous Air Pollutants (NESHAP) based on Maximum Achievable Control Technology (MACT) (40 CFR 63 Subpart EEE). A multi-year emissions inventory and risk assessment effort, and several studies that evaluated how to upgrade the calciner facility to meet the HWC MACT standards, were performed between 1997 and 2001 (Boardman 2001). Data were collected both at the normal operating temperature of 500°C and also at high-temperature conditions. In 2000, after off-gas sampling confirmed that the calciner facility would require modifications to become HWC MACT-compliant, DOE temporarily shut down the calciner pending determination of how the remaining SBW should be treated for final disposal.

It is expected that the NWCF will be regulated as a miscellaneous thermal treatment unit; thus, compliance with MACT emission limits will be imposed. In order to meet these standards, an upgrade to the calciner off-gas treatment train will be required. Specifically, emissions of CO, total hydrocarbons (THC), and mercury releases must be mitigated. In addition, NO_x abatement is highly desirable in order to simplify air-monitoring requirements to demonstrate compliance. Other new equipment and facilities may be required to package the calcine produced for disposal at Waste Isolation Pilot Plant (WIPP) and to treat a small purge of calciner off-gas scrub into an acceptable final waste form.

Table 1-1 is a partial list of the technical engineering design files (EDFs) that describe the proposed Calciner off-gas system upgrade and operating conditions (i.e., feed blend composition, throughput, scrub system recycle, etc.) that can feasibly meet the Settlement Agreement. Several underlying assumptions were invoked in these documents due to the general lack of actual process experience with the high-temperature calcination flowsheet and several challenges associated with removal of mercury from the harsh Calciner off-gas. The reality is that several significant design and operating risks are associated with the Calciner MACT upgrade. It was therefore incumbent on the program to identify the most significant data gaps and to reduce the design risks by operating a pilot-plant calciner with a prototypical MACT-compliant off-gas system, commensurate with the design basis.

In summary, the data gaps and design risks for the Calciner MACT upgrade option for SBW treatment can be mapped to two overarching needs:

3. Data that support calciner throughput projections and calciner production rates

4. Data that support the evaluation and design of a MACT-compliant off-gas cleaning system.

Table 1-1. Key technical calciner MACT upgrade engineering design files.

EDF No.	Title	Key Assumptions, Recommendations, and Data Gaps
3311	MACT Compliance for the "Calcination with MACT Upgrade" SBW Treatment Alternative	• MACT rule applies to NWCF per EPA Region 10 and State communications; new off-gas cleaning equipment will be required to control mercury, THC/CO, and possibly HCl/Cl2 • Reduction of NOx level to 1000 ppm-vol is necessary upstream of the carbon bed to minimize interference with mercury adsorption and possible deleterious impacts on the bed itself • CEM monitoring of THC; CO will be required • Possible CEM monitoring of PM and Hg may be required; Hg monitoring is recommended for process control purposes.
3387	Calcination with MACT Upgrade Process Design	• Sampling and characterization of Tank solids is recommended • Pilot-plant testing to determine the effect of tank solids on calcinations needs to be verified • ANN addition ratios for the expected SBW compositions need to be verified • Necessity of adding $CaNO_3$ to control HF emissions is not known • Cyclone replacement and/or fines recycle may be necessary to meet process throughput requirements • Fines generation reduction is desirable to improve throughput • Pilot-plant testing is recommended to optimize chloride behavior with respect to scrubber performance and adsorption by the carbon bed • Determine and verify ways to reduce O_2 in calciner off-gas, as it relates to operation of the staged combustion • Determine speciation of chloride in the off-gas downstream of the staged combustor • Obtain pilot-plant data to verify the predicted benefits of the staged combustor for CO/THC and NO_x control • Conduct pilot-plant test to demonstrate efficiency and capacity of carbon for mercury control, as well as sorption capacities for HCl and Cl_2. • Provide additional data on scrubber performance to help evaluate scrub recycle rates, process throughput, and scrub treatment alternatives, needs, and benefits.

Table 1-1. (continued).

EDF No.	Title	Key Assumptions, Recommendations, and Data Gaps
3292	Off-gas Mercury Control for the Idaho Tank Farm Project – Calcination with MACT Upgrade SBW Treatment Alternative	• Pilot-plant testing for design purposes is highly encouraged • Hg removal efficiency of 99.9% is significantly greater than other MACT facilities requirements • 3-mm carbon bed testing is needed; this is impractical for laboratory testing • A scale model of the full-size carbon bed design should be demonstrated to determine the MTZ and to verify high HCl and Hg^o sorption efficiency at representative (pilot-plant) calciner off-gas conditions • Sorption of organics such as PCBs and D/Fs by the carbon should be experimentally determined.
2467 & 4451	NO_x Abatement Technology Development and Selection for the NWCF MACT Upgrade Option Modeling of a Multi-Stage Combustor for Off-gas NO_x and PIC Destruction in Support of the NWCF MACT Upgrade	• Pilot-plant verification of a pilot-plant scale of the recommended full-scale unit for representative calciner off-gas conditions will verify modeling calculation and previous technology demonstrations; specifically for THC and CO destruction and NO_x destruction • Optimize stream inputs (natural gas, air, interstage water quench spray, and air injection into the final stage • Determine the fate and speciation of mercury in the process • Test the performance of combustor ceramic liner • Demonstrate startup and operating procedures • Determine process robustness, including such concerns as refractory life at design operating conditions.
2205	Off-gas Chloride Control for the Calciner MACT Compliance Facility	• A pilot-plant test series should be conducted to optimize chloride retention in the calcine solids • Chloride speciation downstream of the staged combustor is recommended for adsorption bed design considerations • A representative test is needed to demonstrate that the carbon bed can provide a Cl removal efficiency of at least 80% • Pilot-plant testing is needed to determine chloride loading and the effect of chloride on mercury removal.
3646	Cyclone Replacement Options for Calcination with MACT Upgrade SBW Treatment Alternative	• Fines generation rate and fines characterization data are based on very limited 15-cm pilot-plant data. Better pilot-plant data are needed to validate the assumptions and conclusions of this EDF. • A more highly efficient cyclone separator for the pilot plant is needed to address assumptions invoked in the EDF.
3212	Calciner Throughput Evaluation for Calcination with MACT Upgrade SBW Treatment Alternative	• Pilot-plant testing needs to be done of feed blends for individual tanks and associated SBW feed solids to confirm an AAR ratio of 2.25 is possible.

AAR = Aluminum to alkali metals atom ratio in feed blend (i.e., Al/[sum or Na and K])
ANN = Aluminum nitrate nano-hydrate cold chemical blended with feed
D/F = Dioxion/Furan (compound)
CEM = Continuous Emissions Monitor
MTZ = Mass transfer zone
NO_x = Nitrogen oxides (x = 1 or 2)
PCB = Polychlorinated biphenyl (compound)
PM = Particulate matter
THC = Total (unburned) hydrocarbons.

1.2 Purpose and Scope

The purpose of the 100-hr pilot-plant calcination tests was to simultaneously address as many of the calciner throughput data gaps as possible and to verify that the conceptual design for the off-gas cleaning system upgrade will meet the MACT standards. The scope of the tests was designed to provide the following information, in accordance with the *Sodium-Bearing Waste Treatment Applied Technology Plan* (INEEL/EXT-03-00477, June 2003):

Calciner Process Throughout Data Needs

- Verify that the recommended AAR of 2.25 is acceptable for a representative SBW feed; and if successful, determine whether an additional step reduction in AAR is feasible
- Verify that the fines generation rate for the high-temperature tests (a) is acceptable for the NWCF process and (b) exhibits a particle size distribution that can be efficiently captured by the NWCF cyclone
- Verify that the NWCF quench/scrubber system will capture the fine particulate that passes through the cyclone separator, and determine the solubility of fines in the scrubber
- Determine volatile elements and compounds (namely, alkali species, chloride species, and mercury) behavior in the calciner, cyclone, and quench/scrubber, and carry over into the off-gas system
- Project NWCF net waste processing rate taking into consideration fines generation, particle and chloride capture in the scrub system, and scrub recycle rates.

Calciner MACT Technology Implementation Needs

- Quantify THC/CO, NO/NO_2, and HCl/Cl emissions rates
- Verify retention of semi-volatile and low volatile metals in the calcine
- Verify the design-basis performance of the multi-stage combustor for NO_x and THC/CO destruction
- Determine optimum operating conditions and control logic with respect to (a) elimination of THC/CO and NO_x and (b) minimizing the amount of natural gas, combustion air, and quench vapor required in the respective stages which collectively increase the staged combustor effluent gas volume
- Examine the performance of the combustor refractory, water spray quench, and burner equipment
- Determine the speciation of mercury leaving the staged combustor and entering the carbon bed
- Verify the design-basis of the carbon bed for mercury removal, including packing diameter and depth, operating temperature, and capacity
- Determine the mass transfer zone of mercury (i.e., axial profile) in the carbon bed.

Calcine and fines product, vapor adsorption tendency, and transport, storage, and retrieval verification tests are not included in the scope of this project. The scope also does not include examination of organic compound deposition on the calcine, although this may be of interest in regard to

addressing organic compound deposition on the calcine bed or cyclone fines. The pilot-plant calciner test samples will be archived for future characterization and testing if necessary.

1.3 Test Objectives and Approach

The main objective was to perform a 100-hr continuous pilot-plant run during which the feed blend composition was varied to test two waste feed blends. The tests were conducted in the DOE fluidized-bed test facility installed and operated by Science Application International Inc. at the SAIC Science and Technology Application Research (STAR) Center in Idaho Falls. Before the 100-run, a 50-hr shakedown of the facility was performed, during which system operating (SO) testing of the new test facility components was verified.

System SO testing was performed under the following calciner test conditions:

- *Test period*. January 12–15
- *Starting bed*. Alumina oxide (54 grit); 1,766 kg/m^3; 14.9 kg initial charge, 1.91 added during test to compensate for bed attrition when initially injecting water through the feed nozzle
- *Feed solutions*. 4–6 L/hr water (~20 hr total), followed by 3-5 L/hr aluminum nitrate, nitric acid and boric acid, water blend commencing 13 January (~45 hr)
- *Kerosene burner*. Adjusted to achieve outlet concentrations per test plan requirements
- *Scrub solution hold/recirculation tank*. Initially charged with 4 kgmol/m^3 nitric acid solution

The SO test produced a suitable starting bed for the 100-hr waste stimulant calcination test. The bed was sieved and sampled before the 100-run. The scrub solution was replenished with fresh 4-molar (4-Mol/L HNO_3) before test startup.

Non-radioactive Tank 180 feed simulate (~300 L) was prepared by SAIC. Aluminum nitrate solution (ANN) was supplied by BBWI in two 55-gal drums. Chemical analysis of the surrogate waste feed and ANN solutions were completed by INEEL Analytical Laboratory to confirm feed composition specifications. The surrogate waste was blended with the ANN to achieve target feed solutions shown in Table 1-2. Summary test conditions were as follows:

- *Test Period*. January 19–23
- *Starting bed*. Amorphous aluminum oxide-borate bed produced by SO test
- *Feed rate*. 4–6 L/hr feed blend
- *0–50 COT*:[a]. Target aluminum-to-alkali-metal ratio (AAR) of 2.25
- *50–100 COT*. Target aluminum-to-alkali-metal ratio (AAR) of 1.75.

The feed solution was analyzed for aluminum, sodium, and potassium in order to ensure proper formulation of the aluminum-to-alkali metal ratio during feed blending. Feed stock aluminum nitrate solution was also analyzed to ensure feed blending is as desired. Posttest analysis of the feed indicated that the amount of fluride in the feed was approximately 50% low; otherwise, feed specifications met the target composition.

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a. COT = cumulative operating time of waste processing. This does not include hours of system operation when liquid waste stimulant feed is interrupted, discontinued, or switched to air, water, or acid feed.

Table 1-2. Target WM-180 supernate composition.

Cations						
Analyte	Molarity	gm/L		Analyte	Molarity	gm/L
Acid	1.1	1.13		Magnesium	1.2E-2	0.292
Aluminum	6.6E-1	17.9		Manganese	1.4E-2	0.775
Boron	1.2E-2	0.133		*Mercury*	*5.4E-3*[a]	*0.271*
Calcium	4.7E-2	1.89		Nickel	1.5E-3	0.086
Cesium	3.2E-3	0.431		Potassium	2.0E-1	7.66
Chromium	3.4E-3	0.174		Rhenium	1.1E-3	0.200
Copper	7.0E-4	0.044		Sodium	2.1	47.4
Iron	2.2E-2	1.21		Zinc	1.1E-3	0.069
Lead	1.3E-3	0.274				
Anions						
Analyte	Molarity	gm/L		Analyte	Molarity	gm/L
Chloride	3.0E-2	1.06		Phosphate	2.9E-2	2.74
Fluoride	4.7E-2	0.901		Sulfate	7.0E-2	6.72
Nitrate	5.3	330		Water	40.6	731

a. Note: Mercury was increased from 1.4e-3 M to 5.4e-3 molar to represent higher mercury concentrations than are present in Tank 189.

Calcium nitrate addition was not considered necessary for the current tests, since the amount of calcium in the feed is sufficient to bind the fluoride and phosphate in the feed. Boric acid is also not necessary for the high-temperature runs. In retrospect, the amount of calcium in the feed was insufficient to properly tie up all the chloride, fluoride, sulfate, and phosphate in the feed.

The SAIC fluidized-bed calciner system uses wall heating to help minimize the higher heat loss to the surroundings that is associated with small-diameter vessels. Pilot-plant test performed at INTEC in the enclosed 10- and 15-cm pilot-plant facilities required a higher amount of heat input through in-bed combustion of the kerosene. This produced a gas environment that is significantly higher in CO_2, CO, and unburned hydrocarbons than NWCF calciner. Through the use of the wall heaters in the SAIC facility, it was possible to control heat losses and to trim the kerosene/oxygen flow rate to more closely match the calciner outlet concentrations of the NWCF. Additional heat tracing on the off-gas line and cyclone separator made it possible to match the off-gas temperature in the cyclone and entrance to the off-gas quench. The overall effect is a system that better represents the chemistry in the calciner bed and off-gas system. This is especially important to evaluate the performance of the scrubber system and NO_x reduction and unburned hydrocarbon destruction in the staged-combustor.

Concurrently with the SO test and 100-run, the off-gas staged combustor was investigated. Variation of operating conditions included the amount of reducing natural gas used to “reburn” the calciner off-gas, stage temperatures, and burnout air injection.

The carbon bed was tested during the 100-hr run. Mercury concentrations in the Tank 180 simulant feed were increased by a factor of four (from 1.4 to 5.4 mmol/L) in order to match and bound the higher mercury concentrations in other SBW storage tanks (i.e., Tank 189).

The specific and measurable test objectives of this test activity are listed in Table 1-3 in conjunction with their quantifiable parameters and measurement techniques. On-line gas monitoring was performed by SAIC using two continuous emissions monitors for major species and criteria pollutants (O_2, CO_2, CO, CH_4, total unburned hydrocarbons, H_2, NO, NO_2, and HCl). Two mercury monitoring trains were used to monitor and speciate elemental (Hg^o) and oxidized mercury ($HgCl_2$) concentrations. Solid and solution samples were collected throughout the test to perform material balances and to help qualify the product. At the conclusion of the tests, the carbon bed was sampled at various axial and radial positions to establish a map of mercury concentrations through the bed. The carbon bed was also analyzed for sulfur, halides, and ammonia to determine the co-adsorption and any possible affects of the gas matrix on the carbon bed.

Table 1-3. SBW Calcination pilot-plant test objectives.

Objective Statement	Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods
Establish steady-state target operating conditions for the calciner fluidized bed and NO_x staged combustor off-gas reburner– 1. 30-50 hr system shakedown operating period	• CO_2/CO/unburned hydrocarbon concentrations downstream of cyclone separator to match prescribed NWCF calciner effluent gas compositions • Off-gas temperature in freeboard zone and downstream of calciner • Natural gas and oxygen rate and mixture ratio to stage combustor primary burner • Excess natural gas injection rate into 1st stage • Temperature in 1st, 2nd, and 3rd stage of reburner • Concentration of CO_2/CO/O_2/ unburned hydrocarbons in gas downstream of off-gas reburner • Water flow rate to 2nd stage quench • Excess air injection rate to 3rd stage (oxidizer).	• CEM 1 Gas monitoring at cyclone • Temperature sensors in off-gas line • Temperature sensors in staged combustor • Oxygen sensor in staged combustor • CEM 2 for gas monitoring at below staged combustor • Mass flow controllers for gas, oxygen, and water injection.
Verify feasibility of the MACT-Upgrade 600°C flowsheet chemistry for Tank 180 simulant waste with addition of ANN– 1. 50-hr COT with feed @ AAR of 2.25:1 2. 50-hr COT with feed @ AAR of 1.75:1 (Note: This will likely work well for WM-180; however, the other waste tanks will probably require higher AARs than 180.)	• 50 hrs continuous operation at an average feed rate of 5 L/hr blended feed • Less than 5 wt% bed agglomeration, with no particles greater than 5 mm diameter • Less than 3 nozzle plugs per hour on anti-beading feed nozzles • Uniform temperature distribution in bed with no greater than ±20ºC axial temperature variation in the bed • Distributor and bed pressure drop not to exceed 25% of starting conditions	• System flow meters, temperature indicators and pressure transducers • Gravimetric measurement of 8-hr bed samples and fines samples • MMPD and HMPD of 4-hr bed and fines samples density, agglomeration, etc. • Material Balances for total mass and individual species based on solids bed and cyclone fines samples, and liquid scrub samples, and condensate samples

Table 1-3. (continued).

Objective Statement	Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods
	• Steady-state MMPD of bed 400-550 μm • Steady-state MMPD of fines 40-75 μm • Fines generation <50% rate of bed weight buildup rate.	
Evaluate product and fines chemical characteristics– 1. Produce a non-agglomerating bed product and fines fraction 2. Produce a non-hygroscopic bed product and fines mixture for acceptable storage 3. Produce a pneumatically retrievable bed product and fines mixture 4. Produce acceptable bulk and true density 5. Minimize particle sintering potential 6. Produce $NaAlO_2$ constituent phase 7. Maximize product to fines ratio.	• <3 wt% nitrate in bed product • <5 wt% nitrate in fines particles MMPD of fines 40-75 μm • <10 wt% carbonate in bed product • <1 wt% organic in bed product • Bed product attrition index of 40-80 • Bed/fines mixture retrieval efficiency of >99 wt% • Bed/fines mixture hygroscopicity of <10 wt% moisture, with <2 wt% crusting of glazing of particles on the surface • Product bulk density 1.2-1.4 g/cm^3 • Bulk density 2.0-3.5 g/cm^3 • <10 wt% particle agglomeration/clustering • >50 wt% Na and $NaAlO_2$ • P/F mass ratio >1 desirable to minimize scrub recycle and maximize the density (minimize the volume) of blended calcine	• Chemical analysis of product per sample analysis plan per sample analysis plan • Bed and fines size particle distribution and density trends • P/F as calculated from measurement of product and fines cumulative mass • SEM/EDX analysis of solids per sample analysis plan • Product attrition index per (not completed under the current tests) • Product hygroscopicity index (not completed under the current tests) • Product retrieval index per (not completed under the current tests) • BET surface and pore volume measurements (not completed under the current tests)
Produce calcine and fines product that is soluble in nitric acid	• >98 wt% solubility in nitric acid scrub-solution.	• Product dissolution bench-top tests.
Demonstrate acceptable material balance closure for major and minor constituents	• Material balance closure of ±10% for major constituents (Al, Na) • Material balance closure of ±30% for minor constituents (K, Cl, F, NO_3-, etc.).	• Bed samples, fines samples, and scrub composition analysis per sample collection log sheet • Off-gas analysis.
Demonstrate off-gas particulate cleaning comparable to NWCF cyclone and scrub system	• Combined fines removal efficiency of 99.9%.	• Gravimetric measure of fines mass recovery by cyclone and scrub system – mass, volume, density • MMPD by INTEC Coulter Counter.
Determine mercury speciation and scrub removal efficiency	• Hg species removal efficiency as a function of scrub composition • 90% material balance closure	• CEM measurement of Hgo and oxidized Hg upstream and downstream of quench/scrub system • Quench/scrub solution samples mercury measurement.
Determine mercury speciation and species reaction/conversion in staged combustor	• Hg species shift from oxidized to elemental mercury • 90% material balance closure (±10% error)	• CEM measurement of Hgo and oxidized Hg upstream and downstream of staged combustor.

Table 1-3. (continued).

Objective Statement	Quantifiable Objective Target or Criteria	Measurable Parameters and Test Methods
Determine mercury removal efficiency, mercury breakthrough, and migration through carbon bed	• Mercury removal efficiency of >99.9% or to MACT standard.	• CEM measurement of Hg^o and oxidized Hg across carbon bed • Analysis of carbon bed samples at conclusion of tests to establish mercury profile in bed.
Investigate pollutant destruction response to temperature, fuel loading, and oxygen concentrations 1. Parametric test during system shakedown and 100-hr calcination test period	• Vary temperature ± 50°C of target operating temperature in the 1st stage • Vary temperature ± 50°C of target operating temperature in the 2nd stage • Vary fuel injection rate ± 20% of target set point in 1st stage.	• CEM measurement of CO, CO_2, O_2, and unburned hydrocarbons at combustor inlet and outlet • CEM measurement of NO/NO_2 in inlet and outlet stream and midstream sample point.
Demonstrate steady staged combustor operating control and pollutant abatement efficiency: 1. NO_x reduction efficiency 2. THC/CO oxidation efficiency	• >25% on-line steady state operating time within optimum specifications • >85% NO_x time-averaged removal (or <1,000 ppm in exhaust gas • <10 ppm continuous HC in exhaust gas • <100 ppm continuous CO in exhaust gas.	• CEM measurement of CO, CO_2, O_2, and unburned hydrocarbons at combustor inlet and outlet • CEM measurement of NO/NO_2 in inlet and outlet stream and midstream sample point.
Determine chloride and fluoride species behavior and fate and emissions rates	• Product and scrub solution analysis accuracy of ± 20 wt% • Exhaust gas chloride emissions measurement with ±10 vol.% accuracy.	• Product, fines, and scrub solution material balance per sample analysis plan • Chloride analysis of carbon bed (before and after samples).

1.4 Calcination Theory

Calcination is a term used at INTEC to describe the process that converts acidic aqueous radioactive wastes liquids into a granular solid oxide product (referred to as calcine). The liquid wastes are sprayed into a hot fluidized-bed where the water and acids in the wastes are evaporated. The dry residue left on the bed, composed mainly of nitrate salts, is converted into chemically stable metal oxides. As the bed of granular particles increases in volume, it is continuously removed and pneumatically transported to dry storage bins where it can be safely stored in bins until final waste treatment can be accomplished.

Calcination of radioactive wastes was developed by the INEEL when it was first recognized that a fluidized-bed process had several advantages over spray-drying, wiped-film, rotary-kiln, and fixed or moving bed thermal treatment processes. Radioactive waste processes typically require a closed system that can be remotely operated. The process must be robust, easily maintainable, and efficient. Vast experience has demonstrated that a rotary kiln is not amenable to liquid waste treatment, often experiencing problems with seal leakage, solids caking, heat transfer and temperature maldistribution, and fugitive dust control problems. Fixed and or moving beds are also clearly not applicable to liquids or fine particulate wastes, while batch processes suffer from low throughput and solids transport challenges. Hence, the best reactor for radioactive waste solutions containing a high content of dissolved salts is a fluidized-bed reactor, especially when:

1. The liquid can be spray-fed

2. Solid bed material can be added via a lock hopper, screw conveyor, pressurized-gas injection inlet, or by solid entrainment

3. Heat deposition to the bed is feasible with in-bed electrical or fluid heat exchangers (steam, molten metal, or molten salt), external electrical resistance heaters, or in-bed exothermic reactions by the burning of a liquid or gaseous fuel such as kerosene

4. Temporal conditions (temperature, time, and composition) are suitable to drive key physical and chemical reactions,

5. The bed particle size distribution can be held approximately constant to maintain adequate bed fluidization and mixing characteristics

6. The particulate is non-agglomerating

7. Cleanup of high volumes of off-gas (due to typical high bed fluidizing gas requirements) is not a deterrent

8. The bed particles and fines generated and carried out with the fluidizing gas can be efficiently recovered and remotely transported and containerized

9. The off-gas can be cleaned to meet applicable emissions standards

10. The preferred mode of particle transport is by pneumatic transport systems that can be remotely operated and maintained.

1.4.1 Calcination Chemistry

In the past, SBW was blended with raffinate waste, which provided aluminum and zirconium to dilute the alkali metals and nitrates contained in the SBW. Upon termination of reprocessing activities at INTEC, all of the HLW raffinate solutions in the Tank Farm were eventually calcined by 2000. Calcination of the remaining SBW without additives cannot be accomplished in the current operating mode of the NWCF for two factors. First the melting points of sodium nitrate and potassium nitrate salts (T_m ($NaNO_3$) = 307°C and T_m (KNO_3) = 337°C) are lower than the typical 500°C operating temperature of the NWCF. Second, mass transfer limitations, kinetic limitations, and the formation of eutectic phases prevent complete thermal decomposition of the nitrates at 500°C, although the decomposition temperature of the pure components (T_d [$NaNO_3$]=380°C and T_d [KNO_3] = 400°C) are lower than the operating temperature of the calciner. Even when sodium nitrate decomposes to sodium hydroxide or to the sodium dioxide dimer, Na_2O_2, these compounds are also molten at an operating temperature above 400°C; consequently, the calcine bed will naturally agglomerate unless a diluent, such as aluminum nitrate, is added to the feed.

To overcome the problem of bed agglomeration, aluminum nitrate nona-hydrate (ANN, $Al(NO_3)_3$*9 H_2O) solutions were blended with the SBW feed. Aluminum nitrate decomposes at a fairly low temperature, and it is initially converted to amorphous aluminum but can be subsequently converted to highly coordinated crystalline phases, such as γ-alumina and α-alumina, at elevated temperatures within hot zones of the bed (i.e., near the in-bed flame zone or heating surfaces). For this reason, boric acid was commonly added batch-wise to the feed to suppress crystallization in the product. This also helped control the particle size and improve the solubility of the product in the scrub system.

Sodium and aluminum can also combine to form a double-metal oxide with a general formula of $NaAlO_2$. The formation of this compound appears to depend on temperature and the availability of amorphous, rather than crystalline, aluminum in the calcine. Through a series of pilot-plant testing, it was shown that when the ratio of aluminum-to-alkali metal ratio (AAR) was greater than 3.1:1, it was possible to calcine SBW at 500°C while avoiding bed agglomeration.

In order to improve SBW process rates, a series of new pilot-plants runs were completed to identify new operating conditions to reduce the amount of cold chemical additives required to process SBW wastes. The processing scheme, known as high-temperature calcination, involving calcining at a higher temperature (600ºC), with lesser amounts of ANN, was developed (Boardman et al. 1997; Nenni 2000, 2003). This flowsheet was tested for a limited time in the NWCF at the end of the H-4 Campaign. The run results were encouraging, but not entirely conclusive. From evaluation of these results an AAR of 2.25 was recommended in EDF-3213. However, some pilot-plant tests indicate that it may be possible to operate at an AAR of only 1.5 and also with possible elimination of additive boric acid (possibly because there is already sufficient boron present in the wastes). If a lower blend ratio is in fact possible, then boric acid addition can be avoided, and a significant savings in SBW processes time can be achieved. The calcine storage volume will also be significantly reduced.

1.4.2 Bed Stability Considerations

Stable fluidized bed particle dynamics requires a balance between the production of fines and control of particle agglomeration in the bed. The production of particles small enough to be elutriated with the upward moving gases must be minimized while producing a sufficient amount of small "seed" particles to provide nuclei for particle growth. Uniform feed deposition on the particles requires a uniform nozzle spray pattern and thorough mixing of the bed while the product is continually drawn from the bed to maintain a constant bed height. Buildup of particle agglomerates (caking) in the bed, on the vessel walls, on the calciner appurtenances, or on the feed nozzles must be avoided. The combined processes that affect the particle size distribution are illustrated in Figure 1-1. In order to maintain steady bed particle fluidization and dynamics, a target mean particle diameter must be achieved while the bed is withdrawn at the same rate as it is generated. This requires a balance between building the bed (increasing the particle diameters) and generating seed particles. If an excessive amount of fines are generated, or if the diameters of the fines are too small, then the fines will be elutriated from the bed, causing excessive loading on the off-gas cleanup equipment and possibly resulting in a calcine product that is difficult to pneumatically transport.

Fines generation is accomplished by two mechanisms: particle attrition and flash vaporization. The product to fines ratio (P/F) is a measure of the mass ratio of the product and fines generated during a test.

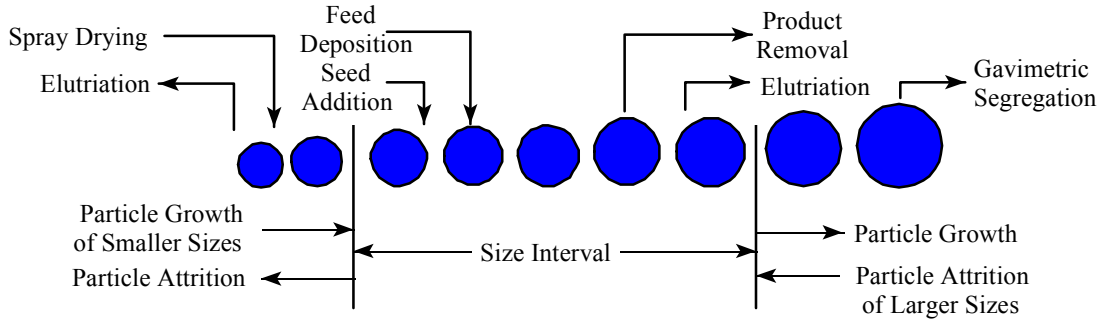


Figure 1-1. Processes that affect the particle size distribution during fluidized bed calcination.

The mass of product includes bed that was built (or lost) during the test; therefore, the P/F can be determined by the following equation:

$P/F = (P + (FB - (SB - COT\ 0\ P\&F)))/F$

where

P/F	=	product-to-fines ratio
P	=	mass of product collected during the test (excluding COT 0)
FB	=	mass of the final bed
SB	=	mass of the starting bed
COT 0 P&F	=	mass of product and fines collected at COT 0 hr
F	=	mass of fines collected during the test (excluding COT 0).

1.4.3 Bed Turnover

Bed turnover plays a significant role in the operation of new blends, and a bed turnover of greater than 90% is generally needed to ensure that the feed and bed material are indicative of the new product versus the behavior and characteristics of the starting bed. Bed turnover for each test is defined as:

$TO = (1 - e^{-(P/W)})*100\%$

where

TO	=	bed turnover percentage
P	=	weight of total product plus final bed minus product drained at COT 0 (kg)
W	=	average bed weight during the test (kg).

1.4.4 Spray Droplet Evaporation

Fine particles are generated by flash evaporation of the liquid droplets before and after adhering to the bed particles. The current feed nozzle design produces a finely divided mist in order to enhance uniform deposition on the bed particles. The atomized feed droplets evaporate according to the "d-squared" evaporation law:

$$d^2 = d_o^2 - [8 \frac{\rho_{air} D_{H_2O,air}}{\rho_l} ln(1 + B)]t \qquad [m^2]$$

where B is the Spaulding transfer number calculated from the following relationship,

$$B = C_{p,l} \frac{(T_\infty - T_s)}{\Delta H_v}$$

(with standard convention for all symbols). Droplet life is thus a direct function of the properties of the gas, the temperature difference between the droplet surface and the surroundings, and, most importantly, the initial diameter of the feed droplets size. Hence, the feed droplet size can be increased to offset enhanced flash evaporation at elevated bed temperatures. However, particles that are too large result in single particle quenching and give rise to possible particle-particle sticking (agglomerating) when the excessive liquid dries on the particle.

Figure 1-2 shows a plot of the theoretical extinction time for a droplet of water in a humid nitrogen gas stream at 600 and 700°C, respectively. The droplet life accounts for particle heating by conduction to the droplet, assuming that the velocity of the droplet is equivalent to the velocity of the surrounding gas. This assumption is a reasonable approximation for droplets that are atomized by the co-flowing atomizing gas. These calculations assume that the atomizing gas is already at the bed temperature. In reality, the atomizing gas must first be heated to the bed temperature; hence, the actual time of flight in non-obstructed space exceeds the correlation shown in Figure 1-2. These charts reveal, for example, that a 0.050-mm (or 50-micron particle) will be flash dried in 0.018 s (or 18 milli-seconds).

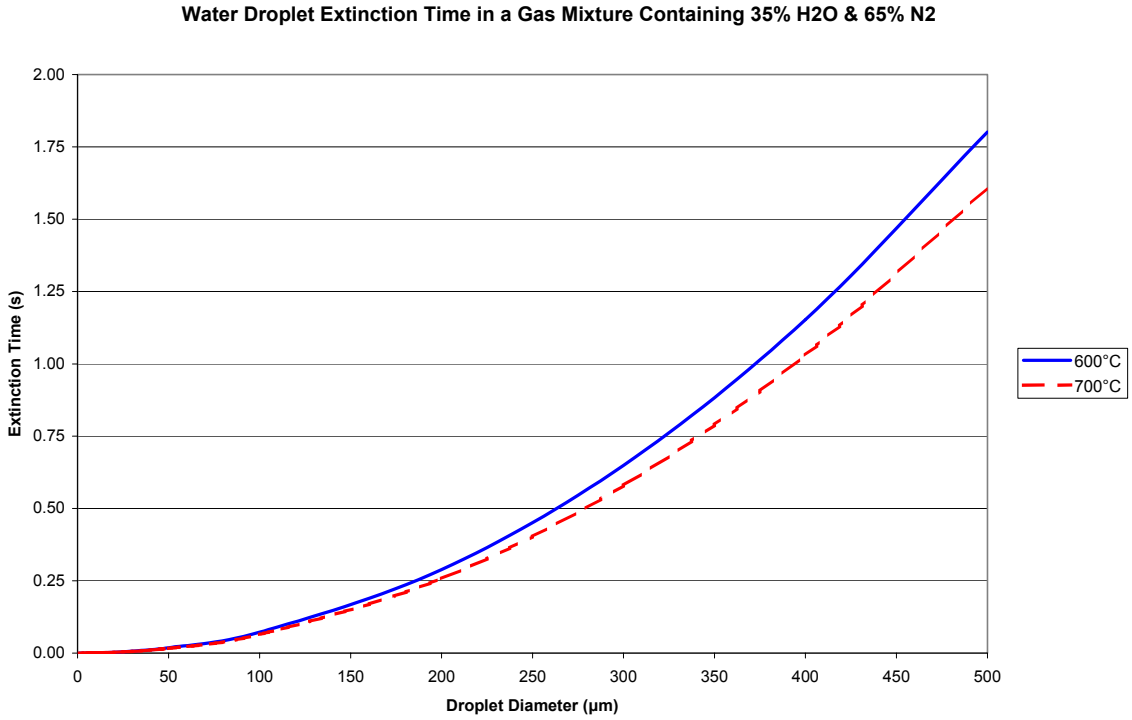


Figure 1-2. Comparison of droplet extinction time is a gas stream of 600 and 700°C (0 to 500-µm-diameter particle size range).

Consider the following example:

Assumptions:

- *Spraying Systems nozzle*. 40/100 liquid cap, 120 air cap
- *Gas orifice surface area*. 2.2 mm^2
- *Liquid injection rate*. 6 $L \cdot hr^{-1}$

- *Nozzle atomizing air volumetric flow*. 3000 L•hr^{-1} (NAR = 500)
- *Gas temperature*. 600°C.

Then, using Figure 1-2 and the gas velocity, the calculated extinction distance for a given water droplet is:

- *0.100 mm droplet*. 27 mm
- *0.200 mm droplet*. 80 mm
- *0.250 mm droplet*. 104 mm.

This example illustrates that a 0.250-mm particle leaving the nozzle at a spray angle of 35 degrees will impinge on the near side of a 150-mm diameter reactor (~91-mm actual distance to the wall) before it is fully evaporated. In order to minimize feed deposit on the wall, two conditions must be avoided; bed slugging and coarse atomization of the feed. Nozzle spray testing with water and stimulant feeds indicate that the minimum NAR of 250–300 is necessary to fully nebulize the waste feeds. Nozzle plugging, however, may disrupt the spray pattern, resulting in large droplet formation that will likely exacerbate bed agglomeration and well and feed deposition on the wall or vessel appurtenances.

The calculations also show that the affect of temperature increase from 600 to 700°C does not greatly affect particle evaporation times. Thus, spray drying of particles is more dependent on initial particle size.

Evaporation by film boiling on the surface of the particles increases at higher temperatures, resulting in the formation of small satellite particles that are easily ejected from the surface of the host particles. Film boiling results when the rate of heat transfer from the bed particles is high enough to cause rapid evaporation, which consequently prevents the droplets from wetting and adhering to the particle surface. Once the moisture is evaporated in the film layer above the particle, there may be insufficient adhesion of the residual solid to the surface of the particle.

Depending on the viscosity and surface tension of the feed and heat capacity of the solids, film boiling is observed at bed temperatures in excess of 600°C. Above 700°C, film boiling has been considered severe for similar calcination flowsheets, and, in fact, resulted in quantitative conversion of liquid feed to fines (i.e., P/F ratio of 0.05–0.1 observed at 700°C in comparison to 0.5–0.75 at 625°C). This phenomenon thus limits the bed operating temperature when feed is being atomized and the objective is to minimize fines generation.

To a lesser degree, the feed atomizing air is also believed to control the particle size through jet grinding. By increasing the velocity of the atomizing air, the momentum of the feed spray is increased. This increases the intensity of the particle-particle collisions in the vicinity of the feed nozzle. The collisions result in particle fracturing (attrition). The fluidizing air circulates the bed and causes particle collisions, but the fraction of fines attributed to the fluidizing air is minor compared to the fuel and feed nozzle atomizing air. A separate jet grinder is recommended to control particle growth in order to conserve feed conditions and to prevent feed nozzle wear.

1.4.5 Fluidizing Gas Velocity Considerations

Particle elutriation is affected by the fluidizing air velocity at the top of the bed and by bubble eruption at the bed surface. As the air bubbles burst at the surface, both large and small particles are thrust up into the particle disengaging section. The fines that are entrained in the gas stream can be

carried into the off-gas system unless they lose momentum and disengage from the off-gas in the freeboard section above the calciner bed. Most of the larger particles fall back to the bed; however, some of the fines remain entrained and are carried over into the off-gas cleanup train. Only those particles that have a terminal velocity that is lower than the velocity in the disengaging section ("freeboard") of the fluidized-bed will be carried out of the reactor. Particle collisions in the freeboard region also results in loss of momentum and particle disentrainment. It is, therefore instructive to understand the relationship between bed fluidizing velocity and particle terminal velocity to bound operating conditions that will result in excess fines carryover.

Figures 1-3 and 1-4 illustrate the concept of (1) the minimum calculated bed fluidization velocity and terminal velocity as a function of particle diameter for various particle densities. Both charts indicate the recommended fluidizing gas velocity of ~2.5 times the minimum for fluidization of a 450-µm-diameter particle with a density of 6 g/cm^3 (or about 0.66 m•s^{-1}). The corresponding terminal velocity plot indicates that all particles of diameter less than about 100 µm can be lost or elutriated from the bed, with all other considerations—such as particle-particle collisions, particle-wall collision, and gas velocity decrease with temperature and expansion in the freeboard section—not being taken into consideration.

1.4.6 Particle Size Distribution

The particle size distribution (PSD) is a good indicator as to whether agglomeration of the bed is occurring. In the context of this report, MMPD signifies the mass-mean particle diameter, while HMPD signifies the harmonic mass mean diameter, which is interpreted as the particle diameter with the average particle surface area. The HMPD is used when calculating pressure drop through the bed using, for example, the Eurgen equation.

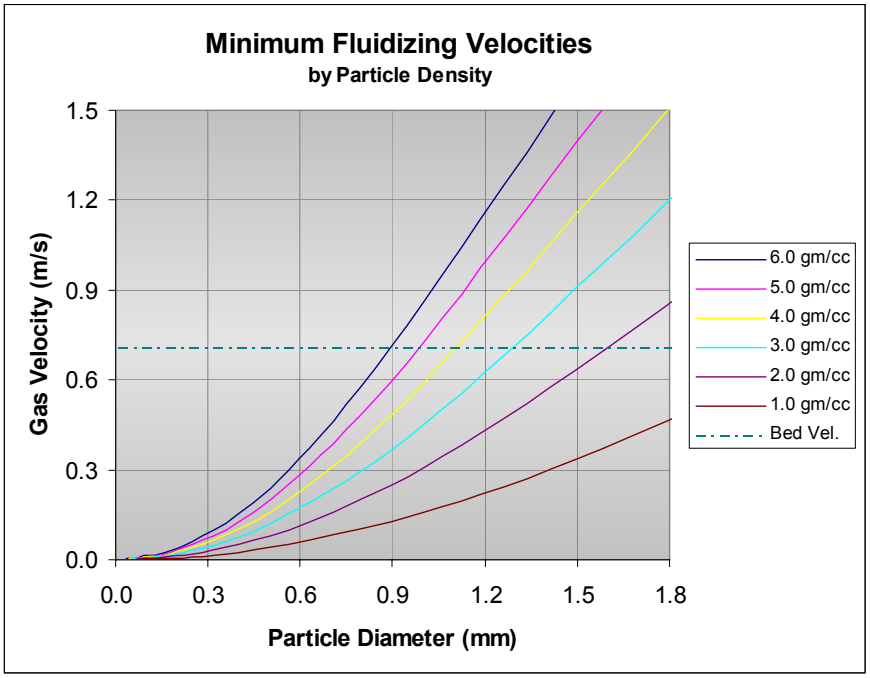


Figure 1-3. Minimum theoretical fluidization velocity as a function of particle diameter and particle density.

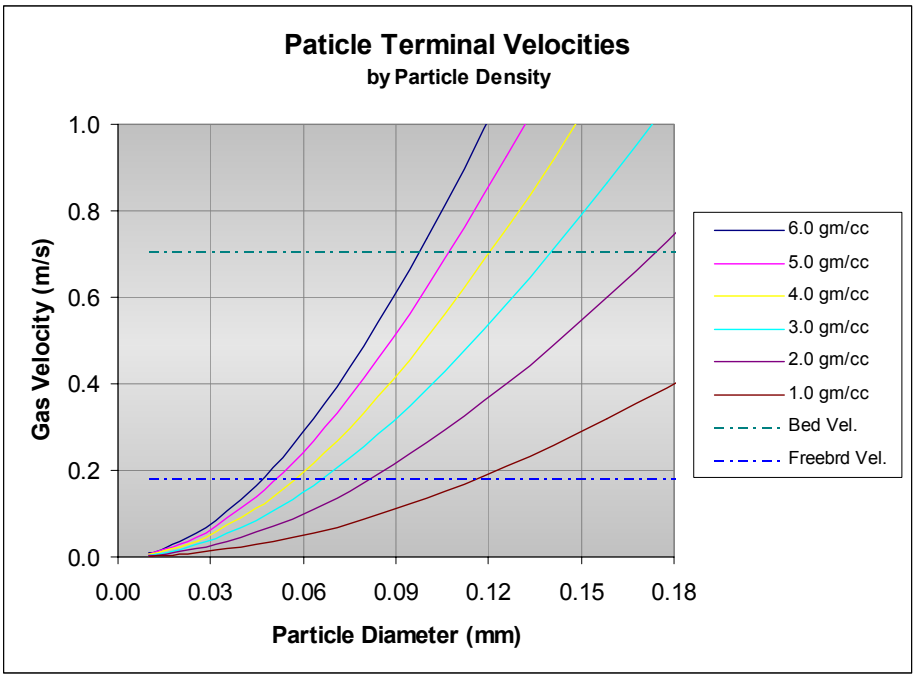


Figure 1-4. Minimum theoretical particle terminal velocity as a function of particle diameter and particle density.

The PSD, if plotted as the cumulative percent less than the screened particle size as a function of the particle size, usually forms an S-shaped curve. A PSD with very little size variation, as with the starting bed for all the tests, is indicated by a very steep center section of the curve. A gradual slope in the center section indicates a wider variation in particle size. Departure from an S-shaped curve indicates two or more dominant chemical or physical mechanisms controlling particle growth. For example, bed agglomeration results in a bi-modal particle distribution with a particle accumulation at a high particle diameter channel. Severe bed attrition can result in particle buildup at a smaller particle channel. Ideally, particle growth will be balanced by particle attrition, resulting in a steady-state MMPD and HMPD.

2. FLUIDIZED BED CALCINATION TEST SYSTEM DESCRIPTION

The High-temperature MACT Test is the sixth test series performed using the fluidized bed primary reactor constructed at the SAIC STAR Center. The prior test series were all fluidized bed steam reformer tests (Marshall 2003a; Marshall 2003b; Soelberg 2003; Soelberg 2004a and 2004b).

The test system (including feed systems, the fluidized bed vessel that includes the bed section and the freeboard (bed disengaging) section, the product collection and solids management systems, off-gas treatment and waste collection components, and the process monitoring and control station) covers a footprint of about 40 × 40 feet. All wetted components are constructed from corrosion-resistant materials. Equipment and piping are fabricated from 300-series stainless steel except for the fluidized bed vessel, which is fabricated from Inconel 800H. The system can be manually controlled or automatically controlled using a programmable logic controller (PLC) system with multiple human-machine interface (HMI) stations.

A simplified process flow diagram is shown in Figure 2-1. Table 2-1 summarizes pilot-plant subsystems and components.

Table 2-1. Fluidized bed test system components.

Fluidized Bed Reactor		
• Bed material feed subsystem, product recovery line, bed drains, product containers	• Fluidizing air compressor, pre-heater, and gas distributor ring	• Kerosene fuel tanks, pumps, delivery line, spray nozzle
• Compressed oxygen cylinders, burner nozzle feed line	• SBW simulant feed makeup, feed metering, and feed injection subsystems	• Liquid feed atomizing air supply line and metering system
• Thermocouple and pressure taps, pressure transducers	• Instrument line purge air supply and metering gauges	
Off-gas Control System		
• Off-gas cyclone separator, fines collection line, fines container	• Full wet quench, venturi scrubber, scrub tank, recirculation pumps, scrub water sample collection location	• Off-gas mist eliminators, and reheaters, condensate traps
• Multi-stage combustor, natural gas supply line, gas flow meters and controllers, water quench, combustion air supply, thermocouples, pressure indicators, oxygen analyzers	• Granular activated charcoal bed, external wall heaters, thermocouples, off-gas sample lines	• Air eductor
• HEPA filter	• Stack discharge	
Programmable Logic Control System and Process Monitoring Equipment		
• Human-Machine Interface computers for automatic process monitoring and process control	• Data collection and data management computers	• Continuous emissions monitors, sample collection probes, sample delivery lines, instrument calibration gases, data collection computers
• Off-gas mercury monitors, sample collection probes, and sample delivery lines	• Particle sieve trays, and shaker	• Balances, solid and liquid sample containers

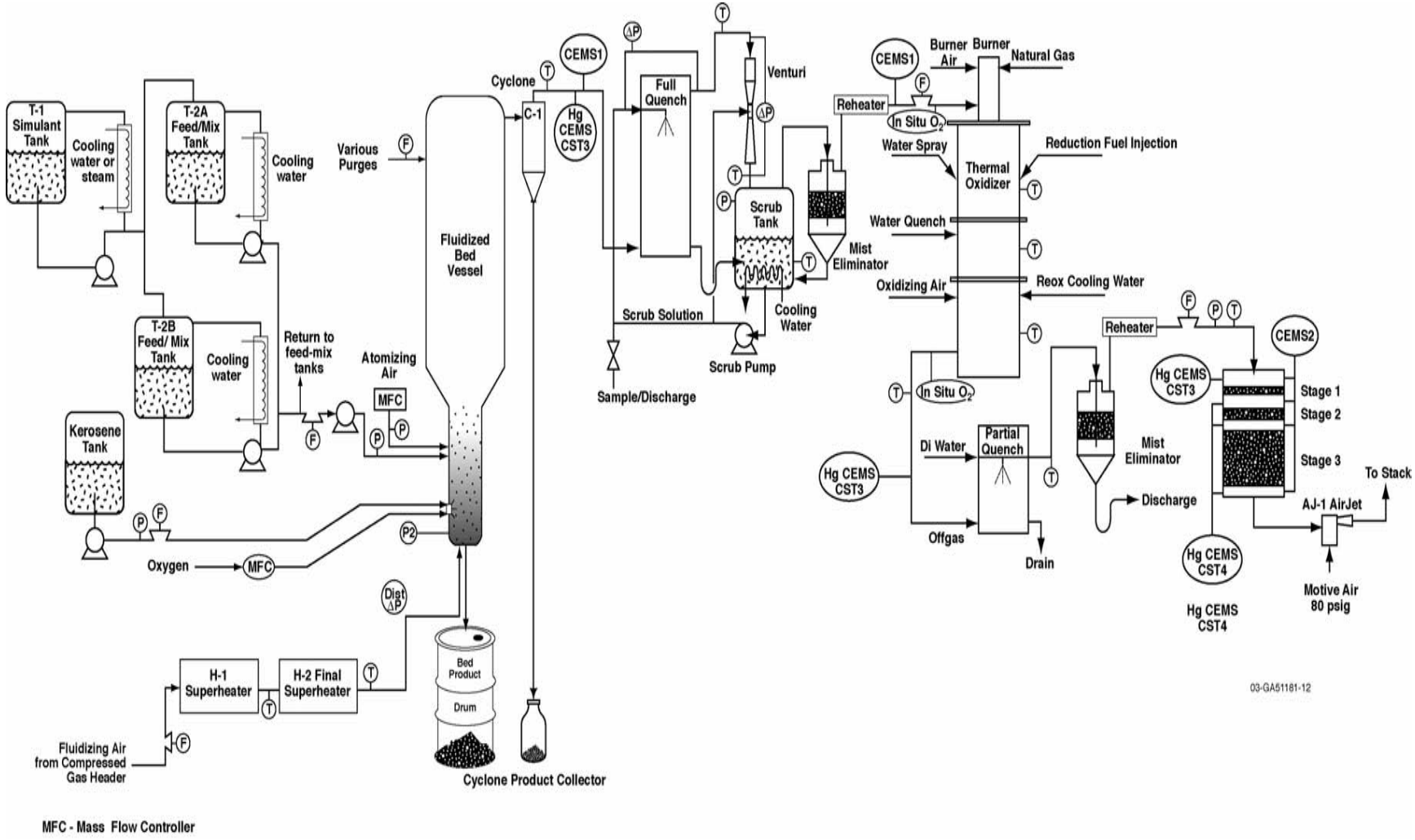


Figure 2-1. Fluidized bed test system process flow diagram.

2.1 Fluidized Bed Vessel

The fluidized bed test system represents an approximate 1/100 scale (liquid feed basis) plant compared to the current NWCF calciner located at the INTEC plant. The fluidized bed vessel has an inside diameter of 6 inches (nominal) because experience at the INEEL with fluidized beds, ranging in diameters from as small as 3 inches up to 12 inches, has shown that a 6-inch diameter bed is typically the smallest size that still provides bed particle attrition and growth dynamics that approach those of larger beds. However, with a 6-inch-bed diameter, the bed operates in a slugging mode, rather than a bubbling mode that is more typical of larger-diameter, full-scale beds. The 6-inch-diameter bed is a reasonable compromise between a bed large enough to provide representative test data and a system small enough to control testing and waste disposal costs.

The fluidized bed vessel (see Figure 2-2) is made of Inconel 800H pipe to tolerate operating conditions, including temperatures that could exceed 700°C, oxidizing or reducing conditions, and the presence of corrosive or hazardous materials.

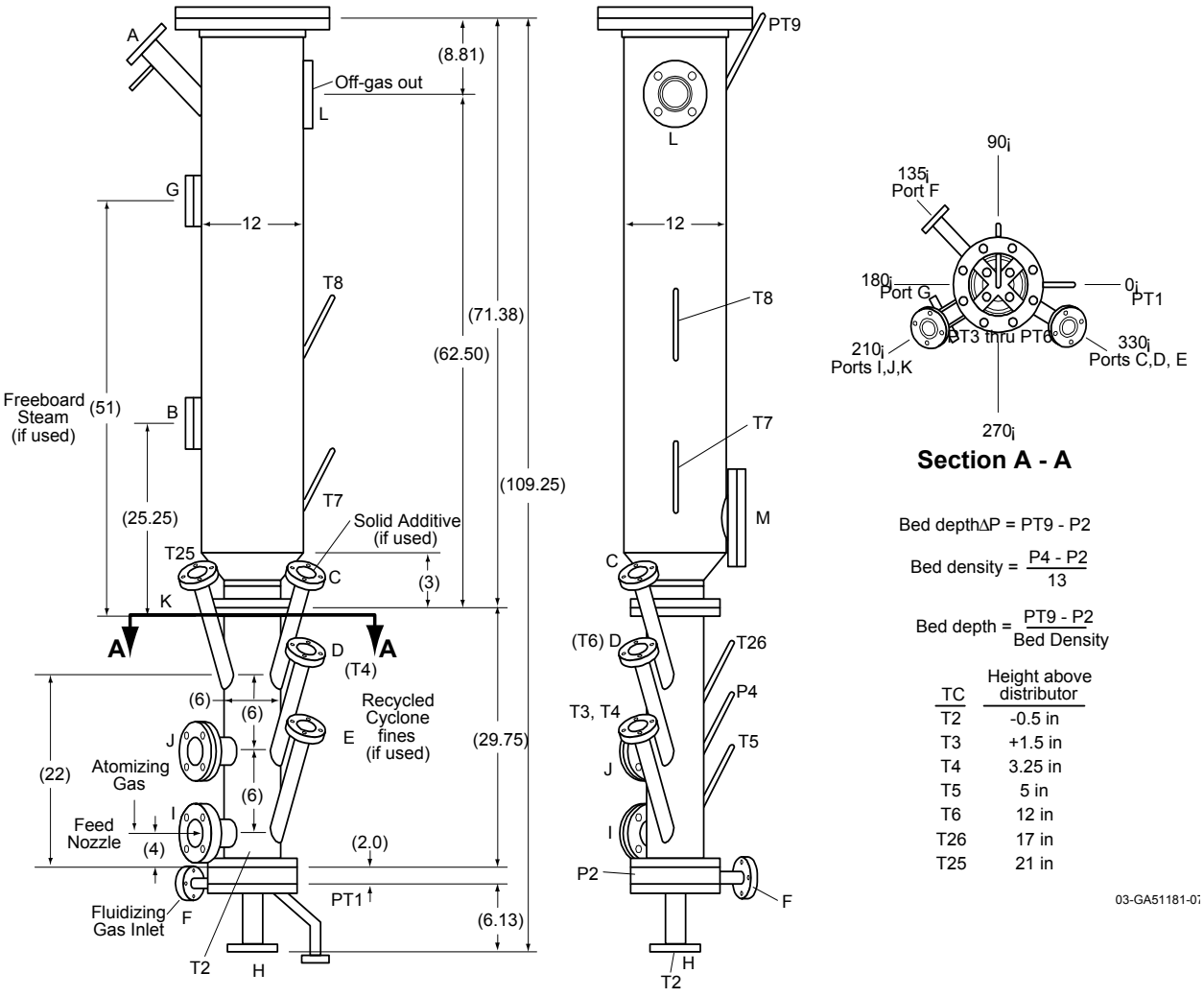


Figure 2-2. Fluidized bed vessel detail.

The main features of the fluidized bed vessel are the distributor plate through which the fluidizing gas enters the vessel below the fluidized bed section, and the freeboard (particle disengaging) section. The vessel is equipped with several process inlet/outlet ports, inspection ports, pressure taps for sensing internal static and differential pressures, and thermocouples for sensing internal and wall surface temperatures.

Three vertical rows of ports are provided, oriented at 120-degree intervals around the vessel circumference. These ports are used to access the vessel interior for material additions and process monitoring instrumentation.

2.1.1 Distributor Plate and Bottom Receiver

The distributor plate used for calcination tests is a 4-inch-diameter sparge ring made of half-inch, 300-series stainless steel tubing mounted in a 316 stainless steel, 6-inch, 150# flange. The ring has several orifices drilled into the ring to distribute the fluidizing gas. Half of the orifices are oriented radially inward at a downward angle of 45 degrees off-vertical, while the other half were oriented radially outward at a downward angle of 30 degrees off-vertical. The ring fully encompasses all of the penetrations/ports from the receiver. The distributor unit is designed to be removable from the fluidized bed vessel for inspection or replacement. Figure 2-3 and 2-4 illustrate the distributor plate and the bottom receiver.

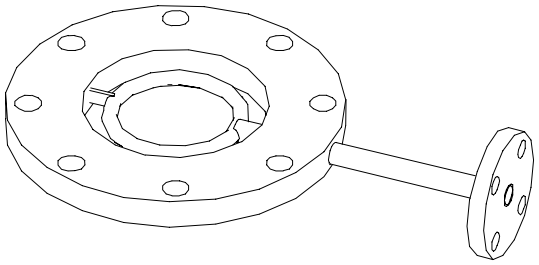


Figure 2-3. Ring distributor plate.

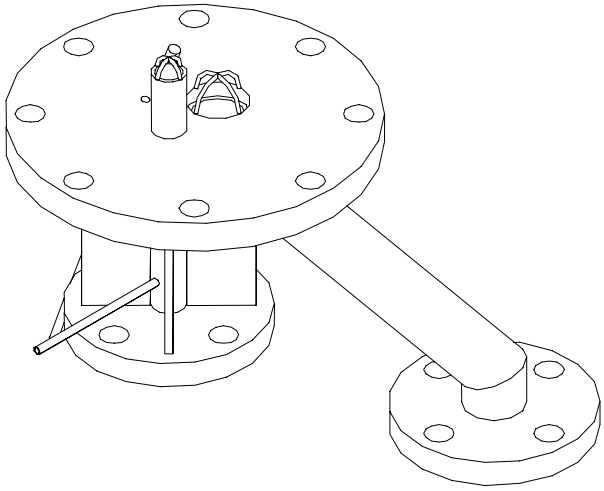


Figure 2-4. Bottom receiver design.

2.1.2 Fluidized Bed Section

The fluidized bed section is a nominal 6-in., schedule 40 Inconel 800H pipe that is 30 inches long and flanged on each end. Six ports are provided, stacked in two groups of three, with approximately 120 degrees between each group. Four of the ports are nominal 1.5-in., schedule 40 pipe, with standard 150-lb flanges that penetrate the bed section at a 60-degree downward angle. Two ports are horizontal 2-in. ports that are covered with outer flanges shaped like top hats. The top hat flanges provide a flat vertical surface (through with feed nozzles or other attachments could be made) that is nearly flush with the interior wall of the bed section and preclude gross quantities of bed material and product from accumulating and stagnating in the port.

Either of the two horizontal ports can accommodate a liquid feed nozzle. For the calcination tests, the SBW feed nozzle was located in the upper horizontal port. The liquid feed nozzle was a custom-designed, water-cooled, air-atomized spray nozzle adapted from a standard Spraying Systems Company externally mixed nozzle. Atomization was accomplished by an annular jet of air that surrounded the central liquid feed flow. The nozzle atomizing ratio (NAR) is the ratio of atomizing gas volume (at 1 atmosphere and 68^{o}F) per volume of liquid feed and is regulated to achieve the desired degree of liquid atomization. The NAR is typically adjusted between 400–800. The higher NAR settings not only atomize the feed but also provide enough turbulence in the feed zone to attrit product from bed particles, thereby reducing the bulk bed particle size.

The kerosene feed nozzle was located in the lower horizontal port. The kerosene was atomized at the nozzle with oxygen provided from a dewar supply system.

A series of nominal 3/8-in. tubes penetrate the bed section for pressure taps and temperature instrumentation. These probes are placed in a column positioned 120 degrees from two rows of larger-diameter ports. Temperatures are monitored at 6-in. intervals, with 1/8-in.-diameter sheathed thermocouples inserted through unused taps and addition ports. The differential pressures across the distributor and between the bottom and the top of the bed are measured to monitor distributor performance, bed mass, bed depth, and bed density.

Externally mounted, custom clam-shell electrical heaters from Watlow provide sensible heat transfer through the fluidized bed vessel walls to maintain the temperature in the fluidized bed and in the freeboard sections. The process control computer can be reconfigured at will to control bed and freeboard temperatures by the signal from any of the internal or externally mounted thermocouples.

2.1.3 Disengagement Freeboard Section

The freeboard section is a nominal 12-inch-diameter, 5-foot-long schedule 40 Inconel 800H pipe with a flanged top and a flanged 12 × 6-inch conical reducer on the bottom, connecting to the top of the fluidized bed section. Optimal bed design is based on the top of the fluidized bed reaching to the bottom of the conical section. The total fluidized bed height would then be 30 inches, equivalent to the 30-inch long bed section height. As the fluidizing gas velocity slows (when the inside vessel diameter increases from 6 to 12 in.), the bed particles disengage from the fluidizing gas and fall back down into the bed. The freeboard height (not including the conical section) is 5 feet, to provide sufficient time and distance for most of the larger particles to disengage from the fluidizing gas before they are carried out of the vessel.

Freeboard temperatures are monitored at several locations by internally and externally mounted thermocouples. Three 1/8-inch-diameter sheathed thermocouples are inserted through 3/8-inch tubing used to provide some mechanical support for the sheathed thermocouples. Another of these tubes serves as a pressure port for measuring the differential pressure of the bed.

The freeboard has a 2-in. flanged port near the top for a rupture disk, a 3-in. outlet port, a 6-in. "hand" port for inspections, and two 2-in. ports to accommodate gas distribution rails for the injection of reactive or tracer gases into the freeboard.

2.2 Fluidized Bed Feed Systems

Several feed systems interface with the fluidized bed vessel. These feed systems provide the capability of delivering different feeds into the fluidized bed system and include blended simulant feed, a solid additive, fresh bed material, bed fluidizing gas, feed atomizing gas, liquid kerosene, oxygen, instrument purge gas, filter pulse gas, and off-gas dilution gas.

2.2.1 SBW Simulant Feed System

SBW simulant makeup and feed preparation tankage is provided to facilitate continuous operation for several days and to enable varying and evaluating flowsheet chemistry. The Simulant Tank (T-1) is a makeup/hold tank for the feed simulant. The tank has a working capacity of 800 liters (200 gallons) and provision for adding both solid and liquid ingredients. A Simulant Transfer Pump (P-1) is used to circulate the simulant to promote suspension and dissolution of solid ingredients and is used to transfer simulant from the simulant tank to the feed/mix tanks. Insoluble solids are not normally added to the simulant makeup tank, but simulated heel solids may be the exception.

Two Feed/Mix Tanks (T-2A, T-2B), each with a working capacity of 200 liters (50 gallons), are used for feed adjustments and to provide the feed mixture to the fluidized bed. The tanks have provision for adding powdered amendments to the simulant transferred from the simulant tank. Each tank is equipped with a variable-speed agitator, cooling coils, and a feed recirculation pump to control feed temperature and to ensure that suspended solids do not settle in the tank or feed line. The process feed stream is taken as a side stream from the feed recirculation loop to the Feed Pump (P-9), which is a peristaltic pump used to transfer the feed mixture to the fluidized bed. The pump speed and direction are controlled by the process computer to maintain a constant process feed rate. The SBW feed stream is atomized with pressurized air at the bed inlet nozzle located in the upper vessel port.

2.2.2 Bed Material Feed System

The Fresh Bed Material Bin (LF-1) is an Acrison weight-loss feeder used to store fresh bed material and deliver it on demand to the fluidized bed. Bed material is generally dense enough to penetrate the fluidized bed without pneumatic or mechanical injection. Small quantities of bed material can also be added by hand through the shuttle valves below the weight-loss feeder.

2.2.3 Gas Injection Systems

Gases supplied to the fluidized bed system include the bed fluidizing gas, atomizing gas, instrument purges, filter pulse gas, and off-gas dilution gas. The system is configured to provide compressed air from a diesel-powered compressor. The fluidizing gas is preheated in Superheaters (H-1 and H-2), which are Inconel tube heaters from MRL Industries with customized 303 stainless steel mesh internals for improved heat transfer to the fluidizing gas. The maximum achievable outlet temperatures may vary as a function of the fluidizing gas properties and mass flow rates, but are generally close to the operating bed temperature. The superheater element (pipe) temperatures are maintained just below the maximum temperature limit of 1,100°C.

2.2.4 In-Bed Combustion Heating

Primary heat to maintain the sustained calcination process is provided by in-bed kerosene combustion. The bed fluidizing air is preheated, and the bed vessel is externally heated to establish initial bed conditions for auto ignition of the injected kerosene. Once ignited, in-bed combustion, augmented with fluidizing gas preheating and external vessel heating, provides calciner heating. The kerosene injection system consists of a kerosene storage tank, a fuel filter, a pressure pump, an injection nozzle, and association piping, valves, and instrumentation.

The kerosene is atomized with oxygen to increase the efficiency and intensity of combustion. The oxygen injection subsystem includes oxygen from a dewar tank, with associated pressure regulators, piping, and valving. Flow is monitored and controlled via the PLC.

2.3 Product Collection and Solids Management

Solid particles elutriated from the bed with the fluidizing gas are collected using the cyclone (C-1). External heaters are used to preheat the cyclone during startup, but they are not needed to maintain cyclone temperature during operation due to its close proximity to the calciner. Solids collected in the cyclone are transferred by gravity to a fines collection pot. Cyclone instrumentation includes the gas inlet and exit temperatures and the vessel differential pressure.

The original cyclone from the Phase 2 steam reforming test series was not designed to provide the efficiency required for the calcination test. The calcination test required a cyclone with up to 95% overall removal efficiency, and the original cyclone only provided about 50% removal efficiency. For this reason a new cyclone (Figure 2-5) was procured from a local manufacturer. The predicted removal efficiencies for the design are presented in the Table 2-2.

Table 2-2. Cyclone design removal efficiencies.

Size Range (um)	Removal Efficiency for that Size Range (%)
<3	50
3–5	70
6–10	90
11–20	95
21–40	98
41–60	99
>60	99.9

2.4 Off-Gas Emissions Control System

The off-gas system includes the following components: an initial partial quench, a wet venturi scrubber, a scrub liquid tank, a scrub liquid makeup tank, a mist eliminator, an off-gas reheater, a multi-stage combustor, a partial quench, a mist eliminator, another reheater following the partial quench, a 3-stage granular activated charcoal bed, an air eductor that induces off-gas flow through the test system, and a stack outlet.

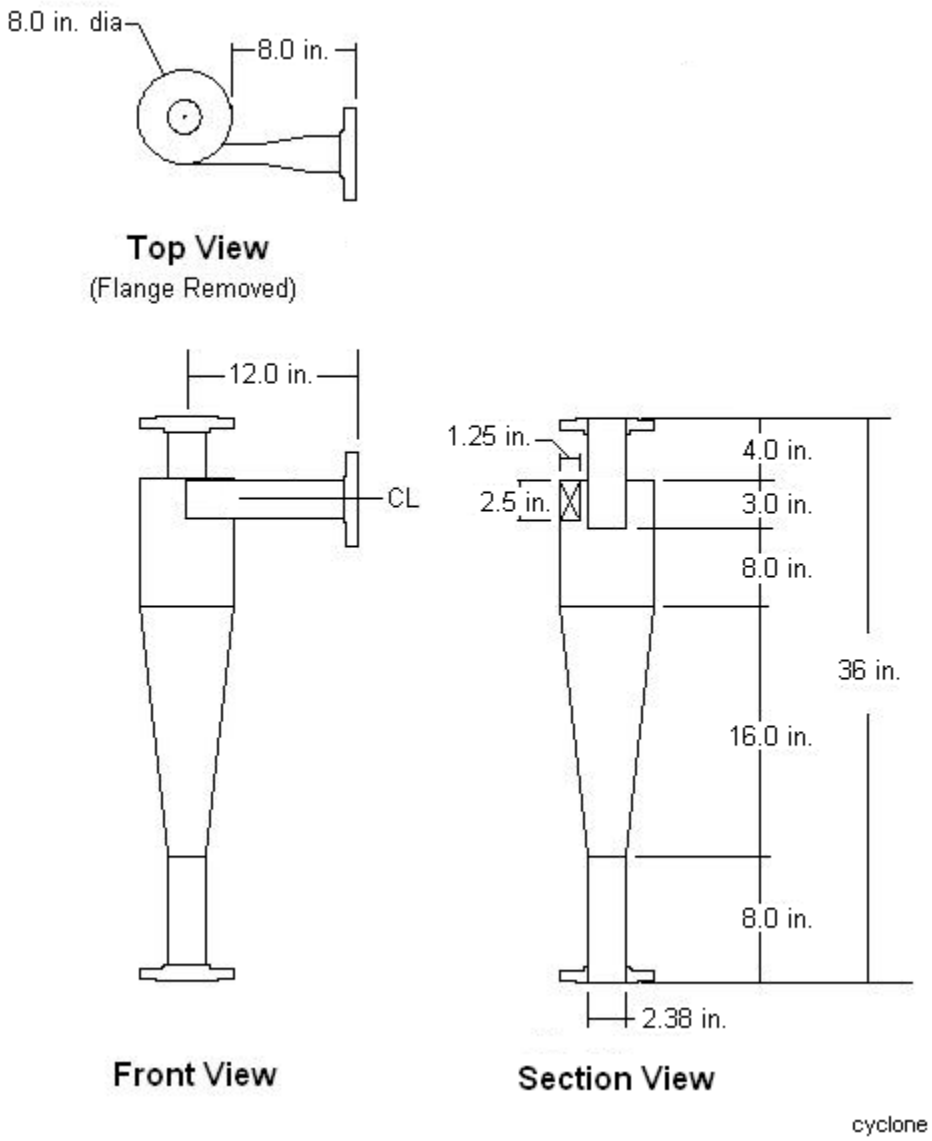


Figure 2-5. Cyclone used in the calcination test.

This off-gas system configuration primarily allows testing of the multi-stage combustion process for the destruction of the high NO_x off-gas emitted from the calciner during simulated sodium-bearing waste thermal treatment. The off-gas system components are instrumented for pressure, temperature, and flow rate monitoring and control. The system is instrumented with four continuous emissions monitoring systems (CEMS). All key off-gas control system instrumentation is electronically monitored and recorded by the PLC.

2.4.1 Quench Vessel

The gas exits the cyclone particulate separate and enters a quench vessel to lower the off-gas temperature to nearly the off-gas dewpoint before the venturi scrubber. The quench vessel (Figure 2-6) consists of a corrosion-resistant, non-lined metal tube with a scrub liquid (water) injection nozzle. Water is injected into the gas stream under pressure at sufficient flow to quench the hot gas stream to a control temperature between 70 and 120°C.

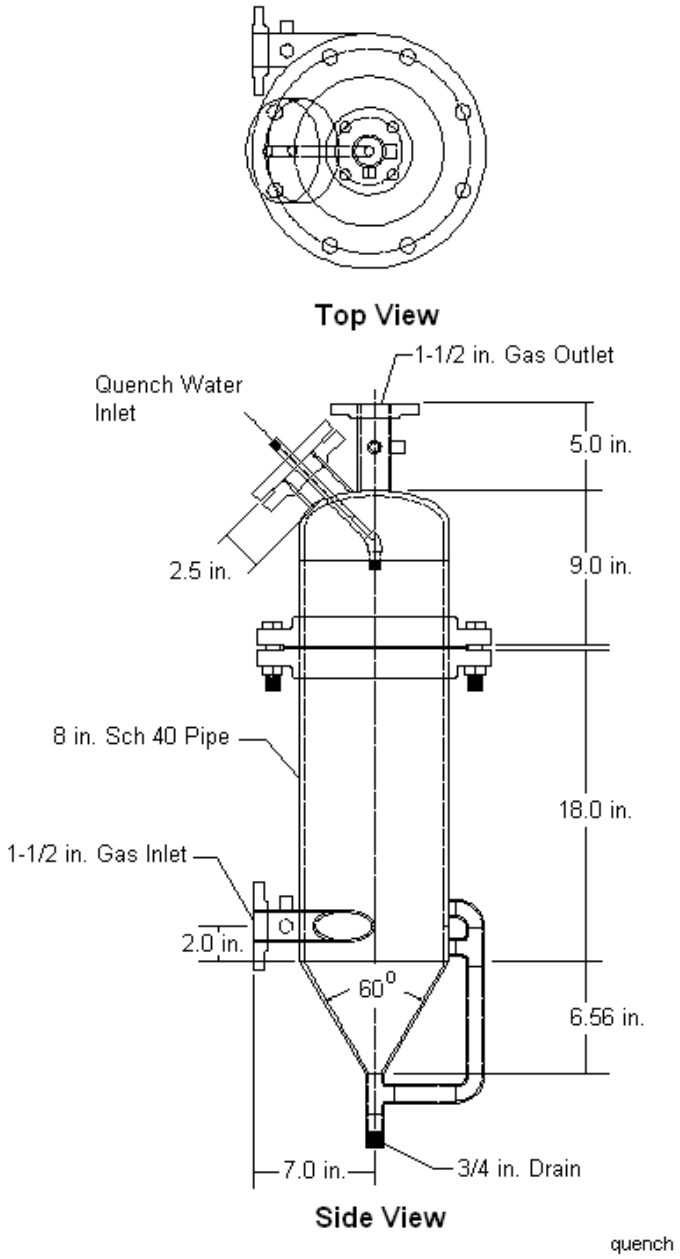


Figure 2-6. Quench vessel.

2.4.2 Venturi Scrubber

The venturi scrubber system was designed to emulate the NWCF scrubber system to provide test data representative of the NWCF scrubber. The venturi scrubber (Figure 2-7) removes particulate matter and scrubs soluble gases by forcing interaction of the gas stream with the scrub water through pressure drop across the venturi. The goal is to cause as much interaction as possible between the scrub liquid and the gas stream. The venturi scrubber runs at 30–50 inches of w.c. differential pressure drop to provide moderately efficient particulate scrubbing. Figure 2-8 presents a graph of generalized scrubber efficiency versus particle diameter for various types of particulate control devices and components (EER 1992).

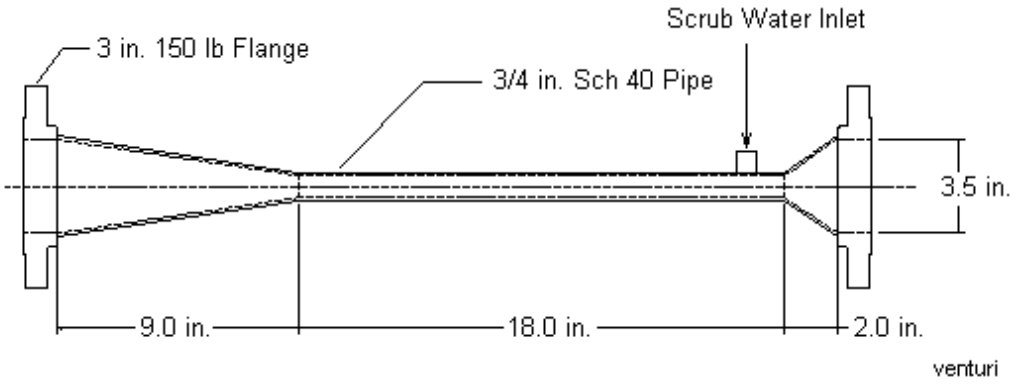


Figure 2-7. Venturi scrubber used in the calcination test.

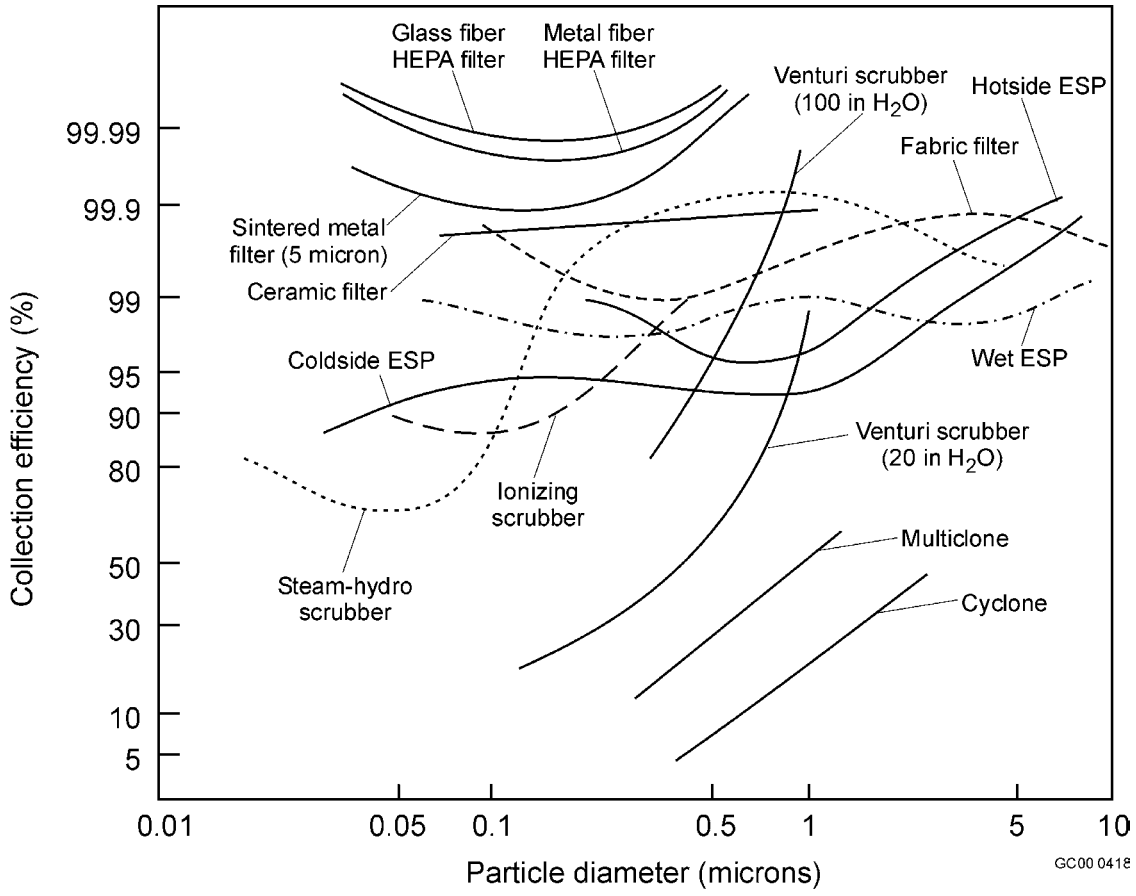


Figure 2-8. Particulate removal equipment efficiencies.

The typical scrubber pressure drop, at about 10 to 30 in. water, is not high enough to capture submicron particulate matter that remains in the off-gas through the fluidized bed freeboard section, the cyclone, and the quench vessel. However, it does provide sufficient interaction of the liquid and gas streams for other non-particulate contaminate control. The scrub solution recycle system includes the scrub tank and recycle pump that circulates scrub solution from the tank to the venturi. The scrub tank is fitted with a mist eliminator at the outlet to reduce scrub droplet entrainment in the off-gas system. The tank is also equipped with cooling coils used to maintain scrubber operation in a near water-level constant

state (i.e., neither condensing nor evaporating water) for waste minimization and mass balances. Depending on test objectives, the scrub solution may be neutralized, acidified, or otherwise adjusted to optimize performance or minimize secondary waste disposal. The Makeup Scrub Tank (T-5) and the Makeup Scrub Pump (P-5) supply scrub solution to the off-gas quench and venturi scrub system as needed.

2.4.3 Scrub Tank/Mist Eliminator

The wet off-gas exits the venturi scrubber, passes through the plenum space of the scrub tank, and exits the tank through a mist eliminator. Liquid drains from both the scrubber and the mist eliminator to the scrub tank. The mist eliminator removes most liquid droplets entrained into the gas stream by the venturi scrubber.

2.4.4 Reheater

Following the scrubber, the off-gas is reheated to approximately 120°C to dry residual aerosols downstream of the mist eliminator and to preclude any condensation of the gas in the lines before entering the multi-stage combustor.

2.4.5 Multi-stage Combustor

The multi-stage combustor (Figure 2-9) consists of 3 stages. The first stage is operated in a high-temperature [1,220ºC (2,200ºF)] reducing mode, with a design residence time of about 2 seconds, to destroy residual NO_x in the off-gas. The second stage is a partial quench, designed to cool the off-gas to a temperature low enough so that the third stage oxidation temperature is controlled below about 1,000°C (1,830°F) to minimize thermal NO_x formation.

The first stage uses a fuel-fired burner to maintain temperature and auxiliary injected fuel to maintain reducing conditions. The goal for the first stage is to react the unburned fuel with NO_x and reduce it to N_2. Mercury compounds such as HgO and $HgCl_2$ will be dissociated into elemental mercury vapor. The halogens (chlorine and fluorine) will pass through the first stage in the gaseous state. Control parameters include excess (auxiliary) natural gas, and residence time (indirectly only by control input flow rates). Water can also be injected to control excess heating in the first stage. This water injection was not required for the calcination test. At the operating temperature of the reducing stage, small amounts of residual particulate matter, if present in the gas, may soften, melt, and adhere to inside refractory surfaces.

The reducing stage has a 150,000 Btu/hr natural gas-fired axially mounted burner used to heat up and maintain chamber temperature at, at least, 1,000°C. The burner is equipped with an ultraviolet (UV) scanner to detect the presence of a flame, and a direct spark flame ignitor. The burner is operated at its optimum flame stoichiometry in order to maintain a stable flame. Off-gas enters the chamber from a tangential inlet port. Reductant fuel is with the off-gas to cause sufficiently reducing conditions to cause thermal non-selective, non-catalytic NO_x reduction (NSNCR).

In the second stage, the off-gas is partially quenched using a water spray atomized with nitrogen to a nominal temperature of 1,400–1,550ºF. The quench section exit temperature is a control parameter for regulating the amount of injected cooling water.

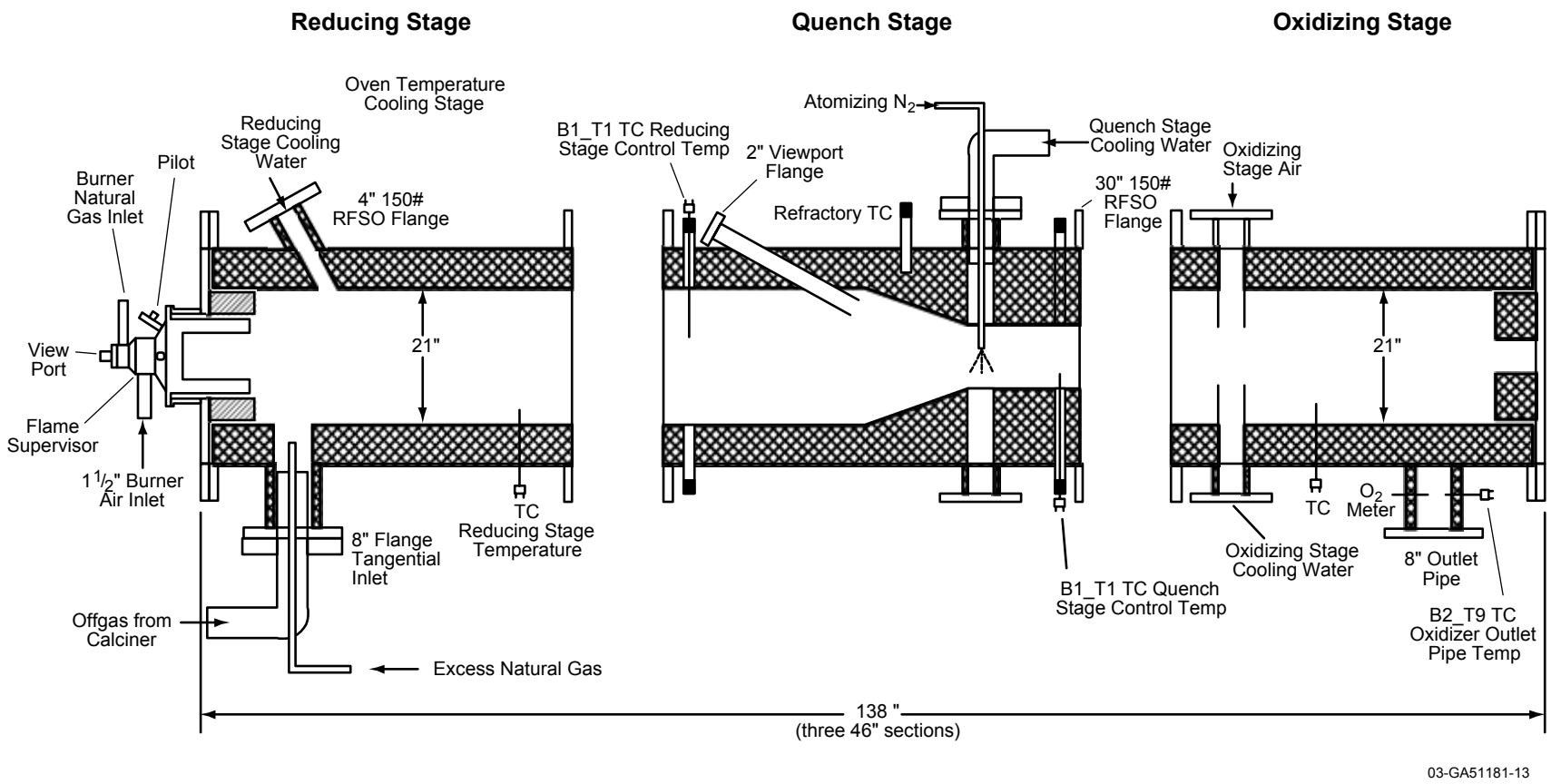


Figure 2-9. Multistage combustor for NO_x and hydrocarbon destruction.

Stage 3 is designed and operated to complete the combustion of residual reduced gas species (primarily CO, CH_4, and other light hydrocarbon gases) from the reducing stage while minimizing NO_x reformation. Air is injected to initiate auto-ignition of the reduced gas species. The air flow rate is controlled to minimize residual oxygen in the off-gas to 2–3% (wet basis), measured by an in situ O_2 analyzer located at the oxidizer stage exit pipe. The oxidizing stage temperature is determined by the temperature of the off-gas exiting the quench stage, the levels of reduced gas species in the off-gas, the amount of excess air (that dilutes the off-gas), and heat losses. Halogen gases and mercury pass through the third stage in the gaseous state.

The vessel is stainless steel and lined with 4.5 in. of high-temperature Greenlite 45L alumina, silica, and calcia refractory. The vessel is configured in three sections, each 46 in. long, for an overall length of 138 in. The inside dimension are 118 in. long (inlet port to outlet port), by 21 in. nominal inside diameter for Stages 1, 2, and 3. Stage 2 also includes a conically reduced section. Stage 1 is sized for a nominal 4-s residence time at a nominal gas flow rate of 97.3 scfm (738 acfm at 982°C and 8.9 psia [0.6 atmosphere]). The reaction chamber is configured with instrumentation and controls to ensure safe operation consistent with commercial burner and thermal oxidizer designs.

2.4.6 Partial Quench

The Partial Quench (PQ-1) is designed to cool the hot oxidizer stage exit gas to a low enough temperature to protect downstream equipment and the carbon bed. The design partial quench gas outlet temperature is 120°C, slightly higher than the gas dewpoint, warm enough to avoid moisture condensation, and cool enough for the carbon bed. The gas cooling is accomplished by spraying de-ionized water directly into the off-gas stream. The amount of water spray is automatically controlled, based on the gas temperature setpoint.

2.4.7 Mist Eliminator

A mist eliminator is located after the partial quench to ensure no moisture droplets are entrained in the off-gas stream and into the carbon beds. The mist eliminator drains to a separate drum.

2.4.8 Reheater

A reheater is located after the second quench and mist eliminator to raise the gas temperature sufficiently high to preclude any condensation of moisture in the carbon bed.

2.4.9 Granular Activated Carbon Bed

The carbon bed (Figure 2-10) is designed with three separate stages of activated carbon. The carbon is sulfur impregnated to aid in removal of elemental mercury from the off-gas. Sample ports between each stage enable gas sample collection for continuous monitoring. When mercury is included in the simulant feed, the carbon bed can be used to sorb mercury and other species, such as Cl, S, trace NO_x, and hydrocarbon species to evaluate carbon bed performance for sorbing these species. The carbon bed temperature is monitored and recorded by the PLC.

2.4.10 Air Eductor

The air eductor jet (AJ-1) induces a vacuum into the off-gas train sufficient to overcome all pressure drops in the system without any rotating mechanical parts that could become an ignition source. It also quickly dilutes the off-gas to a lower dew point and reduces any flammable gas concentrations in the exit gas. The vacuum can be controlled by motive air inlet pressure and/or drawing vacuum control air into the vessel off-gas line from within the enclosure.

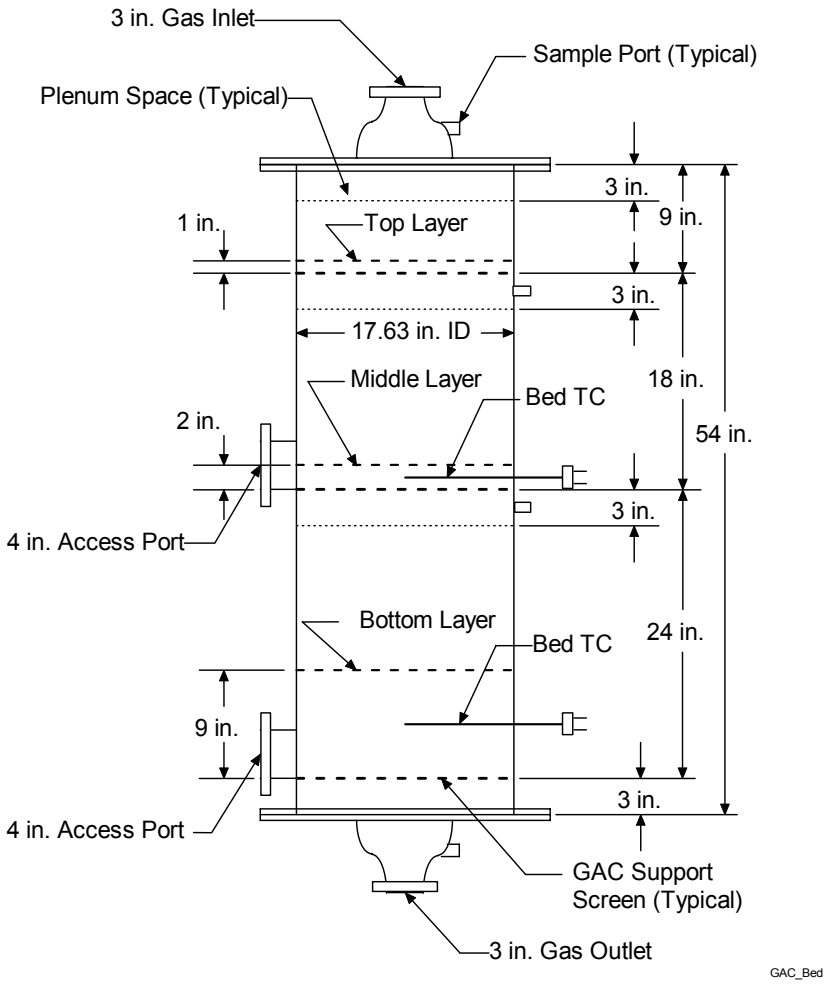


Figure 2-10. Three-stage carbon bed.

3. PROCESS MONITORING AND CONTROL, SAMPLE COLLECTION, AND SAMPLE ANALYSIS

The fluidized bed test system data acquisition and control system (DACS) uses Allen Bradley programmable logic controllers (PLCs) for control and data acquisition, and computer workstations running Rockwell software for human-machine interfaces (HMIs). The HMIs provides the operators with a graphic component view of the system broken into sections (screens) based on unit operations. The operators use these screens to monitor system parameters and control process components with command buttons and set point adjustments. The HMI also provides alarming and allows the operator to view selected process parameters as time-based trends.

Data collection was performed primarily by the PLC. Manually recorded data sheets were also used to collect data periodically throughout the tests. Additionally, mass and scrub solution accountability log sheets were maintained to record product and fines production rates, scrub solution blowdown and makeup additions, and condensate collection volumes. Limited process and off-gas monitor data were recorded manually on operator data sheets to ensure consistency with PLC records. Table 3-1 lists the key process data recorded throughout the calcination test.

3.1 Process Monitoring and Control

The DACS utilizes PC workstations running Rockwell software (RSSql) and Sequel databases for data acquisition and archiving. The PLCs interface with RSSql via an Ethernet connection to ensure the data collected from the various instruments is synchronized and archived in the Sequel database. As the information from the process is archived, the Sequel database performs calculations to determine such things as the theoretical mass and volume concentrations of various constituents in the off-gas at several points in the system. The archived process information and calculated values are available to the operator via a web interface on the HMI workstation.

All of the instrumentation installed in the Fluidized Test Bed Facility has a documented calibration performed by the manufacturer. In addition, the performance of each instrument is verified after installation with documented performance check. Table 3-1 lists key process monitoring and control instruments, with manufacturer, model, and claimed accuracy.

3.1.1 Fluidized Bed Vessel and Cyclone

The DACS components for the fluidized bed vessel and cyclone include monitoring and control of flow rates, temperatures, pressures, and differential pressures. Figure 3-1 shows the operator screen used for monitoring and controlling process conditions in the fluidized bed and cyclone. Thermocouples inserted into the fluidized bed vessel through thermal wells, and thermocouples welded to the outside of the vessel, provide internal and shell temperature measurements. Thermocouples were also placed inside the piping upstream and downstream of the cyclone. Other thermocouples were welded to the outside of the cyclone to measure the cyclone inlet, outlet, and shell temperatures. Electric heaters with discrete controllers heat the vessels. The operator uses the HMI to enter temperature set points and to select control thermocouples. The PLC transmits the selected temperature signals to the discrete temperature controllers.

The system vacuum is controlled by modulating the amount of dilution air added in an air jet to balance the pressure drops created by the column of fluidized bed solids. The measured pressure at the bottom of the fluidized bed vessel just above the gas distributor is the process variable for controlling the

Table 3-1. Key process monitoring during the calcination test.

Tag Name	Description	Manufacturer	Technology	Accuracy
AJ1_F1_VAL	Off-Gas Mass Flow to GAC (kg/hr)	Micro Motion	Coriolis	±0.044%
AJ1_P2_VAL	Off-gas Pressure at Reheater RH-2 Discharge (psia)	Rosemount	Capacitive	0.2% Span
AJ1_T1_VAL	Off-Gas Temperature at GAC Inlet (°C)	Idaho Lab	Type K	±2.2°C
B1_A1_O2	Raw Oxygen Concentration at B-1 Oxidizer Discharge (Wet Basis) (%)	Ametek	Zirconium Oxide	±0.75%(measured)
B1_A2_VAL	Raw Oxygen Concentration at B-1 Oxidizer Inlet (Wet Basis) (%)	Ametek	Zirconium Oxide	±0.75%(measured)
B1_F1_VAL	Natural Gas Mass Flow to B-1 Burner (kg CH_4 / hr)	Micro Motion	Coriolis	±0.044%
B1_F2_VAL	Air Mass Flow to B-1 Burner (kg Air / hr)	Micro Motion	Coriolis	±0.044%
B1_F3_VAL	Excess Natural Gas Mass Flow to Reducing Stage of Combustion Unit (CH_4 kg/hr)	Micro Motion	Coriolis	±0.044%
B1_F4_VAL	Cooling Water Mass Flow to Combustion Unit (kg H_2O / hr)	Micro Motion	Coriolis	±0.044%
B1_F5_VAL	Air Mass Flow to Oxidizing Stage of Combustion Unit (kg Air / hr)	Micro Motion	Coriolis	±0.044%
B1_F5A_VAL	Air Mass Flow to Oxidizing Stage of Combustion Unit (Bypass)(kg Air / hr)	Micro Motion	Coriolis	±0.044%
B1_F6_VAL	Off-Gas Mass Flow at Combustion Unit Inlet (kg Off-Gas / hr)	Micro Motion	Coriolis	±0.044%
B1_F7_VAL	Nitrogen Mass Flow to Partial Quench Stage Purges (kg N_2 / hr)	Micro Motion	Coriolis	±0.044%
B1_T1_VAL	Temperature in Reducing Stage of Combustion Unit (°C)	Idaho Lab	Type K	±2.2°C
B1_T2_VAL	Temperature in Partial Quench Stage of Combustion Unit (°C)	Idaho Lab	Type K	±2.2°C
B1_T3_VAL	Temperature in Oxidizing Stage of Combustion Unit (°C)	Idaho Lab	Type K	±2.2°C
B1_T5_VAL	Temperature in Piping Between Combustion Unit and Partial Quench (°C)	Idaho Lab	Type K	±2.2°C
B1_T8_VAL	Temperature at Reheater RH-1 Exhaust (°C)	Idaho Lab	Type K	±2.2°C
B1_T9_VAL	Temperature at Combustion Unit Exit	Idaho Lab	Type K	±2.2°C
C1_PD_VAL	Differential Pressure Across C-1 Cyclone (in WC)	Rosemount	DP Cell	0.25% Span
C1_T1_VAL	Off-gas Temperature at C-1 Cyclone Inlet (°C)	Idaho Lab	Type K	±2.2°C
C1_T2_VAL	Off-gas Temperature in C-1 Cyclone (°C)	Idaho Lab	Type K	±2.2°C
C1_T3_VAL	Off-gas Temperature at C-1 Cyclone Discharge (°C)	Idaho Lab	Type K	±2.2°C
EVS1_F2_VAL	Scrub Solution Volume Flow to EVS-1 Scrubber (l/hr)	Yokogawa	Mag.	0.25% of Span
EVS1_PD1_VAL	Differential Pressure Across EVS-1 Scrubber (in WC)	Rosemount	DP Cell	0.2% Span
F1_PD_VAL	Differential Pressure Across F-1 Filter Vessel (in WC)	Rosemount	DP Cell	.25% Span
F1_T1_VAL	Off-gas Temperature in F-1 Filter Vessel (°C)	Idaho Lab	Type K	±2.2°C
F1_T2_VAL	Off-gas Temperature at F-1 Filter Vessel Discharge (°C)	Idaho Lab	Type K	±2.2°C
GAC1_PD_VAL	Differential Pressure Across GAC (in WC)	DWYER	DP Cell	2% of Scale
GAC1_T_VAL	Temperature 1 in GAC (°C)	Idaho Lab	Type K	±2.2°C
GAC1_T2_VAL	Temperature 2 in GAC (°C)	Idaho Lab	Type K	±2.2°C
H1_F2_PV	Fluidizing Gas Mass Flow to Fluidized Bed (kg/hr)	Micro Motion	Coriolis	±0.044%
H1_T1_VAL	Process Gas Temperature at H-1 Superheater Inlet (°C)	Rosemount	Mass ProPlate	±.56°C
H1_T2_VAL	Process Gas Temperature at H-1 Superheater Discharge (°C)	Idaho Lab	Type R	±2.2°C
H1_T2B_Val	Pipe Temperature in H-1 Superheater (°C)	Idaho Lab	Type K	±2.2°C
H2_T_VAL	Process Gas Temperature at H-1 Superheater Discharge (°C)	Idaho Lab	Type R	±2.2°C
H2_TB_Val	Pipe Temperature in H-2 Superheater (°C)	Idaho Lab	Type R	±2.2°C
ME1_PD1_VAL	Differential Pressure across the Mist Eliminator (in WC)	Rosemount	DP Cell	0.25% Span
PQ1_F1_VAL	Cooling Water Mass Flow to PQ-1 Partial Quench (kg/hr)	Micro Motion	Coriolis	±0.044%
PQ1_PD1_VAL	Differential Pressure Across PQ-1 Partial Quench (in H2O)	Rosemount	DP Cell	0.25% Span
PQ1_T1_VAL	Temperature at PQ-1 Partial Quench Discharge (°C)	Idaho Lab	Type K	±2.2°C
Q1_F1_VAL	Scrub Solution Volume Flow to Q-1 Quench (l/hr)	Micro Motion	Coriolis	±0.044%
Q1_T1_VAL	Temperature of Q-1 (°C)	Idaho Lab	Type K	±2.2°C
SR1_D1A_VAL	Simulant Feed Density (gm/cc)	Micro Motion	Coriolis	±0.044%
SR1_F1A_VAL	Simulant Feed Mass Flow to Fluidized Bed (kg/hr)	Micro Motion	Coriolis	±0.044%
SR1_F1B_KGH	Atomizing Calculated Mass Flow Rate Based on Raw Value from MFC	Brooks	Thermal Anem	1%of Setpoint
SR1_P1_VAL	Pressure at Bottom of Fluidized Bed (psia)	Rosemount	Capacitive	0.2% Span
SR1_PD1_VAL	Differential Pressure Across Distributor Plate (in WC)	Rosemount	DP Cell	0.25% of Span
SR1_PD2_VAL	Differential Pressure Across Lower 13 in of Fluidized Bed (Density) (in WC)	Rosemount	DP Cell	0.25% of Span
SR1_PD3_VAL	Differential Pressure Across Fluidized Bed (in WC)	Rosemount	DP Cell	0.25% of Span
SR1_T11_VAL	Wall Temperature of Upper Disengaging Section (°C)	Idaho Lab	Type K	±2.2°C
SR1_T12_VAL	Wall Temperature of Mid Disengaging Section (°C)	Idaho Lab	Type K	±2.2°C
SR1_T13_VAL	Wall Temperature of Lower Disengaging Section (°C)	Idaho Lab	Type K	±2.2°C
SR1_T15_VAL	Cooling Water Jacket Temperature on Feed Nozzle (°C)	Idaho Lab	Type K	±2.2°C
SR1_T19_VAL	Wall Temperature of Upper Fluidized Bed (°C)	Idaho Lab	Type K	±2.2°C
SR1_T2_VAL	Bed Temperature at -0.5 inch height in Fluidized Bed (°C)	Idaho Lab	Type K	±2.2°C
SR1_T20_VAL	Wall Temperature of Lower Fluidized Bed (°C)	Idaho Lab	Type K	±2.2°C
SR1_T25_VAL	Steam Reformer Internal Temperature at 21in High	Idaho Lab	Type K	±2.2°C
SR1_T26_VAL	Steam Reformer Internal Temperature at 17in High	Idaho Lab	Type K	±2.2°C
SR1_T3_VAL	Bed Temperature at 1.5 in Fluidized Bed Height (°C)	Idaho Lab	Type K	±2.2°C
SR1_T4_VAL	Bed Temperature at 3.25 in Fluidized Bed Height (°C)	Idaho Lab	Type K	±2.2°C
SR1_T5_VAL	Bed Temperature at 5 in Fluidized Bed Height (°C)	Idaho Lab	Type K	±2.2°C
SR1_T6_VAL	Bed Temperature at12 in Fluidized Bed Height (°C)	Idaho Lab	Type K	±2.2°C
SR1_T7_VAL	Off-gas Temperature in Lower Disengaging Section (°C)	Idaho Lab	Type K	±2.2°C
SR1_T8_VAL	Off-gas Temperature in Mid Disengaging Section (°C)	Idaho Lab	Type K	±2.2°C
SR1_T9_VAL	Off-gas Temperature in Upper Disengaging Section (°C)	Idaho Lab	Type K	±2.2°C
T7_P_VAL	Vapor Space Pressure in T-7 Tank (psia)	Rosemount	Capacitive	0.2% Span
T7_T1_VAL	Scrub Solution Temperature in T-7 Tank (°C)	Idaho Lab	Type K	±2.2°C
T7_T2_VAL	Off-gas Temperature at Tank T-7 Discharge (°C)	Idaho Lab	Type K	±2.2°C
V1_F1_VAL	Gas Supply Mass Flow at System Inlet (kg/hr)	Micro Motion	Coriolis	±0.044%

[PLC instrumentation and accuracy.xls]Sheet1

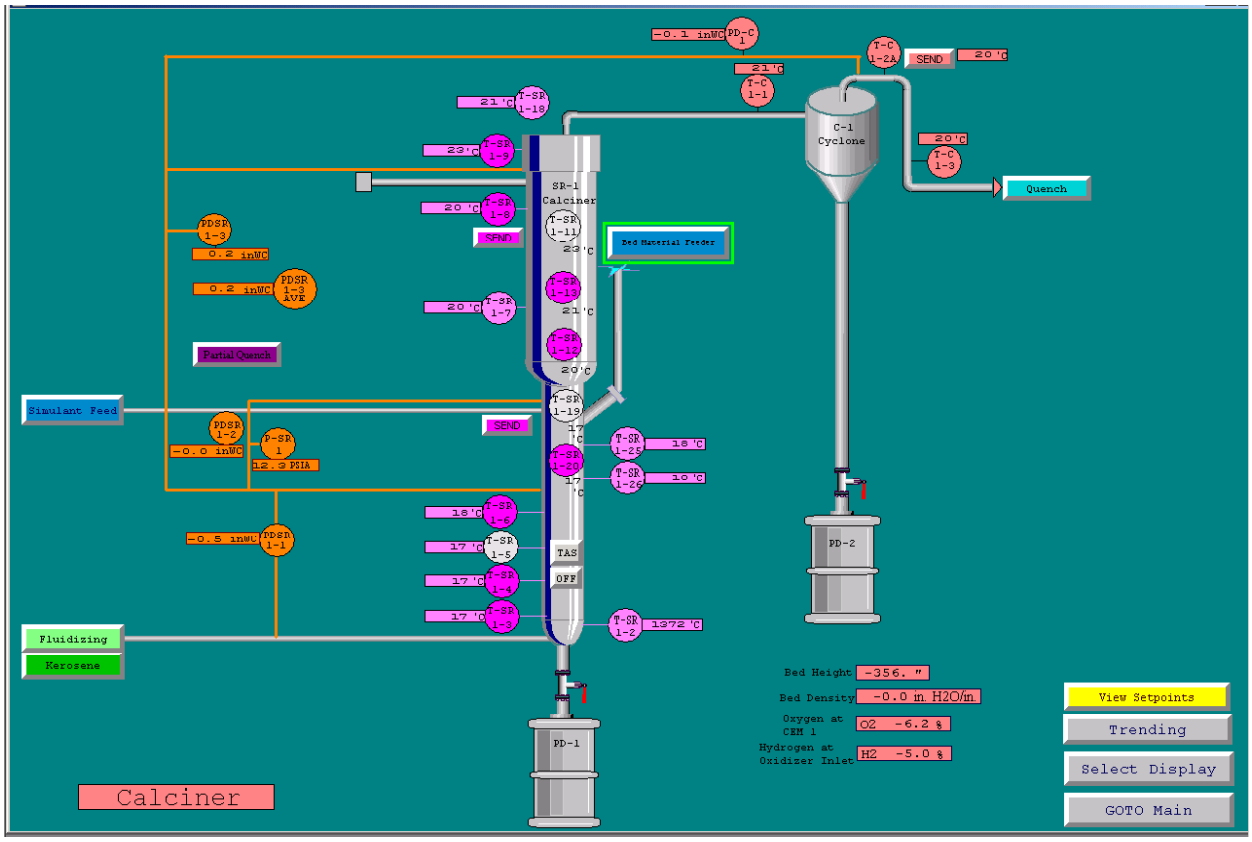


Figure 3-1. HMI control screen for fluidized bed feed rates and fluidized bed and cyclone operating conditions.

vessel pressure. The operator uses the HMI to enter the desired pressure set point; the PLC maintains the pressure in the vessel by adjusting a dilution air valve as the column of fluidized bed solids changes. Three differential pressure measurements are taken at different points in the fluidized bed vessel to monitor fluidization of the bed material. The differential pressure across the cyclone is also measured.

3.1.2 Quench, Venturi Scrub System, Mist Eliminator, and Re-heater

The DACS components for the quench, venturi scrubber, mist eliminator, and re-heater (Figure 3-2) include monitoring and control of flow rates, temperatures, pressures, differential pressures, and liquid levels. The differential pressures across the quench, venturi scrubber, and the mist eliminator are measured. The pressure in the vapor space of the scrub tank is measured, and the liquid level in the scrub tank is approximated by a calculation. The PLC calculates the level in the scrub tank using the differential pressure from the bottom of the scrub tank to atmosphere, tank dimensions, and the density of the scrub solution entered by the operator at the HMI.

Process temperature measurements consist of thermocouples placed inside the quench and scrub tank vessels, as well as in the piping around the scrubber and downstream of the re-heater. The temperature of the off-gas at the exit of the quench vessel is maintained by controlling the flow of scrub solution to a nozzle in the vessel. The temperature of the scrub solution in the scrub tank is maintained by controlling the flow of water to cooling coils in the tank. In both cases, the operator enters a temperature set point at the HMI, and the PLC controls a valve to adjust liquid flow to achieve the set point.

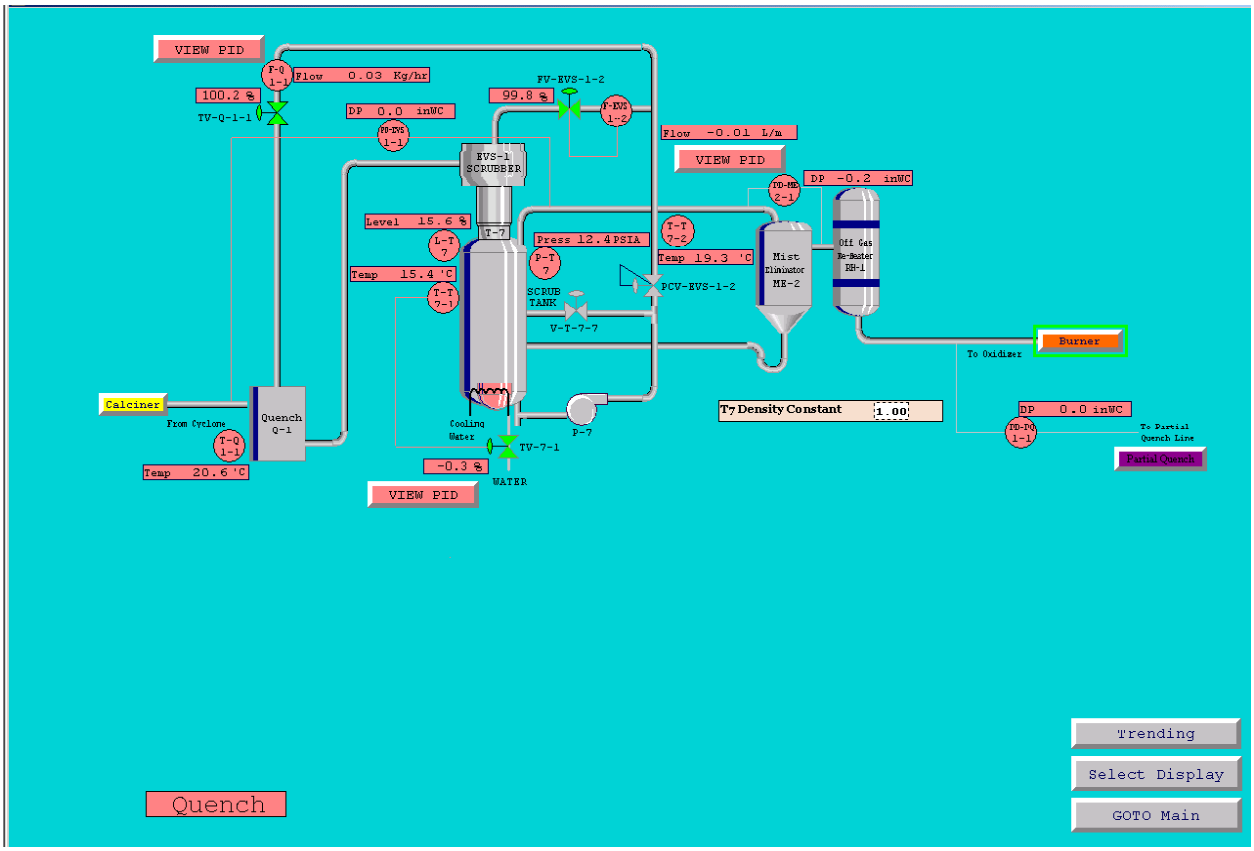


Figure 3-2. HMI control screen for monitoring and controlling the off-gas quench, scrubber, mist eliminator, and reheater.

The flow of scrub solution to the quench and the venturi scrubber are measured independently. The quench flow rate is measured with a Coriolis flow meter, while the flow rate to the venturi scrubber is measured with a magnetic flow meter. The operator enters a flow rate set point at the HMI, and the PLC controls a valve to adjust liquid flow rate to achieve the set point.

3.1.3 Staged Combustor

The DACS for the staged combustor works in tandem with a control panel provided by the burner manufacturer (North American) to safely monitor and control temperatures, oxygen concentrations, and excess fuel in the various stages of the combustion vessel. Figure 3-3 illustrates the HMI screen used to monitor and control the staged combustor. Solenoid blocking valves on the natural gas supply, excess natural gas supply, air to the combustion vessel, and water to the combustion vessel are only allowed to open when specific operational parameters are met which ensure operation within the safety envelope. The operator controls the temperature in the three stages by entering the desired set points at the HMI. The PLC controls valves to adjust natural gas and water flow rates to achieve the set points. Coriolis flow meters are used to measure the following flow rates:

- Off-gas flow to the combustion vessel
- Natural gas to the burner, air to the burner
- Excess natural gas to the first section
- Atomizing nitrogen to the second section

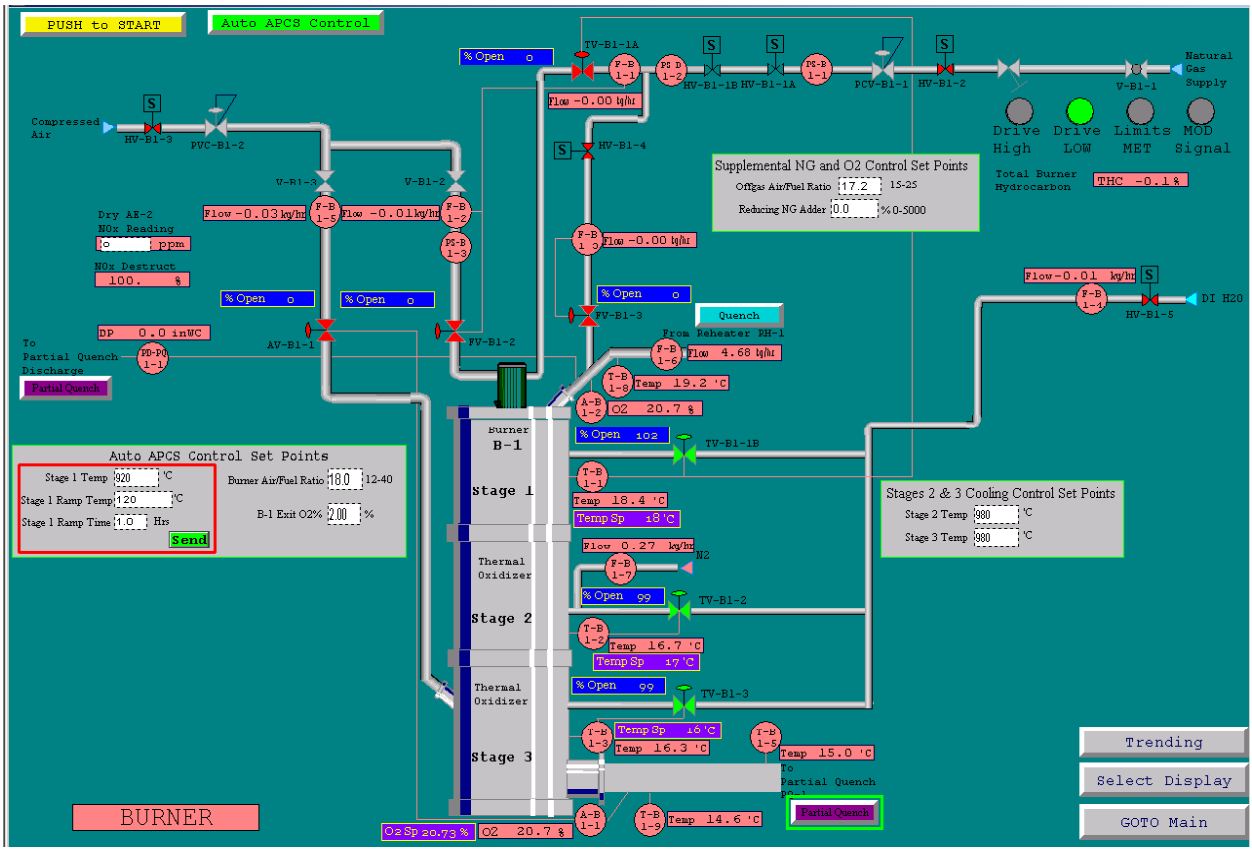


Figure 3-3. HMI control screen for monitoring and controlling the staged combustor.

- Air to the third section
- Bypass air to the third section
- Water spray supplied to all three sections.

Zirconium oxide, in situ oxygen sensors are used to measure the oxygen concentration of the off-gas at the entrance and exit of the combustion vessel. The flow rate of air to the burner is ratio controlled with the flow of natural gas to the burner. The operator enters the ratio at the HMI, and the PLC calculates the set point from the natural gas flow rate and the entered ratio. The flow rate of excess natural gas to the first stage also uses ratio control. The PLC calculates the mass flow of oxygen in the off-gas from the oxygen and mass flow measurements at the entrance to the combustor. The operator enters a ratio and multiplication factor at the HMI, and the PLC calculates the set point from the mass flow of oxygen and the entered values. The calculated set point is averaged over a 20-s period to dampen the affect of spikes in the instrument readings. The flow rate of air to the third stage is controlled by the concentration of oxygen at the exit of the combustion vessel. The operator enters the desired oxygen set point at the HMI.

3.1.4 Partial Quench, Mist Eliminator, Reheater, and Carbon Bed

The DACS components for the partial quench, mist eliminator, reheater, and carbon bed include monitoring and control of flow rates, temperatures, pressures, and differential pressures. Process temperature measurements consist of thermocouples placed inside or at the outlet of each of these components. The temperature of the off-gas at the exit of the partial quench vessel is maintained by

controlling the flow of water to a nozzle in the vessel. The operator enters a temperature set point at the HMI. Coriolis flow meters are used to measure the flow rate of water to the partial quench and the off-gas flow rate at the inlet to the carbon bed. The off-gas pressure is measured at the carbon bed inlet, and the differential pressures across the combustor/partial quench, mist eliminator, and carbon bed are measured.

3.1.5 Simulant Tank, Feed/Mix Tanks, and Feed System

The DACS components for the feed system include monitoring and control of flow rates, temperatures, pressures, differential pressures, and liquid levels. The liquid levels in the simulant and feed/mix tanks are approximated using the differential pressure measurement from the bottom of the tanks to atmosphere, the individual tank dimensions, and the density of the liquid in each tank entered by the operator at the HMI. Level switches are also positioned at the bottom of each tank to alert the operator of a very low liquid level. Temperature measurements consist of thermocouples placed inside the simulant and feed/mix tanks. The feed mixture from the feed/mix tanks is pumped through a re-circulating loop to supply a variable-speed peristaltic feed pump.

The flow rate of the feed mixture to the fluidized bed is measured with a Coriolis flow meter, and the pressure in the feed line is measured between the feed pump and nozzle. A feed flow rate set point is entered at the HMI, and the PLC controls the speed of the pump to reach the set point. The PLC also controls a solenoid valve to supply an air purge to the liquid side of the nozzle whenever the feed pump is off.

Both the flow rate measurement and control of the atomizing air for the feed nozzle is accomplished with a discrete mass flow controller. The set point for the atomizing air flow rate is calculated by the PLC from the volumetric flow rate of simulant feed and nozzle atomizing gas flow ratio (NAR) entered by the operator at the HMI.

3.1.6 Kerosene Fuel System

Kerosene is pumped from a storage tank through a pressure controlled re-circulating loop to supply the kerosene feed system. The operator opens a solenoid-blocking valve from the HMI to enable the flow of kerosene to the feed system. The blocking valve can only be opened after the internal temperature of the fluidized bed has exceeded the auto-ignition temperature of the kerosene. The flow rate of kerosene to the fluidized bed is measured with a Coriolis flow meter. The operator enters the desired flow rate set point at the HMI. The kerosene is injected to the fluidized bed with an oxygen-atomized nozzle. The PLC controls a solenoid valve to supply an air purge to the liquid side of the nozzle whenever the kerosene-blocking valve is closed.

The kerosene and atomizing oxygen flow rate measurements and control are accomplished with a discrete mass flow controller. The set point for the atomizing oxygen flow rate is calculated by the PLC from the volumetric flow rate of kerosene and the kerosene-oxygen nozzle atomizing volumetric ratio (KNAR) entered by the operator at the HMI. The PLC controls a solenoid valve to supply an air purge to the gas side of the nozzle whenever the oxygen-blocking valve is closed.

3.1.7 Compressed Gas Supply System

The compressed gas supply header provides the atomizing, fluidizing, and purge air to the fluidized bed vessel. The fluidizing gas system supplies a controlled flow of superheated air to a distributor plate at the bottom of a vessel to fluidize a solid bed material. The DACS components for the fluidizing gas system and gas supply header include the monitoring and control of temperatures, pressures, and flow

rates. The total flow rate of air supplied by the gas header is measured with a Coriolis flow meter; the temperature of the air is measured by a thermocouple in the supply header pipe.

The flow rate of fluidizing air is measured with a Coriolis flow meter and is controlled by the PLC, with a valve. The flow rate set point for the fluidizing air is calculated by the PLC, using the measured temperature and pressure in the fluidized bed vessel and the bed particle size and density entered by the operator at the HMI.

The fluidizing air passes through two electric super heaters that heat the air temperature close to the fluidized bed temperature. Process temperature measurements are from thermocouples in the pipe at the exit of each super heater. Each super heater also has a discrete temperature controller that uses an independent thermocouple to measure pipe wall temperature. The operator enters set points for the pipe wall temperatures in each superheater at the HMI, and the PLC transmits the set points to the discrete temperature controllers.

3.1.8 Shutdown Procedures

The DACS includes five PLC-controlled safety shutdowns that can be enabled or disabled from the HMI Shutdown Alarm screen. Each shutdown is triggered by a critical control temperature, oxygen level, or pressure. Table 3-2 lists the programmed shutdowns and shutdown actions.

Table 3-2. System shutdown events and automatic actions.

Shutdown Cause or Event	Automatic Shutdown Actions
Low temperature in combustor first stage	• Simulant feed off • Excess natural gas off
Low O_2 at exit of combustor	• Excess natural gas off
Low temperature in fluidized bed	• Kerosene feed off • Simulant feed off
Low temperature at combustor exit	• Simulant feed off • Excess natural gas off
Loss of compressed air to system	• Simulant feed off • Kerosene feed off • Natural gas supply off • Cooling water to burner off • All temperature set points to zero

3.2 Data Acquisition System

The Data Acquisition System (DAS) fluidized bed test system consists of four main parts:

1. *Data Collection*. Interfaces with the control system to collect analog and discrete data, as well as set points and entered variables
2. *Data Storage*. Archives the raw data collected from the control system to a database

3. *Averaging and Calculations*. Averages the raw analog data at minute intervals and performs data reduction calculations

4. *Data View and Retrieval*. Provides a nearly real-time view of the averaged analog data, calculated values, discrete data, as well as set points and entered variables.

Each component of the DACS is loaded on separate PCs to provide the performance and redundancy required for the application. The DACS uses a private Ethernet network for communications between the various machines. Figure 3-4 displays the communications for the data acquisition and control systems.

3.2.1 Data Collection and Storage

A Rockwell software package (RSSql) manages the interface with the control system to collect the data generated by the system during a run. RSSql buffers the information it collects from the control system, and then writes it to a database. Analog values from the control system are polled every 10 s, while set points, entered variables, and discrete values are collected on change of state.

A dedicated Sequel database is used for archiving the raw data generated by the system during a run. The only function of this database is to receive information from RSSql. The database uses three basic tables to receive the data from RSSql. Each record in the database includes the tag-name for the data-point, the value, and a time-stamp. Analog data are polled every 10 s and written to the Analog Table. Discrete data are written to the Discrete Table when it changes state. Set points and entered variables are written on a value change to the Change of State Table.

3.2.2 Averaging and Calculations

The Analog Table from Sequel 1 is replicated to a separate Sequel database, where the information is averaged on 1-min. intervals, pivoted to a time based table format, and then used in a series of data reduction calculations. The calculations are used to determine such quantities as the theoretical mass and volume concentrations of various constituents in the off-gas at several points in the system.

3.3 Continuous Off-gas Monitoring

On-line gas monitoring was accomplished using two continuous emissions monitors (designated as CEMS 1 and CEMS 2), with capability of monitoring major species and criteria pollutants at various locations in the off-gas line. An on-line atomic adsorption mercury analyzer with dual sample collection and sample conditioning trains (designated as CEMS 3 and CEMS 4) was used to measure and speciate mercury emission at key locations throughout the off-gas system. This provided maximum data measurement and process monitoring throughout the run. Sample ports were located at the following positions in the off-gas control system:

- Three sample ports located between the cyclone and quench. These provided a sample port for CEMS 1 (major species and criteria pollutants) and CEMS 3 (for mercury), plus one redundant line in case of sample line plugging due to the presence of fines at this location in the off-gas line. Sampling at this location enabled measurement of gas species exiting the calciner vessel in order to address calcination denitration efficiency, and to verify off-gas compositional similitude with the NWCF calciner system.
- One sample port located between the re-heater and the combustion vessel. This provided a sample port for CEMS 1 downstream of the scrubber and upstream of the staged combustor to determine scrubber removal efficiency of NO_x and the NO_x reduction and unburned hydrocarbon destruction efficiency of the staged combustor.

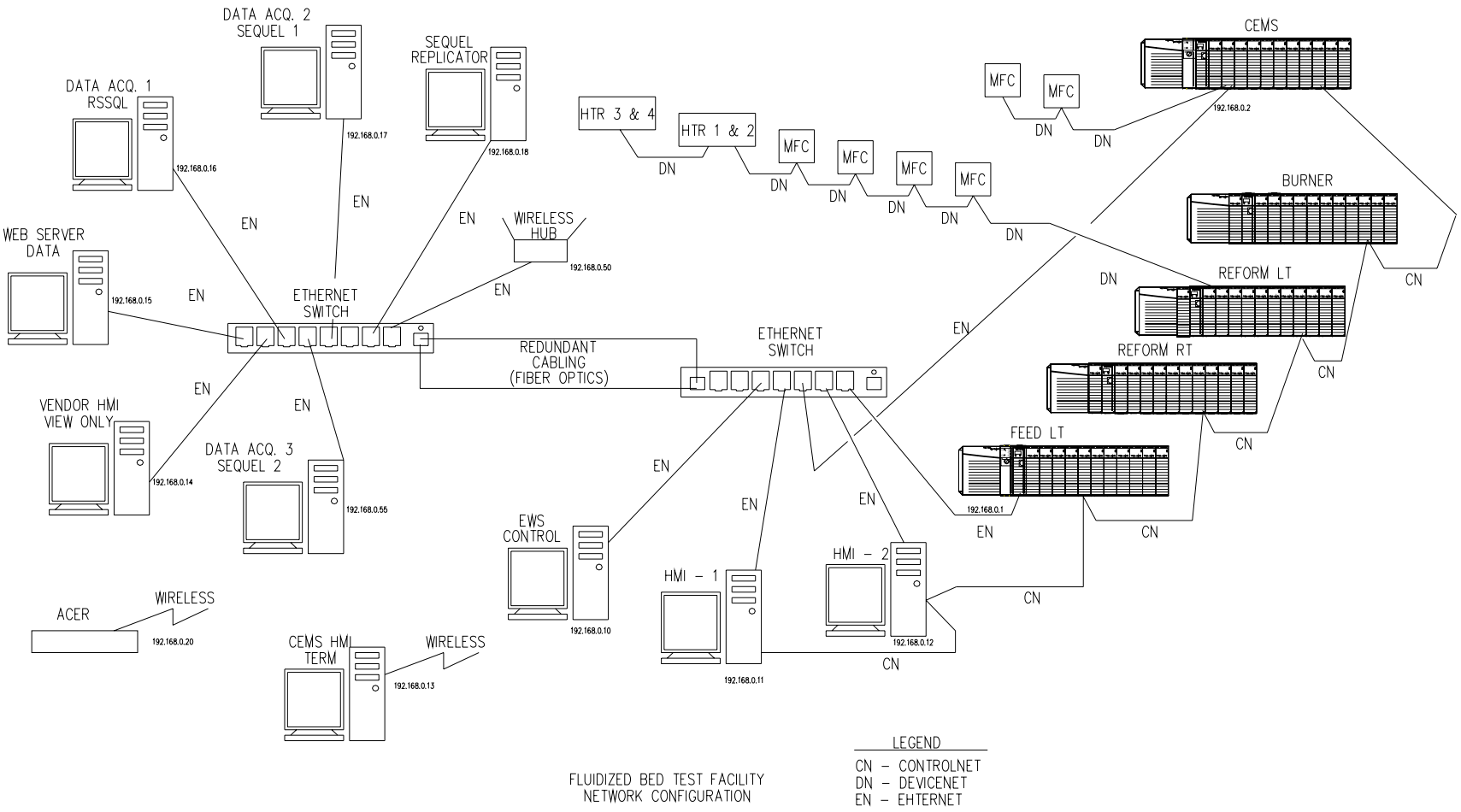


Figure 3-4. Data acquisition system relationships.

- One sample port located between the staged combustor and the partial quench. This port was used for CEMS 3 (mercury analyzer).
- Two sample ports located at the inlet to the carbon bed. These samples ports were designated for CEMS 2 (major species and pollutants) and CEMS 3 (mercury analyzer). Analysis of mercury species at this location provided data to determine both the scrubber removal efficiency as well as the carbon bed mercury removal efficiency. (Note that CEM 2 was left connected to this sample location throughout the course of the calcination test.)
- Two sample ports located between the first and second stages of the carbon bed. Sample collection lines can be routed to CEMS 2 (major species and pollutants) and CEMS 3 (mercury analyzer). CEMS 2 was not connected to its Stage 1 outlet port during the calcination tests.
- Two sample ports located between the second and third stages of the carbon bed. Sample collection lines can be routed to CEMS 2 (major species and pollutants) and CEMS 4 (mercury analyzer). CEMS 2 was not connected to its Stage 2 outlet port during the calcination tests.
- Two sample ports located at the outlet of the carbon bed Stage 3. Sample collection lines can be routed to CEMS 2 (major species and pollutants) and CEMS 4 (mercury analyzer). CEMS 2 was not connected to its Stage 3 outlet port during the calcination tests.

3.3.1 CEMS 1

The CEMS 1 for the off-gas at the cyclone outlet is shown in Figure 3-5. CEMS 1 uses an off-gas sampling and conditioning system with a heated sample probe to continuously extract a portion of the off-gas from the off-gas pipe. A heated filter at the back end of the heated probe removes particulate matter

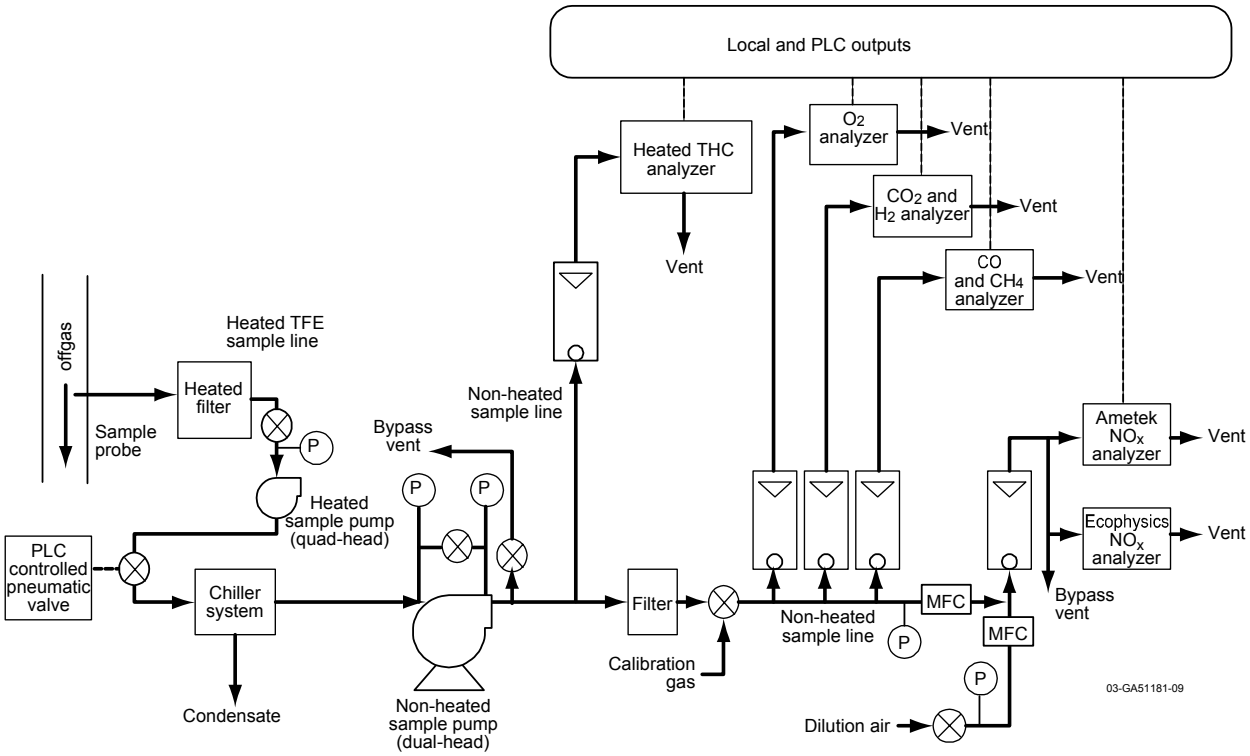


Figure 3-5. CEMS 1 for off-gas measurements upstream of the staged combustor.

from the sample gas. The hot sample gas flows through heated Teflon (TFE) sample line to a heated-head sample pump and through more heated TFE line to the chiller system.

The chiller system cools the sample gas and removes moisture. In this design, some of the water-soluble gases (i.e., NO_2 and HCl) and some higher molecular weight or water-soluble hydrocarbons, if present, could be captured with the water condensate. Results of these analyses from prior tests have shown negligible NO_x scrubbing (Marshall 2003a; Marshall 2003b; Soelberg 2004a; and Soelberg 2004b).

The sample gas is analyzed on a dry basis because the chiller removes moisture from the sample gas. All components downstream of the sample gas chiller system are unheated because condensable moisture is removed in the chiller. An unheated sample pump located after the chiller, in combination with the heated-head pump upstream of the chiller, induces the negative pressure needed to draw the sample gas from the off-gas pipe into the CEMS. Two pumps in series are necessary to overcome the negative pressure in the off-gas pipe and provide sufficient dry sample gas for the analyzers, which are generally configured in parallel. A backup filter located immediately downstream of the unheated sample pump provides added protection for the flow meters and analyzers from particulate matter damage or fouling.

The NO_x analyzer is based on nondispersive infrared (NDIR) measurement of NO and NO_2 species. This analyzer can also detect SO_2 by NDIR. This analyzer replaces the chemiluminescent NO_x analyzer used in prior tests because (a) the chemiluminescent analyzer used at this sample location was subject to interferences and required air dilution of the sample gas to mitigate some of this interference, and (b) the chemiluminescent analyzer was relocated to sample the fully oxidized off-gas downstream the thermal oxidizer, where interferences to the chemiluminescent analysis are mitigated. Since a replacement analyzer was required at the filter outlet sample location, an NDIR analyzer, which is less susceptible to the kinds of interferences than are known to affect chemiluminescent analysis, is used to measure NO_x in the filter outlet gas.

The components of the sample pump, and all other components of the CEMS that contact the sample gas, are constructed of stainless steel, Teflon, glass, or other materials designed to avoid reaction with the sample gas.

3.3.2 CEMS 2

An illustration of CEMS 2 is shown in Figure 3-6. CEMS 2 uses an off-gas sampling and conditioning system similar to CEMS 1. Since off-gas measured by CEMS 2 is similar to more typical combustion off-gas, the analyzers are more typical of those used for typical combustion off-gas. CEMS 2 includes a total hydrocarbon (THC) analyzer along with CO_2 and CO analyzers to monitor the performance of the thermal oxidizer and to characterize THC and CO emissions, which are regulated by the Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) standards. CEMS 2 also includes an HCl analyzer (which, combined with Cl_2, is also HWC MACT regulated). Some of these species could not be reliably measured using a CEMS until the off-gas is fully combusted. They are of particular interest with respect to how the carbon bed sorbs them, and if their presence or sorption affects the sorption of Hg species in the carbon bed.

The THC analysis is made by flame ionization detection of C ions that are produced when hydrocarbon compounds are ionized at high-temperatures in a hydrogen-air flame. NO_x is measured using an Ecophysics chemiluminescent NO_x analyzer. CEMS 2 was used to sample fully oxidized off-gas

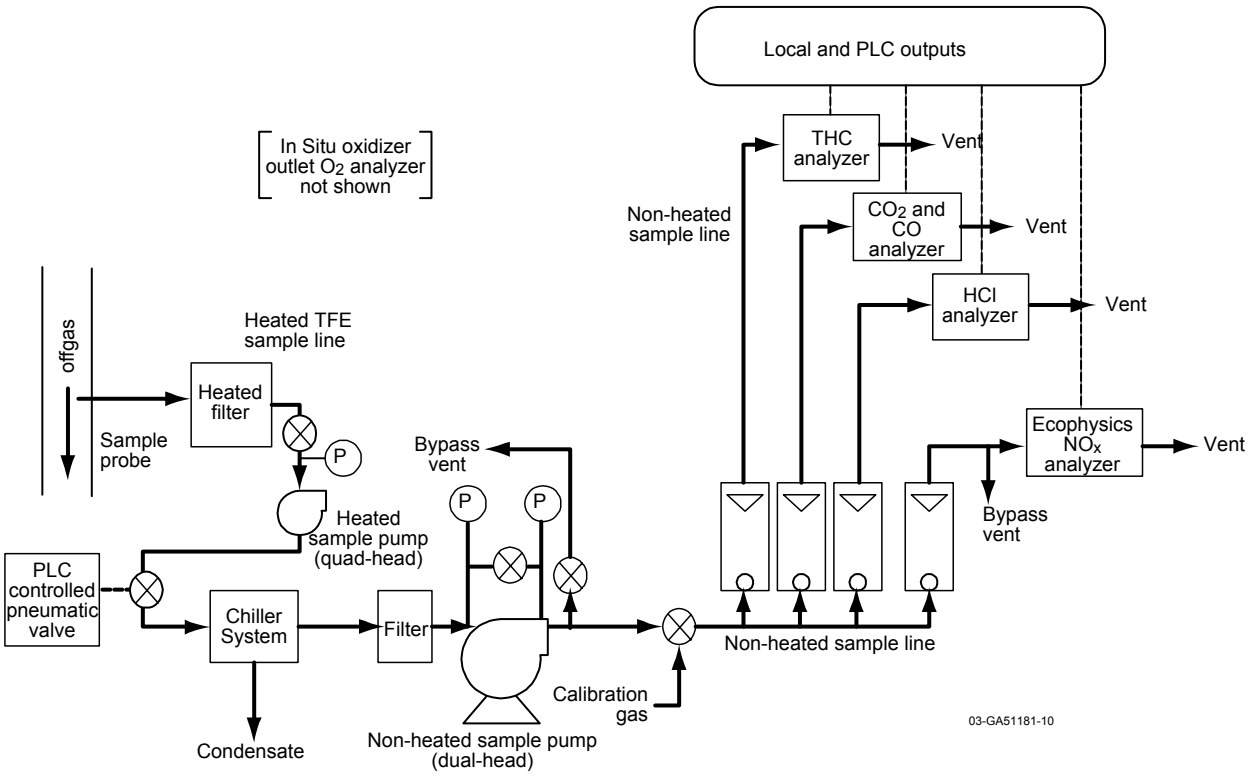


Figure 3-6. CEMS 2 for off-gas measurements downstream of the staged combustor.

downstream of the staged combustor. The staged combustor outlet O_2 was measured using an in situ zirconium oxide O_2 probe, designed for directly and quickly measuring the 3rd stage outlet O_2 concentration for safety and process control.

3.3.3 CEMS 3 and CEMS 4 Mercury Analyzer

Continuous mercury measurements were made using a PSA Analytical Sir Galahad continuous mercury analyzer system, shown in Figure 3-7. This single analyzer is equipped with two separate sampling and conditioning systems (CEMS 3 and CEMS 4), one each dedicated to separate sampling locations. The upper range of the PSA analyzer is 4,000 µg/dscm^3. The projected emissions of the calciner off-gas could range to about 20,000 µg/m^3 (wet basis, as measured). Assuming 80% of the total Hg is scrubbed in the venturi scrubber, the total Hg concentration at the inlet to the carbon bed may range around 4,000 µg/m^{3}g/m^3. At these concentrations, the sample gas requires dilution to lower the Hg levels within the instrument range of 0 to 4,000 µg/m^3.

Both CEMS 3 and CEMS 4 were equipped with a critical-flow orifice to dilute the off-gas concentrations to the analyzer range. A heated head sample pump is used to provide positive pressure to the critical flow orifice to ensure that the flow of sample gas through the orifice is choked flow, typically when the static pressure upstream of the orifice is at least twice the static pressure downstream of the orifice. The orifice upstream pressure, and the flow rate of dilution gas (compressed air or nitrogen) to the diluter jet pump, establish the dilution factor. The upstream pressure is controlled using a manual valve on the sample pump bypass. The flow rate of sample gas through the filter and sample pump is controlled using a bypass valve and rotameter to ensure that, even when the sample gas is diluted, sufficient sample gas flows through the sampling system to minimize Hg measurement bias caused by low sample flow rate.

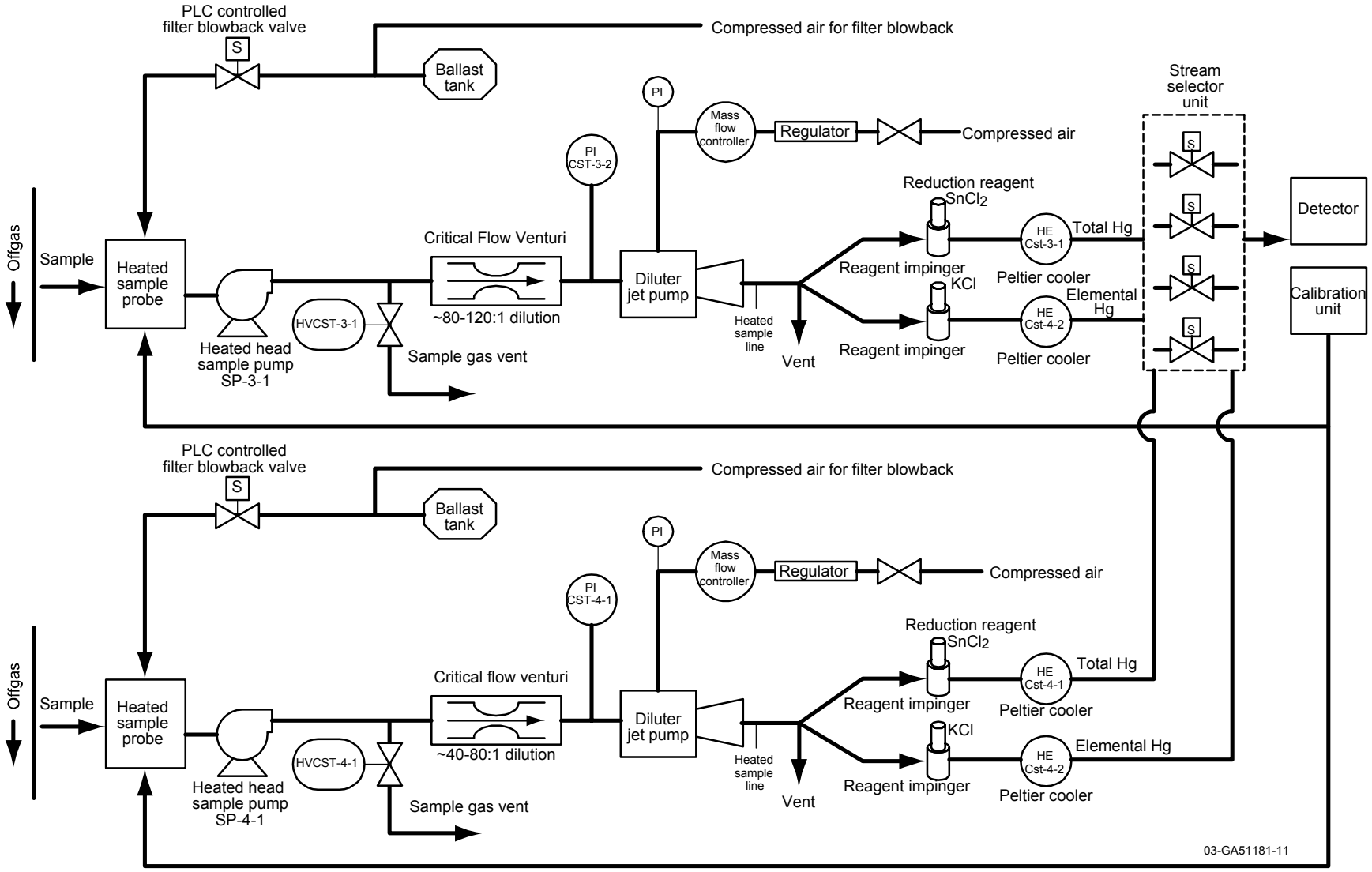


Figure 3-7. PSA Analytical Hg CEMS with dual sampling and conditioning systems.

Unfortunately, the orifices were problematic due to plugging during the calcination test. Therefore, valid off-gas Hg CEMS data were obtained only late in the test. The limited data were still sufficient to assess off-gas Hg concentrations and wet scrubber and carbon bed mercury removal efficiencies.

In the PSA analyzer, the sample gas flows through either of two selectable pathways that enable the separate measurement of either total Hg or only elemental Hg. In the total Hg measurement mode, the sample gas flows through an impinger system containing stannous chloride solution, which converts any oxidized Hg (principally $HgCl_2$) to Hg^0. The sample then flows through a Peltier cooler to the Hg analyzer, where total Hg is measured. In the elemental Hg measurement mode, the sample gas flows through an impinger system containing KCl solution, which scrubs any oxidized Hg species out of the sample gas but allows elemental Hg to pass through. The sample gas flows from this impinger system through a separate Peltier cooler to the Hg analyzer, where only elemental Hg is measured.

3.3.4 Off-gas Measurement Accuracy, Calibrations, and Quality Assurance Checks

Specifications for the gas analyzers are shown in Table 3-3. The analyzers were calibrated with calibration gases before, during, and after each test series. The actual calibration frequency was determined considering calibration error and calibration drift that the CEMS incurs during each test, and considering the schedule for test activities when the analyzers need to be on-line for key test periods. Past experience has shown that CEMS calibrations once per day, or even less frequent, are usually adequate. During each calibration, the following activities were generally performed:

- The system was leak-checked by running the sample pump with the CEMS inlet capped to demonstrate zero gas flow.
- Analyzer zero responses were determined using a zero gas (N_2 gas for all of the analyzers, or N_2 for the O_2 analyzer and air for the other analyzers).
- Analyzer span responses were determined using a calibration gas with the specified gas concentration.
- Interferences of gas species on the detection of other gas species are determined by recording all analyzer responses for each of the calibration gases. Interferences greater than 2% of the instrument span value were corrected after the test.

When the calibrations show that calibrations, drift, linearity, or bias exceed acceptance limits, the CEMS data were corrected following the test.

3.3.5 CEMS Data Logging

A programmable logic controller (PLC) was used for data acquisition and control functions, and a PC workstation was used for the human machine interface (HMI). The HMI allowed the CEMS operator to view system trends, control valves, and make range and set point adjustments. The overall HMI screen for the CEMS operations is shown in Figure 3-8. The CEMS PLC interfaces with the fluidized bed test system data acquisition system via an Ethernet connection to ensure the data collected from the various instruments is synchronized and archived along with the process parameters.

The CEMS operator uses the HMI workstation to enter calibration information to the facility data acquisition system via an Ethernet connection and a Web interface. The calibration information is used to adjust the “raw” data collected from the instruments by the data acquisition system. As the information from the process is archived, the data acquisition system performs calculations to determine such quantities as the theoretical mass and volume concentrations of various constituents (i.e. water content) in the off-gas at several points in the system. The data acquisition system also performs calculations to

Table 3-3. Analyzers used in the CEMS.

Gas Species	Instrument	Detection Principle	Instrument Range	Acceptance Limits (%FS)				Reference Method
				Calibration	Drift	Linearity	Bias	
O_2	Servomex 1440 CEMS 1)	Paramagnetism	0 to 25%	2	3	4	5	40 CFR 60 App. A Method 3A
	In situ ZrO_2 probe (CEMS 2)	Electrochemical						
CO_2	Nova 4230 RM (CEMS 1) CAI (CEMS 2)	Nondispersive infrared (NDIR)	0 to 40% 0 to 100%					
H_2	Nova 4230 RM (CEMS 1)	Thermal conductivity	0 to 5%	—	—	—	—	—
CO	CAI 200 (CEMS 1) CAI (CEMS 2)	NDIR	0 to 1% 0 to 2% (CEMS 1) 0–500 ppm 0–2,500 ppm (CEMS 2)	5	10	2	—	40 CFR 60 App. A Method 10
CH_4	CAI 200 (CEMS 1)		0 to 0.5% 0 to 1%	—	—	—	—	—
NO, NO_x	Ametek M922 (CEMS 1)	Dispersive ultraviolet (DUV)	0-5,000 ppm	2	3	4	5	40 CFR 60 App. A Method 7E
	Ecophysics CLD 70E (CEMS 2)	Chemiluminescence	0 to 5,000 ppm					
THC	CAI 300 HFID (CEMS 2)	Flame ionization detection (FID)	0–3% C_1	5	3	—	—	40 CFR 60 App. A Method 25A
SO_2	Ametek M921 (CEMS 2)	Nondispersive ultraviolet (NDUV)	0–100 ppm	2	3	4	5	40 CFR 60 App. A Method 6C
HCl	Thermo 15C (CEMS 2)	NDIR with gas filter correlation (GFC)	0–100 ppm to 0–5,000 ppm	—	—	—	—	—
Total and elemental Hg	PSA Analytical Sir Gallahad (CEMS 3 and CEMS 4)	Atomic fluorescence	0–3,000 µg/m3	—	—	—	—	—

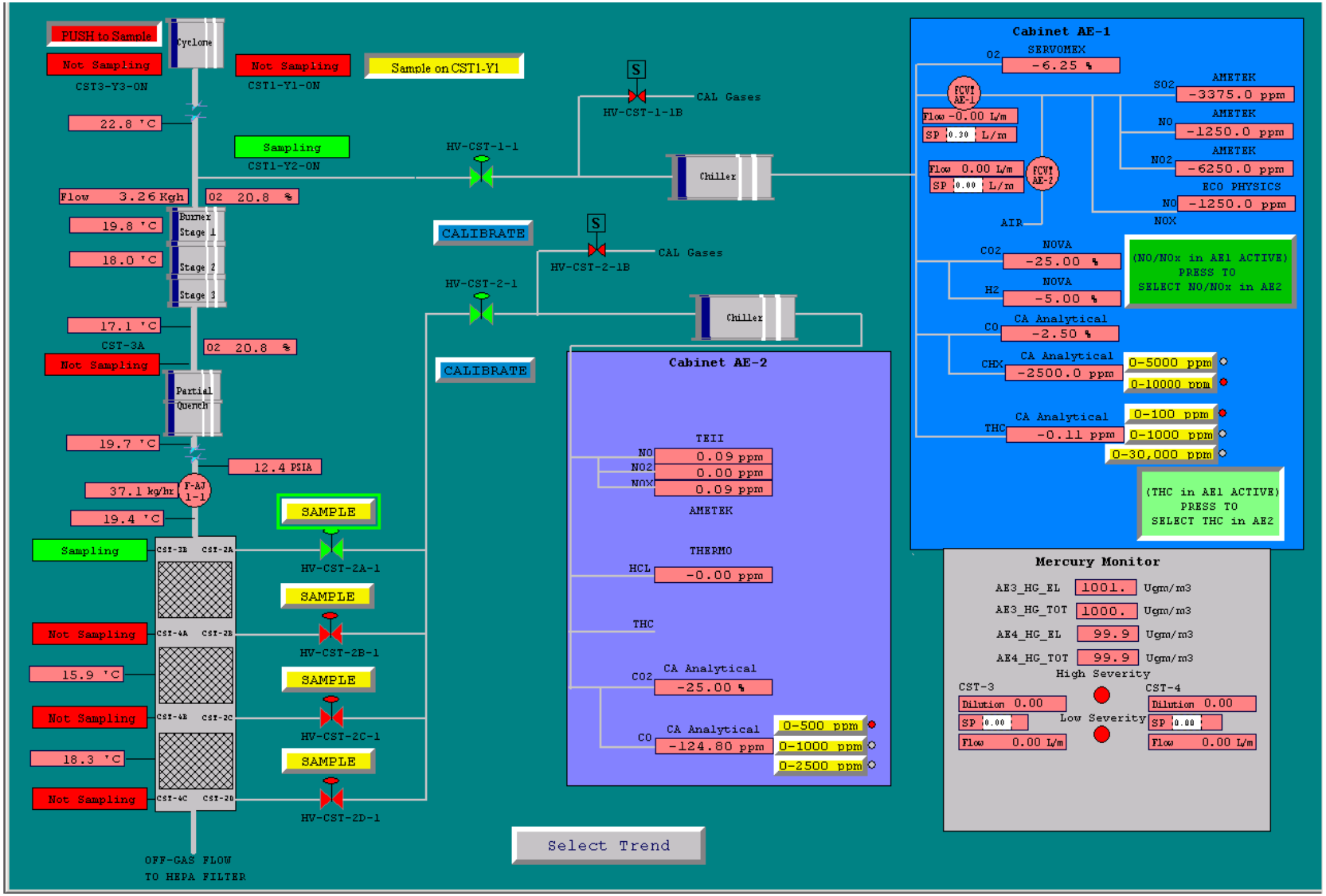


Figure 3-8. HMI screen for the CEMS.

adjust the "raw" CEMS data as they are archived. The CEMS data are adjusted based on the calibration information entered by the operator at the HMI, and the off-gas water content calculated from the process data. The adjusted CEMS data, as well as the archived process information and calculations, are available to the operator via a Web interface on the HMI workstation.

3.4 Manual Data Collection Sheets

In addition to a systems operating logbooks for both the fluidized bed test system and the CEMS, data collection was made using manual data sheets in order to track system operating conditions and to provide a hard-copy data record in addition to the electronically logged data record. The following records shall be archived for future reference:

- *Test Parameter Communications Data Sheet*. General operating conditions were recorded approximately twice each shift, or 6 times daily during normal test operations
- *Staged Combustor Trends Data Sheet*. The staged combustor operating conditions were manually recorded twice each shift, or 6 times daily during normal test operations. Additional data were also collected whenever adjustments to the operating conditions of the combustor are performed.
- *Mass Accountability Data Sheet*. Bed and fines product weights were recorded as samples were collected to provide a running log of the cumulative solids collected. These data were used to calculate bed turnover, product-to-fines ratio, and total theoretical mass carried over and captured by the scrub system.
- *MMPD and HMPD Data Sheets*. Particle size distribution data were entered into manual data sheets and subsequently transferred to an Microsoft Excel Spreadsheet for ongoing calculation of the MMPD and HMPD throughout the run
- *CEMS Data Sheets*. CEM operating conditions and gas analysis results were recorded periodically, by the SAIC CEMS operators or the BBWI technical leads.
- *Sample Collection and Identification Log*. A sample labeling system was set up for identify and tracking individual samples, each with a unique identifying number. The general format for sample labeling is CMACT-XXX, where XXX begins at 500. Over 150 separate samples were collected and submitted to INEEL analytical services.

3.5 Process Sample Collection and Analysis

Process sample collection and analysis were completed to determine the fate of feed constituents, perform process mass balances, and evaluate the properties of the solid and liquid products. The lab results are tabulated in Appendix A. Table 3-4 shows the process sample collection matrix for the calciner pilot plant tests. The sample analysis procedures are summarized in Table 3-5. Particle size and particle density were measured at the STAR Center using a Tyler Mesh screen set and a vibratory shaker throughout the run in order to provide particle size information relevant to setting bed fluidization parameters.

A total of over 150 separate solid and solution sample were collected (see Table 3-4) and analyzed in accordance with the sample and analysis test plan summarized in Table 3-5.

Table 3-4. Sample matrix for calciner test (definitions in table footnotes).

Test	Matrix	Sample	Description	Lab	Analysis
Test 1	Tank 180 Simulant Blend	502A 555	SBW simulant with ANN. Samples were collected at COT 0 and COT 50.	IRC/TRA	pH, SpG TIC/TOC Anions: NO_2, NO_3, Cl, F, SO_4, PO_4 Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn
	ANN	CKJ-ANN-1A CKJ-ANN-2A CKJ-ANN-1B CKJ-ANN-2B	Aluminum nitrate nonahydrate, $Al(NO_3)_3*9H_2O$, used to blend with WM-180 simulant collected COT 0.	ALD	pH, SpG Anions: NO_2, NO_3, Cl, F, SO_4, PO_4 Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn
	Bed	575 576, 576A 577, 577A, 581, 606	COT 0 COT 24 COT 50	IRC/TRA	TIC/TOC, Water soluble, Bulk density, Particle density Anions: NO_2, NO_3, Cl, F, SO_4, PO_4, CrO_4 Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn
	Fines	578, 578A 579, 579A, 580, 607, 608	COT 24 COT 50	IRC/TRA	TIC/TOC, Water soluble, Bulk density, Particle density Anions: NO_2, NO_3, Cl, F, SO_4, PO_4, CrO_4 Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn
	Scrubber Liquor	501A, 501B, 565 516, 516A 566 536A 567, 567A	COT 0 COT 15.4 COT 24 COT 36 COT 50	IRC/TRA	pH, SpG, UDS TIC/TOC Anions: NO_2, NO_3, Cl, F, SO_4, PO_4 Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn
	CEMS I condensate	549	COT 50	IRC/TRA	Anions: NO_2, NO_3, Cl, F, SO_4, PO_4
	CEMS II condensate	550	COT 50	IRC/TRA	Anions: NO_2, NO_3, Cl, F, SO_4, PO_4
Test 2	Tank 180 Simulant Blend	563A, 603A	SBW simulant with ANN. Samples were collected at COT 0 and COT 50.	IRC/TRA	pH, SpG TIC/TOC Anions: NO_2, NO_3, Cl, F, SO_4, PO_4 Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn
	Bed	604, 604A 614, 621, 622, 623	COT 24 COT 50	IRC/TRA	TIC/TOC, Water soluble, Bulk density, Particle density Anions: NO_2, NO_3, Cl, F, SO_4, PO_4, CrO_4 Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn
	Fines	605, 605A 615, 617, 618, 619, 620	COT 24 COT 50	IRC/TRA	TIC/TOC, Water soluble, Bulk density, Particle density Anions: NO_2, NO_3, Cl, F, SO_4, PO_4, CrO_4 Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn

Table 3-4. (continued).

Test	Matrix	Sample	Description	Lab	Analysis
	Scrubber Liquor	568A 583A 596A 616, 616A, 616B, 624, 624A, 624B	COT 12 COT 24 COT 36 COT 50	IRC/TRA	pH, SpG, UDS TIC/TOC *Anions: NO_2, NO_3, Cl, F, SO_4, PO_4* Metals: Na, K, Al, Ca, Fe, Cs, Mn, Mg, Pb, Hg, Re, Cr, B, Ni, Zn
	CEMS I	584 610	COT 24 COT 50	IRC/TRA	Anions: NO_2, NO_3, Cl, F, SO_4, PO_4
	CEMS II	585 611	COT 24 COT 50	IRC/TRA	Anions: NO_2, NO_3, Cl, F, SO_4, PO_4
Test 1 and Test 2	Carbon Bed	657 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650 651, 652, 653, 654, 655, 656	Virgin bed at COT 0 COT 100 Composite bed at COT 100	IRC/TRA	Metals: Hg S Anions: NO_2, NO_3, Cl, F, SO_4, PO_4

Table 3-5. Sample analysis procedures.

Analytes	Method (reference)	Analysis technique	Detection limits	Performed at:	Method summary, comments
Total mass	Good laboratory practice	Calibrated laboratory balance	Depends on range	All laboratories used in the test program	Using an appropriately ranged, calibrated balance, determine the net weight of sample by subtracting the container tare weight from the total weight of the sample and the container.
Bulk density	—	Gravimetric and volumetric analysis	~0.1 g/mL	STAR Center, TRA	Fill a tared graduate cylinder, tap for ~30 seconds to settle, measure the mass and volume
Particle ("true") density	—	Gravimetric and volumetric analysis	~0.1 g/mL	STAR Center, TRA	Determine bulk density, then fill in interstitial space with hexane or other liquid that does not dissolve solid particles, reweigh to determine the void volume, subtract the void volume from the bulk volume, and determine void-free density.
Total Organic Carbon (TOC, Loss on Ignition)	Bear, F. E., Chemistry of the Soil, Van Nostrand, New York, 1964	Colorimetry	0.1 wt%	TRA	Solids—Add concentrated sulfuric acid and chromate to the hydrated sample. Heat the solution with continuous agitation. Add excess ammonia, dilute, and centrifuge. Weigh and read its absorbance.
Total inorganic carbon (TIC) and TOC for liquid samples	Persulfate-Ultraviolet Oxidation/Combustion-Infrared method 5310B/C (PUO-IM)	Combustion infrared spectroscopy	~1 mg/L	IRC	Liquids—Oxidizes the organics with persulfate at an elevated temperature (100^{O}C) in a Teflon lined chamber. Carbon is then measured with combustion infrared spectroscopy.
Elemental	SW-846 6000 or 7000 series or equivalent	Inductively-coupled plasma atomic emission spectroscopy (ICP-AES) for most metals; ICP-mass spectroscopy (ICP-MS) for Cs and Re.	1 mg/L	IRC, (ICP-AES; TRA (ICP-MS)	Completely digest per EPA 3050 or equivalent for all elements. Several digestions were evaluated to determine the best digestion applicable for a sample matrix and analyte. Aqua regia digestion was used on all samples except for 575 and 576, where HF digestion was used. ICP analysis of digested solution. If no solids are present in liquid samples, digestion will not be done.
Hg	SW-846 or equivalent	ICP-MS	1 mg/kg	TRA	Digest sample per SW-846 3050 and analyze by ICP-MS; re-digest solid residues to determine completeness of the first digestion.
Anions Cl, F, SO_4, PO_4, nitrate, nitrite	SW-846 9056 or equivalent	IC	1 mg/L	IRC	Water digestion (of solids) followed by analysis per 9056. If no solids are present in liquid samples, digestion was not done.
S	SW-846 6000	ICP-AES	~0.001 wt%	IRC	Aqua regia digestion per EPA 3050 followed by analysis per 9056.

4. TEST OPERATING CONDITIONS AND RESULTS

The calcination test was performed over a 2-weeks between January 12 and January 23. The fluidized bed was operated from January 12–15 to (a) perform the operability tests for the feed and fluidized bed subsystems, and (b) generate a NO_x-laden calciner off-gas to enable operability tests for the acid scrubber, staged combustor, and other off-gas system equipment. The fluidized bed was operated with kerosene combustion while fluidizing an alumina bed and feeding first water and then a simplified simulant mixture of aluminum nitrate nonahydrate (ANN) solution, nitric acid, and boric acid in water. Following the SO test, a 100-hr calcination run was performed January 19–23.

Two calcination test conditions were performed during the 100-hr test run. The feed mixture for the 100-hr run consisted of a mixture of Tank 180 SBW simulant and ANN solution, supplied in 55-gal drums. No other additive chemicals were used. Nominally, calcium nitrate is added to the feed to help adsorb and tie up chloride, fluoride, sulfate, and phosphate during calcination of the waste. Due to the relatively high concentration of calcium in the Tank 180 wastes, no additional calcium was considered necessary for these tests. A 300 L batch of Tank 180 simulant and ANN was mixed to attain an AAR of 2.25 for the first 50 hr of cumulative operating time (COT). A second 300 L batch was prepared to attain an AAR of 1.75 for the second 50-hr COT.

4.1 Run Summary

Figure 4.1-1 displays the cumulative run time versus cumulative feed processed, bed produced, and fines generated for the two test periods and total run. Except for a brief interruption in feed for 5 hr at COT=3 and then between the two test conditions at COT=50, the feed rate was continuous, about 5 L/hr during the first 15 hr and about 6 L/hr thereafter. A total of 572 L of blended feed was calcined. Bed growth and product collection was also constant, as indicated by the discrete product and fines collection every 2–4 hr COT. The difference between total cumulative solids produced and the theoretical solids production represents the amount of mass carried over to the scrub system.

4.1.1 Calcination Test System Operability Test (January 12–15, 2004)

System operability and optimization testing was performed the week before the calcination testing to verify operational readiness of all calciner subsystems, to verify operation of the three-stage thermal oxidizer operation, and to verify that the pilot plant, as designed, could successfully calcine aluminum nitrate feed. The calciner unit was heated up, and a fresh bed of commercial aluminum oxide abrasive (14.9 kg, 54 grit, 0.33 mm MMPD) was added to the reactor vessel. The calciner was started with water feed followed by aluminum nitrate feed consisting of 1.8 molar aluminum nitrate, 0.2 molar nitric acid, and 0.02 molar boric acid. The aluminum nitrate solution was readily calcined with no apparent feed nozzle plugs and with steady bed fluidization. The final product MMPD was 0.35 mm. The bulk product density at the end of the SO test was 1.44 g/mL, indicative of a dense, non-porous aluminum oxide particulate. The cyclone separator and fines collection systems operated as designed with no apparent bridging of fines. The off-gas quench and scrub system also operated as designed. No plugging in the system was observed while the off-gas was quenched to around 120ºC. A constant pressure drop of 40–50 inch water column (w.c.) was maintained across the venturi scrubber. The scrub solution was essentially clear, indicative of a low fines loading in the scrub.

Once the off-gas system was stabilized, and while calcining the aluminum nitrate feed, excess natural gas flow to the staged combustor was varied to observe the affect of Stage 1 reducing stoichiometry on NO_x destruction. Total NO_x destruction generally trended down with increasing natural gas flow to the first stage, as expected. When the excess natural gas was reduced to zero flow (i.e., oxidizing conditions)

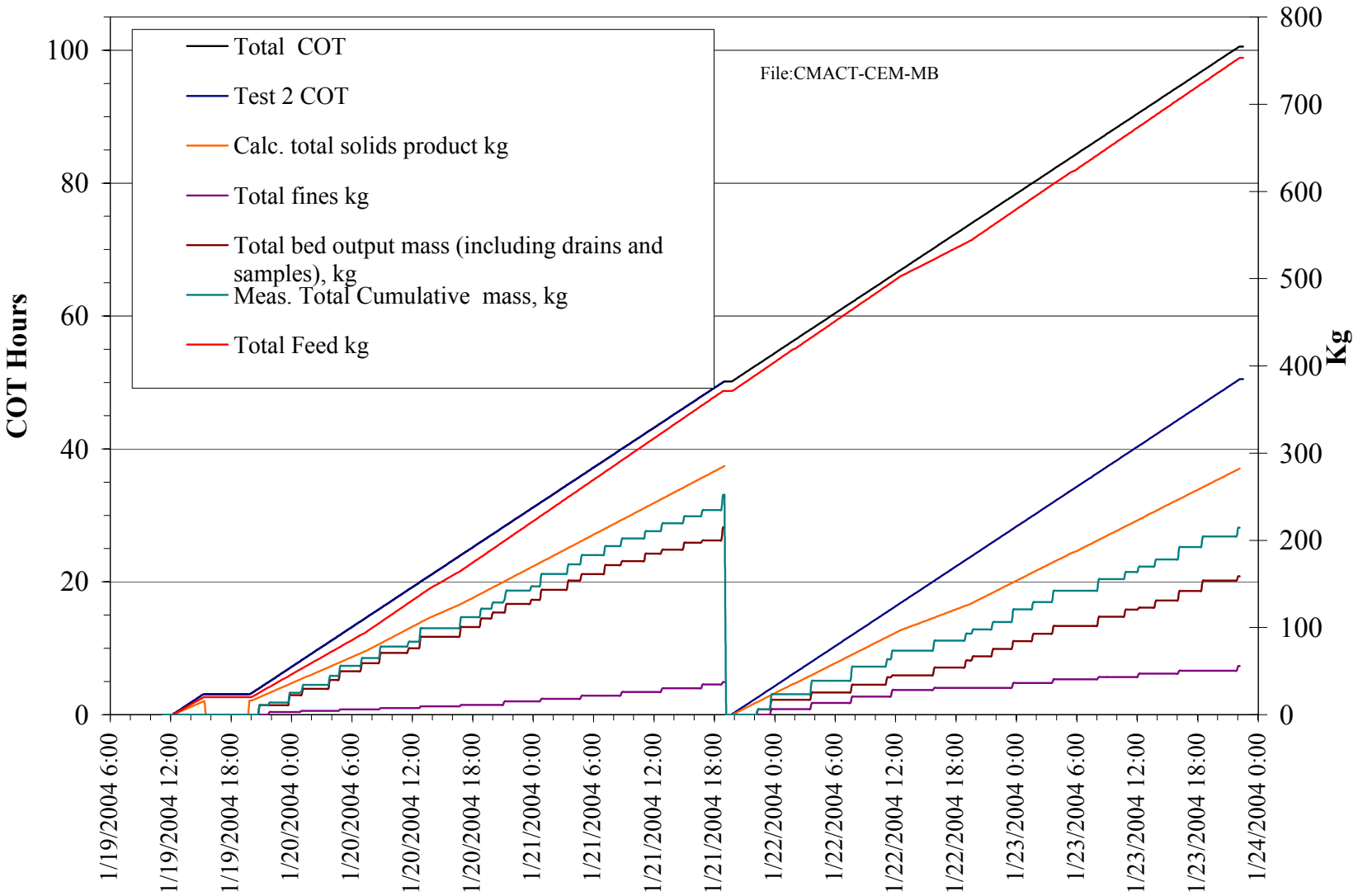


Figure 4.1-1. Summary of cumulative operating time (COT), feed, and solids production.

a NOx reduction of around 70% was still achieved. Emissions of NO_2 were about 0–5 ppm, with NO levels up to 1000 ppm. The stack effluent remained colorless in spite of the relatively high NO levels, since oxidation of NO in the off-gas line was negligible.

The subsystems generally performed as designed during the SO test, requiring only minor adjustments such as tuning the system for control of flows, system pressures, and temperatures. In addition, the automatic shutdown PLC logic was tested successfully at the end of the test.

Flame stability problems were experienced in the staged combustor. The natural gas supply pressure (5 psig) was too low to maintain constant pressure to the burner when the pressure fluctuated in the off-gas system. This caused the burner flame to become unstable when sudden changes in process operating conditions were experienced (e.g., large feed rate changes, fines collection without proper closure of the fines collection column, and clearance of off-gas line plugs). Calciner operators were typically able to re-establish control of the flame stability by adjusting the air jet eductor used to induce draft through the system, and by partially closing the main valve from the natural gas header to improve the pressure differential between the gas line and the oxidizer. This problem is only considered a shortcoming of the current system and can be easily rectified for future tests.

Carbon bed startup was also problematic. The first two beds used began burning as a result of improper heating during startup. Additional details regarding this concern are described in the discussion on carbon bed performance assessment in Section 4.10.

4.1.2 Test 1 (2.5 AAR, January 19, 2004 to January 21, 2004)

Test 1 began at 1210 hrs on February 19, when the calciner feed was switched from water to the simulated WM-180/ANN blend with an AAR mole ratio of 2.25. The alumina bed produced during the SO test was used for the starting bed of this test. The target simulant blend feed rate (5 L/hr) was exceeded, with an average feed rate of 5.5 L/hr (7.1 kg/hr). There was essentially no feed or bed problems throughout this test.

The bed particle size initially decreased, so the NAR was initially reduced from 700 to 600. After continued bed turnover, as the proportion of product (primarily sodium aluminate) increased, the bed particle size grew, and was successfully controlled at about 0.45 mm with a NAR of 800. The design operating time of 50 hr was achieved, during which the design feed volume of 250 L was exceeded. The total feed volume was 283 L, and the net solid product (bed product and cyclone fines, less starting bed) was 25 kg.

Various incidental problems that occurred during Test 1, and their resolutions, included:

- On January 18, before Test 1 start, a high-temperature excursion occurred in the carbon bed. The carbon bed was bypassed, and was brought back on line on January 20 midway through Test 1. The carbon in the bed was replaced and the carbon bed startup procedures were modified while the unit was off-line.

- The off-gas line between the quench vessel and venturi scrubber temporarily plugged with particulate matter about 3 hr after the test start. Feed was shut off for 4.7 hr while a cleanout tap was added to the line to flush it out (with scrub solution or nitric acid). A differential pressure gauge was also installed to better monitor for plugs. Both the Enclosed 15-cm and Enclosed 30-cm Calciner Pilot Plants at INTEC have experienced similar plugging and have used similar cleanout procedures. Plugging of the off-gas piping was not observed in previous steam reforming testing largely because of the presence of the heated filter that efficiently removed particulate matter from

the off-gas upstream of this location. In order to emulate the process configuration of the NWCF, the heated filter was bypassed for the calcination test. This part of the off-gas line was monitored for plugging for the remainder of the test. Line flushing was performed approximately twice daily to keep the off-gas line and the venturi scrubber throat clear of particulate matter.

- At about 24 hr into the test, a consistent amount of small agglomerates began to appear in the product drained from the bed. The mass of agglomerated product was small, about 0.4 wt% of the drained bed product. These small agglomerates were not considered problematic, or indicative of agglomerations caused by, or that could cause, extensive bed defluidization. These small agglomerates may result from solid accretions around the feed nozzle, on a thermocouple that extended into the spray zone, or on the opposite wall from the feed nozzle, which slowly form and break off.

- Feed nozzle plugging was essentially non-existent. Feed nozzle plugging has occurred during prior calcination tests (Nenni 1999, 2001a, 2001b), during prior steam reforming tests, and during NWCF operations. Nitric acid flushing readily cleared nozzle plugging. Nozzle plugging during this calcination test did not significantly hamper operations or impair test results.

- Occasional elevated cyclone pressure drop indicated some plugging in this vessel during the test. Cyclone plugging was resolved with periodic tapping on the cyclone. More severe plugging occurred in the location of the cyclone during the steam reforming test for Savannah River Site Tank 48H waste (Soelberg 2003a). Cyclone plugging has also occurred in previous 15-cm enclosed pilot-plant calcination tests during high-temperature calcination.

- The liquid seal in the quench vessel liquid drain occasionally failed, allowing off-gas to bypass the venturi scrubber. When the off-gas bypassed the scrubber, it was not effectively scrubbed of particulate matter and acid gases. This condition was resolved by briefly closing the seal loop scrub return valve to allow the loop to refill.

- Natural gas flow control to the burner was occasionally upset when staged combustor and vacuum conditions were varied significantly. The SAIC operators became more adept at preventing these upsets by making adjustments to the vacuum jet supply air when activities that affected the system vacuum occurred.

- The Hg CEMS were not operational for most of Test 1. Upon instrument startup, the critical-flow orifices, designed to dilute the sample gas to within the instrument design range were apparently plugged with fine particulate in the off-gas. Efforts to identify and resolve the plugged orifices were generally unsuccessful; therefore, data were eventually collected without diluting the sample stream.

After 50 operating hours during Test 1 (not including any significant time when simulant was not being fed, such as when the off-gas line plug was resolved) the feed was switched from simulant blend to water (1900 on January 21). All systems remained operational, and bed fluidization continued, while the bed drained down to the starting level of 19 in. using the bottom drain in preparation for the second feed blend test. Scrub and fines samples were also taken.

4.1.3 Test 2 (1.75 AAR, January 21, 2004 to January 23, 2004)

Feed was resumed to the calciner at 1910 hrs on January 21 using the second feed blend (1.75 AAR). This feed blend continued to operate smoothly. The 5 L/hr feed rate goal was exceeded

with an average simulant blend feed rate of 5.7 L/hr. The bed product and cyclone fines were routinely recovered and weighed. The total bed product and fines for the test (less starting bed) was 21 kg.

During the first 17 hr of the 1.75 AAR blend test, the bed particle size decreased slightly from 0.44 mm to 0.39 mm, but stabilized after the NAR was reduced from 800 to 700, resulting in a final MMPD of 0.42 mm. The MMPD during Tests 1 and 2 was controllable by varying NAR, and ranged between 0.35 to 0.45 mm throughout the entire 100 hr of testing.

Feed nozzle plugging was more frequent during this test, as often as every 10 minutes for one 12-hr period. Nozzle plugging decreased significantly during the latter part of the test, when nitric acid was used to clear the nozzle plugs. The nozzle plugs were readily removed with acid flushing. Fines plugging in the cyclone also occurred and required frequent tapping on the cyclone to dislodge off-gas flow restrictions. Off-gas line restrictions downstream of the quench vessel that required flushing with scrub continued to be performed approximately twice daily to reduce particle plugging in the off-gas line. Natural gas flow control to the burner continued to require attention when vacuum conditions in the staged combustor were changed.

The amount of small agglomerates formed in the reactor increased in Test 2, but still did not indicate bed defluidization. The amount of agglomerates in the bed product increased to about 2 wt% until COT 76 hr, after which it decreased to 0.8 wt%. There were only a half dozen agglomerates remaining on the distributor plate after the run. Some of these agglomerates were fairly large at ½-in. diameter and they had a distinctive biscuit shape. It is possible that they formed on the feed nozzle (contributing to feed nozzle plugging); however, both the feed nozzle and fuel nozzle had only a light scale on them upon inspection after the test. The biscuits may have formed temporarily on the far wall opposite the feed nozzle, until they reached a size large enough to be broken off of the wall and fall to the bottom of the vessel. Another possibility is that the agglomerates were forming on TC#6 or its 1-in. port, which were both opposite the feed nozzle. There was some scale on the upper part of TC#6 after the test, and it appeared that there also had been some on the lower part of the TC that had flaked off.

During posttest inspections, an annular ring about ½-in. thick was found on the inside wall of the cyclone. The line between the cyclone and the quench tower had ¼ to ½-in. layer of calcine inside it. These deposits were generally soft and could be easily crushed and removed.

4.2 Feed Blends

The feed blends (see Table 4.2-1) were prepared for the two 50-hour calcination tests using a Tank 180 waste simulant prepared by SAIC. Two samples of the waste stimulant were collected for analysis before the tests. Tank WM-180 has only 1.8 g/L undissolved solids; consequently, no UDS simulant solids were added to the feed. Tank WM-180 has a lower mercury content than the other SBW tank wastes. In order to simulate maximum mercury concentrations in Tank WM-189, the mercury concentration was increased from 1.4 to 5.6 mol/L (1.1 g/L) to ensure that the carbon bed was tested at the higher levels that may be encountered in the NWCF. Two drums of ANN solution were provided to SAIC from the NWCF operations. The drums were analyzed and found to contain 2.35 molar Al and 2.51 molar Al, respectively. Stock aluminum nitrate is typically supplied in 2.2 molar Al. Based on the simulant and solution analyses, two 300 L feed blends were prepared, one with an aluminum-to-alkali metal mole ratio (AAR) of 2.25, and the other with an AAR of 1.75. A WM-180/ANN blend with an AAR of 3.1 had previously been tested successfully at both 600°C and 500°C during Run SBW-HT-15a/b in the INTEC Enclosed 15-cm Calciner Pilot Plant (Nenni 1999).

Table 4.2-1. WM-180 simulant composition and blended feed compositions for the calcination test.

Simulant or solution		SBW simulant w/o heel solids or additives						Aluminum nitrate solution					Test 1, SBW with 2.25 AAR				Test 2, SBW with 1.75 AAR			
		Composition			Sample analysis/ calculated	Compos-ition (avg of samples)	RPD of avg sample and recipe	Composition				RPD of the 2 analyses,	Composition			Analy-sis/ calc	Composition			Analy-sis/ calc
		Calculated from simulant recipe		Measured (THOR 2)				Intended concentration		Drum 1 sample avg	Drum 2 sample avg		Calculated		Sample 502A		Calculated		Sample 555A	
Component	Mole weight	*M*	gm/L	gm/L	value, %	gm/L	values, %	*M*	gm/L	gm/L	gm/L	%	*M*	gm/L	gm/L	value, %	*M*	gm/L	gm/L	value, %
Acid	1.0	1.12	1.1	NM	---	---	---	---	---	---	---	---	0.38	0.38	---	---	0.43	0.44	---	---
Aluminum	27.0	0.66	18	17	95%	17	5%	2.5	67	63	68	6%	1.88	51	45	88%	2	46	45	99%
Boron	10.8	0.012	0.13	0.098	74%	0.11	19%	---	---	0	0	---	0.0041	0.045	0.041	92%	0.0048	0.052	0.041	80%
Calcium	40.1	0.047	1.9	1.8	95%	1.7	14%	---	---	0.020	0.018	11%	0.016	0.65	0.69	106%	0.019	0.75	0.69	92%
Cesium	132.9	0.0032	0.43	0.25	57%	0.40	7%	---	---	0	0	---	0.0011	0.14	0.11	77%	0.0013	0.17	0.15	90%
Chromium	52.0	0.0033	0.17	0.16	92%	0.15	18%	---	---	0.0008	0.0004	57%	0.0011	0.059	0.057	97%	0.0013	0.068	0.057	84%
Copper	63.5	0.0007	0.044	0.029	66%	---	---	---	---	---	---	---	0.0002	0.015	---	---	0.0003	0.017	---	---
Iron	55.9	0.022	1.2	1.2	95%	1.00	19%	---	---	0.014	0.012	15%	0.0074	0.42	0.38	92%	0.0086	0.48	0.38	80%
Lead	207.2	0.0013	0.27	0.24	87%	0.25	8%	---	---	0.0005	0.0004	5%	0.0004	0.092	0.056	61%	0.0005	0.11	0.05	51%
Magnesium	24.3	0.012	0.29	0.33	112%	0.31	6%	---	---	0.0004	0.0004	3%	0.0040	0.10	0.13	132%	0.0047	0.11	0.13	115%
Manganese	54.9	0.014	0.77	0.75	97%	0.76	2%	---	---	0.0007	0.0007	10%	0.0048	0.26	0.31	118%	0.0055	0.30	0.31	102%
Mercury	200.6	0.0056	1.12	0.27	24%	---	---	---	---	---	---	---	0.00187	0.38	0.08	22%	0.0022	0.43	0.08	19%
Nickel	58.7	0.0015	0.086	0.080	92%	0.08	11%	---	---	0.0017	0.0015	11%	0.0005	0.030	0.038	126%	0.0006	0.035	0.034	98%
Potassium	39.1	0.20	7.7	7.9	103%	7.4	4%	---	---	0.0027	0.0027	2%	0.066	2.6	2.9	113%	0.076	3.0	2.8	95%
Rhenium	186.2	0.0011	0.20	0.20	98%	0.20	1%	---	---	0.015	0.016	5%	0.0004	0.078	0.052	67%	0.0005	0.087	0.07	78%
Sodium	23.0	2.1	47	50	105%	52	10%	---	---	0.34	0.31	9%	0.77	17.8	19.4	109%	0.89	20	19	94%
Zinc	65.4	0.0011	0.069	0.073	107%	0.07	4%	---	---	0.011	0.011	3%	0.0005	0.030	0.036	119%	0.0005	0.033	0.036	107%
Chloride	35.5	0.030	1.1	1.2	116%	0.63	52%	---	---	0	0	---	0.010	0.36	0.14	40%	0.012	0.41	0.14	34%
Fluoride	19.0	0.024	0.45	0.48	106%	0.20	78%	---	---	0	0	---	0.008	0.15	0.11	75%	0.009	0.17	0.10	59%
Nitrate	62.0	5.3	330	307	93%	182	58%	7.5	465	231	295	24%	6.77	420	341	81%	6.66	413	338	82%
Phosphate	95.0	0.029	2.7	---	---	1.9	36%	---		0	0	---	0.010	0.92	1.8	---	0.011	1.1	1.7	---
Sulfate	96.1	0.070	6.7	7.9	118%	4.2	46%	---		0.055	0.042	27%	0.024	2.3	2.3	102%	0.027	2.6	2.3	88%
Total species	---	9.642	422	397	94%	271	44%	10	532	295	363	21%	10.0	497	415	83%	9.9	489	411	84%
Water	18.0	---	838	---	---	---	---	---	---	1,045	997	5%	---	819	---	---	---	830	---	---
ANN solution, L/L blend		---	---	---	---	---	---	---	---	---	---	---	---	0.66	---	---	---	0.61	---	---
SBW simulant, L/L blend		---	---	---	---	---	---	---	---	---	---	---	---	0.34	---	---	---	0.39	---	---
Al:alkali metal stoichiometric ratio		0.29	---	0.267	---	0.258	13%	---	---	---	---	---	2.24	2.24	1.81	---	1.75	1.75	1.84	---
Ca:(total non-NO3 anion stoich ratio)		0.337	---	---	---	---	---	---	---	---	---	---	0.341	---	---	---	0.341	---	---	---
Density		---	1,260	1,270	101%	1,250	1%	---	---	1,340	1,360	1%	---	1,316	1,310	100%	---	1,319	1,320	100%
Solution used for each feed batch, L			101	Test 1		116.5	Test 2			184	199									

1. The simulant was from prior Phase 2 THOR steam reforming tests (Soelberg 2004). Nitrite was measured in samples at levels under 0.01% of the nitrate levels, and so was not tabulated or included in mass balances.

2. AAR = Aluminum to alkali metal stoichiometric ratio for producing NaAlO2 or KAlO2. Alkali metals used in the calculation were Na and K.

3. The % recovery is the ratio of the concentration from the sample analysis divided by the calculated concentration.

4. The aluminum nonohydrated nitrate solution was in two separate drums. The drums had slightly different compositions. ANN = aluminum nonohydrate, Al(NO3)3*9H2O. While the ANN contained trace levels of several elements, those amounts were negligible, 1% or less, of the levels of the same elements in the simulant. Those amounts were included in the total blended feed composition.

5. ANN drum 2 was used for preparing feed for Test 1, so the drum 2 Al content was used in Test 1 blend calculations. ANN drum 1 was used to prepare feed for Test 2, so drum 1 Al content was used for Test 2 blend calculations. Since the lab analysis for nitrate content is thought to be erroneously low for both drums, the intended nitrate value was used.

6. The anion analyses for Feed 1A and 1B samples and the ANN are all suspiciously low. These analyses are lower than the THOR Sample 2 analyses, the recipe values, and the nitrate in the ANN is lower than indicated based on the vendor ANN and Al concentrations. The recipe and vendor concentrations for all cation and anion species are used in mass balance calculations, except for Na, which was consistently higher in the lab analyses.

7. The recipe concentration for F is half the intended value -- test log indicates 1/2 of the intended amount of F was added. This increases the intended Ca:F ratio.

8. The recipe Hg concentration in the THOR 2 sample was 0.27 gm/L. Hg(NO3)2*H2O was added to raise the recipe Hg concentration to 1.12 gm/L for the CMACT tests, an increase of 4.2 times. The RPD for Hg in the THOR 2 sample is based on the original Hg content of 0.27 gm/L. The blended feed sample analyses only showed about 1/4th of calculated amount of Hg. The calculated amount is used in all mass balance calculations.

9. The calcium:anion stoichiometric ratio is based on the reaction of Ca and the anions Cl, F, PO4, and SO4 to produce CaCl2, CaF2, Ca3(PO4)2, and CaSO4.

10. The logbook shows that only 1/2 of the intended F was added, so the concentration used in product composition calculations and mass balances is 1/2 of the intended (calculated) value.

11. The calculated concentrations of NO3, Hg, and water in the blended feeds agree well with the values used in the PLC to make on-line offgas flowrate, offgas concentration, NOx destruction, and Hg control calculations. The calculated water concentration has been adjusted so the calculated specific gravity nearly matches the measured specific gravity. The on-line calculations require no adjustments.

[2003 Simulant Makeup-II feb 25 NO3.xls]sbw feed comp for CMACT test

It was found during flowsheet development testing for the NWCF high-temperature trial that blends of simulated waste from the SBW tanks with higher fluoride and zirconium, such as WM-189, were more difficult to calcine than blends with lower fluoride and zirconium (O'Brien 2000) due to agglomeration. For example, simulated blends with an AAR of 1.6, fluoride concentrations of 0.05 to 0.1 molar, and zirconium concentrations of 0.005 to 0.007 could be calcined successfully in the INTEC calciner pilot plants, while WM-189/ANN blends with AARs of 1.5 to 1.8, fluoride concentrations of 0.17 and 0.15 molar, and zirconium concentrations of 0.025 to 0.027 could not. Blends with WM-180 waste have $1/10^{th}$ the fluoride and $1/100^{th}$ the zirconium of the WM-185 and WM-189 blends calcined at the NWCF during high-temperature trials (O'Brien 2000; Law 2000, Swenson 2000; Wood 2001). Since both the zirconium and fluoride in the waste came from the dissolution of zirconium fuel cladding with hydrofluoric acid, the ratios tended to follow each other for the WM-185 and WM-189 wastes. It remains uncertain which of those species, or a different species, had promoted agglomeration during the pilot-plant flowsheet development for those WM-185 and WM-189 wastes.

The Tank Farm waste highest in fluoride and zirconium was emptied from the Tank Farm by calcination during the high-temperature calcination trials in 1999 and 2000, such that the projected future blends with WM-187, 188, and 189 will have only 0.03 to 0.06 molar fluoride and will be well within the fluoride concentrations that have been successfully calcined. However, those blends will have 0.03 to 0.04 molar zirconium, due to the high content of zirconium in the Tank Farm heel solids to be distributed between those 3 tanks. Simulated blends of these other SBW tanks with high heel solids must be tested in the pilot plant to determine whether the high zirconium sulfate in the heel solids will remain as unreactive solids or will promote bed agglomeration.

4.3 Test Operating Conditions and Observations

4.3.1 Calciner Operating Parameters

Table 4.3-1 lists the target operating conditions and selection basis for Test 1. Preliminary calculations indicated that a kerosene flow rate of approximately 0.7 L/hr would yield 5.1 vol% CO_2 (wet basis) in the off-gas; however, the actual kerosene rate was higher at an average 0.86 L/hr, and the average CO_2 concentration (at the wet scrubber outlet location) was 7.4% wet basis. Wall heating was simultaneously controlled to maintain the bed temperature at 600°C, while keeping the vessel wall temperature less than 610°C to reduce the possibility of calcine scale formation on the inside walls.

The variation of major test parameters, such as feed rate, fluidizing air rate, system temperatures, etc., for both the 2.25 and 1.75 AAR test periods are shown in Figures 4.3-1 and 4.3-2. Averaged test operating data are shown in Tables 4.3-2 and 4.3-3.

4.3.2 Bed Behavior

4.3.2.1 Bed Fluidization. Proper bed fluidization is necessary because poor fluidization will contribute to bed agglomeration and subsequent calciner shutdown. The primary indicator of proper fluidization is relatively close agreement between the bed thermocouples. Bed locations that are more than about 10°C cooler than the rest of the bed indicate unfluidized sections or formation of feed agglomerates, while spots more than 10°C hotter than the bed can indicate agglomerates that are deflecting the fuel nozzle flame.

Approximate locations of the bed thermocouples for the SAIC calciner fluidized bed section of the calciner are shown in Figure 2-2. All of the bed temperatures except TC#2 and TC#6 tracked within a few degrees of each other, as shown in Figure 4.3-3. Thermocouple TC# 2 is installed on the distributor plate housing and extends into the middle of the distributor sparge ring. The TC#2 temperature

Table 4.3-1. Summary of target and actual operating parameters.

Operating Parameter	Startup Condition, Setpoint or Target	Test 1, 2.25 AAR		Test 2, 1.75 AAR	
		Test Average	Value at End of Test	Test Average	Value at End of Test
Feed blend AAR	2.25 (Test 1) 1.75 (Test 2)	2.25	1.81	1.75	1.84
Liquid feed rate (L/hr)	Start at 3 L/hr, ramp to 5 L/hr. As bed conditions indicate stable operation after COT=40, then raise to 6 L/hr.	5.6	6.0	5.7	6.0
NAR (sL/L)	700 (Adjust to control MMPD)	666	800	731	700
MMPD (mm)	0.3 to 0.5 mm	0.40	0.45	0.44	0.42[a]
Fluidizing Air- Multiple of Minimum Fluidization Velocity	2 (Adjust to control proper bed fluidization)	0.40	0.45	0.44	0.42
Fluidizing Air Velocity (m/s)	~0.11 m/s for MMPD of 0.34 mm	0.16	0.24	0.27	0.27
Pressure (psia)	12.4 psia	12.4	12.5	12.4	12.4
Temperature in lower bed (°C)	600°C	597	596	597	596
Temperature in cyclone separator (°C)	525-575°C, (These temperatures are desired to minimize renitration of fines)	546	548	548	549
Starting bed height (in)	Maintain bed height around 18-24 inch.	22.6	26.0	22.6	25.0
Kerosene	0.6-0.8 L/hr	0.87	0.87	0.87	0.87
O_x/fuel ratio (sL/L)	2000	2,000	2,000	2,000	2,000
Quench exit temperature (°C)	100-130°C	86	86	81	83
Pressure drop across venturi separator (inch w.c.)	40-50 inch w.c.	44	47	44	42
Reburner Stage 1 temperature (°C)	1200°C	1,200	1,200	1,199	1,200
Reburner Stage 2 Temperature (°C)	980-1000°C	980	980	979	980
Reburner Stage 3 Temperature (°C)	660-950°C	897	930	905	902
Excess natural gas percentage (%)	1000-1200	1,384	1,000	1,056	1,150
Reheater 1 Temperature (°C)	120°C	125	131	126	126
Reheater 2 Temperature (°C)	120°C	117	117	117	118

a. This is for the COT 90 hr calcine sample. The screening of a sample of calcine from the end of the 1.75 AAR test gave an MMPD of 0.54 mm; however, this was an improbably large increase for the last 10 hr of the test. It is likely that either the sample taken from the COT 100 product was not representative, or the amount of sample was too large causing blinding of the 30 and 40 mesh screens.

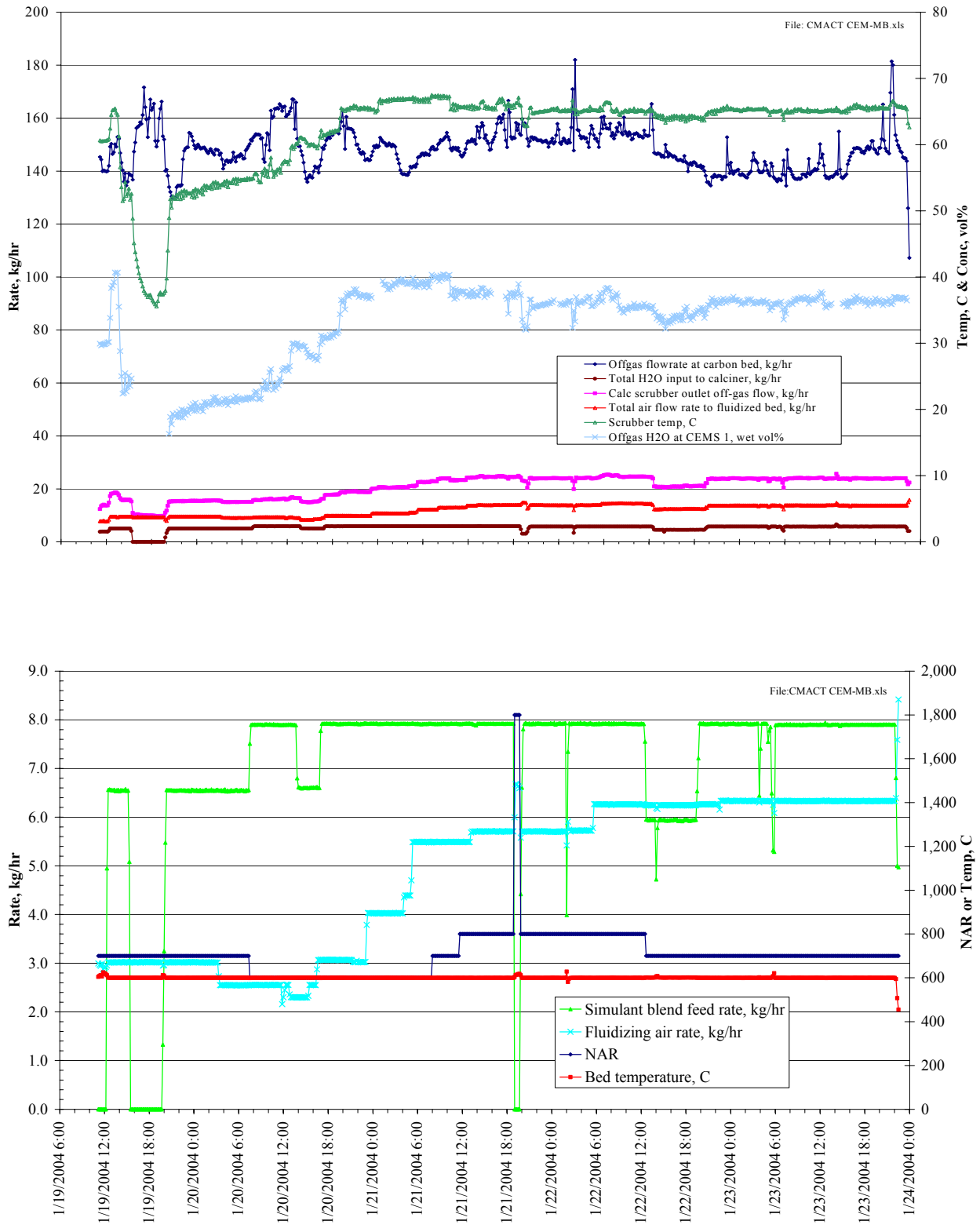


Figure 4.3-1. Trends of selected fluidized bed test system operating conditions.

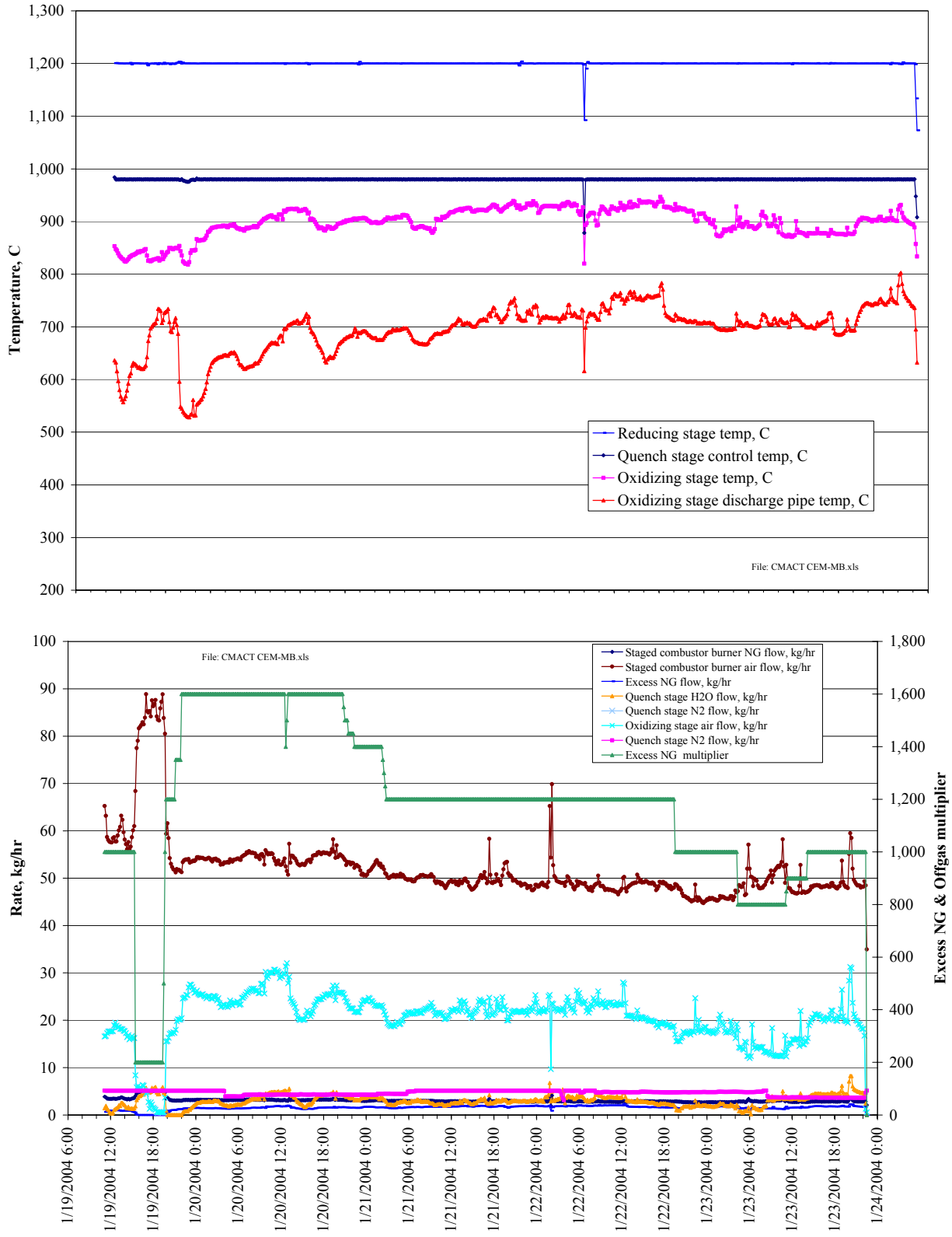


Figure 4.3-2. Trends of selected operating conditions for the staged combustor.

Table 4.3-2. Average fluidized bed system operating conditions during the calcination test.

Averages	Simulant blend feed rate, kg/hr SR1_F1A_VAL	Simulant blend density, gm/cc SR1_D1A_VAL	Simulant blend feed, L/hr SR1_F1A_VFR	Total simulant blend feed, kg	Total simulant blend feed, L	Atomizing air flow rate kg/hr SR1_F1B_KGH	Feed NAR	Fluidizing air rate, kg/hr H1_F2_PV	Fluidized bed bottom pressure, psia SR1_P1_VAL	Fluidizing air temp at H-1 super heater discharge, C H1_T2_VAL	Fluidizing air velocity, m/s	Total air flow rate to fluidized bed, kg/hr V1_F1_VAL
Test 1	7.13	1.31	5.54	182	283	4.45	685	3.75	12.4	766	0.16	10.7
Test 2	7.56	1.32	5.73	381	289	5.03	733	6.20	12.4	850	0.27	13.7
Averages	7.48	1.32	5.40	371	572	4.76	701	4.96	12.4	809	0.21	12.2
STD DEV	1.79	0.07	1.34	0	---	0.93	118	1.55	0.2	109	0.07	2.1

NAR = Nozzle atomizing gas to liquid feed volume ratio (at 1 atm, 68 F). [CMACT CEM-MB feb 25.xls]Tables

Averages	Kerosene flow rate, kg/hr SR1_F1C_VAL	Kerosene flow rate, L/hr	Total kerosene flow rate, kg	Kerosene atomizing O_2 flowrate, kg/hr SR1_F2_KGH	Kerosene NAR	O_2/fuel mass ratio	Bed fluidized density, gm/mL BED_DENSITY	Bed height, in BED_HEIGHT	Bed mass, kg 0.00	Bed control temp (T5), C SR1_T5_VAL	Bed wall control temp (T19), C SR1_T5_VAL	Total air flow rate to calciner, kg/hr V1_F1_VAL
Test 1	0.70	0.86	18.5	2.37	2,021	3.39	0.80	22.5	9.44	600	600	10.7
Test 2	0.69	0.86	35.2	2.34	2,000	3.34	0.65	22.6	7.78	599	599	13.7
Averages	0.70	0.83	36.5	2.35	2,000	3.36	0.72	22.6	8.58	600	600	12.2
STD DEV	0.14	0.18	0.0	0.48	0	0.69	0.15	1.6	1.68	7	7	2.1

Notes:
1. The bed mass was calculated from the bed dP measurements and normalized to match the measured starting bed mass of 11.1 kg.
2. Total flowrate to calciner is measured at the air supply header and is the sum of fluidizing air, atomizing air, and air purges.

	Cyclone			Scrubber						Staged combustor burner and fuel			
Averages	Total H_2O input to calciner, kg/hr H2O_AT_CYC_KGH	Calc offgas flowrate from cyclone, kg/hr TOTAL_KGH_AT_CYC	Off-gas flow after cyclone, scfm SCFM_AT_CYC	Scrubber temp, C T7_T2_VAL	Scrubber pressure, psia T7_P_VAL	Calc scrubber outlet off-gas flow, kg/hr TOTAL_KGH_AFTER_EVS	Off-gas flow after scrubber, scfm SCFM_AFTER_EVS	Meas. scrubber outlet offgas flowrate, kg/hr B1_F6_VAL	Ratio, scrubber outlet meas. off-gas flowrate / calc flowrate	Staged combustor burner NG flow, kg/hr B1_F1_VAL	Staged combustor burner air flow, kg/hr B1_F2_VAL	Excess NG flow, kg/hr B1_F3_VAL	Excess NG multiplier B1_F3_MUL_IN
Test 1	5.50	20.3	10.1	61.1	10.0	18.9	9.1	14.9	0.78	3.11	52.9	1.51	1,384
Test 2	5.59	23.4	11.6	65.1	10.1	23.6	11.7	20.7	0.88	2.85	48.5	1.71	1,056
Averages	5.58	21.9	10.6	63.1	10.1	21.3	10.2	17.9	0.83	2.98	50.7	1.62	1,228
STD DEV	1.21	3.4	1.7	6.7	0.4	4.1	2.3	4.4	0.08	0.44	7.4	0.42	313

Notes:
1. Total H_2O input to the calciner is the sum of water in the blended feed and water of combustion from the kerosene.
2. The calculated cyclone off-gas flow rate is the sum of flow rates of the total calciner air, atomizing O_2, CO_2 from the kerosene, total H_2O, and NO_2 from the feed blend.
3. The volumetric flowrates are based on a standard pressure of 1 atmosphere and a standard temperature of 68 F.
4. The measured scrubber outlet off-gas flow rate is lower than the calculated flow rate and is not as accurate as the calculated value because the flow rate at this location was too low for the coriolus flowmeter measurement range and because the measurement may have been interfered by particulate matter.
5. The staged combustor pressure was calculated as the average of the scrubber pressure and the off-gas pressure at the inlet to the carbon bed.

Table 4.3-3. Average off-gas control system operating conditions during the calcination test.

	Staged combustor reducing stage				Staged combustor quench stage						Staged combustor oxidizing stage				
	Reducing stage total gas flowrate, kg/hr	Reducing stage temp, C	Reducing stage total gas flowrate, acfm	Reducing stage gas residence time, s	Quench stage H_2O flow, kg/hr	Quench stage N_2 flow, kg/hr	Quench stage control temp, C	Quench stage total gas flowrate, kg/hr	Quench stage total gas flowrate, acfm	Quench stage gas residence time, s	Oxidizing stage air flow, kg/hr	Oxidizing stage temp, C	Oxidizing stage total gas flowrate, kg/hr	Oxidizing stage total gas flowrate, acfm	Oxidizing stage gas residence time, s
Averages		B1_T1_VAL			B1_F4_VAL	B1_F7_VAL	B1_T2_VAL				B1_F7_VAL	B1_T3_VAL			
Test 1	73.4	1,200	301	2.97	2.82	4.72	980	80.9	283	0.24	22.98	897	102.9	319	1.74
Test 2	73.7	1,199	296	3.00	3.12	4.58	979	80.9	280	0.24	19.51	905	97.9	299	1.85
Averages	73.6	1,200	299	2.99	2.99	4.64	980	80.9	282	0.24	21.37	902	100.4	309	1.80
STD DEV	---	7	---	---	1.22	0.52	5	---	---	---	5.31	28	---	---	---

Notes:
1. N_2 is used to atomize the quench water.
2. The volume of the reducing stage (14.8 ft^3) was based on a inside diameter of 21 inches and a length of 74 inches, not including the conical reducing section at the inlet of the quench section.
3. The volume of the quench stage (1.1 ft^3) was based on the volume of the frustum (8 inches long) and the throat length (10 inches) and the throat inside diameter (8 inches).
4. The volume of the oxizing stage (9.22 ft_3) was based on an oxidizing stage diameter of 21 inches and a length of 46 inches.

	Carbon bed								Total flows			
	Carbon bed pressure, psia	Carbon bed control temp, C	Carbon bed offgas flowrate, acfm	Carbon bed superficial gas velocity, f/s	Stage 1 superficial residence time, s	Stage 2 superficial residence time, s	Stage 3 superficial residence time, s	Total carbon bed superficial residence time, s	Total gas input to system, kg/hr	Offgas flowrate at carbon bed, kg/hr	Offgas flowrate at carbon bed, scfm	Ratio, carbon bed off-gas rate / total gas input to system
Averages	AJ1_P2_VAL	GAC1_T2_VAL							TOTAL_KGH_AFTER_PQ	AJ1_F1_VAL	SCFM_AFTER_PQ	
Test 1	9.71	108	160	1.56	0.053	0.107	0.481	0.641	147	149	81	1.02
Test 2	9.69	107	156	1.52	0.055	0.109	0.492	0.656	142	147	79	1.03
Total test average	9.70	107	158	1.55	0.054	0.108	0.485	0.647	145	148	81	1.02
STD DEV	0.40	1	---	---	---	---	---	---	8	8	5	0.03

Notes:
1. The superficial volume, velocity, and residence time is calculated from the bed volume assuming 100% void space.
2. The superficial volume of the carbon bed Stage 1 (0.14 ft^3) was calculated using a bed depth of 1 inch and a bed diameter of 17.63 inches.
3. The superficial volume of the carbon bed Stage 2 (0.28 ft^3) was calculated using a bed depth of 2 inches and a bed diameter of 17.63 inches.
4. The superficial volume of the carbon bed Stage 3 (1.3 ft_3) was calculated using a bed depth of 9 inches and a bed diameter of 17.63 inches.

[CMACT CEM-MB feb 28.xls]offgas tables

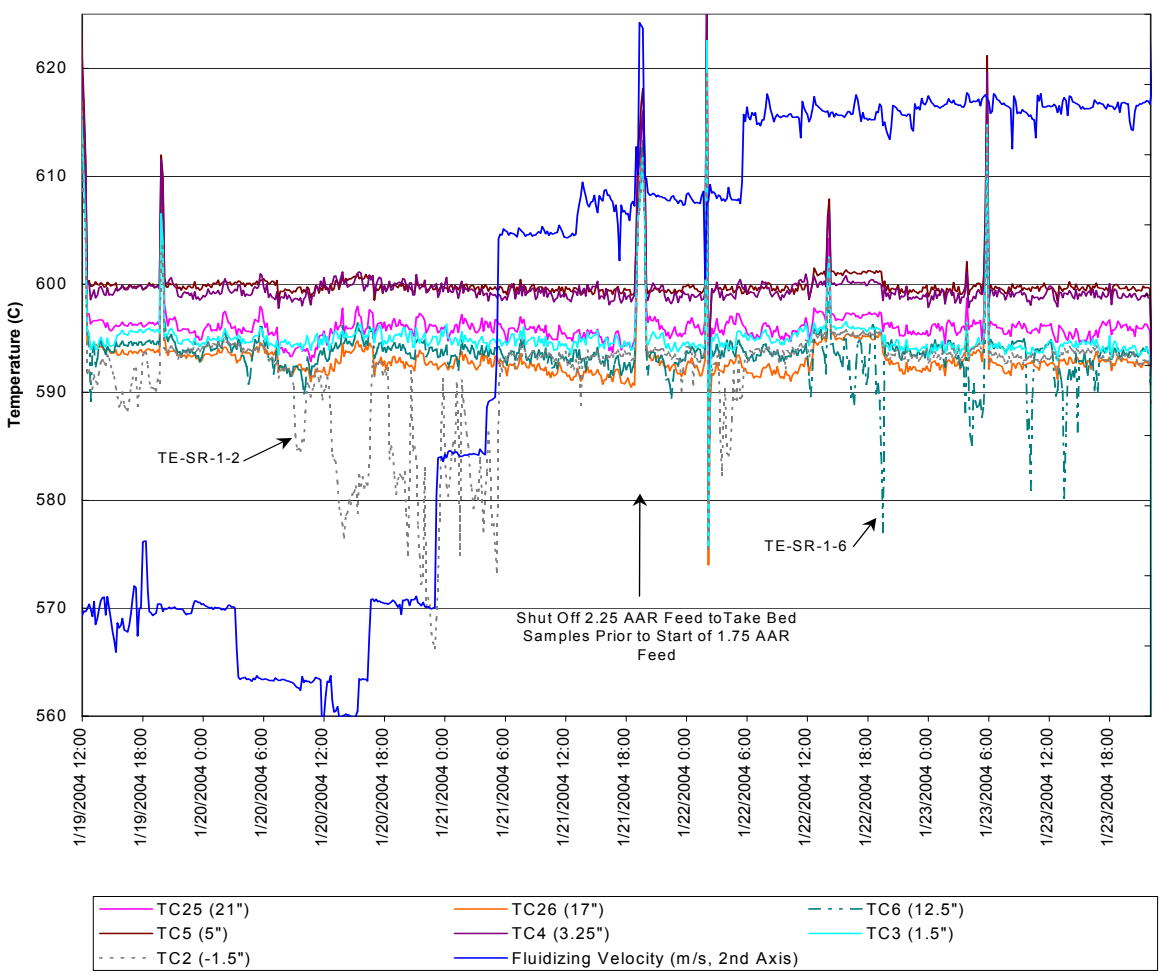


Figure 4.3-3. Fluidized bed temperatures and fluidizing velocity.

measurement diverged from the bulk bed temperature when the liquid feed was shut off to unplug the off-gas line at the beginning of the first test. Later, TC#2 diverged significantly after the fluidizing velocity was reduced to 0.10 m/s (2.25 to 2.5 times the calculated minimum fluidizing velocity). This was attributed to large, non-fluidized particles at the bottom of the bed below the sparge ring. The fluidizing air flow was therefore increased in several steps up to 0.25 m/s to help fluidize the bed. This brought TC#2 back up to the bulk bed temperature. TC#2 again diverged early on 1/22/04, after switching to the 1.75 AAR feed blend. The velocity was raised to 0.27 m/s, which was sufficient to realign the temperature of the bed.

Thermocouple TC#6, which was located on the wall across from the feed nozzle, briefly diverged on 1/20/04, and again on 1/21/04, shortly after feed was switched to the 1.75 AAR blend. Subsequently, it recovered and diverged several more times. This was attributed to feed spray coating and drying on the thermocouple sheath. The depression in temperature is thus attributed to evaporative cooling on the tip of TC#6. The potential deposits on TC#6 likely built up and then sloughed or were dislodged by the bed. The dry deposit layers could not themselves cause a temperature depression, because the wall was heated to 600ºC, and therefore heat would not be conducted from the thermocouple junction to the wall. Hence, there is a likely correlation between nozzle behavior and spray droplet deposition on TC#6. Nozzle plugging was an occasional problem. If the spray pattern was disrupted by partial nozzle plugging on the

air cap, then large droplets could be injected into the bed in the vicinity of TC#6. Posttest inspection of the internal vessel revealed that the bottom inch or two of TC#6 had been coated with calcine sometime during the run, but had flaked off before the end of the run or during bed recovery. The location of this thermocouple was undoubtedly an unnecessary source of agglomerate formation that could be remedied by moving it out of the feed spray zone.

4.3.2.2 Product and Fines Production. The rate that the bed level increases during a test correlates with the amount of feed being calcined and retained in the bed (as new particles or as growth of existing particles). A decrease in the bed build rate, with no change in the feed rate, indicates an increase in fines carryover. The bed build rate can change due to a change in the fluidizing air flow, the atomizing air flow, the feed rate, or the feed blend composition. Production rates for both the 2.25 and 1.75 AAR blends were closely comparable, as shown in Figure 4.3-4 and Figure 4.1-1. The slope of bed height versus time was about the same near the end of the 1.75 AAR test as it was at the end of the 2.25 AAR test. Figure 4.1-1 also shows similar bed removal rates based on product collection throughout the run. In comparison to previous 15-cm Enclosed Pilot Plant high-temperature runs (Nenni 2000), bed production rates are 50–100% higher.

If the new calcine product has a different density than the starting bed, then the change in the fluidized density is a rough indicator of bed turnover. As shown in Figure 4.3-5, the fluidized density decreased dramatically up until the latter part of the 2.25 AAR test, and then remained relatively constant until the end of the 1.75 AAR test. This is due to the gradual decrease in the bed weight fraction of higher density Al_2O_3 particles that were used as the startup bed material. The product density decreased for the first 36 hr of the test, then leveled off at an average of 0.92 ± 0.05 g/mL for the remainder of the

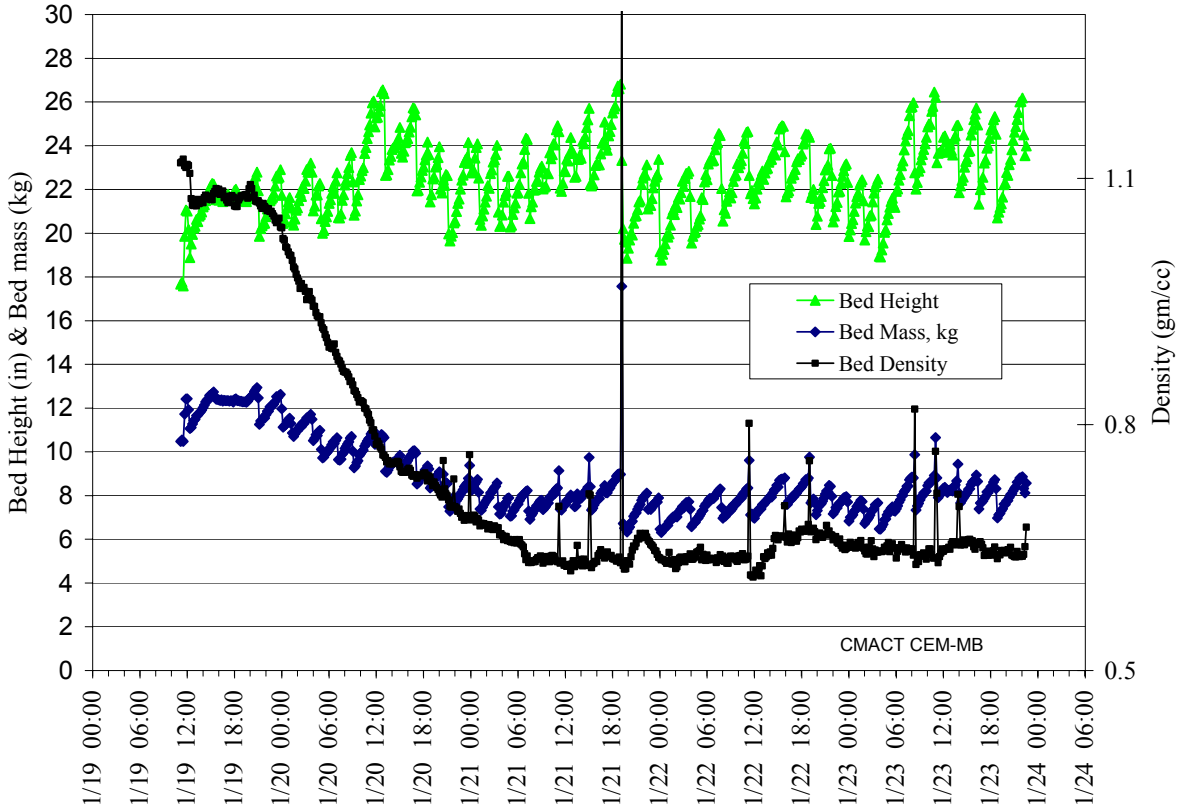


Figure 4.3-4. Bed height, mass and fluidized density.

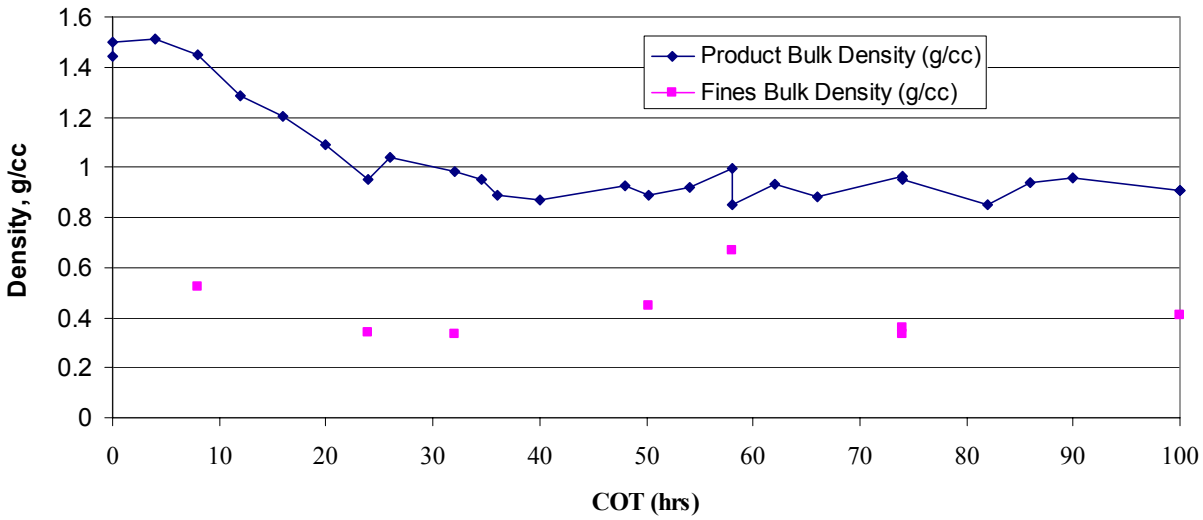


Figure 4.3-5. Product and cyclone fines bulk density.

2.25 and 1.75 AAR tests. The fines density was relatively constant through both the 2.25 and 1.75 AAR test portions, at 0.43 ± 0.13 g/mL. The fines bulk density tends to have more scatter, since it is difficult to reproduce the same consolidation each time when obtaining a "tapped" bulk density in a volumetric cylinder.

Bed turnover plays a significant role in the operation of new blends, and a bed turnover of greater than 90% is generally needed to ensure that the feed and bed material are indicative of the new product versus the behavior and characteristics of the starting bed.

For a fluidized bed, the pressure drop across the bed is equated to the bed weight. Therefore, the average bed weights were calculated from the average bed pressure drop multiplied by the cross-sectional area of the bed. Summary bed data and bed turnover are provided in Table 4.3-4. The bed turnover (97.88 and 98.47, respectively, or 99.9% for both runs combined) was excellent for both the test series, due to their excellent production rates.

The product-to-fines ratios (P/Fs) for the current tests were significantly higher than obtained during previous tests at INTEC, such as the P/F of 0.71 obtained during the previous 3.1 AAR test with WM-180 (Nenni 1999) and the P/F of 1.05 calculated for the high-temperature tests at NWCF (EDF-3387 p. 173). If the P/F ratio of the SBW/ANN blends continue to be near unity, then a mixture bulk density of 0.68 g/mL should be assumed for calcine volume projections.

The high P/F ratio may have been due to the blend, the lower calciner gas flows, or a more concentrated feed. The ANN used for feed makeup was higher, at 2.3 to 2.5 molar, than the normal INTEC ANN concentration of 2.2 molar. The test blends produced 130-g calcine per liter of feed but would have only produced 114 to 120-g calcine per liter of feed if they had been made up using 2.2 M ANN. Experience with dilute 3-way Al/Zr/SBW blends during NWCF Campaign H-3, which are similar to ANN/SBW, showed that blends producing about 120-g calcine per liter of feed build bed better and allow more ability to control particle size (O'Brien 2000). During H3, the product rate was quite sensitive to feed concentration, and the higher feed concentration for the current pilot plant tests likely had a positive affect on the P/F ratio. Therefore, it may be possible to improve NWCF calciner operation, P/F ratio, and mixture bulk density significantly by increasing the minimum ANN concentration in the procurement specification to 2.3 M ANN.

Table 4.3-4. Total product and fines masses, bed turnover, and mixture bulk density.

Test Blend	2.25 AAR	1.75 AAR	Both Tests
Initial bed (kg)	11.1	8.23	11.10
Bed product collected (kg)	28.17	20.72	48.89
Final bed (kg)	8.23	8.27	8.27
Average bed DP (inch w.c.)	18.37	14.68	16.53
Average bed weight (kg)	8.70	6.95	7.83
Net total bed product (kg)	25.29	20.77	46.06
Total cyclone fines (kg)	4.93	7.32	12.25
Product-to-fines ratio (kg/kg)	5.13	2.84	3.76
Bed turnover (%)	97.88%	98.47%	99.90%
Product bulk density (g/cm^3)	0.92	0.92	0.92
Fines bulk density (g/cm^3)	0.43	0.43	0.43
Mixture bulk density based on test P/F ratio[a] (g/cm^3)	0.95	0.90	0.93
Worst case mixture bulk density for P/F of 1 (g/cm^3)	0.68	0.68	0.68

a. Estimated based on bulk densities, product-to-fines ratio from curve fitting of the data in chart G-1 of ENICO-1100 (Childs Donovan and Swenson 1982):

RhoMixture = (-3.4514*(1/(P/F+1))^4 + 11.045*(1/(P/F+1))^3 - 10.61*(1/(P/F+1))^2 + 2.0339*(1/(P/F+1)) + 0.9827)*(RhoProduct-RhoFines)+RhoFines

The decrease in the P/F in Test 2 may be attributed in part, or in total, to the increase in the fluidizing gas rate during Test 2. Test 1 averaged 3.75 kg/hr fluidizing air compared to 6.20 kg/hr in Test 2. This increased flow would have entrained more fines to the cyclone.

A graph relating the bulk densities of mixtures of product and fines with the weight fraction of each was provided in the WCF Campaign 9 report (Childs, Donovan and Swenson, 1982). From this, combined product and fines mixture bulk density for the tests was about 0.93 g/mL. If the P/F ratio for calcination at the NWCF is 1 instead of the high P/F ratios obtained during the current tests, then the product and fines bulk density would be reduced to 0.68 g/cm^3, as shown on the table.

If the cyclone efficiency for the current test is higher that the cyclone used in the previous tests, more fines would be collected with less passing through to the scrubber. Fines that reach the scrubber are dissolved, and the scrub is recycled back to the calciner in full-scale operations. Decreased scrub recycle would reduce the overall feed rate and increase the required time to process all the SBW waste.

4.3.2.3 Feed Nozzle Plugging and Agglomerate Formation. The feed nozzle plugged infrequently during the 2.25 AAR blend test, as shown in Figure 4.3-6. The plugs were easily cleared with either the nozzle plunger or with acid flushing. Feed nozzle plugging became more frequent during the 1.75 AAR test, including one 12-hr period where the plugging occurred as frequently as every 10 minutes. The frequency of plugging then reduced dramatically toward the end of the test. In all cases, the feed nozzle could be cleared with acid flushing, but use of the plunger was less effective.

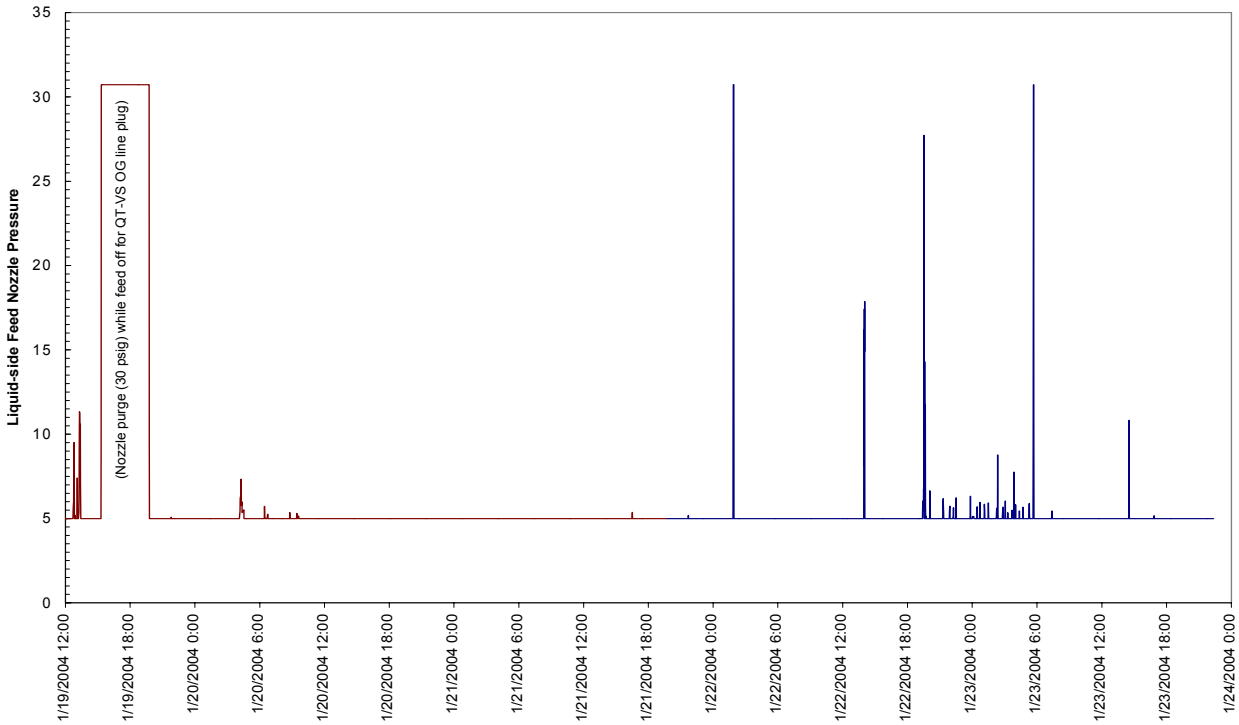


Figure 4.3-6. Liquid-side feed nozzle back-pressure.

During both the 2.25 AAR and 1.75 blend tests, agglomerates were collected in the bed product, with the amount more than doubling during the 1.75 blend test. At about COT 24 hr into the 2.25 AAR test, a consistent amount of small agglomerates began to appear in the product recovered from the bottom drain (about 0.44 wt% of the drained product until the end of the 2.25 AAR test). After switching to the 1.75 AAR blend, the amount of agglomerates in the bed product increased to about 2 wt% until COT 76 hr (COT time here includes the first 50 hr on the 2.25 blend) after which it decreased to 0.8 wt%. There was no buildup on the walls opposite the feed and fuel nozzles after the tests, as shown in Figure 4.3-7. There were only a half dozen agglomerates remaining on the distributor plate after the run (Figure 4.3-8 and Figure 4.3-9). Some of these agglomerates were fairly large at ½-in. diameter and were biscuit-shaped. It is possible that they formed on the feed nozzle (contributing to feed nozzle plugging); however, both the feed nozzle and fuel nozzle had only a light scale on them upon inspection after the test (see Figure 4.3-10). Another possibility is that the agglomerates were forming on TC#6 or the 1-in. port. This thermocouple frequently decreased by about 10 to 15ºC, then recovered without operator intervention. This thermocouple is in the spray zone directly opposite the feed nozzle, and it is likely the spray was building up calcine on the thermocouple and that the calcine dislodged after building up to some point.

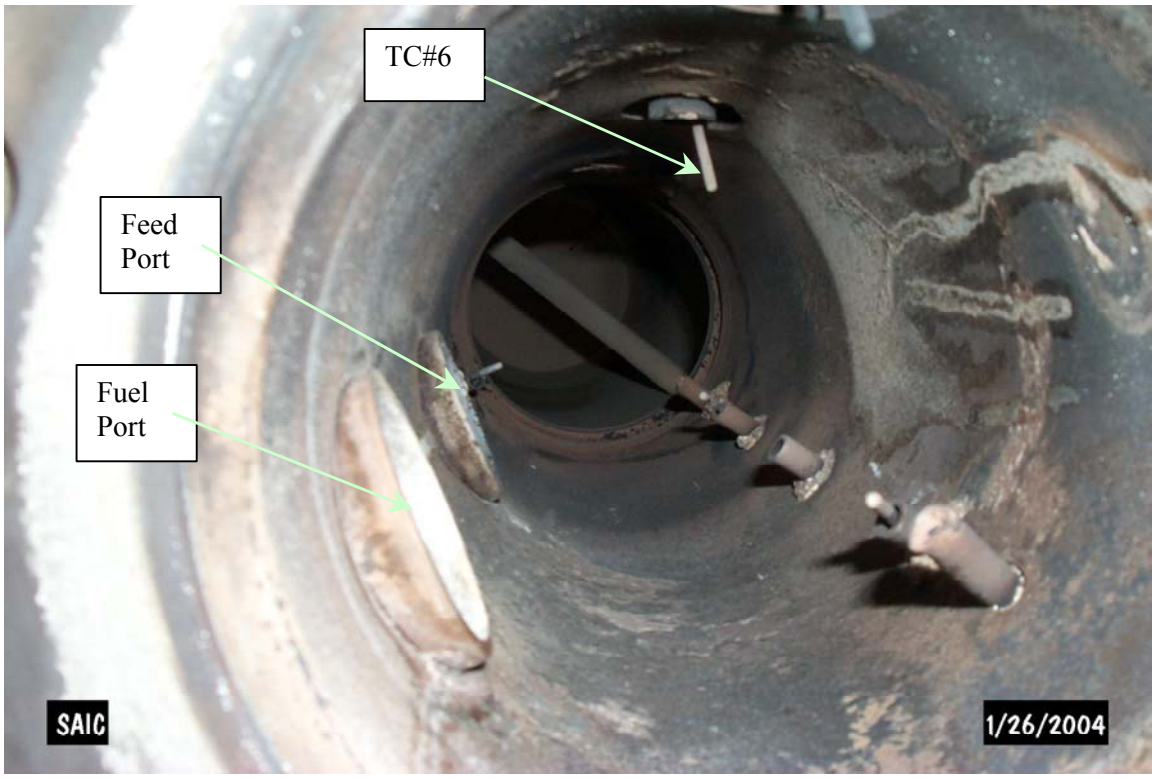


Figure 4.3-7. Interior of calciner bed section looking up—posttest.

Figure 4.3-8. Distributor plate—posttest inspection.

Figure 4.3-9. Agglomerates collected in bed product during operations.

Figure 4.3-10. Feed and Fuel Nozzles—posttest inspection.

Feed nozzle plugging was a frequent problem during tests of SBW/ANN blends, both at 500 and 600°C in the INTEC Enclosed 15-cm Calciner Pilot Plant (Nenni 1999; Nenni 2001a, 2001b). Plugging was worse at 500ºC, compared to the same blend at 600ºC, and was worse during calcination of lower AAR blends (higher sodium content). In Test SBW-HT-15a/b, cone-shaped agglomerates up to ½-in. were found in the bed at the end of the test (the Enclosed 15-cm calciner had smaller bed drain pipes than the SAIC calciner, and therefore, could not be with the bed sample as they were during the current tests). As with the current tests, no cones were found on the feed nozzle after the test, although a ⅛ to ¼-in. coating was found on the vessel walls near the feed nozzle port.

The feed blends that experienced frequent feed nozzle plugging in the INTEC pilot plant were later calcined at the NWCF, with little nozzle plugging (Law 2000; Swenson 2000; Wood 2001); thus, it is likely that the nozzle plugging exhibited by the SBW/ANN feeds in the pilot plants is an artifact of the smaller pilot-plant vessels and their protuberances in the nozzle spray zones.

4.3.2.4 Fines Carryover Past the Cyclone. A coating of fines was found inside the cyclone outlet and the line to the quench tower, as shown in Figure 4.3-11. This indicated that a portion of the calcine fines were not removed by the cyclone. The amount of calcine carried past the bed and cyclone can be estimated from a material balance of the bed product and cyclone fines collected, and the amount of calcine calculated from the components of the feed. As shown in Table 4.3.5, it is estimated that 19 to 24 wt% of the calcine went past the cyclone. From this and the amount of material collected in the cyclone, it is estimated that the cyclone efficiency averaged only 43%. This is less than desired, given a design criteria of 98% overall. It is indicative of the small size of the fires generated during these tests.

The amount of calcine fines carried over to the scrub was estimated from a mass balance of the sodium in the feed and the scrub. The results indicate that 20 to 24% of the sodium, and also the calcine, was carried over into the scrub, as shown in Table 4-3.6.

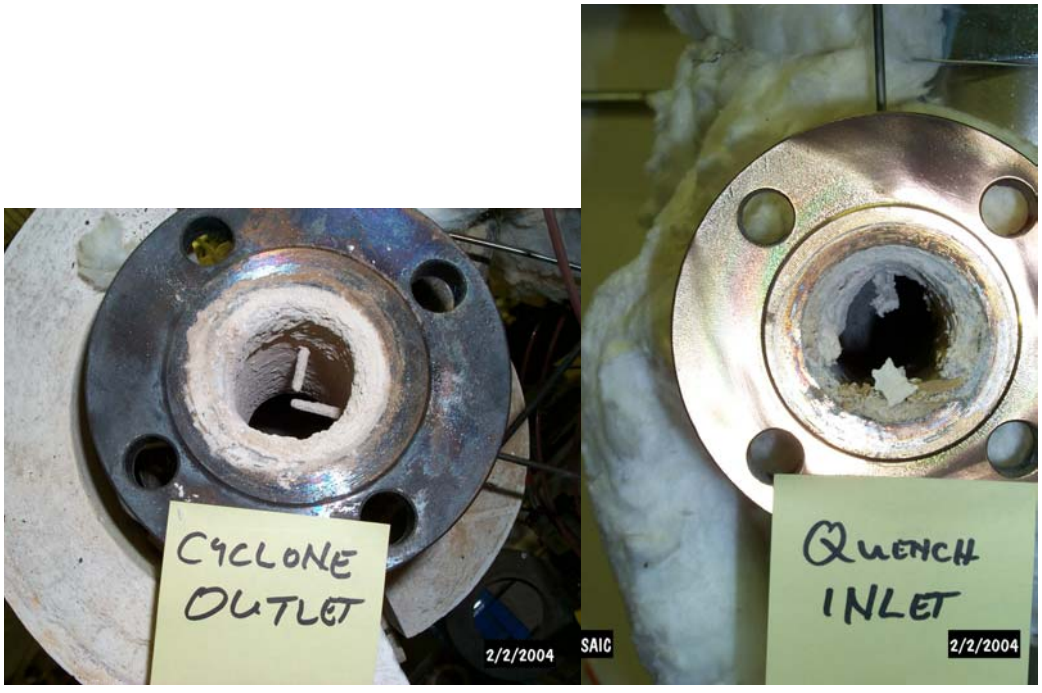


Figure 4.3-11. Cyclone outlet and quench tank inlet—posttest.

Table 4.3-5. Comparison of bed product and fines to calcine predicted from feed.

	2.25 AAR	1.75 AAR	Both Tests
Total feed (L)	283.0	289.0	572.0
Projected calcine production (g/L of feed)	132.2	128.2	130.2
Projected product from feed (kg)	37.4	37.0	74.5
Net total bed product (kg)	25.3	20.8	46.1
Total cyclone fines (kg)	4.93	7.32	12.25
Bed product (as wt% of calcine from feed)	67.6%	56.1%	61.9%
Cyclone fines (as wt% of calcine from feed)	13.2%	19.8%	16.5%
Calcine lost, as wt% of calcine from feed (wt%)	19%	24%	22%
Cyclone removal efficiency based on fines collected versus fines + calcine lost	41%	45%	43%

Table 4.3-6. Calcine carryover to scrub based on sodium balance.

	2.25 AAR	1.75 AAR	Both Tests
Feed volume (L)	283	289	572
Feed Na concentrate (M)	0.838	0.947	0.893
Feed Na (moles)	237	274	511
Scrub Na (moles)	52	66	118

After the run, the inside of the demister downstream of the scrubber was inspected and found to be clean. There was a light dusting of solids inside the pipe between the demister and the staged combustor, and there was a small area coated with very fine crystalline hairs up to 1/8-in. long just downstream of the in situ oxygen monitor. This oxygen monitor began to give erratic readings toward the end of the testing, indicating that it was being affected either by the off-gas or by the solids in the off-gas.

4.3.2.5 Calciner Product. The bed MMPD responded well to adjustments in the NAR for both the 2.25 and 1.75 AAR blends, as shown in Figure 4.3-12. The ability to both increase and decrease bed particle size was demonstrated. The NAR was initially set at 700, based on the value used during test SBW-HT-15a at INTEC, which calcined a WM-180/ANN blend with an AAR of 3.1. The particle size dropped slightly during the first 14 hr, so the NAR was reduced to 600. The particle size then began to increase slowly, but was controlled at 0.44 by increasing the NAR to 800 at COT 44. After switching the to 1.75 AAR blend, the particle size began to decrease but was stabilized at 0.40 mm by reducing the NAR to 700. The MMPD showed a slight increase from COT 84 to 90 hr. The COT 100 bed sample showed a large increase to 0.54 mm; however, it is unlikely that the size would have changed this much in the last 10 hr after being relatively stable for the previous 25 hr. When calcine is handled, the larger particles float to the surface. The MMPD sample of the COT 100 product was taken from the main product bag, and it is likely that there was some segregation of the product before sampling.

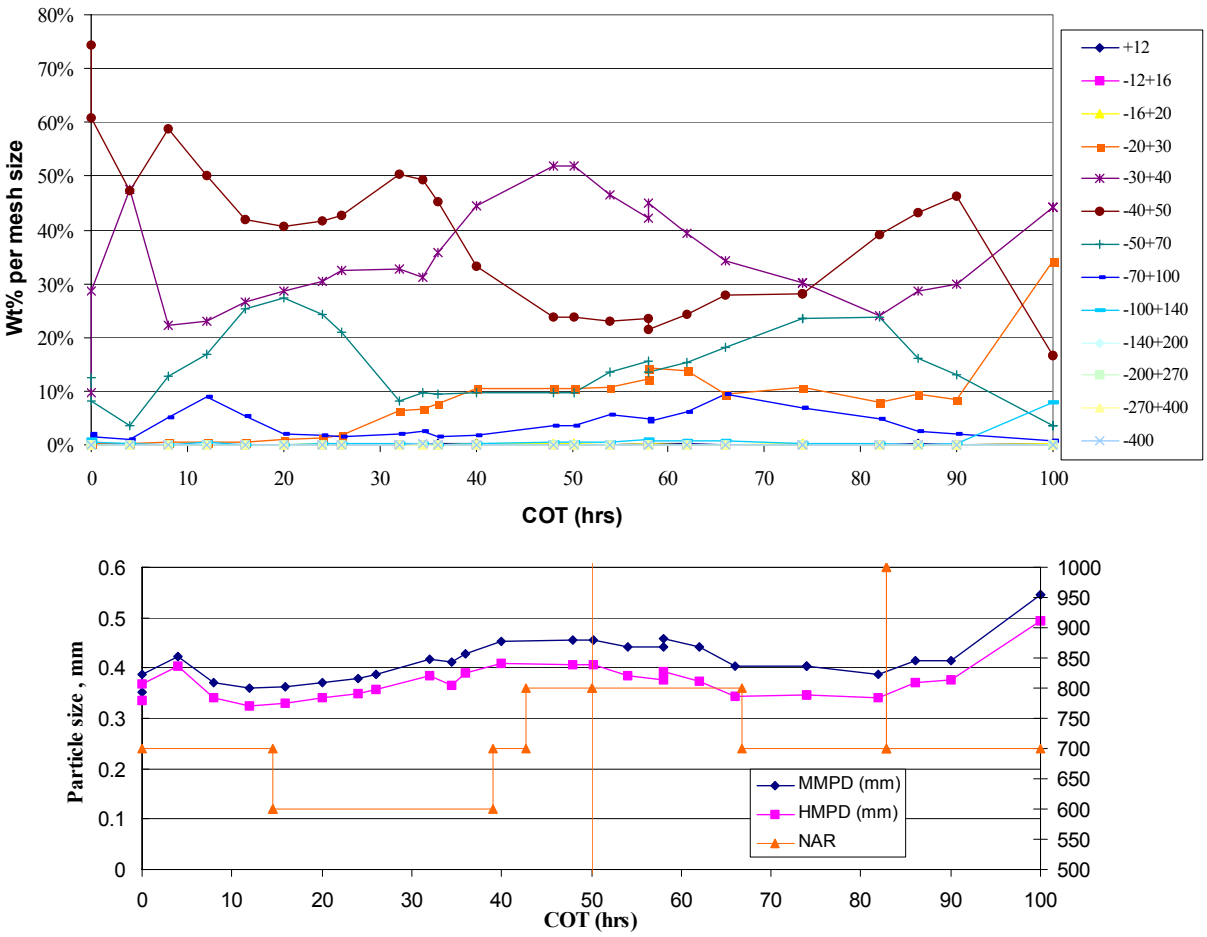


Figure 4.3-12. Bed particle size distribution in mesh size and mm.

4.3.2.6 Cyclone Fines PSD. Particle size distributions were measured for fines from the current tests; these are shown in Figure 4.1-13. As expected, the new cyclone was more efficient and removed smaller particles than the INTEC 15-cm calciner pilot plant; however, the particle size distribution during the tests had much smaller particulate than used for the cyclone design. The average particle size for the current test was approximately 12 µm, compared to 45 µm for the INTEC 15-cm pilot-plant test. Both the SAIC and INTEC data show a bimodal distribution. Partial plugging of the cyclone occurred in both the SAIC and INTEC tests, which necessitated frequent tapping on the cyclone to remove the plug. The peak at the larger particle sizes is likely due to a collection of agglomerates from the cyclone and off-gas line when the vessel was massaged with a ball peen hammer. The PSD of the fines for both the 2.25 and the 1.75 AAR test were closely similar.

4.3.2.7 SEMS/EDX. Scanning electron microscope photographs of the starting bed material, calciner product, and cyclone fines are shown in Figures 4.3-14 to 4.3-18. The calcine product from both the 2.25 and 1.75 AAR tests was smooth and regular. The particle sizes observed in the SEM photographs confirm the PSD measurement. Crystalline flakes can be seen in some of the close-ups of the product (Figure 4.3-16). These have been observed before in calcine product from high-temperature tests.

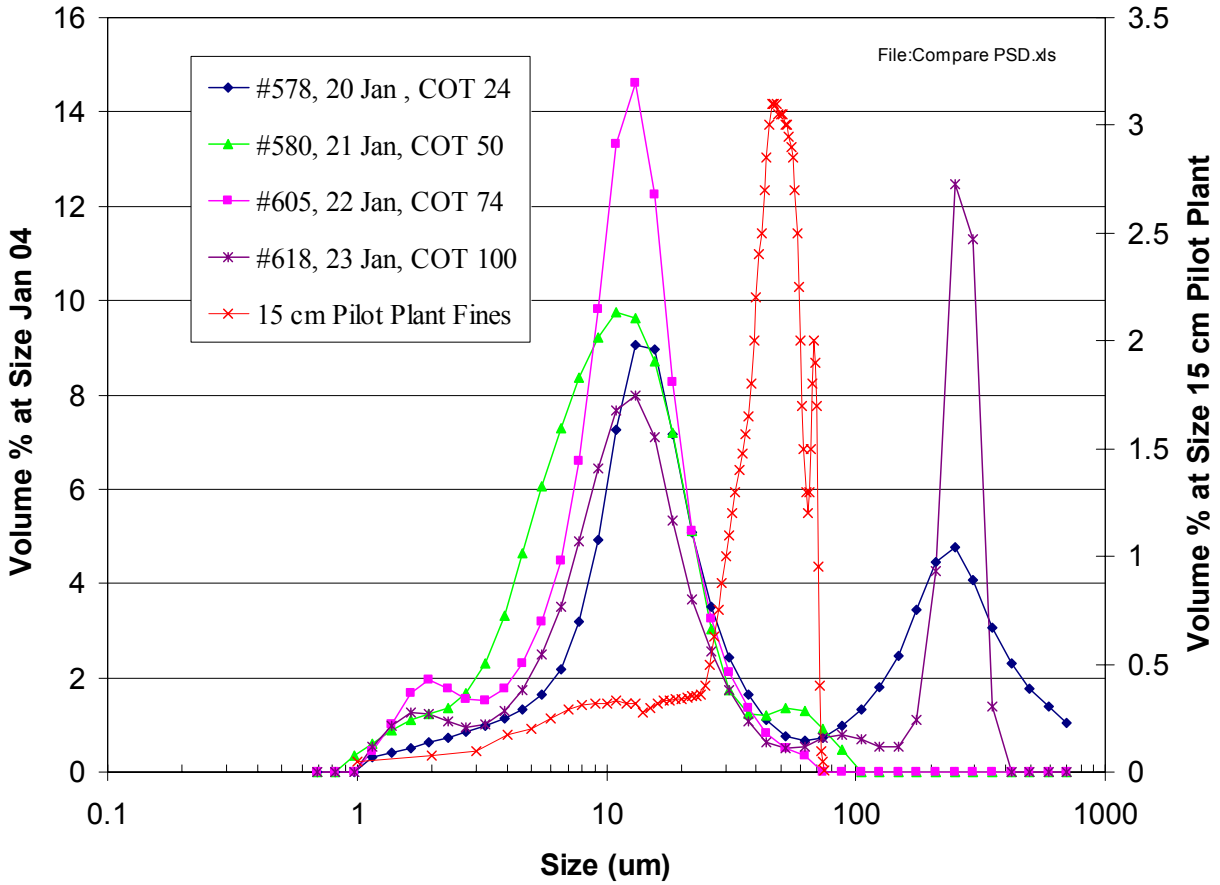
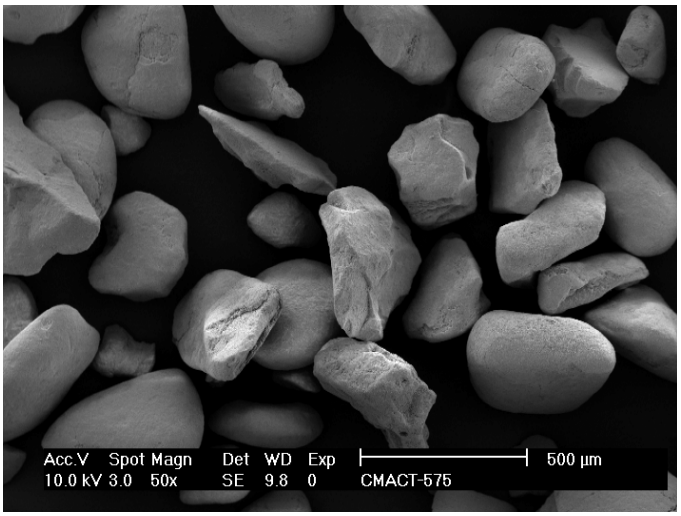


Figure 4.3-13. Comparison of fines size distribution for SAIC 2.25 AAR and 1.75 AAR Tests with INTEC Pilot Plant fines. (15-cm data are plotted on secondary y-scale due to the higher measurement frequency and the resulting lower volume percent per data point).

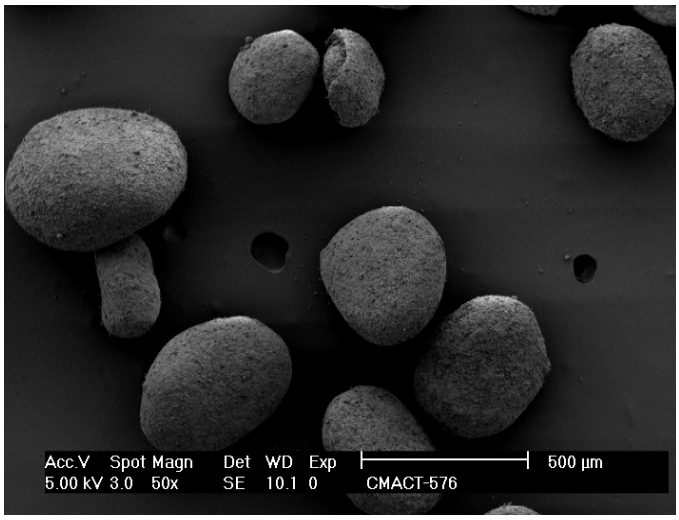
The cyclone fines are similar in appearance to the fines from previous high-temperature calciner tests. The fines are generally irregularly shaped and exhibit some agglomeration. In addition, some very small (<1 um) particles can be seen in Figure 4.3-15, 17, and 18. The smooth surfaces seen on the fines particle indicate that there was a large amount of amorphous material in the fines.

Figure 4.3-19 show SEM photographs of product and fines from test SBW-HT-15a in the Enclosed 15-cm Calciner pilot (Nenni 1999). Test SBW-HT-15a calcined a blend of WM-180/ANN with an AAR of 3.1. Although the scales of the photographs are not shown, the product and fines have a similar appearance to the WM-180/ANN blend 2.25 AAR and 1.75 AAR calcines.

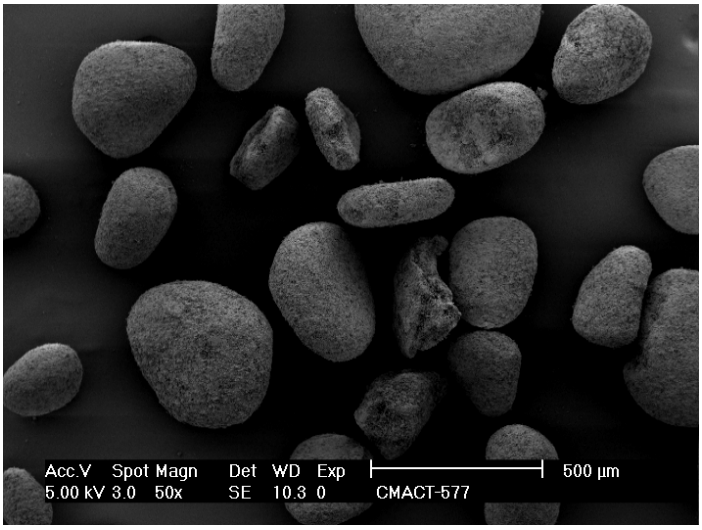
Figure 4.3-20 shows photographs of high-temperature calcine product from NWCF Campaign H-4 in 2000. At the time, the NWCF was calcining a blend of WM-189/ANN with an AAR of 2.5. This blend had an order of magnitude more F, Zr, and Ca than the WM-180 blends, and the calcine had a noduled appearance similar to the Zr/Na/Al waste blends calcined at 500°C during NWCF Campaign H-3. Although noduled calcine does not seem to greatly affect calcination, it is thought to fluidize less well and to have more bed attrition than smooth calcine bed particles.



Sample 575 (2.25 AAR bed product, COT 0)



Sample 576 (2.25 AAR bed product, COT 24)



Sample 577 (2.25 AAR bed product, COT 50)

Figure 4.3-14. SEM photographs of bed product from 2.25 AAR test.

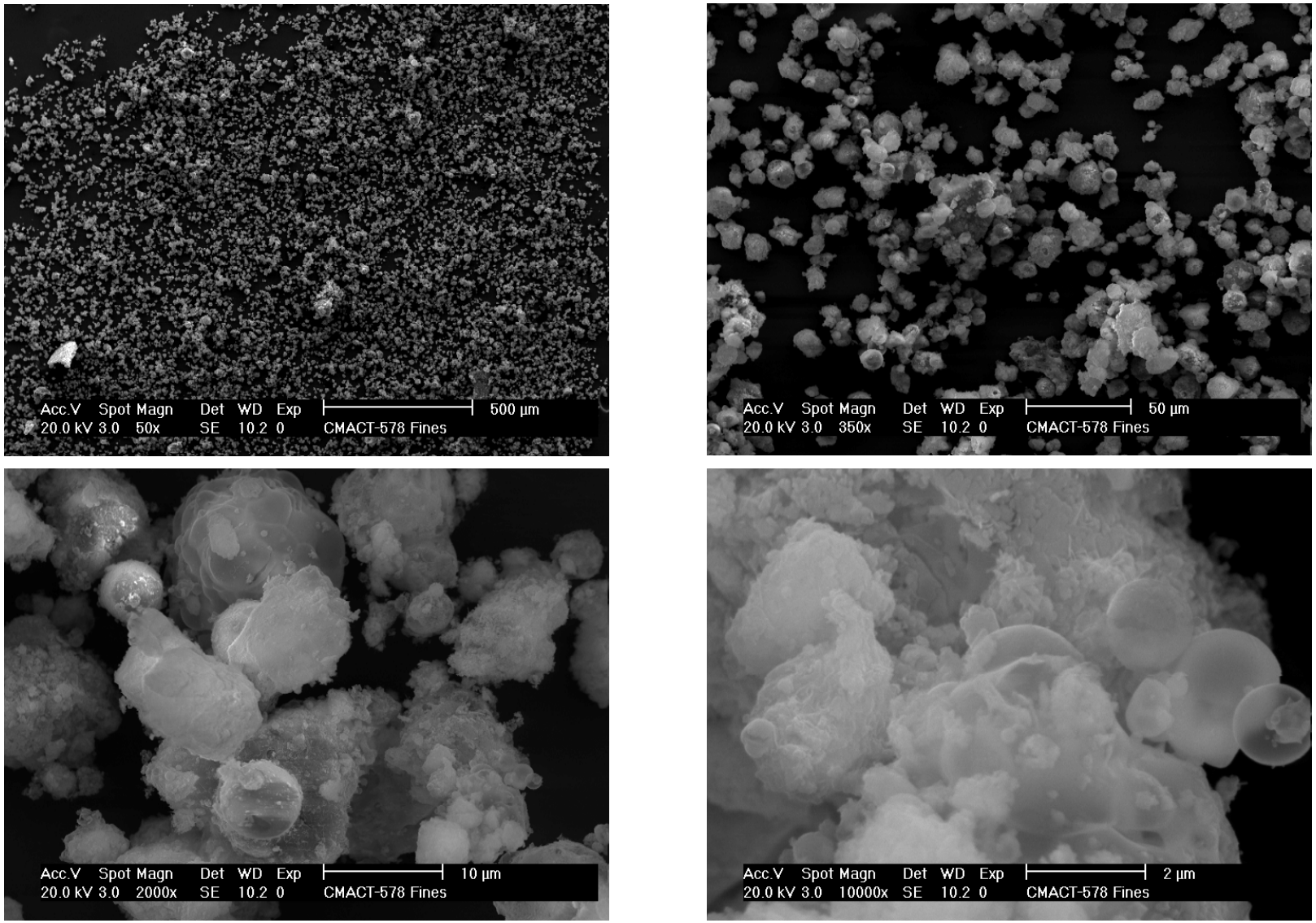


Figure 4.3-15. SEM photographs of cyclone fines from 2.25 AAR testing (Sample 578) at COT 24.

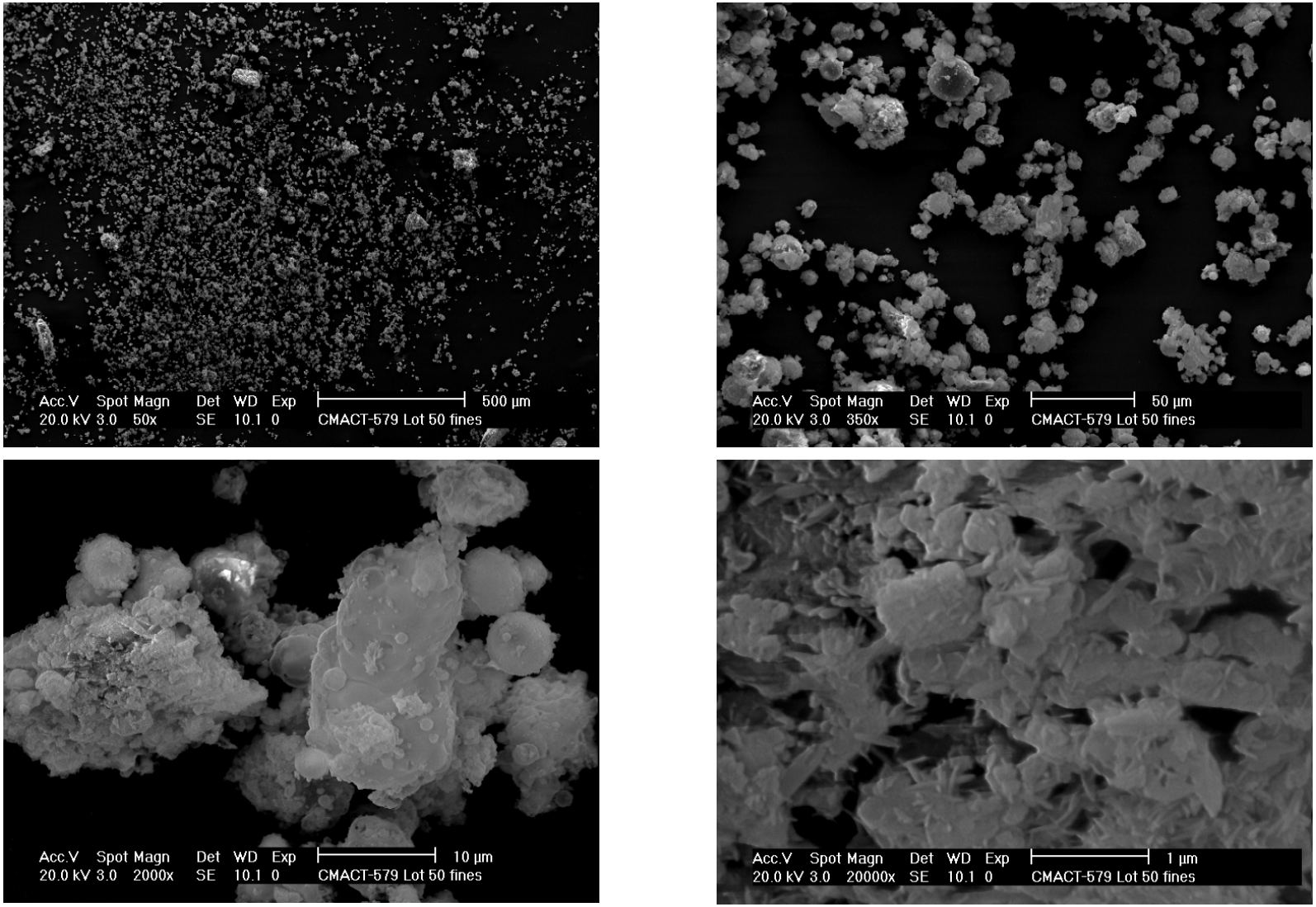
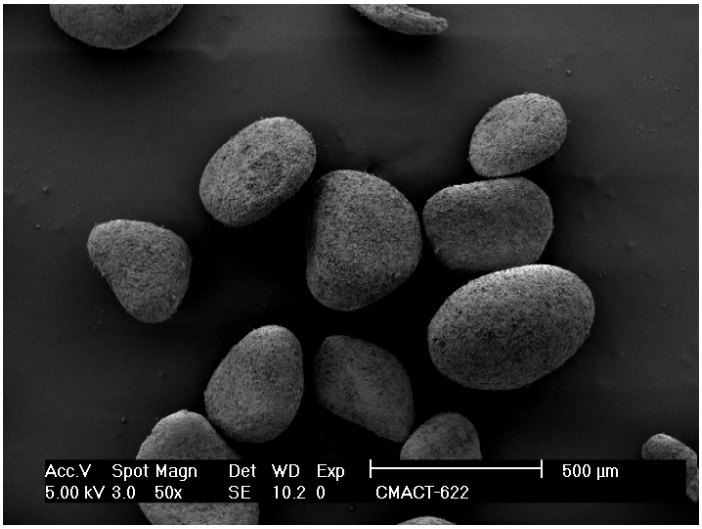
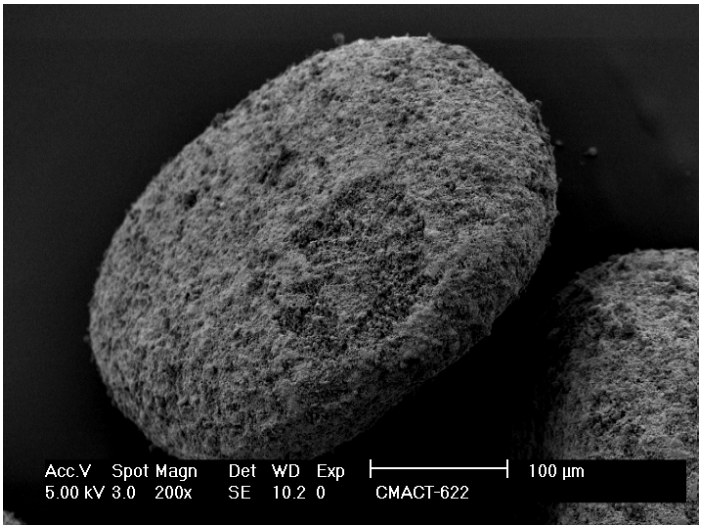


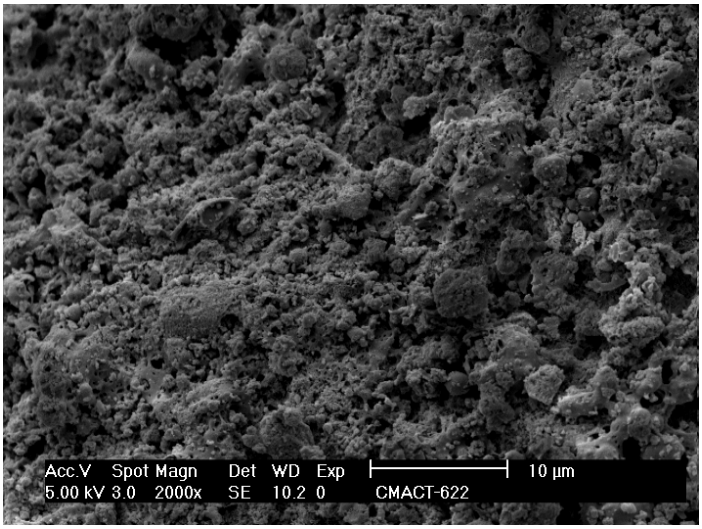
Figure 4.3-16. SEM photographs of cyclone fines from 2.25 AAR testing (Sample 579) at COT 50.



Sample 622 (1.75 AAR bed product, COT 50)



Sample 622 (1.75 AAR bed product, COT 50)



Sample 622 (1.75 AAR bed product, COT 50)

Figure 4.3-17. SEM photographs of bed product from 1.75 AAR test.

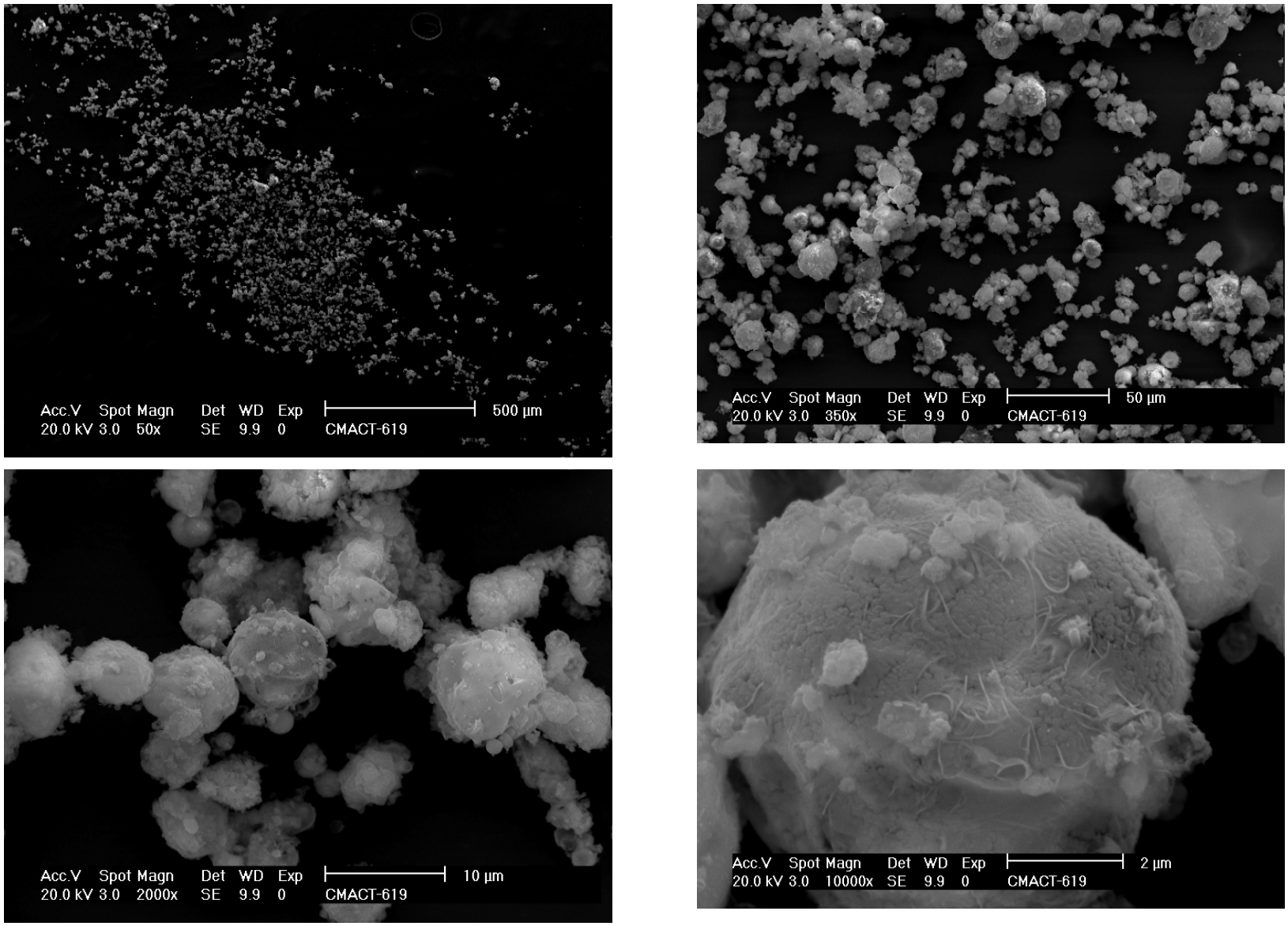


Figure 4.3-18. SEM photographs of cyclone fines from 1.75 AAR testing (Sample 619) at COT 50.

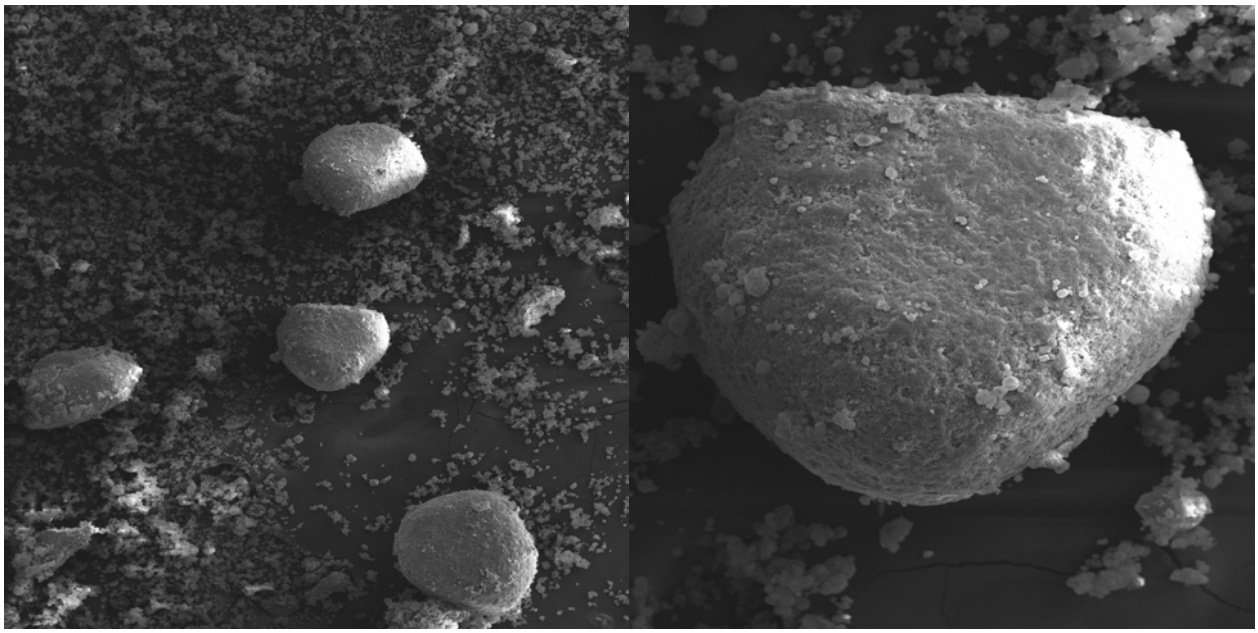


Figure 4.3-19. SEM photographs of product and fines from test SBW-HT-15a in the enclosed 15-cm Calciner pilot plant (Nenni 1999).

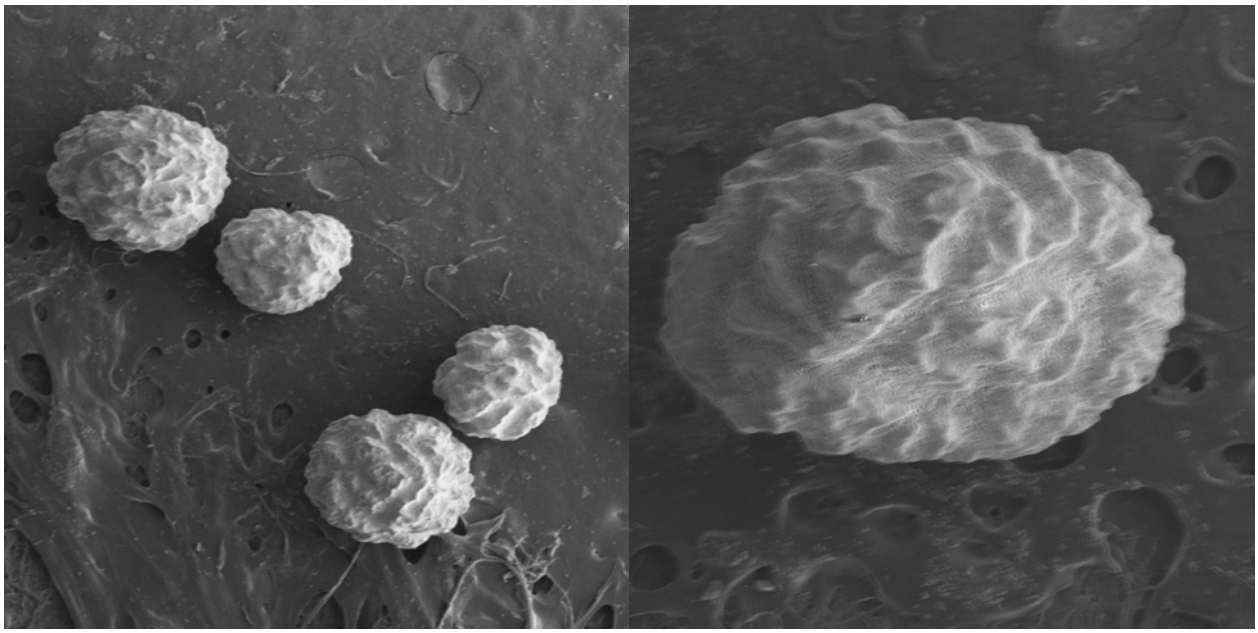


Figure 4.3-20. SEM photographs of high-temperature calcine product from NWCF Campaign H-4.

4.4 Off-gas Concentrations

The off-gas composition at the outlet of the reheater downstream of the scrubber and mist eliminator and upstream of the oxidizer was measured using CEMS 1. For the short time duration of about 1 hr during the 2.25 AAR test, CEMS 1 was also used to measure the off-gas composition at the

cyclone outlet, upstream of the quench and wet scrubber. CEMS 2 was used to measure the off-gas composition at the inlet of the carbon bed exclusively during the current pilot-plant tests.

4.4.1 Cyclone Outlet Off-gas Composition

The average wet-basis off-gas composition at the cyclone outlet is shown in Table 4.4-1. This composition was measured for only two very short time periods of 10 minutes or less each during the 2.25 AAR test. Valid sample periods at this sample location were short because the sample filter was rapidly plugged by particulate in the off-gas at the outlet of the cyclone, upstream of the scrubber system. The cyclone outlet H_2O and NO_x levels tend to be higher than the scrubber outlet measurements. The scrubber outlet H_2O concentration for the 2.25 AAR test was 30.8%, 12% lower than the value of 35% measured at the cyclone outlet, because some of the H_2O is condensed in the wet scrubber.

Some other gas species, especially halides and NO_2, can also be scrubbed in the wet scrubber. Off-gas halide concentrations were not measured upstream of the staged combustor, but the concentrations of HCl downstream of the staged combustor, and the mass of Cl and F captured in the carbon bed, show that show that essentially all HCl and HF that was in the off-gas was scrubbed in the scrubber during the calcination test. This implies that these species might be efficiently wet scrubbed in the NWCF scrubber, but the duration of the calcination test is too short (and the scrubber solution concentrations of Cl, F, etc. were too low) to conclude that the NWCF scrubber indeed does nearly quantitatively scrub halides.

NO_2 is also relatively soluble in even acid solutions. The amount of NO_3^- in the scrub solution corresponds to an average of about 4 ppm NO_2 scrubbing, although a comparison of the short-durations of cyclone outlet off-gas measurements with scrubber outlet off-gas measurements on the same test day indicates that up to 10% of the NO_2 could have been scrubbed at those specific times.

Table 4.4-1. Cyclone outlet off-gas composition.

	Average off-gas composition for each test on a wet basis at the cyclone outlet location											
CEM 1	H_2O, % (a)	O_2, %	CO_2, %	CO, %	NO, ppm	NO_2, ppm	NO_x, ppm	H_2, %	CH_4, ppm	SO_2, ppm	N_2, % (b)	Total, %
After cyclone (c)	35.0	11.7	8.05	1.07	2,559	28,835	31,394	0.61	268	3.06	40.4	100.0

a. The percent H_2O was calculated from input gas flowrates at the cyclone outlet location.

b. Calculated by difference.

c. Data taken from 1/21 14:03 to 14:09 and 14:38 to 14:38.

[CMACT CEM-MB feb 28.xls]Tables

4.4.2 Scrubber Outlet Off-gas Composition

The average wet-basis off-gas composition at the outlet of the wet scrubber (upstream of the staged combustor) is shown in Table 4.4-2 for each test. The wet basis composition was calculated from the dry, as-measured composition by (a) correcting for zero and span calibration error/drift (where necessary), (b) correcting the NO_x measurements for the dilution factor used to lower the actual NO_x concentrations to within measurable levels, and (c) normalizing the dry composition to a wet basis using the off-gas moisture content. The moisture content at the scrubber outlet location was calculated from the dewpoint moisture content of the off-gas at the scrubber outlet, based on the pressure and temperature at that location, assuming that the off-gas was saturated with moisture.

Table 4.4-2. Off-gas composition from CEMS 1 at the outlet of the reheater, downstream of the scrubber and mist eliminator and upstream of the staged combustor.

	Average off-gas composition for each test on a wet basis at the scrubber outlet location											
CEM 1	H_2O, % (a)	O_2, %	CO_2, %	CO, %	NO, ppm	NO_2, ppm	NO_x, ppm	H_2, %	CH_4, ppm	SO_2, ppm	N_2, % (b)	Total, %
AAR 2.25 test	30.8	12.0	8.53	1.29	3,270	32,000	35,270	0.57	380	0.34	43.3	100.0
AAR 1.75 test	35.9	11.2	6.36	1.10	2,904	27,466	30,370	0.54	310	4.32	41.9	100.0
Total test average	33.4	11.6	7.44	1.19	3,086	29,722	32,807	0.55	345	2.34	42.6	100.0
STD DEV	5.99	1.04	1.71	0.27	489	3,838	4,223	0.08	111	5.62	4.1	0.0

a. The H_2O concentration was calculated from the scrubber dewpoint based on the scrubber temperature and pressure.
b. Calculated by difference.

[CMACT CEM-MB feb 28.xls]Tables

The off-gas measurements were continuous and were recorded electronically by the PLC every 10 s. Ten-minute averages are shown in Figure 4.4-1. The trends over time indicate graphically how the gas composition varied during the test series. All valid 10-minute data were averaged over the duration of each test condition to yield the time-weighted average of the test condition averages.

Most of the zero and span calibrations for the CEMS 1 analyzers were within acceptance limits, so few corrections were made to the CEMS 1 data. The O_2, CO, NO_x, H_2, and CH_4 analyzers required no zero, span, or interference corrections. The CO_2 analyzer required a zero correction (of 0.35% CO_2), but no span correction. The SO_2 analyzer required a (–)3.5-ppm zero correction, but no span correction. Since the sample gas for the NO_x analyzer was diluted by a factor of 8 times, all the NO_x data were multiplied by 8 to normalize the as-measured NO_x data to the off-gas conditions.

The concentration of N_2 in the off-gas was calculated by the difference between the sum of the other measured concentrations and 100%.

The CEMS were each equipped with a refrigerated condenser unit to cool the sample gas to below room temperature, and condense water down to the dewpoint of the sample gas at the outlet of the condenser. The condensed water can tend to scrub water-soluble gas species out of the sample gas before those species are measured by the continuous monitors. Table 4.4-3 shows the measured amounts of water-soluble gas species found in CEMS 1 and CEMS 2 condensate samples, and shows calculated concentrations of those gas species that correspond to the amounts those species measured in the condensate.

A significant amount of nitrate and nitrite were found in the CEMS 1 condensate, corresponding to an average off-gas concentration of about 16,000 ppm for the entire calcination test. This value was added to all CEMS 1 NO_2 measurements. The high nitrite concentration in the CEMS 1 condensate samples interfered with the phosphate, sulfate, chloride, and fluoride analyses, causing relatively high detection limits for those species. None of those species were detected above their respective detection limits in the CEMS 1 condensate. The off-gas concentrations for gas species that correspond to the dissolved species were all relatively low, under 6 ppm. Of these other species, only SO_2 was measured by CEMS 1. No corrections were necessary based on the detection limit values of these species for the CEMS 1 condensate.

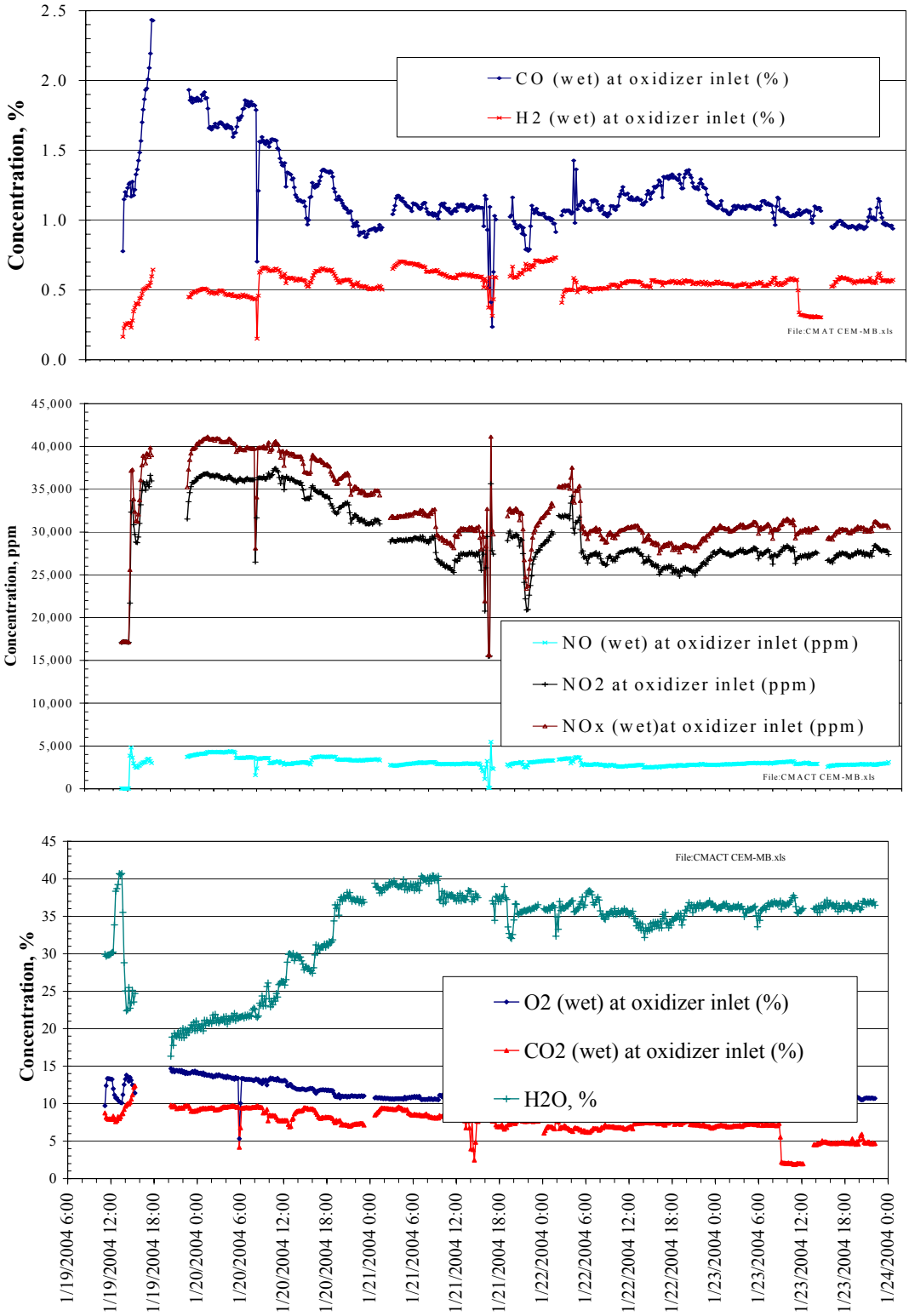


Figure 4.4-1. Wet basis off-gas composition from CEMS 1 downstream of the wet scrubber (upstream of the staged combustor).

Table 4.4-3. Gas species scrubbed in the CEMS condensers.

Test	Sample	Sample Date	COT	Measured concentrations, mg/L NO_3	NO_2	PO_4	SO_4	Cl	F
CEMS 1 condensate									
2.25 AAR	549	1/21/04 18:50	50	165,324	1,465	< 57.6	< 58.5	< 16.3	< 18.4
1.75	584	1/22/04 19:43	24	151,396	2,868	< 57.6	< 58.5	< 16.3	< 18.4
AAR	610	1/23/04 2200	50	176,008	2,415	< 57.6	< 58.5	< 16.3	< 18.4
Averages				**164,243**	**2,249**	**< 57.6**	**< 58.5**	**< 16.3**	**< 18**
CEMS 2 condensate									
2.25 AAR	550	1/21/04 18:50	50	49	2.0	< 0.6	2.4	1.0	1.1
1.75	585	1/22/04 19:43	24	46	2.0	< 0.6	0.4	0.8	1.2
AAR	611	1/23/04 2200	50	166	1.2	< 0.6	0.5	0.8	1.2
Averages				**87**	**1.8**	**< 0.6**	**1.1**	**0.9**	**1.2**

Test	Sample	Sample Date	COT	H_2O, %	Wet-basis off-gas concentrations attributed to species dissolved in CEMS condensate NO_2, ppm	H_3PO_4, ppm	SO_2, ppm	HCl, ppm	HF, ppm
CEMS 1 average				33.4	16,240	< 3.6	< 3.7	< 2.8	< 5.8
CEMS 2 average				51.4	13	< 0.056	0.11	0.23	0.57

Notes:

1. The off-gas concentrations attributed to species dissolved in the CEMS condensate were calculated using H_2O in the offgas and in the condensate as a tie-element, assuming that all moisture in the off-gas is condensed in the CEMS condenser.
2. These concentrations only indicate the concentrations of those species that were scrubbed in the CEMS condensate. The NO_2 concentration was calculated assuming that all of the nitrate and nitrite in the CEMS condensate was from dissolution of NO_2.
3. When only a portion of these species is scrubbed in the CEMS condensate, then the concentrations of these species in the offgas would be higher than the above-calculated values.
4. When a scrubbed species such as NO_2 is measured in the CEMS, then, on average, the total concentration is the sum of the concentration indicated by the CEMS and the concentration indicated by the above calculation.
5. The CEMS 1 NO_x measurements were adjusted for the amount of NO_x in the off-gas calculated above. The CEMS 2 NO_x meausurements were not adjusted for the much smaller amount of NO_2 calculated from the CEMS 2 condensate, because the correction would have biased periods during the test when the staged combustor outlet NO_x levels were lower.
6. No adjustments were made for other species dissolved in CEMS 1 or 2 condensate besides NO_2 in CEMS 1 based on the total NO_3 and NO_2 found in the CEMS 1 condensate. Any other adjustments would have been negligible compared to the measured offgas concentrations or the regulatory limits.

[CMACT RFA 2-25.xls]CEMS Table

Most of the NO_2 in the off-gas was destroyed in the staged combustor, so the CEMS 2 NO_2 concentrations were much lower than the CEMS 1 concentrations. The nitrate and nitrite concentrations in the CEMS 2 condensate samples were also much lower, corresponding to an average NO_2 concentration in the staged combustor outlet gas of 13 ppm. Since this value was so low, no corrections were made to the CEMS 2 NO_2 measurements. With lower nitrate concentrations in the CEMS 2 condensate, the detection limits for the other anions were much lower. While phosphate was still not

detected, sulfate, chloride, and fluoride were all detected, but at low concentrations under 1 ppm each. No corrections were made to the CEMS 2 HCl measurements.

4.4.3 Staged Combustor Exit Off-gas Composition

The average off-gas composition (wet basis) downstream of the staged combustor and partial quench (upstream of the carbon bed) is shown in Table 4.4-4 for each test condition. All of the CEMS 2 measurements were made on a dry basis after condensing off-gas moisture from the off-gas, except for the O_2 measurement. The O_2 measurement was made using a heated extractive ZrO_2 electrochemical sensor, on a wet basis, for thermal oxidizer process control. The wet basis composition was calculated from the dry, as-measured composition by (a) correcting for zero and span calibration error/drift and (b) normalizing the dry composition to a wet basis using the off-gas moisture content.

Table 4.4-4. Off-gas composition (wet basis) at CEMS 2 downstream of the thermal oxidizer and percentage compliance of MACT limits.

	Average off-gas composition for each test on a wet basis from CEM 2 at the outlet of the staged combustor (inlet of the carbon bed)										
CEM 2	H_2O, %	O_2, %	CO_2, %	CO, ppm	NO, ppm	NO_x, ppm	NO_2, ppm	HCl, ppm	THC, ppm	N_2, % (a)	Total, %
AAR 2.25 test	51.4	0.97	4.42	1	201	239	38	0.3	5.1	43.2	100
AAR 1.75 test	53.0	0.94	4.41	3	306	369	63	-0.1	1.0	41.7	100
Total test average	52.2	0.96	4.42	2	254	305	51	0.1	2.7	42.4	100
STD DEV	1.8	0.04	0.58	12	216	271	137	0.4	29.5	1.8	0
a. Calculated by difference.											

CO, HCl, and THC concentrations (dry 7% O_2 basis) compared to the HWC MACT standards						
	CO, ppm	% of MACT CO limit	HCl, ppm	% of MACT HCl/Cl_2 limit	THC, ppm as C_3	% of MACT THC limit
MACT limit	100		21		10	
AAR 2.25 test	2	2.0	0.5	2.5	3.0	30
AAR 1.75 test	5	5.0	0	0.0	0.6	6
Total test average	4	3.5	0.3	1.3	1.6	16

[CMACT CEM-MB feb 28.xls]Tables

The moisture content downstream of the staged combustor and partial quench was not directly measured but was calculated from the off-gas moisture content downstream of the wet scrubber, adjusted for the added gas flow rates and water flow rates through the staged combustor and partial quench, and the water of combustion from the staged combustor fuel.

The concentration of N_2 in the off-gas was calculated by the difference between the sum of the other measured concentrations and 100%.

The average CEMS 2 measurements for CO, HCl, and THC were converted to a dry, 7% O_2 basis for comparison to the HWC MACT standards. The CO and HCl concentrations averaged about 5% or less of the MACT limits. The THC concentrations ranged from 6 to 30% of the MACT limit and averaged 16% for the whole test.

The off-gas measurements were continuous and were recorded electronically by the PLC every 10 s. All valid 10-minute data were averaged over the duration of each test condition to yield the time-weighted average of the test condition averages.

Most of the zero and span calibrations for the CEM 2 analyzers were within acceptance limits, so very few corrections were made to the CEMS 1 data. The O_2, CO_2, NO_x, and HCl analyzers required no zero, span, or interference corrections. The CO analyzer required a (–)8-ppm zero correction, but no span correction. The THC analyzer required a (–)5-ppm zero correction, but no span correction.

4.5 Product, Fines, and Scrub Composition

The compositions of bed product, fines, and scrub solution are discussed below. Various miscellaneous analyses in addition to those discussed below are tabulated in Appendix A.

4.5.1 Bed and Fines Composition

The theoretical bed composition calculated from the feed blend compositions is presented in Table 4.5-1. For greater accuracy, the actual measured nitrate in the product was included in the calculation. The 2.25 AAR blend produced 132 g of calcine per liter of feed and the 1.75 AAR blend produced 128 g of calcine per liter of feed.

The product, fines, and scrub compositions for the tests are tabulated in Table 4.5-2. The aluminum concentration for the starting bed, at 21.7 wt%, was much lower than the value of about 45 wt% expected for aluminum feed. This bed was from the SO testing, which used a starting bed of crystalline alumina frit. Several fusion methods were tried during the analysis of the calcine, but none of the methods—even HF fusion—appeared to adequately dissolve the crystalline alumina for the analysis. This resulted in an under recovery of aluminum based on the test analyses.

Table 4.5-1. Solid calcine composition calculated from the blended feed composition.

Test number		Elemental composition of solid product		Mass of solid product per liter of SBW blended simulant							
		Test 1	Test 2	Test 1		Test 2				Test 1	Test 2
Feed component	Mole weight	2.25 AAR Weight %	1.75 AAR Weight %	2.25 AAR gmol/L	2.25 AAR gm/L	1.75 AAR gmol/L	1.75 AAR gm/L	Product species	Mole weight	2.25 AAR gm/L	1.75 AAR gm/L
Acid	1.0	0	0	0	0	0	0	---	---	0	0
Aluminum	27.0	38	36	1.9	50.8	1.7	46	$Al2O_3$	102.0	58	43
Boron	10.8	0.034	0.040	0.0041	0.045	0.005	0.052	$B2O_3$	69.6	0.14	0.17
Calcium	40.1	0.49	0.58	0.0162	0.65	0.019	0.75	CaO	56.1	0	0
Cesium	132.9	0.110	0.13	0.0011	0.14	0.0013	0.17	Cs_2O	281.8	0.15	0.18
Chromium	52.0	0.045	0.053	0.0011	0.059	0.0013	0.068	CrO_3	100.0	0.06	0.07
Copper	63.5	0.011	0.013	0.0002	0.015	0.00027	0.017	CuO	79.5	0.019	0.022
Iron	55.9	0.31	0.37	0.0074	0.42	0.0086	0.48	FeO	71.9	0	0
Lead	207.2	0.070	0.083	0.00045	0.092	0.00051	0.11	PbO	223.2	0.099	0.11
Magnesium	24.3	0.075	0.089	0.0040	0.098	0.0047	0.11	MgO	84.3	0	0
Manganese	54.9	0.20	0.24	0.0048	0.26	0.0055	0.30	MnO	114.9	0.55	0.63
Mercury	200.6	0	0	0	0	0	0	---	---	0	0
Nickel	58.7	0.023	0.027	0.00051	0.030	0.00059	0.035	NiO	74.7	0.038	0.044
Potassium	39.1	1.95	2.32	0.066	2.6	0.076	3.0	$KAlO_2$	98.1	6.5	7.5
Rhenium	186.2	0.059	0.068	0.00042	0.078	0.00047	0.087	Re_2O_3	420.4	0.088	0.10
Sodium	23.0	13	16	0.77	17.8	0.89	20	$NaAlO_2$	82.0	55	63
Zinc	65.4	0.023	0.026	0.00046	0.030	0.00051	0.033	ZnO	81.4	0.038	0.042
Chloride	35.5	0.27	0.32	0.010	0.36	0.012	0.41	$CaCl_2$	111.0	0.56	0.65
Fluoride	19.0	0.06	0.07	0.0040	0.08	0.0046	0.09	CaF_2	78.1	0.16	0.18
Nitrate	62.0	3.1	3.8	0.066	4.1	0.078	4.9	$NaNO_3$	85.0	5.6	6.7
Phosphate	95.0	0.70	0.83	0.0097	0.92	0.011	1.1	$Ca_3(PO_4)_2$	215.2	0.66	0.75
								Na_3PO_4	163.9	0.59	0.69
Sulfate	96.1	1.7	2.1	0.024	2.3	0.027	2.6	$FeSO_4$	151.9	1.1	1.3
								$MgSO_4$	120.4	0.49	0.56
								Na_2SO_4	142.0	1.8	2.0
Oxide	16.0	39	37		---		---	---	---	---	---
Total	---	100	100	2.9	81	2.8	80	Total	---	132	128

Notes:

1. Not including any starting bed material, and assuming no volatilization except for water, acid, and nitrate.
2. Several simplifying assumptions were made to estimate the elemental speciation in the calcine and the calcine product mass per liter of feed.
3. Al is assumed to react with K and Na to form aluminates. Remaining Al is assumed to be Al_2O_3. Cr is assumed to form CrO_3, based on lab analyses that indicate Cr as Cr^{+6}.
4. The residual nitrate concentration is based on the average nitrate concentration of 3.11 wt% in the Test 1 bed product sample 577, and 3.79 wt% in the Test 2 bed product sample 617.
5. Oxides are assumed for all other cations except (a) Ca is assumed combine with F, Cl, and PO_4, until it is consumed; (b) Mg and Fe are assumed to react with SO_4 until they are consumed; (d) remaining PO_4 and SO_4 are assumed to react with Na; (e) no CO_3 is assumed, and (f) no residual H or NO_2 is assumed.

[2003 Simulant Makeup-II feb 25 NO3.xls]CMACT test calcd product

Table 4.5-2. Bed, cyclone fines, and scrub solution composition for the calcination test.

				Measured concentrations, wt% except where indicated																				
Test	Sample	Sample Date	COT	TOC	NO_3	NO_2	PO_4	SO_4	Cl	F	Al	B	Ca	Cr	Cs	Fe	Hg, mg/kg	K	Mg	Mn	Na	Ni	Pb	Re	Zn
Calculated solid product composition based on feed composition																									
Test 1	---	---	---	0	3.1	0	0.7	1.7	0.27	0.06	38	0.034	0.049	0.045	0.11	0.31	0	1.95	0.074	0.2	13	0.023	0.07	0.059	0.023
Test 2	---	---	---	0	3.8	0	0.83	2.1	0.32	0.07	36	0.040	0.058	0.053	0.13	0.37	0	2.32	0.089	0.24	16	0.027	0.083	0.068	0.026
Average	---	---	---	0	3.5	0	0.77	1.9	0.30	0.065	37	0.037	0.0535	0.049	0.12	0.34	0	2.135	0.082	0.22	14.5	0.025	0.077	0.0635	0.0245
Note: The NO_3 concentration in the calculated product composition is based on the sample analyses.																									
Bed product																									
Test 1	575	1/19/04 12:00	0		0.01	0.005	0.004	0.01	0.001	0.002	21.7	0.240	0.048	0.006	0.001	0.071	---	0.039	0.010	0.010	1.2	0.005	0.002	0.000	0.006
	576	1/20/04 16:50	24		3.07	0.137	0.381	1.19	0.173	0.009	26.6	0.040	0.266	0.030	0.056	0.188	---	1.169	0.065	0.155	10.8	0.017	0.018	0.031	0.019
	577	1/21/04 18:50	50	0.038	3.18	0.190	0.625	1.26	0.180	0.009	34.7	0.056	0.422	0.035	0.069	0.269	0.17	1.610	0.093	0.238	13.7	0.025	0.026	0.038	0.029
Test 2	604	1/22/04 19:43	24		2.18	0.119	0.786	1.45	0.201	0.008	34.7	0.037	0.444	0.034	0.057	0.290	---	1.605	0.108	0.267	14.8	0.026	0.031	0.033	0.028
	614	1/23/04 21:58	50	0.032	2.66	0.139	0.898	1.42	0.182	0.009	35.0	0.032	0.478	0.034	0.063	0.302	0.24	1.660	0.112	0.277	15.4	0.028	0.032	0.037	0.028
Notes: 1. TIC (CO_3) was not detected (at a detection limit of 0.2 wt%) and so is not tabulated here. 2. The Al concentration in the starting bed (COT 0) should have been about 48 wt%. The measured COT 0 Al concentration is only about 1/2 of the expected value, because the laboratory analysis does not adequately dissolve and detect crystalline Al.																									
Cyclone fines																									
Test 1	578	1/20/04 16:50	24		1.72	0.217	0.516	2.38	0.373	0.009	33.2	0.091	0.655	0.069	0.153	0.274	---	2.49	0.085	0.176	14.4	0.023	0.057	0.068	0.023
	579	1/21/04 18:50	50	0.086	4.70	0.336	0.538	2.56	0.371	0.009	33.1	0.043	0.580	0.077	0.053	0.381	---	2.52	0.095	0.197	14.6	0.024	0.051	0.069	0.026
Test 2	605	1/22/04 19:43	24		1.32	0.176	0.864	3.10	0.466	0.008	34.2	0.026	0.682	0.086	0.145	0.312	1.4	3.39	0.103	0.212	14.3	0.026	0.075	0.092	0.027
	615	1/23/04 21:58	50	0.081	3.79	0.350	0.770	3.06	0.506	0.130	33.0	0.025	0.634	0.083	0.127	0.282	0.5	3.15	0.101	0.210	14.5	0.025	0.069	0.087	0.026
Note: TIC (CO_3) was not detected (at a detection limit of 0.2 wt%) and so is not tabulated here.																									
Scrub solution				Measured concentrations, mg/L																					
Test 1	501B	1/19/04 12:00	0		251,577	6	29	109	273	9	585	53.5	1.5	3.3	0.02	18	0.1	1	0.2	0.3	6	2.3	0.1	0.0	1.1
	516A	1/20/04 8:10	15.4	35.1	195,765	98	18	489	121	52	4,627	90.7	75	9.1	19	54	19	287	10.8	23	1,612	5.0	5.5	7.8	4.1
	566	1/20/04 16:50	24	38.8	205,563	6	323	645	149	65	6,480	77.5	122	13.3	27	68	34	444	16.5	35	2,677	6.3	9.7	12.0	7.7
	536A	1/21/04 4:50	36	40.5	222,319	6	160	874	283	90	9,547	69.9	178	20.0	20	87	56	778	22.7	49	4,264	8.1	15.0	21.5	7.4
	567	1/21/04 18:50	50	50.2	205,316	6	493	1,286	311	112	14,070	72.5	249	33.0	70	125	82	1,115	40.1	77	6,177	11.8	24.4	28.6	13.1
Test 2	568A	1/22/04 7:30	12	61.8	210,013	6	664	1,594	398	133	18,193	86.0	341	38.6	116	162	174	1,719	50.6	102	8,495	15.2	34.8	45.7	14.1
	583A	1/22/04 19:43	24	76.6	238,230	6	1,125	1,876	583	150	21,363	80.0	423	46.4	147	194	141	2,170	60.2	121	10,150	17.7	43.6	61.2	16.5
	596A	1/23/04 8:10	36	79.8	224,680	6	1,211	2,184	624	160	24,483	75.5	491	54.8	174	221	160	2,572	71.3	144	11,635	20.5	52.5	71.4	19.2
	616	1/23/04 2200	50	93.4	245,677	6	1,284	2,462	576	141	28,543	78.0	592	65.5	211	261	179	3,029	84.1	170	13,560	23.7	64.3	84.2	22.4
Notes: 1. Sample 516A was identifed as scrubber blowdown; other scrub samples were identifed as scrub liquor. 2. NO_2 was not detected, with a detection limit of about 6 mg/L, in any of the scrub samples except in 516A, which was 98 mg/L, still only 0.05% of the measured NO_3 levels. NH_4 was not detected in any of the scrub samples. 3. Phosphate, chlorine, flourine, potassium, and lead were not detected in sample 501B which was the starting scrub solution.																									

[CMACT RFA 2-25.xls]concentration tables

Figure 4.5-1 shows the increase in sodium content of the bed product during the tests, which appeared to approach an asymptote toward the end of the tests. The final sodium contents for the two tests, at 13.7 and 15.4 wt%, respectively, were very close to the theoretical sodium contents of 13 and 16 wt%. This is indicative of the good bed turnover achieved during the tests.

The cyclone fines composition varied little throughout each test, indicating that the calcine elutriated from the bed was mostly spray-dried droplets rather than attrited bed particles.

The ratio of nitrate to sodium plus potassium for past high-temperature tests averaged 0.23. The averages for the 2.25 and 1.75 AAR tests were only 0.06 mole of nitrate per mole of sodium plus potassium for the product and 0.09 for the fines. Therefore, denitration of the calcine product was better than previous high-temperature tests. Part of this may have been because of the relatively large amount of bed product, which experiences a longer residence time in the heated bed relative to the residence time of the fines at elevated temperature.

4.5.2 Scrub Solution Composition

The volume of scrub drained during the tests was minimal. Scrub was generally drained to allow for the addition of concentrated nitric acid in order to compensate for neutralization of the scrub solution by the fines. Figure 4.5-2 shows that the aluminum and sodium concentrations in the scrub increased linearly throughout the test, which indicates that calcine solids carryover to the scrub solution was at a relatively constant rate. The concentrations of most of the other species also increased throughout the run, except for chloride and flouride, which appeared to reach equilibrium values of 600 mg/L and 150 mg/L, respectively, after COT 24 of the 1.75 AAR test. The chloride reached equilibrium at a concentration much lower than the NWCF of 3,000 mg/L.

The undissolved solids concentration increased throughout the test but was still relatively low. These equilibrium concentrations are much lower, compared to the NWCF high-temperature trial, which reached equilibrium at 3,000 mgCl/L.

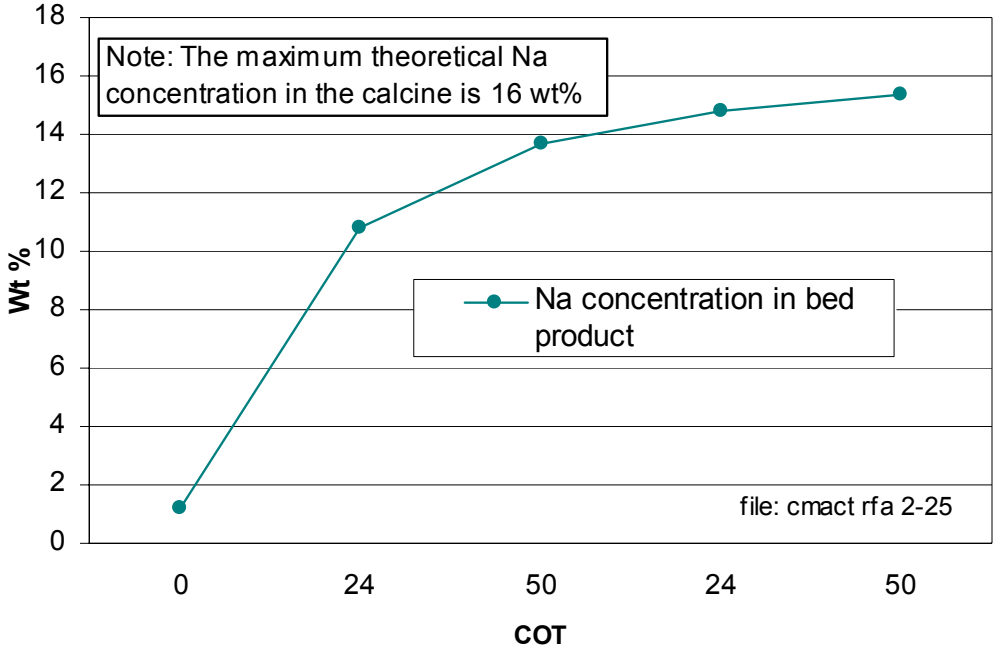


Figure 4.5-1. Asymptotic increase in sodium concentration in the bed product during the calcination test.

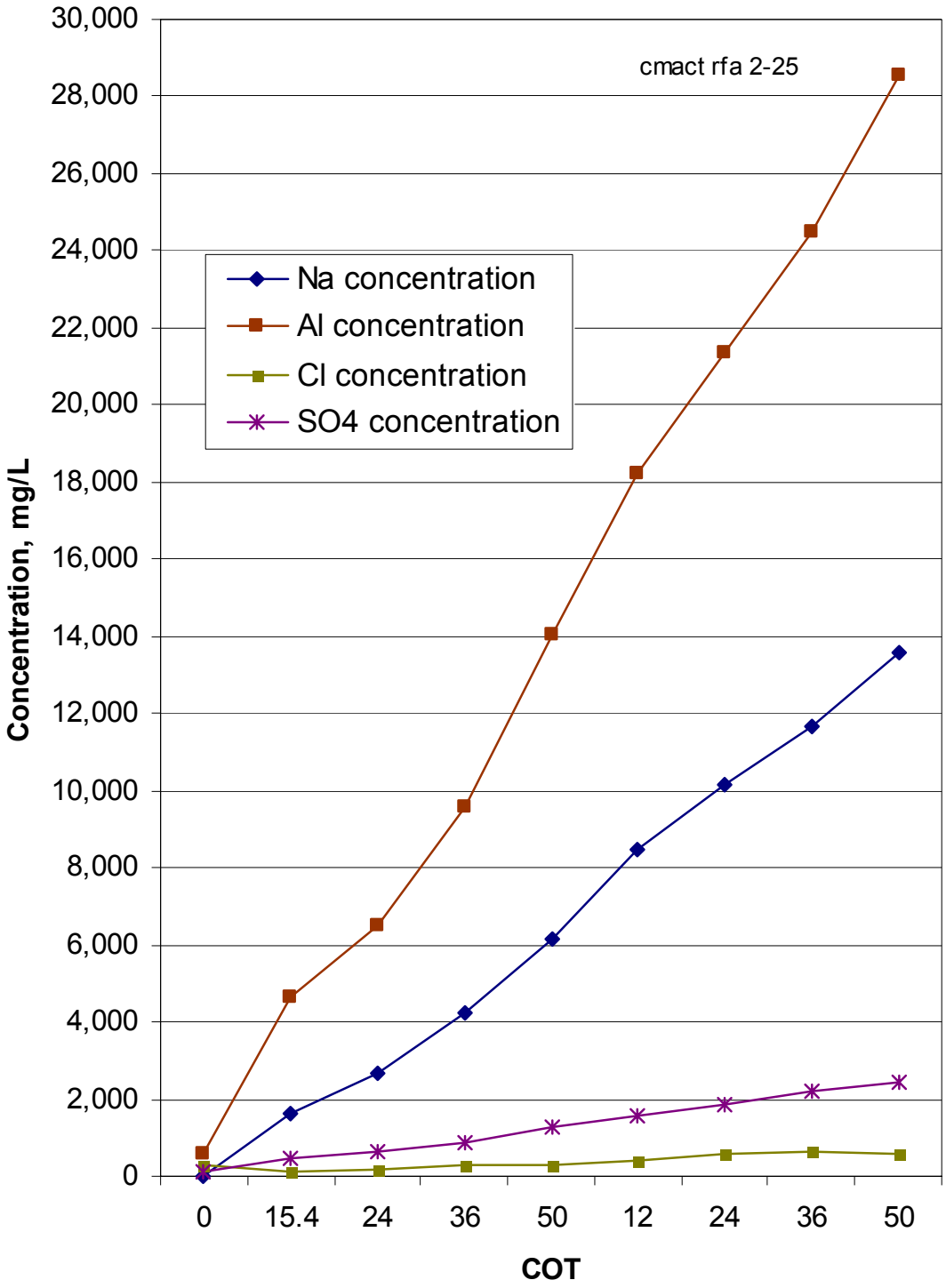


Figure 4.5-2. Linear increase in scrub solution concentrations during the calcination test.

4.5.2.1 Scrub Volume and Acidity. The scrub system was operated at a temperature of about 70°C to minimize buildup of condensate in the scrub. Scrub was drained and 15.8 M HNO_3 was added only four times during the tests.

About 93.5 liters of water and 62.5 liters of 15.8-molar HNO_3 were added to the scrub tank and a total of 282 liters of scrub was collected during the tests. Figure 4.5-3 shows the instantaneous volume of scrub solutions during the test.

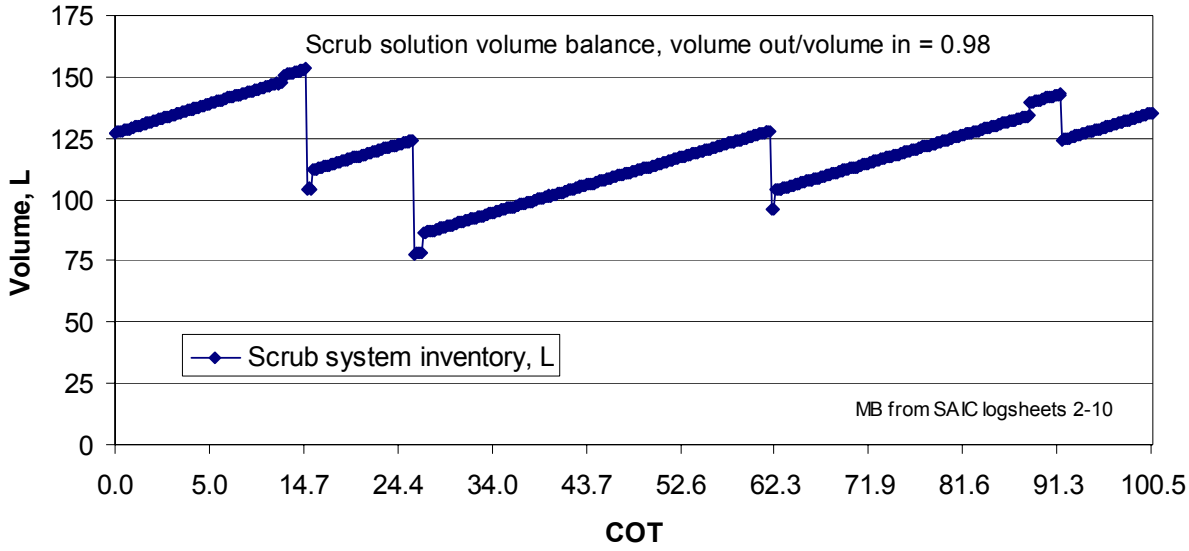


Figure 4.5-3. Volume of scrub solution during the calcination test.

4.5.2.2 Undissolved Solids (UDS). The scrub solution was relatively free of undissolved solids, approaching only 700 mg/L in the final scrub at the end of the tests. This indicates that the cyclone fines were soluble in the scrub. The amount of UDS exhibited in these tests was well within the desired operating range for the NWCF, where a UDS of less than about 10,000 mg/L is desired.

4.5.2.3 Total Inorganic Carbon/Total Organic Carbon (TIC/TOC). The total inorganic carbon analyses of the bed product and cyclone fines showed that no detectable carbon was present in the solids as carbonates. Total organic carbon of 380 ppm was present in the product, and 320 ppm was present in the fines. Total organic carbon in the scrub increased throughout the run, reaching 93 mg/L. Analysis of the organic species was not included in the present sample analysis plan.

4.6 Feed Component Distribution and Mass Balance Closure

Input and output mass balances were performed to determine the fate of feed components. Key calculations include (a) determination of nitrate and NO_x destruction, (b) the fate of the main SBW simulant components (Na, Al, and K), (c) hazardous metals and radionuclide surrogates (Cr, Hg, Pb, Cs, and Re), and anions in the SBW simulant, and (d) overall mass balance closure.

4.6.1 Off-gas Mass Balance Closure

Gas-phase mass balance calculations were performed for the fluidized bed test system from the calciner up to just after the scrubber at CEMS 1, and also for the entire system, from the calciner up to the inlet of the carbon bed. These mass balances were performed by accounting for all input flow rates that

contributed to the total off-gas flow rate, and by ratioing the off-gas flow rates measured by the Coriolis meters to the calculated mass of the inputs to the system that form gaseous components. The system inputs into the system included blended feed, kerosene, oxygen (and their combustion products), fluidizing and atomizing air, various purges, and quench water. The staged combustor natural gas, burner air, water quench and nitrogen dilution were also included. Gas-phase mass balances are presented in Table 4.6-1.

Table 4.6-1. Summary of gaseous species mass balance.

TEST	Calc scrubber outlet off-gas flow, kg/hr TOTAL_KGH_AFTER_EVS	Meas. scrubber outlet offgas flowrate, kg/hr B1_F6_VAL	Ratio, scrubber outlet meas. off-gas flowrate / calc flowrate	Total gas input to system, kg/hr TOTAL_KGH_AFTER_PQ	Offgas flowrate at carbon bed, kg/hr AJ1_F1_VAL	Ratio, carbon bed off-gas rate / total gas input to system
AAR 2.25 test	18.9	14.9	0.78	147	149	1.02
AAR 1.75 test	23.6	20.7	0.88	142	147	1.03
Total test average	21.3	17.9	0.83	145	148	1.02
STD DEV	4.1	4.4	0.08	8	8	0.03

[CMACT CEM-MB feb 26.xls]Tables

The gaseous mass balance closure (measured gas flow rate divided by the gas flow rate calculated from the input flow rates) after the scrubber averaged 83%. The major cause of the difference is measurement error in the Coriolis meter. The measured off-gas flow rate, at around 15-21 kg/hr, was too low for the minimum design value of 50 kg/hr recommended by the manufacturer. For this reason, the calculated flow rate values were considered more accurate, and were used in all calculations, such as mass balances, that use the off-gas flow rate determined for the scrubber outlet (staged combustor) location.

The gaseous mass balance closure through the entire system up to the inlet of the carbon bed averaged 102%. The Coriolis meter at this point was measuring in the middle of the suggested operating range of the meter. The design accuracy of this meter is ±0.044%. The measured values of the mass flow rate were used in all calculations that depend on the off-gas flow rate at this location. The close correlation between the calculated and the measure values provide increased confidence in the calculated off-gas flow rate at the scrubber outlet location, which is based on the input flow rates.

4.6.2 Water Balance for the Wet Scrubber

The wet scrubber system is equipped with a cooling coil in the scrub tank that can be used to cool the scrub solution, removing heat from the scrubber system. When the cooling coil is not used for cooling, the water must evaporate from the scrubber system to cool the hot cyclone outlet off-gas to the dewpoint of the combined off-gas and evaporated water. Makeup water (or fresh acid) is required to replace the evaporated water and provide for any scrub solution blowdown. When the heat removed by the cooling coil matches the heat removed from the off-gas, no net moisture evaporation or condensation occurs and the scrubber operates in a "water-neutral" mode. When the cooling coil removes more heat than needed to cool the hot off-gas, then some moisture is condensed out of the off-gas.

The scrubber system was operated in a slight condensing mode during the calcination tests. The water content of the scrubber outlet gas was slightly lower than the water content of the cyclone outlet gas. The difference in the off-gas water content at the scrubber outlet and cyclone outlet locations was calculated to be 1.2 L/hr. For the duration of the test, combined with the added volume of 15.8 M nitric acid (used to maintain necessary scrub solution acidity) and added makeup water, the total input liquid volume was 289 L. The total amount of scrub solution discharge for the run, including 7 L of scrub solution samples, was 283 L. The output amount of scrub solution was 98% of the input amount.

4.6.3 Species Distribution to Solid Products, Scrub Solution, and Carbon Bed

The masses of each species was calculated for the sample analyses of the bed product, cyclone fines, scrub, carbon bed, and off-gas and is presented in Table 4.6-2. Overall recovery was 91% for Al, 104% for Na, and 109% for sulfate (SO_4). Recovery for all minor constituents was within 25%, except for Pb, which had a low recovery at only 58%. Since lead is a semi-volatile metal, it is possible that it plated out preferentially in the off-gas lines; however, the low recovery could also be due to sample analysis uncertainties or other errors.

The alumina calcine starting bed that was obtained from the SO test apparently still had a significant crystalline alumina that did not show up in the analytical results; however, the aluminum balance was still quite good.

The nitrate mass balance shows that 99% of the nitrate in the feed was destroyed or otherwise separated from the calcine. In addition, except for mercury, the solid material was almost entirely captured as bed product, cyclone fines, or in the scrubber. Only a small amount of solid fines passed through the scrubber, evidenced by a small amount of residue found in both the staged combustor and the carbon bed after the test. This amount of material was not quantified, and does not indicate the amount of material that would pass through the staged combustor and carbon bed in a calciner MACT upgrade, because the calciner MACT upgrade would be located downstream of the NWCF HEPA filters that efficiently capture any material that passes through the NWCF wet scrubber.

4.6.3.1 Distribution of Mercury in the Fluidized Bed Test System. Table 4.6-3 shows the corresponding Hg removal efficiency results (and Hg mass balance closure) for the wet scrubber and carbon bed based on the amounts of Hg found in scrub solution and carbon bed samples. The amount of Hg removed by the scrubber for each test was based on scrub solution analyses and inventory and volumes of discharged scrub solution for each test. Based on these analyses, 16% of the mercury fed to the calciner was collected in the scrub, 72% in the scrub tank solids from the final scrub tank rinse after the test, and 12% was collected in the carbon. Overall recovery for the mercury was 94%. It is unclear why so much mercury collected in the sludge in the bottom of the scrub tank.

4.6.3.2 Halide Partitioning and Emissions. The calcium concentration in the feed was only 0.36 of the stoichiometric amount required to react with all the chloride, fluoride, sulfate, and phosphate in the feed. Calcium addition to achieve 1.4 times stoichiometric has typically been used during past high-temperature tests. Even though no additional calcium nitrate was added than what was present in the feed, the chloride retention in the solids was adequate at 57%. This met the criteria for calciner pilot-plant testing of better than 50% chloride retention in the calcined solids. This was likely because the sodium oxide compounds formed from decomposition of sodium nitrate are highly reactive with chloride.

Even though fluoride carryover to the scrub was high, at 73%, the calcium concentration in the scrub was such that all the fluoride present in the scrub could all be attributed to carryover as calcium fluoride. Therefore, there was no appreciable fluoride carryover as volatile HF. The aluminum to fluoride mole ratio was about 400 in the feed, but was only about 100 in the scrub. These ratios are much greater than that needed to complex the fluoride in solution.

4.6.3.3 Sulfate and Phosphate Partitioning. Sulfate and phosphate, like chloride and fluoride, form stable species with calcium. Since a substoichiometric amount of calcium was present in the feed blend for the tests, some volatility of sulfate and phosphate would be expected. The sulfate and phosphate partitioned at 31% and 35% in the scrub, respectively. This was greater than the 22% carryover of calcine to the scrub but less than the fraction of the total of chloride and fluoride collected in the scrub.

Table 4.6-2. Species distributions and mass balance closure for the SBW simulant blend components.

			Species mass, gm																				
		Total mass, kg	TOC	NO_3	NO_2	PO_4	SO_4	Cl	F	Al	B	Ca	Cr	Cs	Fe	Hg	K	Mg	Mn	Na	Ni	Pb	Re	Zn
Input streams																							
Starting bed media		11	0.00	1.3	0.6	0.4	1.1	0.1	0.2	2,409	27	5.3	0.7	0.1	7.9	0.0	4.3	1.1	1.1	133	0.6	0.2	0.0	0.7
Total feed product		74		194,194	0	567	1,407	221	49	27,628	27	399	37	89	256	229	1,590	61	161	10,925	18	57	47	18
Total inputs		85	64,000	194,195	1	568	1,408	221	49	30,036	54	405	37	89	264	229	1,594	62	162	11,058	19	57	47	19
Output bed product and cyclone fines																							
Test	Sample	COT	Differential mass, kg																				
Bed product																							
Test 1	575	0	2.9	1.0	110	0.0	0	0	0.0	0.1	629	0.0	0.0	0.0	0.0	0.0	---	0	0.0	0.0	0	0.00	0.00	0.00	0.00
	576	24	18.2	6.4	559	24.9	69	217	31.5	1.6	4,841	7.3	48.4	5.5	10.2	34.2	---	213	11.8	28.2	1,966	3.09	3.28	5.64	3.46
	577	50	11.6	4.1	369	22.0	73	146	20.9	1.0	4,025	6.5	49.0	4.1	8.0	31.2	0.02	187	10.8	27.6	1,589	2.90	3.02	4.41	3.36
Test 2	604	24	10.2	3.6	222	12.1	80	148	20.5	0.8	3,539	3.8	45.3	3.5	5.8	29.6	---	164	11.0	27.2	1,510	2.65	3.16	3.37	2.86
	614	50	14.3	5.0	380	19.9	128	203	26.0	1.3	5,005	4.6	68.4	4.9	9.0	43.2	0.03	237	16.0	39.6	2,202	4.00	4.58	5.29	4.00
Totals			57	20	1,640	79.0	350	713	98.9	4.8	18,040	22	211	17.9	33.0	138	0.05	801	49.7	123	7,267	12.7	14.0	18.7	13.7
Cyclone fines product																							
Test 1	Average		4.9	4.2	157	13.5	26	121	18.2	0.4	1,624	3.3	30.3	3.6	5.0	16.0	---	123	4.41	9.1	711	1.15	2.65	3.36	1.20
Test 2	Average		7.3	5.9	187	19	60	225	35	5.0	2,456	2.5	46.1	5.9	7.2	25.3	0.10	215	7.23	14.9	1,055	1.83	4.60	5.88	1.93
Totals			12.2	10.1	344	32.7	85	346	53.7	5.5	4,081	5.8	76.3	9.5	12.3	41.3	0.10	338	11.6	24.1	1,765	2.98	7.25	9.23	3.14

	TOC	CO2	CO	CH4
Offgas				
Test 1	42,704	36,951	5,588	165
Test 2	37,252	31,627	5,470	154
Total	79,955	68,578	11,058	319

Notes:

1. Input mass: The input elemental mass of the starting bed is based on the COT 0 sample analysis. The input TOC is from the organic content of the kerosene feed, assuming kerosene contains 87.5 wt% C. TOC input for test 1 was 34 kg, including about 6 hours idle time near the test start. TOC input for Test 2 was 30 kg.

2. Input mass: The species mass in the total input feed solid product was calculated by averaging the calculated product composition from tests 1 and 2, since the total amounts of feed for each test were nearly identical.

3. Bed product: The differential total mass is the mass associated with the sample analysis at that COT. For the bed product, the product mass associated with COT 0 is differential mass up to about COT 8 (because the product concentration in the bed increases rapidly in the first part of the test).

4. Bed product: The differential mass for COT 24 is the mass between COTs 8 and 36. The differential mass for COT 50 is the mass between COT 36 and COT 62.

5. Bed product: The differential mass for Test 2 COT 24 (COT 74 cumulative) is the mass between COT 62 and COT 87. The differential mass for Test 2 COT 50 (cumulative COT 100) is the mass between COT 87 and COT 100.

6. Bed product: The species mass for each COT time was calculated from the differential total mass and the composition for that COT time.

7. Bed product: Only 2 bed samples were analyzed for TOC, 1 for Test 1 COT 50 and 1 for Test 2 COT 50. These concentrations were averaged and used for the entire test.

8. Cyclone fines: The species mass in the cyclone fines was calculated using the average of the two analyses in each test.

9. Offgas: TOC in the offgas was calculated from the amounts of C in CO2, CO, and CH4 measured by CEMS 1 at the outlet of the scrubber.

[CMACT RFA 2-25.xls]elemental mass balance

Table 4.6-2. Species distributions and mass balance closure for the SBW simulant blend components (continued).

Test	Sample	COT	Differential volume, L	Species mass, gm TOC	NO_3	NO_2	PO_4	SO_4	Cl	F	Al	B	Ca	Cr	Cs	Fe	Hg	K	Mg	Mn	Na	Ni	Pb	Re	Zn
Output scrub solution, scrubber sludge, and carbon bed streams																									
Fines captured in the scrub solution																									
Test 1	516A	15.4	51	1.8	9,984	5.0	1	25	6.2	2.6	236	4.6	3.8	0.5	1.0	2.8	0.95	15	0.55	1.19	82	0.26	0.28	0.40	0.21
	566	24	47	1.8	9,661	0.3	15	30	7.0	3.1	305	3.6	5.7	0.6	1.3	3.2	1.61	21	0.77	1.63	126	0.29	0.46	0.56	0.36
	536A	36	1	0.0	222	0.0	0	1	0.3	0.1	10	0.1	0.2	0.0	0.0	0.1	0.06	1	0.02	0.05	4	0.01	0.01	0.02	0.01
	567	50	1	0.1	205	0.0	0	1	0.3	0.1	14	0.1	0.2	0.0	0.1	0.1	0.08	1	0.04	0.08	6	0.01	0.02	0.03	0.01
Test 2	568A	12	33	2.0	6,930	0.2	22	53	13.1	4.4	600	2.8	11.2	1.3	3.8	5.4	5.75	57	1.67	3.36	280	0.50	1.15	1.51	0.46
	583A	24	1	0.1	238	0.0	1	2	0.6	0.1	21	0.1	0.4	0.0	0.1	0.2	0.14	2	0.06	0.12	10	0.02	0.04	0.06	0.02
	596A	36	19	1.5	4,269	0.1	23	41	11.9	3.0	465	1.4	9.3	1.0	3.3	4.2	3.04	49	1.35	2.73	221	0.39	1.00	1.36	0.36
	616	50	130	12.1	31,938	0.8	167	320	74.9	18.4	3,711	10.1	76.9	8.5	27.5	33.9	23.3	394	10.9	22.1	1,763	3.08	8.4	10.9	2.92
Totals			283	19.5	63,449	6.4	230	473	114	31.8	5,362	23	108	12.0	37.1	49.8	34.9	539	15.4	31.2	2,493	4.56	11.3	14.9	4.35
			44		43,798	NO3 in 15.8 M HNO3 added to scrubber																			
					19,651	NO3 in scrub from offgas & fines																			
			Mass, kg																						
Scrubber sludge			5.5														154								
Species captured in carbon bed					0	---	---	---	5.3	2.9	---	---	---	---	---	---	26	---	---	---	---	---	---	---	---
Total output masses				80,005	---	118	666	1,532	272	45	27,482	51	395	39	82	229	215	1,678	77	178	11,525	20	33	43	21
Elemental mass distribution, % of mass in the output stream divided by the total mass in all output streams																									
Bed product				0.025	---	67	53	47	36	10.7	66	44	53	45	40	60	0	48	65	69	63	63	43	44	65
Cyclone fines				0.013	---	28	13	23	20	12.2	15	11.4	19	24	15	18	0	20	15	14	15	15	22	22	15
Scrub solution				0.024	---	5.4	35	31	42	71	20	45.0	27	31	45	22	16	32	20	18	22	23	35	35	21
Scrub sludge				---	---	---	---	---	---	---	---	---	---	---	---	---	72	---	---	---	---	---	---	---	---
Carbon bed				---	---	---	---	---	1.95	6.44	---	---	---	---	---	---	12	---	---	---	---	---	---	---	---
Off-gas				100	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Total outputs				0	---	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Total elemental mass balance closure, sum of total output mass divided by sum of total input mass																									
				1.25	0.010	---	1.17	1.09	1.23	0.92	0.91	0.94	0.98	1.06	0.92	0.87	0.94	1.05	1.24	1.10	1.04	1.07	0.57	0.91	1.12

Notes: 1. The calciner denitration efficiency is 99.0 % based on the amount of residual NO3 in calcine product and fines compared to NO3 in the feed blend.

2. The TOC mass balance closure is 25% high, probably because the CO2 measurements may have been biased high. The CO2 analyzer was calibrated on a 0-100% CO2 scale. An positive error of only 2% CO2 (an acceptable error on a 0-100% range) would have caused the CO2 measurements to be about 25% high.

3. The elemental distribution of primary components of the calcine to cyclone fines (15% for both Al and Na) indicates the amount of total fines elutriation to cyclone fines.

4. The elemental distribution of primary calcine components to the scrubber (20% for Al and 22% for Na) is an independent indicator of the amount of fines carryover to the scrubber.

5. Several elements and species are enriched in the fines and the scrub solution compared Al and Na. Species enriched in the fines compared to Al and Na are SO4, Cl, Cr, K,Pb, and Re. These same species and also PO4, F, B, Ca, and Cs are enriched in the scrubber compared to Al and Na.

6. Scrub solution: The amounts of scrub solution that correspond to the COTs are defined by the amounts of addded nitric acid and scrub solution blowdown during times bracketed by the COT times when samples were collected. The scrub solution times that corresponds to each of scrub sample analyse times are:

Sample COT	Start COT	End COT	Sample COT	Start COT	End COT	Sample COT	Start COT	End COT
0.0	0.0	8.0	36.0	30.0	43.0	24.0	18.0	30.0
15.4	8.0	20.0	50.0	43.0	6.0	36.0	30.0	43.0
24.0	20.0	30.0	12.0	6.0	18.0	50.0	43.0	end

7. Mass of sludge was estimated as: ~25 wt% sludge in about 12 liters (14.4 kg) = ~4 kg; plus ~0.5 kg of sludge on tank bottom; plus ~1 kg sludge that was cleaned out of system.

[CMACT RFA 2-25.xls]elemental mass balance

Since the results of the halide, sulfate, and phosphate retention in the calcine were acceptable, the calcium present in the WM-180 waste was sufficient. Calcium addition may still be necessary for the other sodium-bearing-wastes, especially because they have high amounts of sulfate from the heel solids.

No phosphate was detected in the carbon bed.

4.7 Cyclone Efficiency

Greater amounts of fines carried over to the cyclone and the scrub system are detrimental to calciner operation. Excessive fines can overwhelm the cyclone and fines column, resulting in more carryover to the scrub. Carryover to the scrub will exacerbate dissolved solids build up in the scrub, necessitating larger amounts of scrub recycle to the feed and resulting in proportionally less waste throughput. A product-to-cyclone fines ratio greater than unity is therefore desired. It was estimated that the product to cyclone fines ratio was about 1.0 during the NWCF high-temperature calcination in May 2000 (EDF-3387, p. 173), but that the cyclone efficiency was only 65%, based on the amount of dissolved calcine measured in the scrub. This is likely because the SBW/ANN blends tend to make finer spray-dried particulate at 600°C than at 500°C.

4.7.1 Fines Removal Efficiency

A new, high-efficiency cyclone particle separator was designed by SAIC and fabricated by a local shop. The cyclone design basis was for 98% removal of fines based on the fines distribution measured for a previous INTEC Enclosed 15-cm Calciner Pilot Plant test. The removal efficiencies for the design pressure drop of 5-inch w.c. are provided in Table 4.7-1. Unfortunately, the cyclone fines size distribution was much smaller than projected, and the cyclone pressure drop, at 0.6 to 0.7-inch w.c., was less than the design pressure differential. Both of these factors would have decreased the efficiency of the cyclone during the current tests.

Table 4.7-1. General cyclone removal efficiencies for a pressure drop of 5-inch w.c.

Size Range (μm)	Removal Efficiency (%)
<3	50
3-5	70
6-10	90
11-20	95
21-40	98
41-60	99
>60	99.9

However, because of the better design efficiency for the cyclone, the fines capture should have been greater than that which would be obtained by the current NWCF cyclone. Nevertheless, the product-to-fines ratio for the 2.25 AAR test was 5.1, and that for the 1.75 AAR test was 2.8. These product-to-fines ratios are quite good for SBW/ANN blends.

The amount of calcine produced can be estimated from the known feed composition and the theoretical oxides formed by calcination. The simulated blends were estimated to produce 132 and 128 g/L of feed. Using the projected calcine production mass and the actual bed product and fines collected during the test, Table 4.7-2 shows that approximately 19–24 wt% of the calcine produced was

apparently lost to holdup in the off-gas lines, solids collection in the scrub tank, and particulate and mist loss to the off-gas downstream of the scrubber. Even though the product-to-fines ratios for the tests were quite good, the cyclone was calculated to have an overall removal efficiency of only 40–43%.

The calcine fines from the current tests had a median particle size of about 12 μm (see Figure 4.3-13) but the cyclone was effective at removing particles as small as 2 μm. By comparison, the fines removed by the cyclone in the INTEC 15 cm Calciner Pilot Plant had a median particle size of about 45 μm and the 15-cm cyclone was only effective at removing particles as small as 20 μm. This indicates the size of particles being elutriated from the SAIC calciner were less than normal, but also that the SAIC pilot-plant cyclone was more effective at removing smaller particles. It is likely that if the median size of particulate elutriated had been 50 μm for the SAIC tests, then the overall efficiency would have been much higher.

Table 4.7-2. Fines removal efficiency for cyclone.

	2.25 AAR (%)	1.75 AAR (%)	Both Tests (%)
Bed product (as wt% of calcine from feed)	67.6	56.1	61.9
Cyclone fines (as wt% of calcine from feed)	13.2	19.8	16.5
Calcine fines past cyclone, as wt % of calcine from feed	19	24	22
Total fines (wt% of calcine from feed)	32	44	37
Cyclone removal efficiency based on cyclone fine collected versus total fines	41	45	43

4.7.2 Comparison to NWCF

The Enclosed 15-cm calciner cyclone was designed to remove 91% of 10 μm particulate, while the NWCF cyclone design was for 99.5% removal of 10 μm particulate (O'Brien 1998). In reality the Enclosed 15-cm cyclone removed very little particulate below 10 μm as shown previously in Figure 4.3-13. The NWCF cyclone was designed for two calciners, so is greatly oversized and is therefore not meeting its design removal rate for small particulate emitted by only one calciner.

Although the removal efficiencies for the current tests cyclone were not as good as expected, and were less than the calculated efficiency of the NWCF cyclone at about 65%, it is likely that this was an artifact of the good solids retention in the bed, the small size of the particulate elutriated from the bed, and operation at a much lower pressure drop than design. Even though the cyclone was operated outside its design, it exhibited a better at removal of fine particulate (<1–20 μm) compared to the cyclone in the INTEC 15-cm Calciner Pilot Plant.

4.8 Scrubber Efficiency

The new separator venturi separator in the SAIC pilot plant was designed to remove 90% of particulate matter penetrating the cyclone separator. The venturi was operated with an average pressure drop of 44 ± 9 inches w.c. during the 2.25 AAR test and 44 ± 4 inches w.c. during the 1.75 AAR test.

The scrubber removed nearly all of the particulate from the off-gas such that the amount that was carried over to the staged combustor and beyond could not be determined within the accuracy of the

system mass balance. Only a thin light dusting of material was found in the piping downstream of the demister, and on the top surface of the carbon bed.

4.9 NO_x/PIC Staged Combustor Performance

The staged combustor at the Star Center was previously operated as part of the steam reforming process testing (Soelberg 2004a, 2004b). However, during those tests, the combustor was operated as a single-stage thermal oxidizer (i.e., under oxygen-rich conditions). Before the calcination flowsheet trial, some modifications were made to the combustor, including adding the interstage quench and adding thermocouples in the reducing and reoxidizing stages. With these hardware modifications, and some changes to the control logic, the combustor is now capable of operating as a true multi-stage combustor. The fuel-rich stage is used to destroy NO_x, while the oxygen-rich stage is used to burn out any remaining products of incomplete combustion (PICs). The interstage quench is used for temperature control to ensure that NO_x is not reformed while burning out the PICs. A performance summary of the combustor during the calcination tests is presented graphically in Figure 4.9-1.

4.9.1 NO_x Destruction

Reducing conditions are required in order to effectively destroy NO_x. The equivalence ratio (ϕ) is one means of specifying the relative degree of oxidizing or reducing ability of a flame. The equivalence ratio is defined as follows:[b]

$$\phi = \frac{[\mathrm{Fuel/O_2}]_{Actual}}{[Fuel/O_2]_{Stoichiometric}} \quad .$$

Hence, for stoichiometric combustion, ϕ=1. Values of ϕ>1 indicate a reducing flame, while values of ϕ<1 indicate an oxidizing flame. To simplify process control, however, a similar variable (referred to throughout this report simply as "excess NG" or "excess NG multiplier") was defined and used during the trial to monitor and control the reducing potential of the flame:

$$natural\ gas\ to\ reduction\ chamber = \frac{mass\ O_2\ in\ offgas}{\left(\frac{mass\ O_2}{mass\ CH_4}\right)_{Stoichiometric}} \times (1 + Excess\ NG\ Multiplier) \quad .$$

In this equation, the mass of oxygen in the off-gas was calculated automatically by the control system, whereas the stoichiometric mass ratio of oxygen to methane and the excess NG multiplier were user inputs. Unfortunately, the stoichiometric mass ratio of oxygen to methane was incorrectly entered as 17.2 rather than 4.0 during testing. Hence, absolute values for the excess NG multiplier are not meaningful. Nevertheless, setpoint changes to the excess NG multiplier during these tests can still be viewed as an indicator of the relative reducing ability of the flame.

In addition to the reducing ability of the flame, the temperatures maintained in the combustor also impact NO_x destruction. The kinetic reaction rate for NO_x destruction under reducing conditions is optimal between about 1,150–1,300°C. However, in the presence of excess oxygen (i.e., in the

b. For purposes of this analysis, the O_2 concentration includes oxygen from the combustion air and off-gas, as well as oxygen bound as NO_x in the off-gas.

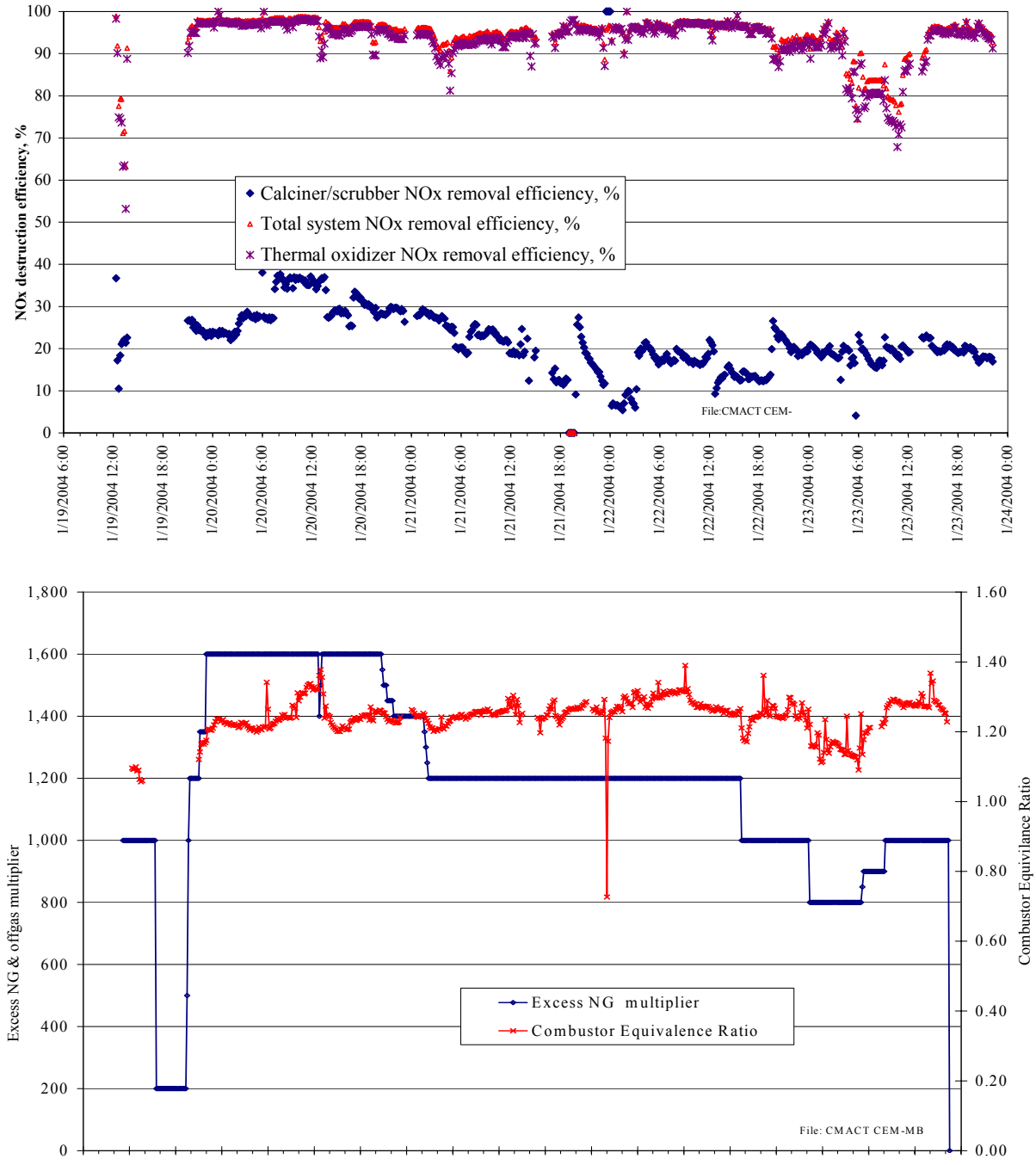


Figure 4.9-1. Summary thermal combustor operation parameters and NO_x destruction by subsystem.

reoxidation chamber), the temperature must be maintained below 1000°C to prevent N_2 and O_2 from rapidly reacting to reform NO_x. Table 4.9-1 summarizes NO_x destruction performance of the combustor during the calcination trials. In this table, the NO_x destruction and removal efficiency (DRE) are defined as follows:

$$NO_X\ DRE = \frac{[moles\ NO_X]_{Inlet} - [moles\ NO_X]_{Outlet}}{[moles\ NO_X]_{Inlet}} x100\% \quad .$$

Table 4.9-1. NO_x destruction summary.

Excess NG Multiplier	Inlet NO	Inlet NO_2	Equivalence Ratio	Reduction Chamber Temp.	Interstage Quench Temp.	Reoxidation Chamber Temp.	Outlet NO	Outlet NO_2	NO_x DRE
	(ppmv)	(ppmv)		(°C)	(°C)	(°C)	(ppmv)	(ppmv)	(%)
1,000	3,152	29,585	1.06	1,200	980	838	945	-1	75.6
1,600	3,562	35,125	1.22	1,200	980	897	106	18	96.5
1,400	3,008	29,859	1.21	1,200	980	905	200	32	94.2
1,200	2,825	26,988	1.23	1,200	980	920	206	25	94.6
1,000	2,890	27,335	1.21	1,200	980	892	323	67	91.8
800	3,047	27,495	1.13	1,200	980	878	794	220	79.0
900	2,806	27,209	1.17	1,200	980	877	599	69	86.0
1,000	2,847	27,510	1.25	1,199	979	903	200	34	94.8

Note: Concentrations are reported on an "as measured" basis. [CMACT CEM-MB feb 28.xls]NOx PIC

Note the trend between NO_x DRE and ϕ. At equivalence ratios below 1.20, a more reducing flame results in better NO_x destruction. Further increases to the equivalence ratio above 1.25 appear to have a less pronounced impact on NO_x DRE. This trend is shown graphically in Figure 4.9-2. Also note that the predominant NO_x species in the combustor exit gas is NO rather than NO_2. This is significant, as NO_2 in the NWCF stack has historically been responsible for the visible yellow-brown plume. Hence, from these results, it can be concluded that staged combustion is capable of achieving excellent NO_x destruction in the calcination flowsheet. Operation at an equivalence ratio above 1.25 will destroy greater than 90% of the NO_x in the off-gas stream. A peak NO_x DRE of 98% was achieved during testing when operating with the Excess NG Multiplier set at 1600.

4.9.2 PIC Destruction

Two process variables must be considered to ensure adequate destruction of PICs in the combustor. First, the reoxidation chamber temperature must be maintained above the autoignition temperature for the PICs (autoignition temperature for CO = 609°C). Second, excess oxygen must be present to completely oxidize the PICs in the off-gas to CO_2.

Gas residence time is also an important parameter related to PIC destruction. However, this was a design variable that could not be easily changed during experimentation and varied slightly based on changes to the upstream calcination process. In order to gauge performance of the combustor against MACT standards for PICs, both CO and THC were measured at the outlet of the combustor. Table 4.9-2 summarizes PIC destruction performance of the combustor during the calcination trials. Note that for most test conditions, effluent CO and THC concentrations are well below the MACT limits (100 ppmv and 10 ppmv, respectively). The only exception was when running with an excess NG multiplier of 1,400, where the outlet THC value averaged 21.5 ppmv. For this test, the average includes 24 data points, which represent 10-minute data averages. Two of the 10-minute averages exceeded 10 ppmv (143 ppmv and 372 ppmv), which adversely skews the tabulated average value. No anomalies in operating conditions were noted during this period; therefore, these values were not omitted from the data set. As evidenced by Figure 4.9-3, reoxidation chamber temperature does not appear to have a significant impact on PIC destruction, at least over the range of conditions tested during the calcination trials.

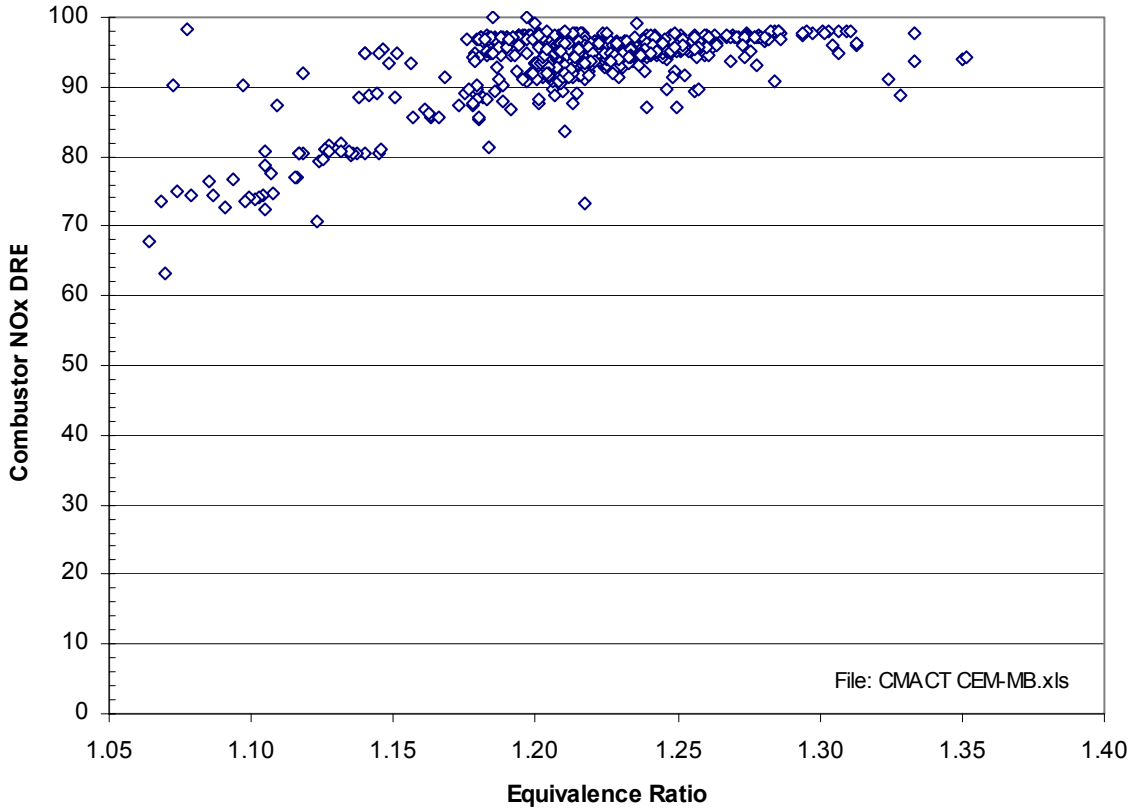


Figure 4.9-2. NO_x destruction as a function of equivalence ratio (φ).

Table 4.9-2. PIC destruction summary.

Excess NG Multiplier	Inlet CO (vol.%)	Reoxidation Chamber Temp. (°C)	Outlet O_2 (vol.%)	Outlet CO (ppmv)	Outlet THC (ppmv)
1,000	2.22	838	2.00	-1.89	-
1,600	1.88	897	2.00	3.38	2.70
1,400	1.71	905	2.00	8.88	21.50
1,200	1.73	920	2.01	1.78	-0.20
1,000	1.74	892	2.00	2.60	0.55
800	1.67	878	2.00	1.19	1.24
900	1.62	877	2.01	13.37	1.44
1,000	1.55	903	2.03	11.40	0.70

Note 1: All concentrations reported on a dry basis.
Note 2: Outlet CO and THC have been corrected to 7% O2.
Note 3: Outlet THC is reported on an "as propane" basis.

[CMACT CEM-MB feb 25.xls]NOx PIC

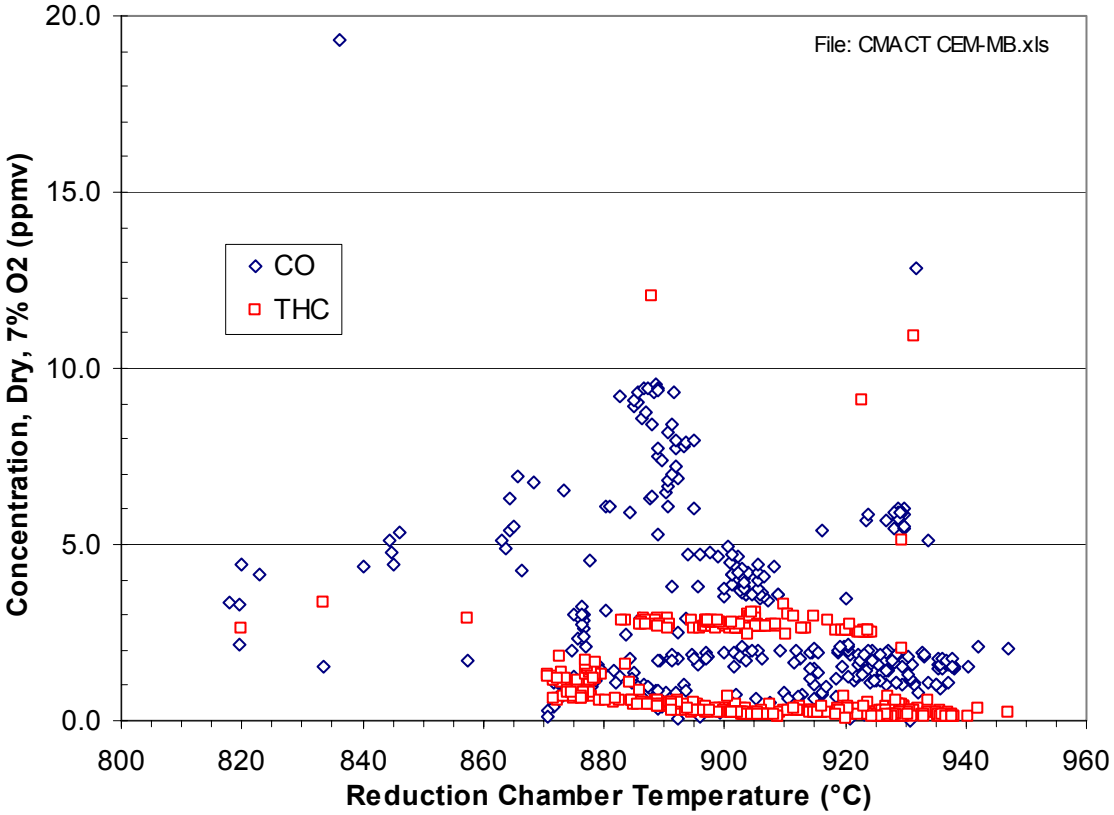


Figure 4.9-3. CO and THC concentrations as a function of reoxidation chamber temperature.

Note that a more rigorous trial burn-type test and analysis were beyond the scope and budget of this trial. Hence, it is not possible to calculate a DRE for principal organic hazardous constituents for comparison with the MACT standard. A more rigorous trial is recommended if calcination is ultimately selected as the treatment option for SBW. This said, it can be concluded from the limited results of these tests that a staged combustor in the calcination flowsheet appears to be well-suited for meeting MACT requirements for PICs.

4.9.3 Combustor Mass and Energy Balance Analysis

One objective for the CMACT design is to minimize the size of the new facility. By keeping the size to a minimum, overall facility costs will be reduced. In addition, due to the location of existing equipment at INTEC that the CMACT facility must interface with, the plot space available for the CMACT facility is extremely limited. To support the design objective of minimizing facility size, it is desirable to minimize the total gas flow exiting the combustor, as this will reduce the required size of downstream unit operations (carbon bed, HEPA filters, off-gas blowers, etc.).

Due to the small size of the SAIC Star Center combustor, significant heat loss was anticipated. To compensate for this heat loss, additional fuel and air must be added to the reduction chamber to maintain the optimal temperature for NO_x destruction. This, in turn, increases the amount of water and air that must be added to the combustor in subsequent stages. Hence, excessive heat loss in the combustor results in a significant increase in effluent off-gas flow.

Based on the discussions above, data were taken during the calcination tests to allow calculation of heat loss from the combustor. In addition, the increase in off-gas flow through the combustor was calculated for each test condition. It is anticipated that these data will be useful for two purposes: (1) to optimize operation of the multi-stage combustor in future pilot-scale trials, and (2) to use in design and scale-up of the CMACT combustor.

An existing Aspen Plus model of the combustor was used to calculate heat losses for the reduction and reoxidation stages (Wood 2004). A flowsheet of this model is shown in Figure 4.9-4, and heat loss results are summarized in Table 4.9-3. The average heat loss from the combustor during the calcination tests was 44%, based on the HHV of the fuel. Due to excessive heat losses, the outlet flow from the combustor increased on average by a factor of 7.6 over the inlet off-gas flow.

Results from these tests indicate the need to minimize heat loss in the CMACT design in order to reduce off-gas flow and ultimately reduce the size of the facility. As shown in Figure 4.9-5, one way to reduce the off-gas flow is to operate at the minimum natural gas flow to the reduction chamber that produces acceptable NO_x destruction. In addition, using multiple refractory layers in the combustor and increasing the thickness of the refractory could further minimize heat losses. Finally, minimizing pilot gas flow would also reduce effluent off-gas flow from the combustor by reducing the required flows of combustion air and quench water. However, additional testing and analyses would be required to define a safe lower limit for the size of the pilot flame.

4.9.4 Control and Operability

In general, control and operability of the combustor was manageable from the HMI throughout the calcination tests. However, two issues were identified that resulted in operational difficulties during the course of testing. Each issue is briefly summarized below.

4.9.4.1 Inlet O_2 Analysis. Oxygen analysis at the inlet to the combustor was sporadic at times. An upward spike in the O_2 analysis at the combustor inlet adversely affected control of the combustor as follows:

- Natural gas flow to the combustor would increase in response to the O_2 analyzer spike.
- Significant quantities of unburned fuel would then flow through the quench stage into the reoxidation chamber.

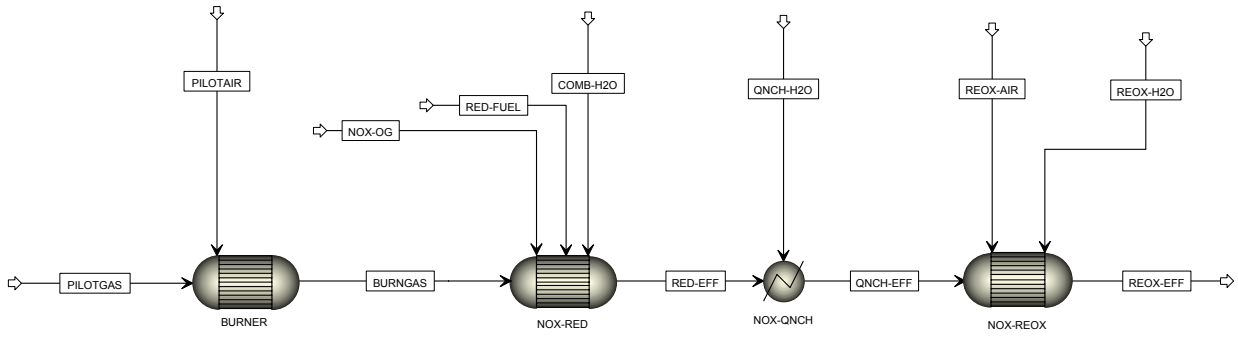


Figure 4.9-4. Aspen Plus flowsheet used to calculate combustor heat losses.

Table 4.9-3. Combustor heat loss and off-gas flow increase summary.

Excess NG Multiplier	Total Fuel Input (kg/hr)	Heat Input From Fuel (kW)	Combustion & Reduction Chamber Heat Loss (kW)	Quench & Reoxidation Chamber Heat Loss (kW)	Total Heat Loss (% Input)	Inlet Offgas Flow (scfm)	Outlet Offgas Flow (scfm)	$\frac{Flow_{Out}}{Flow_{In}}$
1,000	4.3	66.6	20.7	11.2	48	8.8	78.2	8.9
1,600	4.7	72.3	15.8	16.1	44	7.4	81.5	11.0
1,400	4.7	72.1	14.0	16.6	42	9.9	81.0	8.2
1,200	4.7	72.1	13.2	17.3	42	11.6	81.8	7.0
1,000	4.4	67.6	12.8	18.1	46	11.8	75.2	6.4
800	4.3	66.8	15.9	14.5	46	11.9	74.8	6.3
900	4.4	67.4	14.1	15.7	44	11.9	74.5	6.2
1,000	4.7	72.1	12.9	16.8	41	11.9	81.7	6.9
Average	4.5	69.6	14.9	15.8	44	10.7	78.6	7.6

Note 1: Fuel heat input is based on the HHV for methane of 52,668 Btu/kg
Note 2: Flow ratio is volume based.

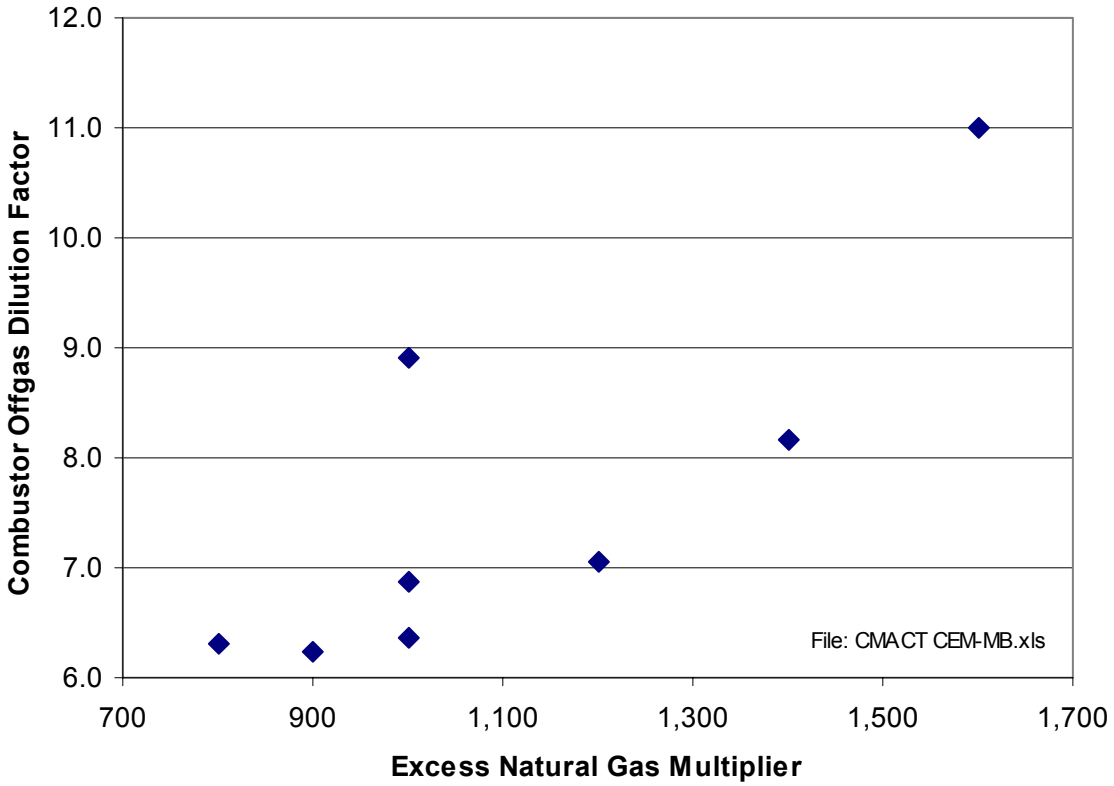


Figure 4.9-5. Off-gas dilution as a function of the excess NG multiplier.

- The O_2 flow valve to the reoxidation chamber would peg wide open in an attempt to provide sufficient oxygen to consume the unburned fuel. Insufficient oxygen flow would result in an O_2 analysis at the outlet of the combustor below 0.2%.

- If the low combustor outlet O_2 reading were to persist for more than 20 s, automatic system shutdown would have been initiated. Fortunately, this did not occur during testing.

This problem underscores the need for reliable gas analyses to ensure stable combustor operation. In addition, it also indicates the need for data averaging as part of the control strategy. It is likely that the data averaging used during the calcination tests prevented numerous undesirable automatic system shutdowns.

4.9.4.2 System Pressure Fluctuations. On numerous occasions during testing, pressure fluctuations were encountered in the off-gas train. The causes of these fluctuations were varied, from feed nozzle plugging to cyclone plugging. These fluctuations typically resulted in instability in natural gas feed to the burner and/or the reduction chamber. In some instances, these fluctuations were severe enough to cause loss of flame in the burner. During testing, a potential solution was identified to reduce the adverse impact of pressure fluctuations on the combustor. By increasing the natural gas supply pressure, the severity of fluctuations in fuel flow as a result of system pressure fluctuations was reduced.

From subsequent inspection of the run data, it appears that inlet O_2 analysis spikes may correspond with system pressure fluctuations. It is likely that these pressure fluctuations were responsible for the oxygen analyzer spikes. Hence, it can be concluded that fluctuation of system pressure was the single largest operability concern for the staged combustor during the calcination tests.

4.9.5 Combustor Reliability

Due to the short duration of the calcination tests, it is not possible to realistically assess reliability of the combustor. This stated, a visual inspection of the reduction chamber refractory was performed following the run. The following observations were made during this inspection:

- No buildup was observed on the vertical cylindrical walls of the reduction chamber; the walls were relatively clean.

- A few hairline cracks were observed in the refractory lining the cylindrical walls of the reduction chamber. However, these cracks were not severe, and appeared fairly typical for a refractory after firing. No significant degradation of the refractory was observed.

- A small amount of buildup was observed on the horizontal plate separating the reduction chamber from the burner. This buildup appeared as orange-brown spots on the refractory surface, and covered approximately ¼ of the refractory surface area. The depth of this buildup was not measured, but appeared to be less than $^1/_8$ in. thick.

- The 316 stainless fuel nozzle in the reduction chamber (aligned flush with the chamber wall during operation) appeared to be in good shape—no spalling was observed. The nozzle was black, but this appeared to be due to a thin covering of soot rather than carburization of the steel.

Obviously longer-term testing is required to adequately assess the reliability of the combustor. In addition, all three stages of the combustor should be carefully inspected (including quench nozzles) after a long-term trial rather than just the reduction chamber. However, based on the limited inspection performed, no significant combustor reliability issues were identified. Note that the refractory used in

this combustor is a Greenlite 45L. This refractory is rated for 1370°C, which is less than 200°C above the target operating temperature of 1200°C for the reduction stage. Hence, the lack of refractory degradation in this stage of the combustor is encouraging. In the full-scale design, it is anticipated that multiple layers of refractory would be used. A potential choice for the innermost refractory layer would be Greencast 94, which has a much higher temperature rating (1870°C) than Greenlite 45L.

4.9.6 Implications for CMACT Combustor Design

Based on the results of these tests, staged combustion is capable of destroying greater than 90% of the NO_x in the inlet stream. In addition, treating calciner off-gas using staged combustion will meet MACT standards for CO and THC. However, as previously stated, additional testing is required to demonstrate a DRE of 99.99% for principal organic hazardous constituents, as required by the MACT standard.

Results from these tests also indicate the need to minimize heat loss in the CMACT design in order to reduce off-gas flow and ultimately reduce the size of the facility. One way to minimize heat loss is to increase the thickness of the combustor's refractory lining and to consider using multiple refractory layers. In addition to minimizing heat loss, another way to reduce the off-gas flow is to operate at the minimum equivalence ratio that produces acceptable NO_x destruction. Finally, minimizing pilot-gas flow can also reduce gas flow from the combustor by reducing the required flows of combustion air and quench water. Additional testing and analyses are recommended to better define minimum limits for equivalence ratio and pilot gas flow.

Operability of the combustor was non-eventful and manageable from the HMI, with the exception of disturbances caused by system pressure fluctuations. As previously discussed, increasing the fuel supply pressure may be sufficient to alleviate this problem. However, additional testing is recommended to completely resolve this operability issue. Note that pressure fluctuations may not be as significant an issue in the CMACT design due to the pressure dampening effect of the calciner's existing constant-speed off-gas blowers.

No significant combustor reliability issues were identified during these tests. However, longer-term testing is recommended to increase confidence in the combustor's reliability.

The SAIC Star Center combustor design is different from the currently proposed CMACT design. The CMACT combustor is a John Zink Co. design, which has previously been tested on simulated calciner off-gas at MSE's facility in Butte, Montana (MSE 2000, MSE 2001). In the CMACT combustor design, off-gas is fed directly to the combustion chamber; hence, the off-gas acts as the oxidizer for combustion. In this design, the oxygen content of the off-gas must be sufficient to ensure a stable flame within the combustion chamber. The Star Center combustor differs in that the off-gas does not pass directly through the combustion chamber. Instead, a large pilot flame is used in the combustion chamber. The fuel-to-air mixture in this pilot is kept at a stoichiometric ratio to ensure stable combustion. The off-gas is then introduced into the reduction furnace, where additional fuel is introduced to create the reducing environment required for NO_x destruction. Based on results of testing each design, the following observations can be made:

- For operation in the same equivalence ratio range, NO_x DREs for the John Zink Co. design in the MSE tests (90–96%) were comparable to the Star Center design in these calcination tests (90-98%). A comparison of the outlet NO_x concentration from the two processes indicates comparable performance (100–500 ppmv). Both designs demonstrated the ability to destroy >90% of the NO_x entering the combustor.

- THC and CO levels in the effluent gas are comparable—both designs have demonstrated the ability to meet MACT requirements.

- The Star Center design resulted in a slightly lower dilution of the off-gas (~7.6x) than the John Zink Co. design (~9.7x). However, further modeling and testing is required to directly compare these values, as heat loss has a significant impact on the effluent gas flow from the combustor.

- The Star Center design provides greater flexibility for startup and shutdown, because the pilot burner allows an increased degree of independence from the off-gas composition and flow rate.

Further modeling and analysis of each of these designs is recommended in order to select the optimal design for the CMACT facility.

4.10 Off-gas Hg Concentrations and Carbon Bed Performance

Mercury is a unique hazardous metal because of its toxicity and its volatility. It was expected that essentially no Hg would be retained in any of the solid products, though this speculation was not confirmed with sample analyses. It was assumed that the Hg in the SBW simulant feed quantitatively evolved to the off-gas. The Hg is highly volatile, but depending on its speciation can be scrubbed in the wet scrubber. Elemental Hg is highly insoluble in water, and much evidence exists that when Hg in the off-gas is in its elemental form, it is not efficiently scrubbed in wet scrubbers (Chambers 1998; Soelberg 1998, Soelberg 2004a, 2004b). However, oxidized forms of Hg such as HgO and $HgCl_2$ are highly water-soluble or have lower volatilities than elemental Hg and are scrubbed in a wet scrubber with high efficiencies.

The calcination tests were performed with an acidic wet scrubber to emulate the NWCF scrub system, by adding nitric acid to lower the scrub solution pH to less than 1. The fixed carbon bed downstream of the scrubber and staged combustor emulates the proposed design for the NWCF MACT upgrade.

4.10.1 Carbon Bed Design and Operation

The carbon bed was designed with three stages in order to (a) show the potential loading capacity (mass of total Hg sorbed per mass of carbon sorbent) and (b) the potential total Hg removal efficiency from the steam reformer off-gas. These two objectives are mutually exclusive in discrete small-scale pilot tests. The theoretical sorption capacity for NUCON sulfur-impregnated carbon is up to 20 wt%, so a carbon bed designed to demonstrate the breakthrough capacity of Hg for small-scale pilot tests in a reasonable testing time would need to be too small to be appropriately designed according to vendor recommendations and design criteria for maximum superficial velocity, minimum residence time, and geometry (Soelberg 2003b).

The operating conditions of the carbon bed are compared to nominal carbon bed design criteria in Table 4.10-1. The design and operating parameters are not generally within the recommended parameters because of the constraints of the pilot-scale test system. Complying more rigorously with these recommendations was not possible within the test system and schedule constraints. The inlet and outlet pipe gas velocities are higher than recommended, which could cause a gas flow distribution profile in the carbon bed that would be higher than desired in a full-scale design.

Table 4.10-1. Carbon bed operating conditions for the calcination tests.

Parameter	Recommended (a)		Conditions During the Calcination Test			
			Stage 1	Stage 2	Stage 3	Total
Inlet pipe gas velocity (ft/s)	≤	40	120	120	120	120
Gas superficial residence time (s)	≥	2	0.052	0.10	0.47	0.63
Gas temperature (C)	≤	150	107	107	107	107
Gas superficial velocity (ft/s)	≤	1	1.6	1.6	1.6	1.6
Maximum gas relative humidity (%)	≤	90	<52%	<52%	<52%	<52%
Minimum bed depth (in.)	≥	24	1	2	9	12
a. From Soelberg 2003b for the NWCF MACT upgrade.						

The gas superficial residence time is lower than recommended, especially for Stages 1 and 2. This was purposefully done so that the mass of carbon, especially in Stage 1, was low enough to enable the concentration of Hg in this stage to approach breakthrough levels within a reasonable test duration. The cumulative residence time of all three stages was still only about 1/3 of the recommended gas residence time, limited by the mass of carbon added to the bed for this test. The capacity of the bed vessel was high enough to use a 36-in. total carbon depth, which would have provided the recommended gas residence time of 2 s. However, after the existing bed used in prior steam reforming tests was replaced due to high-temperature excursions during startup, it was not possible to use a full 36-in. bed depth. The Hg removal efficiency data confirm that the first stage alone is in fact not designed appropriately for ultra-high Hg removal efficiency, but the control efficiency of the three total stages was very high during the calcination test.

4.10.2 Hg Concentrations and Removal Efficiency from Hg CEMS Measurements

Table 4.10-2 shows the speciation and concentrations of Hg downstream of the staged combustor and at the outlet of each stage of the carbon beds based on the Hg CEMS measurements. As expected, downstream of the wet scrubber and staged combustor, most of the measured Hg is elemental Hg, not oxidized Hg. This table also shows the Hg removal efficiency results for the wet scrubber and carbon bed based on the CEMS measurements. The removal efficiency for Hg in the wet scrubber based on the CEMS measurements averaged about 78%. The amount of Hg removed in the scrubber was probably oxidized Hg.

The total Hg removal efficiency for each carbon bed averaged 81, 99, and 94%, respectively. The total carbon bed removal efficiency averaged 99.99%, and the total system removal efficiency (including all retention of Hg in any test system component) was 99.997%.

The combined first, second, and third stages have sufficient depth to achieve high Hg removal efficiencies during the calcination test. The Hg removal efficiency shown at the end of the second and third stages confirms that this bed design accomplishes very efficient Hg control. The off-gas Hg concentration at the carbon bed outlet, corrected to a dry, 7% O_2 basis, averaged 0.7 μg/dscm, under 2% of the HWC MACT limit for Hg of 45 μg/dscm.

Table 4.10-2. Hg speciation, concentrations, and system removal efficiencies based on Hg CEMS measurements.

	Process conditions			Measured offgas concentrations in ug/m^3, wet basis													
				Exit of multistage combustor			Carbon bed inlet			Exit of carbon bed Stage 1			Exit of carbon bed Stage 2			Exit of carbon bed Stage 3		
Averages	Simulant feedrate, l/hr	Carbon bed off-gas flow, wscfm	Hg MTEC at carbon bed inlet, ug/m^3, wet	Hg el corr	Hg tot corr	Hg ox corr	Hg el corr	Hg tot corr	Hg ox corr	Hg el corr	Hg tot corr	Hg ox corr	Hg el corr	Hg tot corr	Hg ox corr	Hg el corr	Hg tot corr	Hg ox corr
Test 1	5.41	81	14,210	25,699	24,361	-1,339	2,395	2,492	7	686	806	120	---	---	---	---	---	---
Test 2	5.73	79	17,429	19,030	19,324	294	3,953	4,442	781	148	171	72	7.4	7.9	0.5	0.5	0.5	0.0
Total test average	5.63	80	15,964	20,434	20,384	-50	3,174	3,501	587	568	667	111	7.4	7.9	0.5	0.5	0.5	0.0
STD DEV	0.76	5	2,272	3,909	3,207	1,934	1,949	2,167	787	259	351	217	0.5	0.6	0.6	0.6	0.5	0.4
				Average off-gas total Hg concentration, dry basis, corrected to 7% O2, ug/dscm													0.8	
				HWC MACT standard for Hg concentration, ug/dscm at 7% O2													45	
				Total off-gas Hg concentration, % of HWC MACT standard													2	

	Total system removal efficiency %	Scrubber removal efficiency, %	Total carbon bed removal efficiency, %	Carbon bed stage 1 removal efficiency, %	Carbon bed stage 2 removal efficiency, %	Carbon bed stage 3 removal efficiency, %
Test 1	---	82.5	---	67.7	---	---
Test 2	99.997	74.5	99.99	96.1	95.4	93.7
Total test average	99.997	78.1	99.99	80.9	98.8	93.7

Notes:
1. MTEC = maximum theoretical emission concentration, calculated from the input Hg rate and the measured off-gas flowrate.
2. The total system removal efficiency includes Hg removal in system components and subsystems including the scrubber and carbon bed.
3. The scrubber removal efficiency was calculated from the carbon bed inlet off-gas Hg concentration and the carbon bed inlet Hg MTEC.
4. Hg removal in each carbon bed stage was calculated from the inlet and outlet Hg concentrations in the offgas.

[CMACT CEM-MB feb 16.xls]Hg

4.10.3 Hg Removal Efficiency from Scrub Solution and Carbon Bed Analyses

The amount of Hg sorbed by each stage of the carbon bed was determined by sampling and analyzing each stage at several locations and averaging the results. Figure 4.10-1 shows the sampling program for the carbon bed. By separating the carbon bed cross-section area into three equal areas, each of which was sampled, the linear average of these samples provides the average radial Hg concentration. By analyzing the top and bottom of each stage (and the middle of Stages 2 and 3), the average Hg concentration for each stage in the axial direction was estimated by averaging the top, bottom, and middle samples.

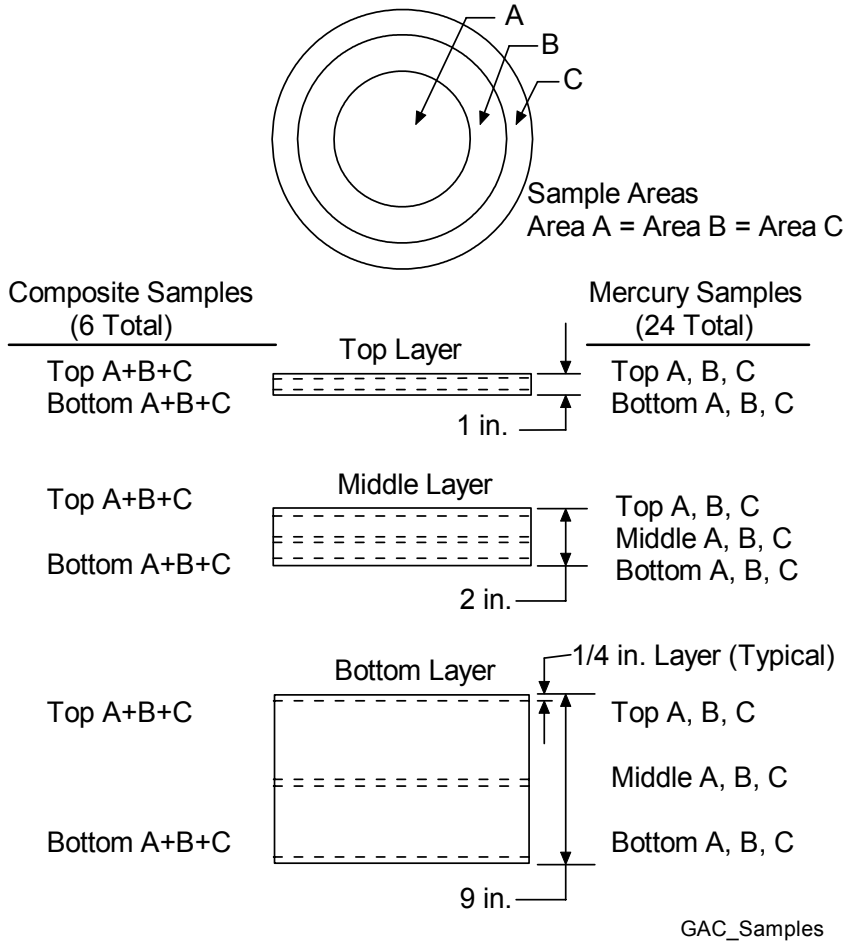


Figure 4.10-1. Carbon bed sample matrix.

Table 4.10-3 shows the Hg concentrations, mass, and removal efficiency for the 3-stage carbon bed based on carbon sample analyses. Figure 4.10-2 shows that, as expected, the highest Hg concentrations and masses of sorbed carbon are in Stage 1, followed by Stages 2 and 3. This is because of the high affinity that sulfur-impregnated carbon has for Hg. Hg is rapidly sorbed onto sulfur impregnated carbon. The zone in which Hg is actively being absorbed is called the "mass transfer zone" (MTZ). As the carbon bed becomes depleted during use, the MTZ travels in the direction of gas flow from the bed inlet to the bed outlet. The amount of Hg sorbed on the carbon between the bed inlet and the MTZ will approach the maximum capacity for the carbon under the operating conditions (temperature, pressure, humidity, etc.) for the carbon bed. The amount of Hg sorbed on the carbon in the MTZ increases as the Hg in the gas is actively absorbed in this zone. The amount of Hg sorbed on the carbon between the MTZ and the bed

Table 4.10-3. Hg concentrations, mass, and removal efficiency for the 3-stage carbon bed based on carbon sample analyses.

Stage	Sample number	Location	Total axial distance form the front of the bed, inches	Radial distance from bed center-line, inches	Total Hg concentration, wt %			Total mass of carbon per stage, kg	Total mass of Hg per stage, gm	Hg removal efficiency, %
					Each sample at the axial location	Avg at the axial location	Avg for the stage			
1	627	Center top 1-inch bed face	0	0	1.151	1.37	1.10	2.0	22.5	87.9
	628	Annulus top 1-inch bed face		6.1	1.367					
	629	Wall top 1-inch bed face		8.0	1.597					
	630	Center top 1-inch bed bottom plane	1	0	1.444	0.83				
	631	Annulus top 1-inch bed bottom plane		6.1	0.757					
	632	Wall top 1-inch bed bottom plane		8.0	0.281					
2	633	Center middle 2-inch bed face	1	0	0.1027	0.1218	0.061	4.2	2.5	81.7
	634	Annulus middle 2-inch bed face		6.1	0.1763					
	635	Wall middle 2-inch bed face		8.0	0.0864					
	636	Center middle 2-inch bed mid plane	2	0	0.0540	0.0440				
	637	Annulus middle 2-inch bed mid plane		6.1	0.0460					
	638	Wall middle 2-inch bed mid plane		8.0	0.0321					
	639	Center middle 2-inch bottom plane	3	0	0.0127	0.0163				
	640	Annulus middle 2-inch bottom plane		6.1	0.0245					
	641	Wall middle 2-inch bottom plane		8.0	0.0118					
3	642	Center lower 9-inch bed face	3	0	0.0062	0.0074	0.003	18.4	0.57	98.8
	643	Annulus lower 9-inch bed face		6.1	0.0062					
	644	Wall lower 9-inch bed face		8.0	0.0098					
	645	Center lower 9-inch bed mid plane	7.5	0	2.2E-03	1.7E-03				
	646	Annulus lower 9-inch bed mid plane		6.1	1.4E-03					
	647	Wall lower 9-inch bed mid plane		8.0	1.6E-03					
	648	Center lower 9-inch bottom plane	12	0	1.4E-04	1.3E-04				
	649	Annulus lower 9-inch bottom plane		6.1	1.2E-04					
	650	Wall lower 9-inch bottom plane		8.0	1.3E-04					
Totals for all 3 stages								24.6	25.6	99.97

Notes:

1. The samples at each axial location are located radially within equal areas, so the linear average of the Hg concentrations in the samples at each axial location indicates the average Hg concentration at that axial location.
2. The average Hg concentration for each stage is the linear average of all of the samples from that stage.
3. The mass of carbon per stage was recorded in the operating logbook on 15 January 2004.
4. Hg removal efficiency for Stage 1 was calculated based on the total amount of Hg captured in Stage 1 compared to Hg in the offgas at the inlet of Stage 1, which was estimated from the total Hg captured in all three stages. This efficiency calculation assumes that the total Hg capture for all three stages is quantitative, which is a good assumption as long as breakthrough has not
5. Hg removal efficiency for Stage 2 was calculated based on the total amount of Hg captured in Stage 2 compared to Hg in the offgas at the inlet of Stage 2, which was estimated from the total Hg captured in the last two stages. This efficiency calculation assumes that the total Hg capture for all three stages is quantitative, which is a good assumption as long as breakthrough has not occurred.
6. The removal efficiency of Stage 3 was calculated based on the total amount of Hg captured in stage 3 compared to the total Hg in the Stage 3 exit gas measured by the Hg CEM, which averaged 0.5 ug/m3. At the average offgas flowrate of 81 wet scfm over a duration of 100 hours, the Hg mass exiting the carbon bed was 0.007 gm.

[Carbon bed Hg feb 26.xls]Hg in carbon table

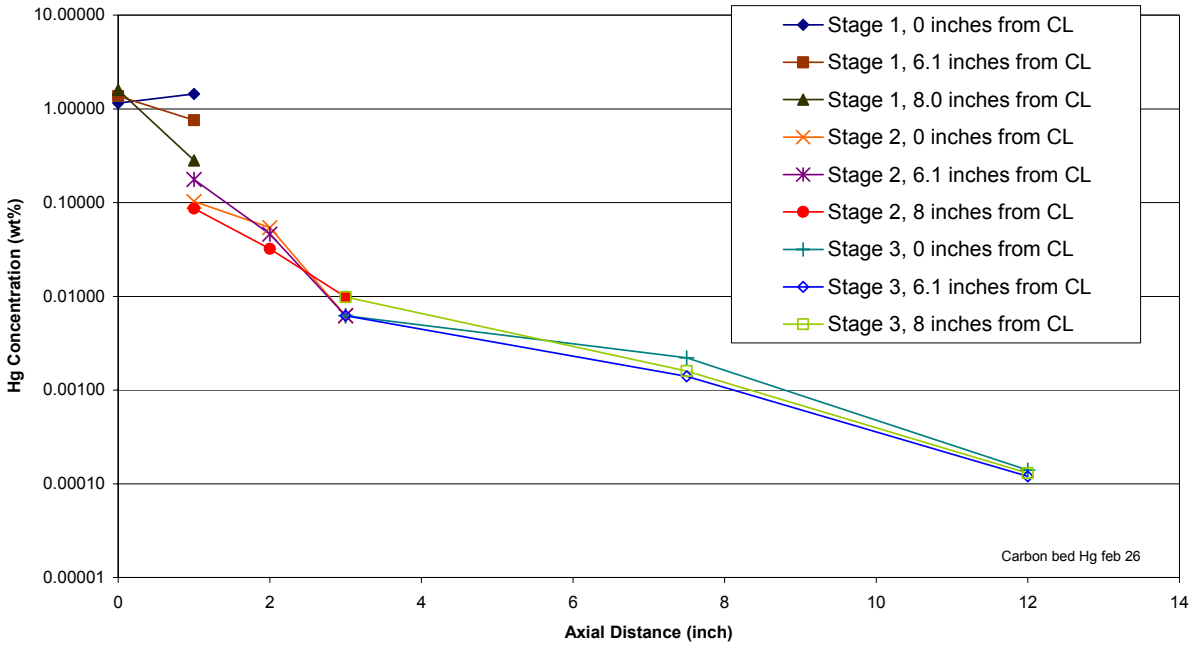


Figure 4.10-2. Axial Hg concentration distributions in the carbon bed samples.

outlet is very small, because nearly 100% of the Hg has been absorbed by the time the gas exits the MTZ. The total bed depth must be longer than the MTZ for the bed to provide highly efficient Hg capture.

Breakthrough occurs when the outlet Hg levels start to increase from a relatively constant baseline level, asymptotically approaching the inlet level. This occurs when the MTZ passes through the depth of the carbon bed, and Hg sorption rapidly approaches zero because the carbon, even at the back end of the carbon bed, approaches saturation with Hg at the operating conditions of the bed. Two indicators show that even the first stage did not reach breakthrough in the duration of the calcination test. First, the Hg CEMS measurements at the outlet of the first stage never increased significantly to levels near the carbon bed inlet concentrations. Second, the Hg concentration in Stage 1 samples were significantly lower than the levels of 10–20 wt%, which is the expected range at which breakthrough might be reached.

Since none of the stages in the carbon bed reached breakthrough, the measured Hg concentrations from this test do not accurately indicate the maximum Hg concentration in the carbon at the time breakthrough would occur. The capacity of the carbon for Hg at the time breakthrough would occur under the operating conditions of this test could be much higher than the highest Hg concentration (1.6 wt%) of this test.

Figure 4.10-3 shows that the Hg concentrations in the Stage 1 and Stage 2 beds tended to be lower near the wall. This result suggests that, as expected, the gas velocity was higher near the center of the bed and lower near the wall. This can occur when, as in the test system design, the inlet and outlet gas pipes are in the center of the cylindrical carbon bed, there are no baffles to distribute the entering gas across the diameter of the bed, and the gas velocity entering the carbon bed vessel is higher than the design criteria. The radial concentration profile for Stage 3 suggests that the gas flow has become reasonably well distributed by the time the gas enters Stage 3.

Based on the carbon bed analyses, a total of 25.6 gm of Hg was sorbed onto the carbon. The first stage sorbed about 10 times more Hg than the second stage. The second stage sorbed about 10 times

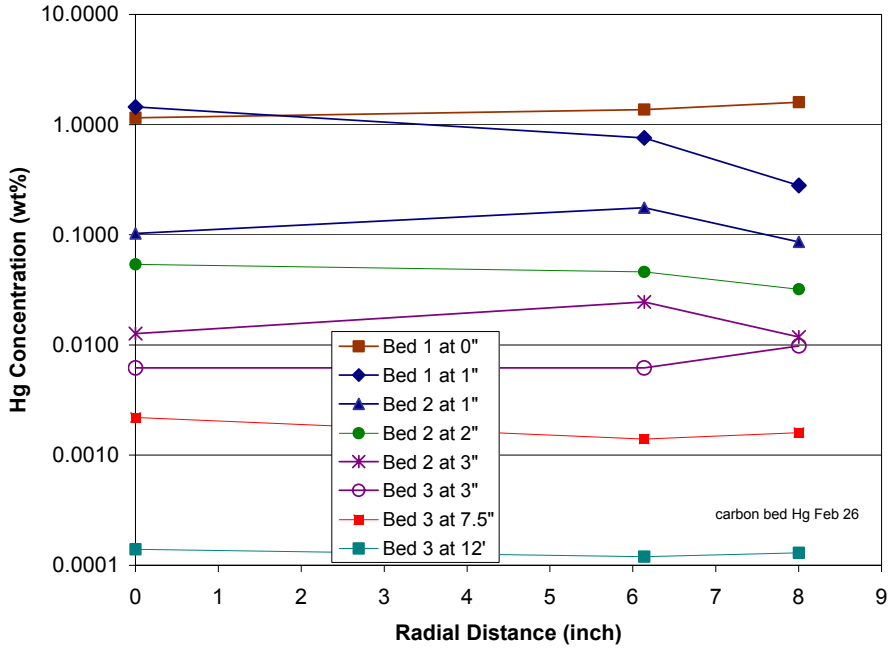


Figure 4.10-3. Radial Hg concentration distributions in the carbon bed samples.

more Hg than the third stage. The carbon bed removal efficiency for Hg was calculated based on the amount of Hg captured in each stage of the carbon bed based on the carbon sample analyses. Based on the carbon sample analyses, the Hg capture efficiencies for the carbon bed averaged about 88% for Stage 1, 82% for Stage 2, 99% for Stage 3, and 99.97% for the entire carbon bed. This overall Hg capture efficiency is less than the Hg capture efficiency for the carbon bed based on the Hg CEMS analyses (99.99%). This is because the amount of total Hg entering the carbon bed based on the Hg CEMS measurements was 48 gm, almost twice the amount of Hg in the spent carbon based on the carbon bed sample analyses.

4.10.4 Halide Adsorption

The carbon bed samples were analyzed for Cl and F ions to assess whether, if these species or precursors of these species (such as HNO_3 or NO_2) were in the off-gas, they would be appreciably sorbed. Both Cl and F were detected at low levels, shown in Table 4.10-4.

The axial concentration profile for Cl and F in the carbon bed is shown in Figure 4.10-4. These species appear to sorb onto the carbon as Hg does, with high concentrations near the front of the bed that rapidly decrease with bed depth. The concentration of F decreases to below the F detection limit after the first stage (a 1-in. depth). The Cl concentration decreases after the second stage (a total 3-in. depth for Stages 1 and 2) to a relatively constant, but still detected, value.

The masses of F and Cl sorbed in the carbon bed are shown in Figure 4.10-5. While the F and Cl axial concentration profiles in the carbon suggest that the carbon will sorb these species, the carbon bed was not adequately challenged with HCl and HF in the off-gas to reliably assess the ability of the carbon bed to sorb these species. The HCl concentration measured by the CEMS at the inlet to the carbon bed was only 0.1 ppm (wet basis), already just a fraction of the HWC MACT standard.

Table 4.10-4. Halide concentrations and masses detected in the carbon bed samples.

Stage	Sample	COT	Description	Total axial distance from the front of the bed, inches	Total Cl concentration, wt%			Total mass of carbon per stage, kg	Total mass of Cl per stage, gm
					Each sample at the axial location	Avg at the axial location	Avg for the stage		
1	651	100	Composite of top 1-inch bed face samples	0	0.067	0.067	0.056	2.0	1.1
	652	100	Composite of top 1-inch bed bottom plane samples	1	0.044	0.039			
2	653	100	Composite middle 2-inch bed face samples	1	0.034		0.027	4.2	1.1
	654	100	Composite middle 2-inch bottom plane	3	0.019	0.018			
3	655	100	Composite lower 9-inch bed face	3	0.017		0.017	18.4	3.0
	656	100	Composite lower 9-inch bottom plane	12	0.016	0.016			
Total for all 3 stages								24.6	5.3

Notes:

1. The halides were digested prior to analysis using water in order to avoid interferences that would occur if acid solutions containing HCl, HF, or HNO_3 were used. Three sequential digestions were done for Cl analysis in order to assess whether the water digestion procedure quantitatively dissolved Cl.

2. The first sequential digestion dissolved averaged 77% of the Cl in the carbon determined after all three digestions. The Cl concentrations shown above are the sum of the Cl detected in all three digestion solutions.

Stage	Sample	COT	Description	Total axial distance from the front of the bed, inches	Total F concentration, wt%			Total mass of carbon per stage, kg	Total mass of F per stage, gm
					Each sample at the axial location	Avg at the axial location	Avg for the stage		
1	651	100	Composite of top 1-inch bed face samples	0	0.048	0.048	0.047	2.0	0.94
	652	100	Composite of top 1-inch bed bottom plane samples	1	0.046	0.027			
2	653	100	Composite middle 2-inch bed face samples	1	< 0.009		< 0.009	4.2	0.36
	654	100	Composite middle 2-inch bottom plane	3	< 0.008	0.008			
3	655	100	Composite lower 9-inch bed face	3	< 0.008		< 0.009	18.4	1.56
	656	100	Composite lower 9-inch bottom plane	12	< 0.009	0.009			
Total for all 3 stages								24.6	2.86

1. Sequential digestions and analyses, which were done for Cl, were not done for F. The single digestion values for F were multiplied by the scaling factor of about 1.3 determined by the amount of Cl digested in the first digestion compared to the total amount of Cl in all 3 Cl analyses.

2. No F was detected in the Stages 2 and 3. The detection limit was not multiplied by thescaling factor, and is used in mass balance calculations instead of 0.

[Carbon bed S, Cl and F feb 28.xls]F and Cl in carbon table

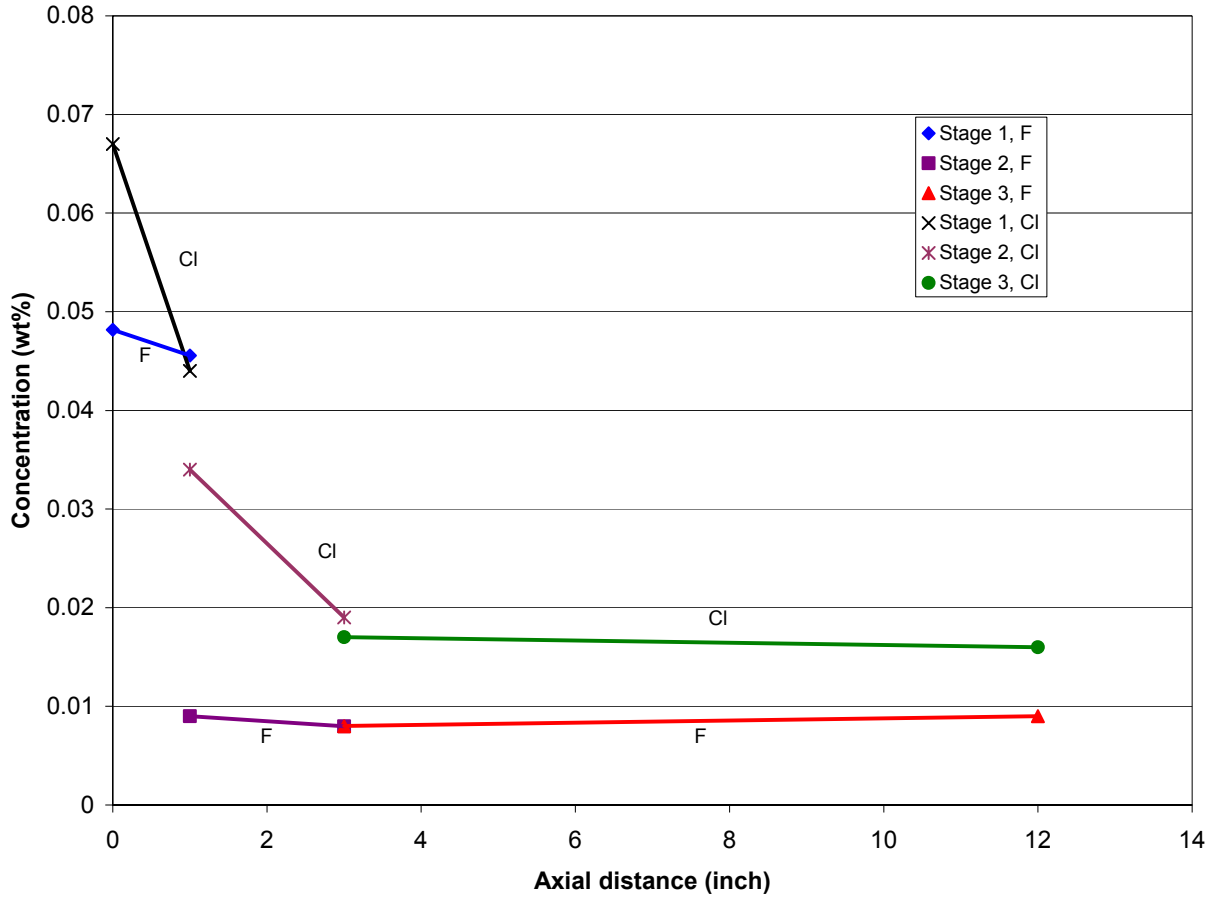


Figure 4.10-4. Sorbed Cl and F concentrations decrease with carbon bed depth.

4.10.5 Nitrate Adsorption

The carbon bed samples were analyzed for nitrate and nitrite ion to assess whether, if these species or precursors of these species (such as HNO_3 or NO_2) were in the off-gas, they would be appreciably sorbed. The analyses were nondetectable for these species, at a detection limit of 0.02 wt% (for nitrate ion) and 0.006 wt% (for nitrite ion).

4.10.6 Ammonium Adsorption

The carbon bed samples were analyzed for ammonium ion to assess whether, if ammonium species (such as ammonium chloride) were in the off-gas, they would be appreciably sorbed. The analytical detection limit was about 0.004 wt%. No ammonium ion was detected at levels above the detection limit range.

4.10.7 Carbon Bed Temperature Excursions

Temperature excursions have sometimes occurred in carbon beds when they are used to sorb contaminants from gaseous streams. When a temperature excursion occurs, it is usually at startup of an idle bed, when heatup is excessive or when exothermic reactions occur. Sorption of contaminants in the

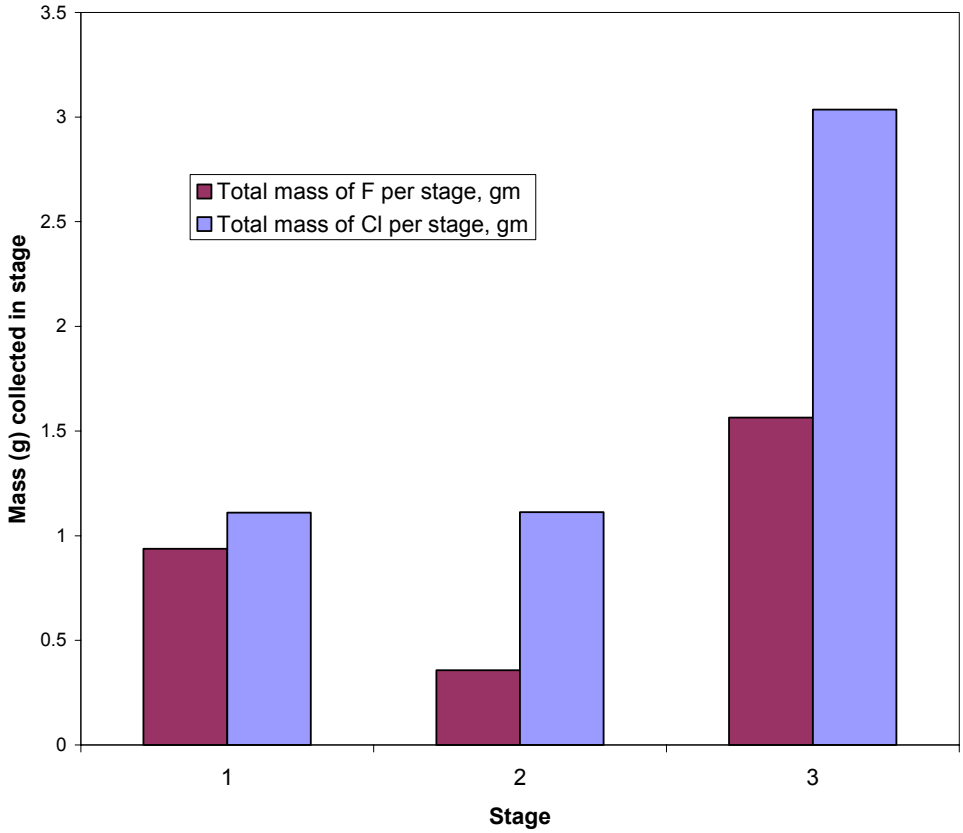


Figure 4.10-5. Masses of sorbed F and Cl in the activated carbon (the masses of F in Stages 2 and 3 are based on detection limit values).

gas stream, including gaseous water, is exothermic. Temperature spikes in a carbon bed are a certainty when a gas that contains high levels of gaseous water begins to pass through a carbon bed that has not been exposed to such a high-moisture-content gas. As water sorbs onto the carbon, heat is released. When an equilibrium is reached between sorbed water and gaseous water vapor, the heat release ends, and the carbon bed temperature stabilizes. Sorption is an exothermic process, so the sorption of any other gas species (such as volatile organic compounds or Hg) will also generate heat. However, the concentrations of other gas species that tend to sorb onto carbon are usually too low to cause temperature spikes high enough to reach oxidation temperatures.

If the bed media heats up to a temperature at which sorbed contaminants such as volatile organic compounds (VOCs), or the carbon bed media itself, begin to oxidize in the presence of air or other sources of oxygen, then the bed temperature can continue to increase and begin to smolder or burn. Temperature excursions typically start in a local region or regions in the bed. If the gas flowing through the bed contains oxygen, or if other sources of oxygen are present, then the smoldering/burning in the carbon bed can continue or even increase, and local hot spots can get hotter and grow in size.

The most common remedy for preventing temperature spikes from reaching oxidation temperatures is to (a) limit the input gas flow temperature, and (if present) only use carbon bed wall heater temperatures, to within design operating limits, typically under 150^{o}C, and (b) ensure a continuous, relatively high gas flow rate through the carbon bed. The gas flow draws heat of sorption away from the bed, preventing temperature spikes from reaching temperatures at which sorbed organic species or the carbon itself to begin to oxidize.

Temperature excursions occurred two different times during startup of the test system before the calcination test. These temperature excursions, and their resolutions, are discussed below.

4.10.7.1 Carbon Bed Temperature Excursion 1. A temperature excursion in the carbon bed occurred during initial heat-up of the carbon bed on January 12, before the operability tests. The carbon bed startup at this time included using the electric heaters clamped on the vessel to preheat the carbon bed, while an air flow rate of about 30 kg/hr air flowed through the calciner, scrub system, and oxidizer. The air temperature, after passing through the upstream equipment, was nominally 120°C. During this preheat, the temperature of the second carbon bed stage increased rapidly up to about 500°C. At the time of this excursion, the Stage 1 temperature was about 120°C, and the Stage 3 temperature was about 80°C. The inlet air and the external heater were shut off, and the bed was purged with nitrogen, eliminating the source of oxygen to the bed. After these actions, the bed temperature rapidly cooled. The carbon bed remained valved out for the remainder of the operability test. Inspection showed that a portion of one side of the middle bed (near the external heater) had oxidized, leaving some ash residue where some of the carbon initially was.

At the time, this temperature excursion was thought to be due to how the external heaters on the carbon bed vessel were controlled, which was based on the temperature inside the carbon bed. With this control design, the shell of the carbon bed could reach a high, unmeasured temperature, even when the temperature inside the bed was low.

Other factors that could have contributed to this carbon bed temperature excursion were the (a) operating history and composition of the carbon, (b) exothermic adsorption of water during startup, and (c) adsorption and reactivity of nitric acid aerosolized from the 5 M nitric acid scrub solution. The carbon in the carbon bed was the same carbon used for four prior steam reforming test weeks performed in October and November 2003. The same carbon was intentionally used in order to achieve highest practical loadings of Hg and other species in order to reach Hg breakthrough (at least in Stage 1) and to evaluate longer-term carbon bed performance. The carbon contained sorbed Hg and other species that tend to sorb into carbon, possibly including halides, products of incomplete combustion (PICs), and water vapor. Oxidation of sorbed PICs, if present, may have contributed to the temperature excursion.

Wetting of the carbon and subsequent acidification of the wet carbon by condensed nitric acid (entrained or volatilized in the gas stream from the 5-M acidified scrubber) was theorized as a possible contributor to the temperature excursion, by providing an oxidant in the carbon. H_2O-HNO_3 equilibrium data show that, as a solution of nitric acid evaporates, the HNO_3 in even a low-concentration acid will increase, eventually reaching an azeotropic concentration of about 15 M, until all H_2O and HNO_3 is evaporated at about 117°C (at 12.3 psia) (Holaday 1986). However, this theory is not a likely contributor, because (a) the nitric acid, and liquid water, is evaporated before the carbon bed temperature reaches a temperature high enough to cause extensive, uncontrollable oxidation, and (b) high nitric acid molarities in water depend on high nitric acid concentrations in the gas stream. While the air passed through the wet scrubber, the scrub solution recirculation line was not in operation, so the likelihood of high HNO_3 levels, and even high H_2O levels, was low.

The theory of oxidation of sorbed species such as VOCs as a contributor to the temperature excursion was discounted because the greatest amounts, if any, of sorbed VOCs would have been in the Stage 1 carbon. The temperatures in Stage 1 never exceeded the design operating temperature for the carbon bed.

The most likely and biggest contributor to this temperature excursion was the excessive wall temperature caused by the heater, when it was controlled by the bed thermocouple. The wall temperature could have reached up to about 800°C and caused the oxidation of the carbon that resulted in ash residue

left in the area of the second bed near the wall heating element. This temperature would have overwhelmed any temperature spikes caused by any other factors. The continual relatively cool temperatures of Stages 1 and 3 during this time confirm that possible contributions from other factors were negligible.

After the temperature excursion, thermocouples were placed on the shell of the carbon bed so that, when monitored, the heaters could be manually controlled to prevent high shell temperatures. The entire bed of carbon was replaced with fresh 1.5-mm Mersorb in the same configuration (3-in.-deep in Stage 1, 9-in.-deep in Stage 2, and 24-in.-deep in Stage 3).

The carbon bed was bypassed for the rest of the system operability tests to avoid any other process upsets that could have occurred during the operability tests.

4.10.7.2 Carbon Bed Temperature Excursion 2. A second temperature excursion in the carbon bed occurred during heatup of the carbon bed on January 18, 2004, during startup before the 100-hr calcination run. The external heaters, with manual control based on wall temperatures, were used to preheat the bed, while an air flow rate of about 30 kg/hr flowed through the calciner and scrub system. Lower heater settings were used this time, and the new top and bottom shell thermocouples only reached 105°C and 186°C, respectively, before the temperature excursion. The staged-combustor and partial quench were by-passed. The temperature excursion occurred again only in the second stage, this time reaching over 800°C. At the time of the excursion, the upper bed temperature was 80°C, and the lower bed temperature was only 36°C. Immediately after the temperature escursion occurred, the inlet air was shut off, and the bed was purged with nitrogen.

The carbon bed was valved out of the rest of the off-gas system so that test startup could continue while startup and operation of the carbon bed was resolved. Again, the 1.5-mm Mersorb carbon was replaced with fresh carbon procured from NUCON and installed in the carbon bed by January 20, partway through the 2.25 AAR test. The replacement carbon bed depths were shorter, at 1 in., 2 in., and 9 in., than the original depths.

The cause of this temperature excursion appears to still be related to the use of the external wall heater during preheating, perhaps in combination with a temperature spike from heat of water sorption.

4.10.7.3 Resolutions of Carbon Bed Temperature Excursions. The carbon bed was successfully placed on line on January 20 by preheating to above the dew point of the off-gas (about 70°C) with preheated (90 to 95°C) air bled into the carbon bed. The air was preheated using a temporary air heater, so the preheat was done using a heated air stream that was completely separate from the calciner off-gas that continued to operate during the 2.25 AAR test while the carbon bed was preheated. After the bed was preheated to a temperature above 70°C, the carbon bed was valved into the off-gas system so that calciner off-gas from the staged combustor, partial quench, and reheater passed through the bed. A brief temperature spike of about 30°C occurred right after the bed was placed on-line, but the temperature then dropped back and continued along the previous heat-up curve. This temperature spike was most likely due to heat of sorption as gaseous water in the calciner off-gas was sorbed. The temperature spike was of short duration and rapidly dropped after the sorbed water in the carbon reached an equilibrium with the gaseous water in the off-gas.

Implications of carbon bed temperature excursions on mixed waste operations are significant, because they could cause process upsets, downtime, and frequent carbon bed replacements, with associated delays in process operations, costs, and waste generation. However, the operating experience of the calcination test, and vendor experience, indicate that such temperature excursions can be prevented by appropriate startup procedures. Most important, preheating using external wall heaters should be

avoided. Maintaining a reasonably high gas flow rate through the carbon bed during startup is also important, so that if hot spots occur due to exothermic sorption of off-gas species, the carbon is cooled by the sweep of gas through the bed.

Preheating the carbon bed is probably not necessary. Without preheating, flowing hot moist off-gas through the carbon bed would certainly cause condensation of moisture. Other condensible or water-soluble gas species, if present, would also tend to condense or be dissolved into the condensed water. Condensed water or other condensed/dissolved species would interfere with Hg sorption during the time that the bed temperature is cool enough to allow liquid water. After the bed temperature exceeds the gas dewpoint, the water and dissolved species such as HNO_3 should evaporate, leaving only the level of sorbed water on the carbon in equilibrium with the concentration of water in the off-gas.

If allowing the carbon to become wetted during startup is not desired, the carbon can be preheated using preheated air until the carbon temperature exceeds the dewpoint of water in the off-gas. In this scenario (which was done during the third startup in the calcination test), a temperature spike is certain to occur when the gas flow is switched to the moisture-laden off-gas and exothermic water sorption occurs until the amount of sorbed water equilibriates with the off-gas moisture content. The height of this spike can be controlled below temperatures that initiate oxidation by maintaining a relatively high gas flow rate to cool the carbon, and by slowly increasing the moisture content of the gas flow instead of rapidly switching from a low-moisture gas to a high-moisture gas.

While not present in the fluidized bed test facility because of location of the CEMS, an operating facility should be designed so that a CO monitor located downstream of the carbon bed (used for regulatory emissions monitoring) can also indicate, along with bed temperature sensors, whether bed oxidation begins to occur. While bed temperature sensors may not always quickly detect local hot spots, a sensitive CO monitor should be able to detect a step-change increase in off-gas CO levels that could be caused by partial oxidation of carbon or organic compounds sorbed on the carbon. While a CO step-change detected by the CO monitor may also be caused by upsets of the upstream combustion process, operators should also consider, in the event of a CO concentration step-change, the possibility of a carbon bed temperature excursion.

In the event of a temperature excursion in an operating facility, the bed should be bypassed from the process gas and purged with an inert gas such as nitrogen. The nitrogen would both cool the bed and eliminate oxygen in the off-gas. While species such as sorbed NO_2 or HNO_3 may continue to provide a source of oxygen, the calcination test results that show no detectable NO_3 in the carbon bed samples indicate that such oxidizer species would not sorb in large amounts.

5. EVALUATION OF RESULTS

5.1 High-Temperature Flowsheet Assessment

The specific and measurable test objectives designed to meet SBW Technology Plan needs are listed in Table 5.1-1 in conjunction with the quantifiable parameters and measurement methods that will be used to accomplish these objectives.

Table 5.1-1. Comparison of SBW calcination pilot-plant test results with test objectives.

Objective Statement	Quantifiable Objective Target or Criteria	Test Results
Verify feasibility of the MACT-Upgrade 600°C flowsheet chemistry for Tank 180 simulant waste with addition of ANN: 1. 50-hr COT with feed @ AAR of 2.25:1 2. 40-hr COT with feed @ AAR of 1.75:1	• 50 hrs continuous operation at an average feed rate of 5 L/hr blended feed • Less than 5 wt% bed agglomeration, with no particles greater than 5 mm diameter. • Less than 3 nozzle plugs per hr on anti-bearding feed nozzles • Uniform temperature distribution in bed with no greater than ±20ºC axial temperature variation in the bed • Distributor and bed pressure drop not to exceed 25% of starting conditions • Steady-state MMPD of bed 400-550 μm • Steady-state MMPD of fines 40-75 μm • Fines generation <50% rate of bed weight buildup rate.	Met – System operated 100 hrs at an average blended feed rate of 5.7 L/hr. Met – Agglomerates were 0.44 wt% of bed for 2.25 AAR and 0.8 to 2 wt% for 1.75 AAR . Partially Met – Nozzle plugging was infrequent during the 2.25 AAR test, but was up to 6 plugs per hr for part of the 1.75 AAR test. The plugs were readily removed with acid flushing. Met – Bed temperatures were generally within 10°C. The bottom thermocouple (TC#2) dropped by up to 30°C during portions of the run but was corrected with increased fluidizing air. TC#6 dropped by as much as 20°C at times, but this was apparently due to feed spray buildup on the TC. Not Met – Bed pressure drop met the criteria, but the distributor pressure drop increased from 12 inch w.c. at the start of the test to 56 inch w.c. by the end of the test due to increases in the fluidizing air flow from 0.11 to 0.27 m/s during the test. Met – Particle size was controlled at about 420 to 440μm Not met – Fines size median was about 10 μm Met – Product to fines mass ratios were much better than previous high-temperature calcination tests at 5.1 for the 2.25 AAR test and 2.8 for the 1.75 AAR test.
Product and fines chemical characteristics: 1. Produce a non-agglomerating bed product and fines fraction	• <3 wt% nitrate in bed product • <5 wt% nitrate in fines particles • <10 wt% carbonate in bed product • <1 wt% organic in bed product	Not Met for 2.25 AAR – The nitrate in the final 2.25 AAR bed product was 3.1 wt%, which was barely over the test objective. Met for 1.75 AAR – The nitrate in the final bed product was 2.65%. Met – The final cyclone fines nitrate was 4.7% for the 2.25 AAR test and 3.6% for the 1.75 AAR test.

Table 5.1-1. (continued).

Objective Statement	Quantifiable Objective Target or Criteria	Test Results
2. Produce a non-hygroscopic bed product and fines mixture for acceptable storage 3. Produce a pneumatically retrievable bed product and fines mixture 4. Produce acceptable bulk and true density 5. Minimize particle sintering potential 6. Produce $NaAlO_2$ constituent phase rather than carbonate, nitrate or hydroxide 7. Maximize product to fines ratio	• Product bulk density 1.2–1.4 g/cm^3	Not met – Product bulk density was only 0.92 g/cm^3. This agrees well with the bulk density of 1.0 g/cm^3 from a previous 3.1 AAR test of WM-180 simulant at INTEC.
	• Particle density 2.0-3.5 g/cm^3	Met – Particle density was 2.5 to 2.8 g/cm^3 for cyclone fines and 2.8 to 3.7 g/cm^3 for bed product.
	• Low product TIC/TOC content	Met – Total Inorganic carbon (TIC) analysis of the final beds indicated no detectable inorganic carbon as carbonates. Met – Total Organic Carbon (TOC) analysis of the final bed product showed insignificant amounts of organics.
	• 50 wt% Na and $NaAlO_2$	Not Met for 2.25 AAR – Total $NaAlO_2$+$KAlO_2$ was calculated to be 46.3 wt%. Met for 1.75 AAR – Total $NaAlO_2$+$KAlO_2$ was 54.9 wt% Total Na in the final product was 13.4 wt% for the 2.25 AAR test and 14.4 wt% for the 1.75 AAR test. Sodium nitrate in the final product was 4.26% for the 2.25 AAR test and 5.20% for the 1.75 AAR test.
	• P/F mass ratio > 1 desirable to minimize scrub recycle and maximize the density (minimize the volume) of blended calcine	Met – Product to fines mass ratios were much better than previous high-temperature calcination tests at 5.1 for the 2.25 AAR test and 2.8 for the 1.75 AAR test. Previous high-temperature tests at the INTEC pilot plants and NWCF have had a P/F ratio of only about 1.
Produce calcine and fines product that is soluble in nitric acid	• >98 wt% solubility in nitric acid scrub-solution	Met – Undissolved solids in the scrub was only 670 mg/L, indicating that the fines were soluble in the scrub.
Demonstrate acceptable material balance closure for major and minor constituents	• Material balance closure of ±10% for major constituents (Al, Na, K)	Met – Overall recovery was 91% for Al, and 104% for Na.
	• Material balance closure of ±30% for minor constituents (Cl, F, SO^{2-}, PO_4^{3-}, etc.)	Met – Recovery for other constituents ranged from 86 to 124%, except for Pb recovery being low at only 58%.
Demonstrate off-gas particulate cleaning comparable to NWCF cyclone and scrub system	• Combined fines removal efficiency of 99.9%	Nearly all the fines were removed by the cyclone and the scrub within the accuracy of the material balance, and only a light dusting was found downstream of the scrubber demister. The amount was too small too be quantified.

5.2 NWCF Throughput Assessment

A throughput assessment for the Calciner with MACT Upgrade was prepared in FY-03. This assessment determined that for an AAR of 2.25, calcination of all of the SBW would require almost 4 years (EDF-3212). The historical average feed rate for the NWCF was determined to be 182 gph, and the average on-stream efficiency to be 73.1%. The minimum turnaround time between major campaigns in the NWCF was 273 days.

The results of the calciner pilot-plant tests at SAIC were favorable, and indicate that (a) blends with an AAR of 1.75 are feasible, (b) an improved cyclone design can significantly reduce carryover to the scrub, and (c) use of ANN with a concentration of 2.3 to 2.4 molar Al instead of 2.2 molar Al greatly improves blend performance.

The high-temperature SBW/ANN blends generate a large amount of very fine particulate, which is not removed effectively by the existing NWCF cyclone. The fines size distribution measured during the WM-180/ANN tests showed that about one-half of the fines were less than 12 μm. The removal efficiency for the NWCF cyclone was calculated to be only 65% during trial of SBW/ANN at 600°C at the NWCF in 2000, and this resulted in a scrub recycle rate of 20 vol% of the blended feed. An improved cyclone might be expected to reduce solids carryover to the scrub such that scrub recycle could be reduced by at least half, to 10% of the blended feed. With these improvements in blend AAR and scrub recycle, the SBW waste can be calcined in 3 years, as shown in Table 5.2-1, assuming a calciner on-stream efficiency of 73.1% and total turnaround time of 273 days. The Calcination with MACT Upgrade alternative therefore could meet the requirement to remove all the waste from the Tank Farm by 2012.

Table 5.2-1. Projected campaign length (including turnaround) for improved AAR and modified cyclone.

	Feed rate (gph)	Campaign Length[a]			
		Al/Na+K Ratio of 2.25	Scrub Recycle Reduced from 20% to 10%	Al/Na+K Ratio of 1.75	Al/Na+K Ratio of 1.75 and 10% Scrub Recycle
Ratio blended feed to waste[b]		3.37 L/L	3.00 L/L	2.84 L/L	2.53 L/L
Expected campaign average feed rate	182	3.8 yr	3.4 yr	3.3 yr	3.0 yr
NWCF design feed rate	214	3.3 yr	3.0 yr	2.9 yr	2.7 yr
Maximum historical sustained feed rate	223	3.2 yr	2.9 yr	2.8 yr	2.6 yr

a. Campaign lengths are based on the historical on-stream efficiency of 73.1% and the minimum historical campaign turnaround time of 273 days (EDF-3212).

b. Waste Volume is 1,061,500 gal per campaign, M. Barnes projection updated in FY-04.

5.3 Chloride and Volatile Fluoride Control

Table 5.3-1 summarizes how the test accomplished chloride and fluoride control objectives. A chloride retention of better than 50% in the calcine solids is the general criterion for assessing the viability of a calciner flowsheet. Chloride retention in the calcined solids has generally been quite good for high-temperature calcinations, both in the pilot plants and the NWCF. This is likely because the sodium and potassium nitrates decompose to oxides, which will readily react with chloride in the off-gas

to form NaCl and KCl. Therefore, chloride did not build up in the scrub during high-temperature trial tests at the NWCF, and, in fact, the chloride concentration in the scrub decreased after the temperature was increased from 500°C to 600°C at the start of the high-temperature test in 1999 (Woods 2001).

A small amount of chloride will still volatilize out of the scrub as HCl, but this does not cause corrosion in the NWCF, where all of the streams are so high in nitrates that the stainless steel is passivated for chloride attack. The Calcination with MACT Upgrade will include a staged combustor to remove NO_X from the calciner off-gas. The off-gas systems downstream of the staged-combustor would then be exposed to chloride without the benefit of nitrates for passivation of the stainless steel. It was calculated that condensate in this portion of the line could be up to 0.3 molar HCl (EDF-2205). The Calciner MACT Upgrade design currently assumes that Hastelloy would be needed from the oxidizer through the carbon beds because of concern for chloride attack (EDF-2205). Gaseous HCl removal may also be required to meet the MACT standard for HCl/Cl_2 emissions. The current calciner MACT Upgrade assumes that the carbon bed employed for mercury control will also remove HCl, although at a lower efficiency.

Table 5.3-1. Comparison of chloride and fluoride test results with test objectives.

Objective Statement	Quantifiable Objective Target or Criteria	Test Results
Determine chloride and fluoride species behavior and fate and emissions rates	• Product and scrub solution analysis accuracy of ± 20 wt%	Met – The accuracy of the calcine and scrub analyses is evidenced by the good material balance closure.
	• Exhaust gas chloride emissions measurement with ± 10 vol.% accuracy	Met – HCl emissions averaged less than 1 ppmv due to the low levels. The measurement accuracy was within ±10% of the analyzer calibrated range.
	• Chloride retention in calcine solids >50%	Met – Chloride retention in the calcine solids was 57% for the combined test, even though no additional calcium nitrate was added to the feed to enhance chloride retention.
	• Volatile Flouride Carryover <1%	Met – All fluoride collected in the scrub could be attributed to carryover as CaF_2, with calcine fines and no volatile fluoride collected in the scrub. The overall fluoride balance was only 87%, indicating that some fluoride may have escaped past the scrub system and carbon bed; however, the aluminum-to-fluoride ratio was >400 in the feed, scrub, and calcine, so any fluoride lost would have had sufficient Al for complexing.

5.4 MACT Upgrade Design Feasibility

5.4.1 Unburned Hydrocarbon Control

Results from the calcination tests indicate that staged combustion can easily meet MACT requirements for CO emissions. During testing, CO was consistently measured at least one order of magnitude below the MACT limit of 100 ppm. In addition, staged combustion was also shown to be acceptable for reducing THC below the MACT limit of 10 ppm, typically by an order of magnitude. Measuring the DRE for principal organic hazardous constituents was beyond the scope of this test, but is recommended for inclusion in subsequent calcination flowsheet trials. Performance of the combustor against test objectives is summarized in Table 5.4-1.

Table 5.4-1. Comparison of staged combustor test results with test objectives.

Objective Statement	Quantifiable Objective Target or Criteria	Test Results
Establish steady-state target operating conditions for the calciner fluidized bed and staged combustor	• CO_2/CO/unburned hydrocarbon concentrations downstream of cyclone separator to match prescribed NWCF calciner effluent gas compositions • Off-gas temperature in freeboard zone and downstream of calciner • Maintain steady control of temperature in 1st, 2nd, and 3rd stage of staged combustor • Measure concentration of CO_2/CO/O_2/ unburned hydrocarbons in gas downstream of staged combustor	Met – CO_2, CO, THC, NO_x and O_2 off-gas concentrations exiting the pilot-scale calciner were matched well with historical NWCF off-gas measurements. Met – Calciner exit off-gas temperatures recorded in the trials match well with historical NWCF temperature measurements. Met – Control of temperatures in the 1st and 2nd stages of the combustor was exceptional during the trial. Reoxidation chamber temperature is not controlled directly, but was maintained within an acceptable range during the trial. Met – These gas species were measured.
Investigate pollutant destruction response to temperature, fuel loading, and oxygen concentrations 1. 20-hr parametric test	• Vary temperature ± 50 °C of target operating temperature in the 1st stage • Vary temperature ± 50 °C of target operating temperature in the 2nd stage • Vary fuel injection rate ± 20% of target set point in 1st stage	Not Met – Temperature optimization studies were not performed during this test due to lack of time. Instead, significant time was devoted to optimizing the fuel/O_2 level in the reduction chamber. Met – Extensive time was devoted to optimizing fuel/O_2 level in the reduction chamber. This study was conducted the week before to formal testing. During testing, additional experimentation was conducted to explore the effect of varying the excess natural gas flow to the reduction chamber. Based on these tests, it is recommended to operate with an equivalence ratio of 1.25 in order to balance efficient NO_x destruction with off-gas flow minimization.
Demonstrate steady staged combustor operating control and pollutant abatement efficiency: 1. NO_x reduction efficiency 2. PIC oxidation efficiency	>75% on-line steady state operating time within optimum specifications > 95% NO_x time-averaged removal (or <1,000 ppm in exhaust gas) < 10 ppm continuous THC in exhaust gas < 100 ppm continuous CO in exhaust gas	Met – Combustor operation was smooth and reliable during testing, except for maintaining a stable flame during process pressure fluctuations. Increasing the supply pressure of the natural gas header may alleviate the instability observed. Met – 90–98% NO_x destruction was achieved in the staged combustor. Met – THC destruction was up to 1 order of magnitude below the MACT limit of 10 ppmv. Met – CO destruction was generally one order of magnitude below the MACT limit of 100 ppmv.

5.4.2 Mercury Control

The performance of the tests against the test objectives for mercury control is provided in Table 5.4-2.

Table 5.4-2. Comparison of mercury control test results with test objectives.

Objective Statement	Quantifiable Objective Target or Criteria	Test Results
Determine mercury speciation and scrub removal efficiency	• Hg species removal efficiency as a function of scrub composition. 90% material balance closure	Met – Hg removal in scrub was 78.1%. Scrubbed Hg is presumed to be oxidized Hg species. Mass closure was 94%.
Determine mercury speciation and species reaction/conversion in staged combustor	• Hg species shift from oxidized to elemental mercury. 90% material balance closure	Met – Hg CEMs data confirm that mercury downstream of the scrubber and staged combustor is primarily elemental mercury. Most of the oxidized mercury is captured by the scrubber.
Determine mercury removal efficiency, mercury breakthrough, and migration through carbon bed	• Mercury removal efficiency of >99.9% or to MACT standard	Met – Hg removal efficiency for the calciner-MACT system exceeded 99.99% removal. The Hg mass balance closure (Hg measured in the output streams divided by input Hg) was very good at 0.94. Hg in the carbon did not reach the carbon sorption capacity, so Hg breakthrough was not determined.

6. CONCLUSIONS

The purpose of the 100-hr pilot-plant calcination tests was to simultaneously address as many of the Calciner MACT Upgrade data gaps as possible and to verify that the conceptual design for the off-gas cleaning system upgrade will meet the MACT standards. The scope of the tests was designed to close the high and medium risk issues identified in the *Sodium-Bearing Waste Treatment Applied Technology Plan* (INEEL/EXT-03-00477, June 2003).

In summary, the objectives of this research and testing activity were mapped to two main needs:

(1) Calciner Process Throughput Data Needs

- Verify that the recommended AAR of 2.25 is acceptable for a representative SBW feed, and if successful, determine whether an additional step reduction in AAR is feasible (AAR was reduced to 1.75 in the current tests)
- Verify that the fines generation rate for the high-temperature tests (a) is acceptable for the NWCF process and (b) exhibits a particle size distribution that can be efficiently captured by the NWCF cyclone
- Determine the potential impact of the fines loading on the NWCF quench/scrubber system with respect to undissolved solids buildup and scrub recycle rates
- Determine the disposition, fate, and behavior of volatile elements and compounds (namely, alkali species, chloride species, and mercury) during high-temperature calcination, including carryover into the off-gas system and adsorption by the quench/scrub system
- Project NWCF net waste processing rate, taking into consideration fines generation, particle and chloride capture in the scrub system, and scrub recycle rates.

(2) Calciner MACT Technology Implementation Needs

- Quantify THC/CO, NO/NO_2, and HCl/Cl emissions rates
- Verify retention of semi-volatile and low volatile metals
- Verify the design-basis performance of the multi-stage combustor for NO_x and THC/CO destruction
- Determine optimum operating conditions and control logic with respect to (a) eliminating THC/CO and NO_x and (b) minimizing the amount of natural gas, combustion air, and quench vapor required in the respective stages that collectively increase the staged combustor effluent gas volume
- Examine the performance of the combustor refractory, water spray quench, and burner equipment
- Determine the speciation of mercury leaving the staged combustor and entering the carbon bed
- Verify the design basis of the carbon bed for mercury removal, including packing diameter and depth, operating temperature, and capacity
- Determine the mass transfer zone of mercury (i.e., axial profile) in the carbon bed.

All of the main test objectives were met or exceeded, as discussed in Section 5. The DOE-owned fluidized-bed calcination pilot plant facility (built and operated by SAIC at the SAIC STAR Center) performed as designed. Pilot-plant operating conditions closely matched conditions at the NWCF, with emulation of the bed temperatures and off-gas gas conditions. Temperature conditions in the off-gas line

and cyclone separator were similar to the full-scale system. The off-gas quench and scrubber operating conditions also compared closely to the full-scale system. The main difference between the two systems, apart from the scale, is that a higher efficiency cyclone separator was installed in the pilot plant to determine whether a higher efficiency cyclone can improve fines collection, and hence reduce fines loading in the scrub system.

6.1 Summary of Calciner Test Results

There were no significant design issues to resolve during the 50-hr SO test performed to demonstrate system operability. The 50-hr test provided operating data for the staged combustor, while demonstrating operability of the calciner feed, calcination vessel, product collection, fines separation, and off-gas quench/scrubber. Aluminum nitrate solution was calcined during the SO test, which provided a starting bed for the 100-hr calcination tests.

The 100-hr high-temperature test was completed without any significant operating difficulties. Bed growth was consistent throughout the run, with steady bed fluidization. The mean particle size of the bed was stabilized at 400–450 μm with NAR levels of 600–800. Some nozzle plugging occurred during the tests; however, the plugs were readily cleared with the liquid orifice plunger or by short nozzle flushes with nitric acid. The nozzle plugs likely contributed to some agglomeration of the feed; however, the amount of agglomeration was considered minor and was not attributed to the high-temperature chemistry.

Fines generation was minimal; however, the particle size distribution of the fines exhibited a lower mean diameter than has been typically measured in previous 15-cm Enclosed Pilot Plant tests and high-temperature trials at the NWCF. The high-efficiency cyclone installed at the SAIC STAR Center pilot plant achieved higher fines removal efficiency, with minimal plugging during the 150 hr of total run time during the SO test and the 100-hr flowsheet verification tests. The pilot-plant tests may be summarized as follows.

Both the AAR 2.25 and AAR 1.75 flowsheets were successfully tested. A bed turnover of 97.9% was achieved for the first test (2.25 AAR). Bed turnover for the second test (1.75 AAR) was 98.5%. For the 100-hr run, a bed turnover of 99.9% was achieved. The high bed turnover is an indication that the bed chemistry of both flowsheets is acceptable. Nitrate decomposition was acceptable, with 3.2 wt% and 2.7 wt% in the bed product of the 2.25 AAR and 1.75 AAR tests, respectively. Nitrate levels in the fines were slightly higher, at 4.7 wt% for the AAR 2.25 flowsheet, and 3.8 wt% for the AAR 1.75 flowsheet. None of the levels are high enough to cause particle agglomeration in the bed or off-gas line. Bed composition and scrub solution concentration trends match bed turnover progression.

The product to fines ratio (P/F) for the two cases was 5.1 and 2.8 respectively. This exceeds all previous SBW high-temperature pilot-plant calcination tests in the 10-cm and 15-cm Enclosed Pilot-Plant Calciners. During the previous NWCF H4 high-temperature trial, a P/F of 1.0 was observed. Therefore, the P/F ratio for the current tests in comparably excellent.

A relatively low cyclone separation efficiency (43% fines capture) was lower than desired, and is attributed to the low particle size distribution (~12-μm diameter average). The amount of fines carried over to the scrub solution was approximately 20%. However, due to the relatively overall low rate of fines generation, the buildup of undissolved fines and soluble compounds was acceptable. At equilibrium, the scrubber undisolved solids (UDS) concentration approached 700 mg/L, which is well under the accepted limit of 10,000 mg/L. Chloride buildup in the scrub solutions level off at 690 mg/L, again under the accepted limit of 3,000 mg/L. The mercury concentration in the scrub climbed to 170 mg/L.

Mass closure was achieved for all major species, with accountability of Al, Na, Ca, and K being 91%, 104%, 98%, and 105%, respectively. Minor species mass closure was also exceptional, with 1.21% accountability of chlorine, 86% of fluorine, 109% of sulfate, and 117% of phosphate. Mercury accountability was 94% of the mass input. With the exception of mercury, the ratio of all cations in the bed and fines was consistent with the feed composition. This indicates negligible volatility of the alkali metal compounds.

Approximately 88% of the feed mercury and virtually 100% of the feed chloride were captured in the scrub solution. Although a trace amount of mercury was detected in the bed samples and cyclone fines, the majority of the mercury was volatilized and released from the fluidized bed. This result compares closely with NWCF operations and indicates similitude between the pilot plant and the full-scale system. Chloride, sulfate, and phosphate retention in the bed product and fines solids exceeded 50% of the input due to the sorption capacity of the alkaline solids. Most of the fluoride (~72% of the input mass) was captured and complexed in the scrub solution. These results reflect the observation that off-gas emissions of acid gases, specifically HCl, were less than 1 ppm.

6.1.1 Flowsheet Recommendations

The WM-180/ANN flowsheet performed acceptably at an AAR of 1.75, and therefore an AAR of 1.75 should be assumed for future NWCF throughput projections for SBW. No boron addition was necessary for calcination of the blend. No calcium nitrate above that which is already in the WM-180 waste (at only 36% of stoichiometric) was necessary to control chloride and fluoride volatility; however, additional calcium nitrate may still be required for calcination of the other SBW wastes that have higher sulfate content that may reduce the effect of calcium to suppress chloride and fluoride volatility. In addition, the use of ANN with a concentration of 2.3 to 2.4 molar Al instead of 2.2 molar Al greatly improves blend performance.

With these improvements in blend AAR and scrub recycle, and with modifications to the NWCF cyclone, the SBW waste can be calcined in 3 years, assuming a calciner on-stream efficiency of 73.1% and total turnaround time of 273 days. The Calcination with MACT treatment alternative therefore could meet the requirement to remove all the waste from the Tank Farm by 2012.

6.2 MACT Off-gas Treatment Results

6.2.1 Staged Combustor Performance

Performance of the pilot-plant MACT off-gas system demonstrated that CO, THC, Hg, and HCl/Cl_2 emissions can achieve the MACT standards. Less than 1 ppm HCl was measured in the off-gas at the staged combustor outlet. Chloride emissions were inherently controlled by the acidified off-gas quench and scrubber. A large portion of the chloride was retained by the bed and fines as chloride salts. Both calcium and sodium oxide are effective sorbents of acid gases, including chlorine and fluorine. The nitric solution effectively scrubbed all remaining chloride in the off-gas.

The staged combustor consistently reduced CO to <10 ppmv (dry, 7% O_2). This is well below the limit of 100 ppmv required by MACT. THC emissions were reduced to <5 ppmv (dry, 7% O_2) on average, which exceed the standard of 10 ppmv. A full-scale staged combustor will likely achieve even better control of staged combustor operating conditions with lower heat losses than were characteristic of the pilot-plant combustor. Reoxidation of the gas was shown to meet the MACT limits over a stage temperature of 840–920ºC).

Overall, the staged combustor achieved a NO_x reduction of 90–98% when the reducing stage equivalence ratio (φ) was 1.2 or higher. Above an equivalence ratio of 1.2, there is little additional NO_x removal. The staged combustor virtually eliminated all NO_2, which is thermally unstable at elevated temperatures in the combustor. Nitric oxide emissions averaged less than 300 ppmv for the tests. When the reducing stage was operated in oxidizing mode, emissions of NO_2 were negligible, while NO concentration rose to 900 ppmv. This result implies that NO_x reduction efficiency remains acceptable over a wide range of operating conditions; therefore, optimization may need to focus on maintaining THC and CO levels to the MACT standards.

6.2.2 Carbon Bed Performance

The sulfur-impregnated carbon bed helped achieve 99.99% removal of mercury during the 75-hr of on-line testing. Outlet mercury concentrations were <0.7 $\mu g/m^3$ (dry, 7% O_2), which exceeds the MACT standard of 45 $\mu g/m^3$. Due to the short length of operating time, mercury loading on the bed was only 1.6 wt%, which is significantly less than the theoretical capacity of about 20 wt%. Halogen compound and nitrate loading on the bed was low due to the relatively low concentrations of acid gases in the off-gas downstream of the off-gas scrubber. There was no apparent interference by NO, chloride, or other off-gas constituents. No ammonium was detected on the bed.

Although additional testing will be necessary to determine long-term effects of matrix components on the carbon bed, the current tests are encouraging and greatly reduce the design risks. A mass transfer zone (MTZ) of 3-4 inches in the bed was observed for test conditions with a gas velocity of 1.6 ft/s. Further testing will also help confirm the Calciner MACT design life for the carbon bed.

Electrical heating of the carbon bed vessel prompted ignition and burning of the carbon bed during startup prior to the tests. Additional testing of adsorption isotherms and bed startup conditions will help determine an acceptable method of reactor startup. Successful heatup of the carbon bed was achieved using air heated to 90–95°C.

6.3 Future Test Recommendations

Future testing should be performed using simulated WM-187 or other waste containing a high amount of simulated heel solids—preferably including zirconium sulfate as a solid simulant. This would determine whether the high amount of zirconium sulfate in the heel solids will detrimentally affect calcination chemistry, or whether the solids will pass through the calciner as inert solids. Future tests need not include calcium nitrate addition unless chloride and fluoride volatility becomes poor during the early tests. Testing at lower AARs than 1.75 should be attempted in the future to determine if further improvements in NWCF throughput can be achieved. Future blends for testing should be made up using concentrated ANN (2.3 to 2.4 molar) to improve performance of the blends.

Parametric testing of the staged combustor may help to optimize conditions further, with one possible objective being the minimization of the effluent volume. This would necessitate a parametric testing of the stage temperature in conjunction with variation in the reducing zone equivalence ratio and quench stage water spray. The pilot-plant system should be insulated to reduce heat loss, in order to better simulate a larger-scale unit.

Long-term testing of the carbon bed is needed to better establish the mass transfer zone, ultimate capacity (weight loading) of mercury, and co-adsorption of species over continuous operation. The affect of the off-gas matrix on the carbon bed quality should also be established with additional testing. The pilot-plant system provides an acceptable platform for testing.

The carbon bed heat-up method and start-up procedures need further evaluation before future testing. Although there is reasonable assurance that the bed can be safely started, additional testing will alleviate concerns pertaining to possible excursion in off-gas concentrations, exothermic vapor adsorption, or startup conditions that may cause a local temperature excursion.

6.4 Pilot-Plant Modification Recommendations

The following modifications to the calciner pilot-plant equipment and continuous emissions monitors are recommended for future testing, in order of decreasing importance:

6.4.1 Pilot-Plant Modifications

- The automatic control of the system vacuum at the staged combustor needs to be improved to reduce upsets in the main burner for the staged combustor, either by resizing the air jet supply valve and/or changing the system to control vacuum at the staged combustor rather than the calciner.

- The 1-inch port in the fluidized vessel containing TE-SR-1-6 should be plugged off flush with the inside vessel wall to prevent possible agglomerate collection.

- TC#6 should be moved out of the feed spray zone.

- The seal loop on the scrub tank should be lengthened and/or a small scrub bypass should be added from the pump to the loop to keep the loop filled and help flush out accumulated solids.

- An additional scrub cleanout port should be added to the off-gas elbow on top of the scrub tank.

- A better vibrator that operates at a lower frequency and has a larger force should be installed on the cyclone off-gas outlet to assist in dislodging the cyclone plugging that required frequent massaging with a ball peen hammer during the run.

- The quench flow control valve (TV-Q-1-1) was not well-suited for control of the quench liquor flow and may be oversized for the current quench nozzle/flow configurations.

- The quench vessel nozzle was not properly sized for the flows. A new nozzle that can properly atomize the quench liquid at lower flows while still having large enough openings to prevent plugging is desirable for more optimized operation of the quench vessel.

- Options are possible for carbon bed modifications to mitigate potential bed ignition during startup.

6.4.2 Continuous Emissions Monitors Recommendations

- Better vacuum ventilation is needed for the condensate collection carboys and the CEMS cabinets to prevent operator exposure to NO_x for the calciner configuration and NH_3 for the steam reformer configuration.

- There is a general need to improve autonomous operation and reliability of the CEMS units. A single operator is only able to repair or work on one of the systems at a time (either the Hg trains or CEMS 1 and 2).

- Additional solids filters are needed that are easily cleaned or replaced to keep solids from plugging the sample lines while sampling from between the cyclone and the quench tower, and/or redesign the sample probe to reduce solids entry (e.g., a reversed pitot tube). An air purge to allow periodic blowouts of the sample lines into the off-gas line is also desirable.

- Spare critical flow nozzles for Hg CEMS sample dilution should be obtained before testing, or the dilution system should be modified.

- Revision/writing of more comprehensive set of CEMS "Operating Procedures" to encompass pretest maintenance and cleaning activities—especially for the Hg analyzers—is warranted

- Additional 3-way valves and solenoids to CEMS 1 and CEMS 2 are needed to facilitate analyzer comparisons and instrument diagnostic capabilities. Alternatively, valve switching and sample locations should be documented on data sheets.

- Additional proximity sensors to sample port locations should be installed to automatically time stamp DACS data when new sampling configurations are employed during test operations. Alternatively, valve switching and sample locations should be documented on data sheets.

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Appendix A
Laboratory Analyses of Solids and Liquids

Table A-1. Miscellaneous sample analyses.

Test	Sample	Sample Date	COT	Measured values						
				pH	Specific gravity	Particle density, g/mL	Bulk density, g/mL	UDS, g/mL	Water solubility, wt%	CrO_4, wt%
WM-180 Simulant										
2.25 AAR	502A	1/19/04 12:30	0	0.5	1.30	---	---	---	---	---
	555A	1/21/04 20:00	50	1.47	1.31	---	---	---	---	---
1.75 AAR	563A	1/22/04 3:43	0	1.25	1.32	---	---	---	---	---
	603A	1/23/04 21:00	50	0.99	1.31	---	---	---	---	---
Bed Product										
2.25 AAR	575C	1/19/04 12:00	0	---	---	3.57	1.17	---	---	---
	576A	1/20/04 16:50	24	---	---	3.73	0.59	---	---	---
	606	1/21/04 18:50	50	---	---	2.87	0.89	---	48	0.004
1.75 AAR	604	1/22/04 19:43	24	---	---	2.91	0.56	---	---	---
	622	1/23/04 21:58	50	---	---	2.83	0.91	---	55	0.004
Cyclone Fines										
2.25 AAR	578A	1/20/04 16:50	24	---	---	2.52	0.34	---	---	---
	608	1/21/04 20:00	50	---	---	2.65	0.66	---	54	0.009
1.75 AAR	605A	1/22/04 19:43	24	---	---	2.82	0.36	---	---	---
	620	1/23/04 21:58	50	---	---	2.63	0.58	---	54	0.010
Scrub Solution										
2.25 AAR	565	1/19/04 12:00	0	0.36	1.13	---	---	50	---	---
	516	1/20/04 8:10	15.4	<0.1	1.11	---	---	---	---	---
	566	1/20/04 16:50	24	0.53	1.12	---	---	---	---	---
	536A	1/21/04 4:50	36	<0.1	1.14	---	---	---	---	---
	567	1/21/04 18:50	50	0.49	1.14	---	---	140	---	---
1.75 AAR	568A	1/22/04 7:30	12	<0.1	1.16	---	---	---	---	---
	583A	1/22/04 19:43	24	<0.1	1.18	---	---	---	---	---
	596A	1/23/04 8:10	36	<0.1	1.19	---	---	---	---	---
	616	1/23/04 2200	50	<0.1	1.21	---	---	670	---	---

[CMACT RFA 2-25.xls]MISC Table

Table A-2. Bed product sample analyses for cations.

					IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC
Sample	Date	Time	COT	Description	Al	B	Ca	Cr	Cs	Fe	Hg	K	Mg	Mn	Na	Ni	Pb	Re	Zn
First Test AAR 2.25					wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
575A	1/19	1200	0	Fusion Analysis; Starting Bed prior to feed initiation	10.9	0.391	0.026	0.003	0.000	0.023		<0.038	0.005	0.001		<0.001	<0.004	<1E-5	0.000
575B	1/19	1200	0	Fusion Analysis; Split Starting Bed prior to feed		0.370	0.023	0.004	0.001	0.017		<0.044	0.007	0.001		<0.001	<0.004	1.0E-04	0.006
575	1/19	1200	0	HF Digestion; Starting Bed prior to feed initiation	21.7	1.437	0.048	0.006	0.001	0.071		<0.039	0.010	0.010	1.2	0.005	<0.002	1.0E-04	0.006
575	1/19	1200	0	Aqua Regia Digestion; Starting Bed prior to feed	8.4	0.277	0.013	0.002	0.000	0.014		<0.009	0.003	0.001	0.1	0.002	0.002	4.0E-05	0.002
575	1/19	1200	0	HCl Digestion; Starting Bed prior to feed initiation	7.7	0.243	0.010	0.001	0.000	0.014		<0.008	0.002	0.001	0.1	0.002	<0.002	3.0E-05	0.001
575	1/19	1200	0	Nitric Acid Digestion: Starting Bed prior to feed	10.8	0.351	0.016	0.001	0.000	0.012		<0.01	0.003	0.001	0.1	0.002	<0.002	3.0E-05	0.005
576	1/20	1650	24	Fusion Analysis; Bed	27.0	0.107	0.263	0.023	0.020	0.129		1.044	0.062	0.149		0.004	<0.004	2.3E-02	0.015
576	1/20	1650	24	HF Digestion; Bed	26.6	1.512	0.266	0.030	0.056	0.188		1.169	0.065	0.155	10.8	0.017	0.018	3.1E-02	0.019
576	1/20	1650	24	Duplicate Aqua Regia Digestion; Bed	25.3	0.117	0.253	0.026	0.054	0.191		1.145	0.064	0.154	9.0	0.021	0.020	3.0E-02	0.017
576	1/20	1650	24	HCl Digestion; Bed	26.9	0.105	0.291	0.028	0.054	0.210		1.256	0.068	0.165	9.9	0.018	0.019	3.0E-02	0.020
576	1/20	1650	24	Nitric Acid Digestion; Bed	26.3	0.092	0.279	0.025	0.049	0.198		1.201	0.064	0.155	9.5	0.017	0.018	2.7E-02	0.018
576A	1/20	1650	24	Fusion Analysis; Split Bed	26.9	0.085	0.277	0.019	0.010	0.171		0.908	0.078	0.141		0.014	<0.004	2.1E-02	0.025
576A	1/20	1650	24	Aqua Regia Digestion, Split, Bed	24.4	0.151	0.253	0.030	0.061	0.152		1.167	0.056	0.137	9.4	0.015	0.016	3.3E-02	0.016
577	1/21	1850	50	Fusion Analysis; Bed	34.4	0.045	0.413	0.030	0.032	0.195		1.402	0.087	0.214		0.005	<0.005	2.9E-02	0.032
577	1/21	1850	50	Aqua Regia Digestion, Bed	34.7	0.050	0.422	0.035	0.069	0.269	1.7E-05	1.610	0.093	0.238	13.7	0.025	0.026	3.7E-02	0.029
577A	1/21	1850	50	Fusion Analysis; Split Bed	34.1	0.029	0.383	0.019	0.013	0.221		1.269	0.090	0.216		0.010	<0.004	2.8E-02	0.019
577A	1/21	1850	50	Aqua RegiaDigestion, Split, Bed	32.2	0.056	0.392	0.035	0.069	0.239		1.524	0.090	0.218	12.9	0.022	0.025	3.8E-02	0.025
Second Test AAR 1.75																			
604	1/22	1943	24	Fusion; Bed	34.1	0.023	0.450	0.025	0.013	0.267		1.212	0.109	0.260		0.012	<0.004	2.5E-02	0.027
604	1/22	1943	24	Aqua Regia Digestion, Bed	34.7	0.037	0.444	0.034	0.057	0.290		1.605	0.108	0.267	14.8	0.026	0.031	3.3E-02	0.028
614	1/23	2158	50	Fusion; Bed	35.0	0.020	0.453	0.016	0.020	0.254		1.292	0.113	0.265		0.018	<0.004	2.7E-02	0.028
614	1/23	2158	50	Aqua Regia Digestion, Bed	35.0	0.032	0.478	0.034	0.063	0.302	2.E-05	1.660	0.112	0.277	15.4	0.028	0.032	3.7E-02	0.028
621	1/23	2158	50	Fusion; Split Bed	34.7	0.027	0.447	0.015	0.020	0.258		1.328	0.102	0.246		0.011	<0.004	2.8E-02	0.017
621	1/23	2158	50	Aqua Regia Digestion, Bed	34.5	0.027	0.431	0.032	0.063	0.272	<1E-03	1.492	0.106	0.260	15.3	0.026	0.030	3.7E-02	0.027

[CMACT RFA 2-25.xls]Bed-elemental

Table A-3. Bed product anion and miscellaneous analyses.

					IRC	IRC	IRC	IRC	IRC	IRC	TRA	TRA	TRA	TRA	TRA	TRA	TRA	TRA
Sample	Date	Time	COT	Description	NO3	NO2	PO4	SO4	Cl	F	Particle Density	Bulk Density	TOC	TIC	NO3	NO2	Water Soluble	CrO4
First Test AAR 2.25					wt%	wt%	wt%	wt%	wt%	wt%	g/mL	g/mL	wt%	wt%	wt%	wt%	wt%	wt%
Bed	1/18	12:00	0	Virgin Bed	<27.7mg/L	<6.5mg/L	<12.4mg/L	<636mg/L	549.2mg/L	<2.9mg/L								
575B	1/19	1200	0	Fusion Analysis; Split Bed	0.01	0.00	<0.005	0.01	<0.002	<0.002								
575C	1/19	1200	0	Split Starting Bed	0.01	0.01	<0.004	0.01	<0.001	<0.001	3.57	1.17						
576	1/20	1650	24	Aqua Regia Digestion, Bed	2.74	0.12	0.36	1.06	0.15	<0.008								
576A	1/20	1650	24	Fusion Analysis; Split Bed							3.73	0.59						
576A	1/20	1650	24	Aqua Regia Digestion, Split, Bed	3.07	0.14	0.38	1.19	0.17	<0.009								
577	1/21	1850	50	Aqua Regia Digestion, Bed	3.04	0.18	0.57	1.31	0.17	<0.009								
577A	1/21	1850	50	Aqua RegiaDigestion, Split, Bed	3.18	0.19	0.63	1.26	0.18	<0.009								
606	1/21	1850	50	Split Bed							2.87	0.89	0.04	<0.2	3.13	0.18	48.00	0.004
Second Test AAR 1.75																		
604	1/22	1943	24	Aqua Regia Digestion, Bed	2.18	0.12	0.79	1.45	0.20	<0.008								
604A	1/22	1943	24	Split Bed							2.91	0.56						
614	1/23	2158	50	Aqua Regia Digestion, Bed	2.66	0.14	0.90	1.42	0.18	<0.009								
621	1/23	2158	50	Aqua Regia Digestion, Bed	2.64	0.11	0.44	1.34	0.18	<0.006								
623	1/23	2158	50	Split Bed							2.83	0.91	0.03	<0.2	2.44	0.13	55.00	0.004

[CMACT RFA 2-25.xls]Bed Anions

Table A-4. Cyclone fines sample analyses.

Sample	Date	Time	COT	Description	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC
					Al	B	Ca	Cr	Cs	Fe	Hg	K	Mg	Mn	Na	Ni	Pb	Re	Zn
First Test AAR 2.25					wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
578	1/20	1650	24	Fusion Analysis; Cyclone	34.8	0.08	0.67	0.06	0.07	0.23		2.16	0.09	0.17		0.01	0.01	0.05	0.02
578	1/20	1650	24	Aqua Regia Digestion, Cyclone	33.2	0.09	0.66	0.07	0.15	0.27		2.49	0.09	0.18	14.40	0.02	0.06	0.07	0.02
579	1/21	2000	50	Fusion Analysis; Cyclone	33.9	0.03	0.59	0.05	0.02	0.20		1.90	0.09	0.18		0.02	<0.004	0.05	0.02
579	1/21	2000	50	Aqua Regia Digestion, Cyclone	32.6	0.04	0.58	0.08	0.05	0.38		2.48	0.10	0.20	14.20	0.02	0.05	0.07	0.03
579A	1/21	2000	50	Fusion Analysis; Split Cyclone	33.5	0.02	0.57	0.05	0.03	0.26		2.00	0.09	0.19		0.01	0.01	0.05	0.02
579A	1/21	2000	50	Aqua Regia Digestion, split, Cyclone	33.1	0.23	0.58	0.07	0.15	0.29		2.52	0.09	0.19	14.60	0.02	0.05	0.07	0.03
Second Test AAR 1.75																			
605	1/22	1943	24	Fusion; Cyclone	34.3	<0.02	0.64	0.06	0.04	0.27		2.60	0.10	0.21		0.02	0.03	0.07	0.02
605	1/22	1943	24	Aqua Regia Digestion, Cyclone	34.2	0.03	0.68	0.09	0.15	0.31	1.E-04	3.39	0.10	0.21	14.30	0.03	0.08	0.09	0.03
615	1/23	2158	50	Fusion; Cyclone	32.6	<0.02	0.61	0.05	0.04	0.23		2.41	0.10	0.21		0.01	0.02	0.06	0.02
615	1/23	2158	50	Aqua Regia Digestion, Cyclone	32.3	0.03	0.63	0.08	0.07	0.28	5.E-05	3.15	0.10	0.21	14.30	0.02	0.07	0.09	0.03
617	1/23	2158	50	Fusion; Split Cyclone	33.2	<0.02	0.64	0.05	0.06	0.25		2.66	0.11	0.22		0.01	0.04	0.07	0.02
617	1/23	2158	50	Aqua Regia Digestion, Cyclone	33.0	0.02	0.59	0.08	0.13	0.27	4.E-05	2.90	0.10	0.21	14.50	0.03	0.07	0.09	0.03

Sample	Date	Time	COT	Description/Analysis	IRC	IRC	IRC	IRC	IRC	IRC	TRA	TRA	TRA	TRA	TRA	TRA	TRA	TRA	
					NO3	NO2	PO4	SO4	Cl	F	Particle Density	Bulk Density	TOC	TIC	NO3	NO2	Water Soluble	CrO4	
First Test AAR 2.25					wt%	wt%	wt%	wt%	wt%	wt%	g/mL	g/mL	wt%	wt%	wt%	wt%	wt%	wt%	
578	1/20	1650	24	Aqua Regia Digestion, Cyclone	1.72	0.22	0.52	2.38	0.37	<0.01									
578A	1/20	1650	24	Split Cyclone							2.52	0.34							
579	1/21	2000	50	Aqua Regia Digestion, Cyclone	4.70	0.34	0.52	2.56	0.35	<0.01									
579A	1/21	2000	50	Aqua Regia Digestion, split, Cyclone	4.60	0.33	0.54	2.44	0.37	<0.01									
608	1/21	2000	50	Split Cyclone							2.65	0.66	0.09	<0.2	4.24	0.31	54.00	0.01	
Second Test AAR 1.75																			
605	1/22	1943	24	Aqua Regia Digestion, Cyclone	1.32	0.18	0.86	3.10	0.47	<0.008									
605A	1/22	1943	24	Split Cyclone							2.82	0.36							
615	1/23	2158	50	Aqua Regia Digestion, Cyclone	3.54	0.35	0.28	2.96	0.51	0.13									
617	1/23	2158	50	Aqua Regia Digestion, Cyclone	3.79	0.31	0.77	3.06	0.47	<0.008									
620	1/23	2158	50	Split Cyclone							2.63	0.58	0.08	<0.2	3.81	0.30	54.00	0.01	

[CMACT RFA 2-25.xls]Cyclone-elemental-Anions

Table A-5. Simulant and ANN sample analyses.

					IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC
Sample	Date	Time	COT	Description	Al	B	Ca	Cr	Cs	Fe	K	Mg	Mn	Na	Ni	Pb	Re	S	Zn
					mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
First Test AAR 2.25																			
Feed 1A	1/15	12:00	0	WM-180 simulant	17035.7	109.0	1643.2	146.0	399.0	998.3	7450.4	307.0	764.7	52352	76.1	251.0	195.2		67.9
Feed 1B	1/15	12:00	0	WM-180 simulant	17137.7	110.1	1649.8	144.8	404.0	1000.3	7312.6	311.8	759.3	52046	78.1	252.3	198.3		66.2
ANN-1A	1/15	12:00	0	ANN	63246.2	<0.03	20.7	0.8	<0.03	13.6	2.3	0.4	0.7	342.5	1.7	0.4	14.6		11.3
ANN-1B	1/15	12:00	0	ANN	63623.6	<0.03	20.4	0.8	<0.03	13.7	3.1	0.4	0.7	339.7	1.7	0.5	14.6		11.4
ANN-2A	1/15	12:00	0	Split of ANN-1A; ANN	67959.1	<0.03	18.4	0.4	<0.03	12.0	3.2	0.4	0.7	317.6	1.6	0.5	16.0		10.8
ANN-2B	1/15	12:00	0	Split of ANN-1B; ANN	67469.4	<0.03	18.1	0.4	<0.03	11.6	2.1	0.3	0.6	308.0	1.5	0.4	15.5		10.6
502A	1/19	1230	0	Start composite feed A	44910.0	40.8	686.8	57.4	111.7	383.0	81.3	2915.3	130.1	308.4	2E+04	33.8	56.0	52.0	36.1
555A	1/21	2000	0	End composite feed blen	45127.5	41.1	686.1	57.3	150.7	383.2	82.3	2822.5	129.6	307.6	2E+04	33.8	54.8	68.1	35.6
Second Test AAR 1.75																			
563A	1/22	343	0	Start composite feed A	46062.5	46.5	726.3	63.8	171.6	408.4	93.6	3163.0	144.5	345.6	21762	37.4	67.4	77.4	37.9
603A	1/23	2100	0	End composite feed B	46167.5	44.5	763.6	64.3	169.3	426.8	94.1	3226.3	144.8	345.0	21782	37.6	67.9	79.7	38.1

					IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC				
Sample	Date	Time	COT	Description	NO3	NO2	PO4	SO4	Cl	F	pH	SpGr	UDS	TIC	TOC				
First Test AAR 2.25					mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		gm/mL	mg/L	mg/L	mg/L				
Feed 1A	1/15	12:00	0	WM-180 simulant	175127.7	<8.86	1575.6	4007.8	598.0	216.4	<0.21	1.25							
Feed 1B	1/15	12:00	0	WM-180 simulant	189284.7	<8.86	2291.1	4449.9	651.0	179.8	<0.21	1.24							
ANN-1A	1/15	12:00	0	ANN	232085.9	29.0	<12.74	62.9	<7.55	<3.05	0.93	1.34							
ANN-1B	1/15	12:00	0	ANN	272235.4	26.1	<12.74	45.9	<7.55	<3.05	0.96	1.34							
ANN-2A	1/15	12:00	0	Split of ANN-1A; ANN	326540.1	38.0	<12.74	45.0	<7.55	<3.05	0.81	1.36							
ANN-2B	1/15	12:00	0	Split of ANN-1B; ANN	261876.7	28.9	<12.74	38.1	<7.55	<3.05	0.79	1.35							
502A	1/19	1230	0	Start composite feed A	341411.1	354.5	1836.9	2342.4	142.2	114.1	0.50	1.30		1.93	59.26				
555A	1/21	2000	0	End composite feed blen	338150.4	236.8	1683.2	2320.4	138.5	103.3	1.47	1.31		1.97	60.55				
UDS-1A	1/15	12:00	0	WM-180 simulant									1301						
UDS-1B	1/15	12:00	0	WM-180 simulant									1233						
Second Test AAR 1.75																			
563A	1/22	343	0	Start composite feed A	358042.0	400.9	1767.6	2560.4	202.3	99.1	1.25	1.32		1.31	64.17				
603A	1/23	2100	0	End composite feed B	392999.6	253.4	1734.6	2583.1	176.3	99.9	0.99	1.31		3.47	61.97				

[CMACT RFA 2-25.xls]Feed-Elemental-Anions

Table A-6. Scrub solution sample analyses for cations.

					IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC
Sample	Date	Time	COT	Description	Al	B	Ca	Cr	Cs	Fe	Hg	K	Mg	Mn	Na	Ni	Pb	Re	Zn
First Test AAR 2.25					mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
501A	19-Jan	1200	0	Scrub							6E-6 wt%								
501B	19-Jan	1200	0	Split Scrub	585.0	53.5	1.5	3.3	0.0	17.5	0.1	<0.964	0.2	0.3	5.9	2.3	<0.07	0.0	1.1
565	19-Jan	1200	0	Split Scrub	452.5	50.4	1.4	3.4	0.0	16.5	<0.049	<0.964	0.3	0.4	6.0	2.2	<2.4	0.0	3.0
516	20-Jan	810	15.4	Scrubber Blowdown				9.2	18.9				10.9	23.5	1611.1	5.1	5.8	7.9	3.0
516A	20-Jan	850	15.4	Split Scrubber Blowdown Sa	4627.5	90.7	74.6	9.1	18.9	54.4	18.7	286.5	10.8	23.3		5.0	5.5	7.8	4.1
566	20-Jan	1650	24	Scrub	6480.0	77.5	122.3	13.3	27.1	67.6	34.3	443.8	16.5	34.6	2676.8	6.3	9.7	12.0	7.7
536A	21-Jan	450	36	Scrub Samples	9547.5	69.9	177.9	20.0	19.7	87.3	56.4	777.8	22.7	49.4	4263.8	8.1	15.0	21.5	7.4
567	21-Jan	1850	50	Scrub	14070	72.5	249.3	33.0	70.3	124.5	82.0	1115.0	40.1	77.3	6177.3	11.8	24.4	28.6	13.1
567A	21-Jan	1850	50	Split Scrub		72.5	245.8	33.2		126.3	82.6	1191.0	40.4	77.8		11.8	25.1		12.3
Second Test AAR 1.75																			
568A	22-Jan	730	12	Scrubber Blowdown Sample	86.0	340.6	38.6	116.1	162.4	174.2	1719.0	50.6	101.9	8495	15.2	34.8	45.7	45.7	14.1
583A	22-Jan	1943	24	Scrub	80.0	422.8	46.4	147.3	194.1	141.0	2169.8	60.2	121.4	10150	17.7	43.6	61.2	61.2	16.5
596A	23-Jan	810	36	Scrub	75.5	490.7	54.8	174.3	221.1	160.0	2572.3	71.3	143.8	11635	20.5	52.5	71.4	71.4	19.2
616	23-Jan	2200	50	Final Scrub	78.0	591.8	65.5	211.4	260.6	178.9	3029.0	84.1	169.7	13560	23.7	64.3	84.2	84.2	22.4
616A	23-Jan	2200	50	Split Final Scrub															
616B	23-Jan	2200	50	Split Final Scrub	74.5	578.6	64.9	211.3	261.6	175.6	3076.5	83.8	168.8	13525	23.6	63.4	84.4	84.4	22.6
624 Filtrate	27-Jan	NA	50	Scrub Rinsate, solids sludge	79.0	642.8	70.3	226.1	261.8	180.0	3386.5	309.4	184.6	14770	25.5	67.4	90.0	90.0	25.0
				Units	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
624A (Soli	27-Jan	NA	50	Fusion; Duplicate Scrub Rin	0.1	0.2	0.1	<2E-5	0.5		0.3	0.04	0.1		0.1	<0.004	0.0	0.004	0.01
624A (Soli	27-Jan	NA	50	Aqua Regia Digestion, Dupl	0.1	0.1	0.4	0.01	1.6	2.8	0.3	0.02	0.1	0.9	0.3	<0.002	0.0	0.01	0.01

[CMACT RFA 2-25.xls]Scrub-elemental-anion

Table A-7. Scrub solution anion and miscellaneous analyses.

					TRA	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	TRA	TRA	TRA	TRA
Sample	Date	Time	COT	Description	NH4	NO3	NO2	PO4	SO4	Cl	F	pH	SpG	TOC	TOC	NO3-	NO2-	UDS
First Test AAR 2.25					mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		gm/m	mg/L	wt%	mg/L	wt%	mg/L
501A	19-Jan	1200	0	Scrub										12.0	0.0	171326		50
501B	19-Jan	1200	0	Split Scrub		251577	<5.9	<28.8	109	273	<9.186							
565	19-Jan	1200	0	Split Scrub		228774	<5.9	<28.8	89	270	<9.186	0	1	11.9				
516	20-Jan	810	15.4	Scrubber Blowdown Sample		197335	84.9	15.9	479	126	58	<0.1	1					
516A	20-Jan	850	15.4	Split Scrubber Blowdown Sample		195765	97.6	17.5	489	121	52			35.1				
566	20-Jan	1650	24	Scrub		205563	<5.9	323	645	149	65	1	1	38.8				
536A	21-Jan	450	36	Scrub Samples		222319	<5.9	160	874	283	90	<0.1	1	40.5				
567	21-Jan	1850	50	Scrub		205316	<5.9	493	1286	311	112	0	1	50.2	0.0	189870		140
567A	21-Jan	1850	50	Split Scrub		203182	<5.9	487	1275	331	119							
Second Test AAR 1.75																		
568A	22-Jan	730	12	Scrubber Blowdown, pre-blowdown		210013	<5.9	664	1594	398	133	<0.1	1	61.8				
583A	22-Jan	1943	24	Scrub		238230	<5.9	1125	1876	583	150	<0.1	1	76.6				
596A	23-Jan	810	36	Scrub		224680	<5.9	1211	2184	624	160	<0.1	1	79.8				
616	23-Jan	2200	50	Final Scrub	4.E-04	245677	<5.9	1284	2462	576	141	<0.1	1	93.4				
616A	23-Jan	2200	50	Split Final Scrub											0.0	224520	<0.0199	670
616B	23-Jan	2200	50	Split Final Scrub		254610	<5.9	1264	2554	507	146			91.4				
624 (liquid	27-Jan	NA	50	Scrub Rinsate, liquid	4.E-05	285221	<5.9	1237	2617	443	158							
624 (Solid)	27-Jan	NA	50	Duplicate Scrub solids												226316	<0.0199	212
624 (Solid)	27-Jan	NA	50	Aqua Regia Dig. solids		7	<1E-3	0.03	0.02	0.02	0.01							
624	27-Jan	NA	50	Split Scrub solids sludge										12				

[CMACT RFA 2-25.xls]Scrub-elemental-anion

Table A-8. CEMS condensate sample analyses.

Sample	Date	Time	COT	Description	IRC	IRC	IRC	IRC	IRC	IRC
					NO3	NO2	PO4	SO4	Cl	F
First Test AAR 2.25					wt%	wt%	wt%	wt%	wt%	wt%
549	21-Jan	1850	50	CEMS I Condensate	165323.8	1465.1	<57.6	<58.511	<16.302	<18.371
550	21-Jan	1850	50	CEMS II Condensate	48.8	2.0	<0.576	2.4	1.0	1.1
Second Test AAR 1.75										
584	22-Jan	1943	24	CEMS I Condensate	151396.4	2868.1	<57600	<58511	<16302	<18371
585	22-Jan	1943	24	CEMS II Condensate	46.1	2.0	<0.576	0.4	0.8	1.2
610	23-Jan	2200	50	CEMS I Condensate	176008.3	2414.9	<57600	<58511	<16302	<18371
611	23-Jan	2200	50	CEMS II Condensate	166.3	1.2	<0.576	0.5	0.8	1.2

[CMACT RFA 2-25.xls]CEMS

Table A-9. Carbon bed sample analyses.

Sample	Date	Description	NH4	NO3	NO2	PO4	SO4	Cl	F	Hg	S
			wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
657	1/19	Virgin GAC Bed	2.E-05	<0.027	<0.006	0.048	2.677	0.027	<0.009	0.00001	12.807
657	1/19	2 leach Virgin GAC Bed					0.113	0.001			
657	1/19	3 leach Virgin GAC Bed					0.053	0.003			
627	1/26	Center top 1-inch bed face								0.45810	3.255
628	1/26	Annulus top 1-inch bed face								0.54440	2.756
629	1/26	Wall top 1-inch bed face								0.63580	10.954
629	1/26	Split 1 leach Wall top 1-inch bed face								0.6062	
629	1/26	Split 2 leachWall top 1-inch bed face								0.5281	
629	1/26	Split 3 leach Wall top 1-inch bed face								0.1207	
629	1/26	Dupe 1 leach Wall top 1-inch bed face								0.7343	
629	1/26	Dupe 2 leach Wall top 1-inch bed face								0.5299	
629	1/26	Dupe 3 leach Wall top 1-inch bed face								0.0943	
651	1/26	Composite of top 1-inch bed face samples	4.E-04	<0.027	<0.006	0.033	4.209	0.050	0.037		
651A	1/26	2 leach of Composite of top 1-inch bed face					0.244	0.010			
651A	1/26	3 -leach of Composite of top 1-inch bed face					0.068	0.007			
630	1/26	Center top 1-inch bed bottom plane								0.57480	12.022
631	1/26	Annulus top 1-inch bed bottom plane								0.30150	11.626
632	1/26	Wall top 1-inch bed bottom plane								0.11170	6.142
652	1/26	Composite of top 1-inch bed bottom plane samples	1.E-04	<0.027	<0.006	<0.027	3.257	0.034	0.035		
652A	1/26	2 leach of Composite of top 1-inch bed bottom plane					0.125	0.005			
652A	1/26	3 leach of Composite of top 1-inch bed bottom plane					0.045	0.005			
633	1/26	Center middle 2-inch bed face								0.04090	8.855
634	1/26	Annulus middle 2-inch bed face								0.07020	11.968
635	1/26	Wall middle 2-inch bed face								0.03370	11.864
653	1/26	Composite middle 2-inch bed face samples	1.E-04	<0.028	<0.006	<0.028	1.415	0.027	<0.009		
653A	1/26	2 leach of Composite middle 2-inch bed face					0.047	0.003			
653A	1/26	3 leach of Composite middle 2-inch bed face					0.018	0.004			

[CMACT RFA 2-25.xls]C Bed

Table A-9. Carbon bed sample analyses (continued).

Sample	Date	Description	NH4	NO3	NO2	PO4	SO4	Cl	F	Hg	S
			wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
636	1/26	Center middle 2-inch bed mid plane								0.02150	11.146
637	1/26	Annulus middle 2-inch bed mid plane								0.01830	11.143
638	1/26	Wall middle 2-inch bed mid plane								0.01280	10.345
639	1/26	Center middle 2-inch bottom plane								0.00505	13.401
640	1/26	Annulus middle 2-inch bottom plane								0.00975	11.777
641	1/26	Wall middle 2-inch bottom plane								0.00468	10.638
654	1/26	Composite middle 2-inch bottom plane	4.E-05	<0.025	<0.005	<0.025	1.195	0.014	<0.008		
654A	1/26	2 leach of Composite middle 2-inch bottom plane					0.036	0.002			
654A	1/26	3 leach of Composite middle 2-inch bottom plane					0.010	0.003			
642	1/26	Center lower 9-inch Bed Face								0.00247	10.455
643	1/26	Annulus lower 9-inch Bed Face								0.00248	9.455
644	1/26	Wall lower 9-inch Bed Face								0.00389	11.776
655	1/26	Composite lower 9-inch Bed Face	2.E-04	<0.023	<0.005	<0.024	1.520	0.012	<0.008		
655A	1/26	2 leach of Composite lower 9-inch Bed Face					0.061	0.002			
655A	1/26	3 leach of Composite lower 9-inch Bed Face					0.029	0.003			
645	1/26	Center lower 9-inch bed mid plane								0.00089	12.536
646	1/26	Annulus lower 9-inch bed mid plane								0.00055	12.966
647	1/26	Wall lower 9-inch bed mid plane								0.00065	13.229
648	1/26	Center lower 9-inch bottom plane								0.00005	11.686
648	1/26	Split 1 leachCenter lower 9-inch bottom plane								0.00021	
648	1/26	Split 2 leach Center lower 9-inch bottom plane								0.00026	
648	1/26	Split 3 leach Center lower 9-inch bottom plane								0.00011	
648	1/26	Dupe 1 leach Center lower 9-inch bottom plane								0.00012	
648	1/26	Dupe 2 leach Center lower 9-inch bottom plane								0.00016	
648	1/26	Dupe 3 leach Center lower 9-inch bottom plane								0.00005	
649	1/26	Annulus lower 9-inch bottom plane								0.00005	11.899
650	1/26	Wall lower 9-inch bottom plane								0.00005	9.986
656	1/26	Composite lower 9-inch bottom plane	8.E-05	<0.027	<0.006	<0.028	1.104	0.012	<0.009		
656A	1/26	2 leach of Composite lower 9-inch bottom plane					0.027	0.001			
656A	1/26	3 leach of Composite lower 9-inch bottom plane					0.008	0.003			

[CMACT RFA 2-25.xls]C Bed

Table A-10. Bed product sample analysis QA results.

					IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC
Sample	Date	Time	COT	Description	B	B	Ca	Ca	Cr	Cs	Cs	Fe	Fe	Hg	K	K	Mg	Mn	Ni	Pb	Re	Re	Zn
First Test AAR 2.25					%RPD	%Rec	%RPD	%Rec	%Rec	%Rec	%RPD	%RPD	%Rec	%RSD	%RPD	%Rec	%Rec	%Rec	%Rec	%Rec	%Rec	%RPD	%Rec
575A	1/19	1200	0	Fusion Analysis; Star	0.7		10.7					9.7											
576	1/20	1650	24	Fusion Analysis					100.8								101.9	108.0	97.4	107.0			105.8
576	1/20	1650	24	Aqua Regia Dig					106.8	95.1							114.8	108.1	100.0	111.1	104.0		107.3
576	1/20	1650	24	HF Digestion; Bed		88.9																	
576A	1/20	1650	24	Aqua Regia Digestio	0.7			0.1				0.5			1.0								
577	1/21	1850	50	Fusion Analysis; Bed										6.2									
577	1/21	1850	50	Aqua Regia Dig							0.2											1.1	
577A	1/21	1850	50	Fusion Analysis;Split				109.1								87.4							
Second Test AAR 1.75																							
604	1/22	1943	24	Aqua Regia Dig						103.4													
614	1/23	2158	50	Fusion; Bed						96.1													
614	1/23	2158	50	Aqua Regia Dig										12.0									
621	1/23	2158	50	Aqua Regia Dig				89.9					90.7										

[CMACT QA-QC 3-1.xls]Bed-elemental

Table A-11. Cyclone product sample analysis QA results.

Sample	Date	Time	COT	Description/Analysis	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC
					NO3	NO3	NO2	NO2	PO4	PO4	SO4	SO4	Cl	Cl	Cs	Hg	Re
First Test AAR 2.25					%RPD	%Rec	%RPD	%Rec	%RPD	%Rec	%RPD	%Rec	%RPD	%Rec	%RPD	%RSD	%RPD
578	1/20	1650	24	Fusion Analysis											1.70		1.40
578	1/20	1650	24	Aqua Regia Digestion,	2.50		0.50		9.10				1.20				
579	1/21	2000	50	Aqua Regia Digestion,	2.00						1.60						
Second Test AAR 1.75																	
605	1/22	1943	24	Aqua Regia Digestion												5.2	
615	1/23	2158	50	Aqua Regia Digestion,	2.30	97.80		96.30		92.90	6.60	103.80		100.80		4.4	
617	1/23	2158	50	Aqua Regia Digestion												2.8	

[CMACT QA-QC 3-1.xls]Cyclone-elemental-Anions

Table A-12. Feed blend sample analysis QA results.

					IRC	IRC	IRC
Sample	Date	Time	COT	Description	SpGr	TIC	TOC
First Test AAR 2.25					SD	RPD%	RPD%
502A	1/19	1230	0	Start composite feed A	0.001	Concentration too low to determine accurate RPD.	7.29
555A	1/21	2000	0	End composite feed blend	0.001		7.77
Second Test AAR 1.75							
563A	1/22	343	0	Start composite feed A	0.001		5.22
603A	1/23	2100	0	End composite feed B	0.003		6.38

[CMACT QA-QC 3-1.xls]Feed-Elemental-Anions

Table A-13. Scrub solution sample analysis QA results.

					IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC
Sample	Date	Time	COT	Description	Al	B	B	Ca	Cr	Cr	Cs	Fe	Fe	Hg	Hg	Hg	K	K
First Test AAR 2.25					%Rec	%RPD	% Rec	%RPD	%RPD	%Rec	%RPD	%RPD	%Rec	%RPD	%RSD	%Rec	%RPD	% Rec
501B	19-Jan	1200	0	Split Scrub					1.8						1.2			
516	20-Jan	810	15.4	Scrubber Blowdown														
565	19-Jan	1200	0	Split Scrub														
566	20-Jan	1650	24	Scrub												100.1		
536A	21-Jan	450	36	Scrub Samples		0.4		1.0				3.1						
567	21-Jan	1850	50	Scrub						105.1				1.3				
Second Test AAR 1.75																		
568A	22-Jan	730	12	Scrubber pre-blowdown														
583A	22-Jan	1943	24	Scrub	90.2		100.2											98.8
596A	23-Jan	810	36	Scrub		12.3		1.9				1.0					0.1	
616	23-Jan	2200	50	Final Scrub														
616B	23-Jan	2200	50	Split Final Scrub						107.6	0.5							
624 (Solid)	27-Jan	NA	50	Fusion; Duplicate solids					2.4									
624 (Solid)	27-Jan	NA	50	Aqua Regia Duplicate					1.7									
624A (Solid	28-Jan	NA	51	Aqua Regia Digestion, Dupl	91.7				0.6				104.2		2.9			

[CMACT QA-QC 3-1.xls]Scrub-elemental-anion

Table A-13. Scrub solution sample analysis QA results (continued).

					IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC	IRC
Sample	Date	Time	COT	Description	Mg	Mg	Mn	Mn	Na	Ni	Ni	Pb	Re	Zn	Zn	SpG	TOC
First Test AAR 2.25					%RPD	%Rec	%RPD	%Rec	%Rec	%RPD	%Rec	%Rec	%RPD	%RPD	%Rec	SD	%RPD
501B	19-Jan	1200	0	Split Scrub	2.2		1.4			1.1				0.5			
516	20-Jan	810	15.4	Scrubber Blowdown												0.001	7.8
565	19-Jan	1200	0	Split Scrub												0.003	20.0
566	20-Jan	1650	24	Scrub												0.002	5.1
536A	21-Jan	450	36	Scrub Samples												0.002	9.2
567	21-Jan	1850	50	Scrub		105.6		105.7			99.4	107.7			105.6	0.004	9.2
Second Test AAR 1.75																	
568A	22-Jan	730	12	Scrubber pre-blowdown												0.001	6.3
583A	22-Jan	1943	24	Scrub					97.4							0.002	6.3
596A	23-Jan	810	36	Scrub												0.001	1.6
616	23-Jan	2200	50	Final Scrub												0.001	4.7
616B	23-Jan	2200	50	Split Final Scrub		114.5		105			102.7	109.0	2.5		104.9	0.002	1.0
624 (Solid)	27-Jan	NA	50	Fusion; Duplicate solids	2.8		4.1			3.6				22.7			
624 (Solid)	27-Jan	NA	50	Aqua Regia Duplicate	0.6		1.2			2.1				4.1			
624A (Solic	28-Jan	NA	51	Aqua Regia Digestion, Dupl	1.4		2.6		98.1	2.6				4.8			

[CMACT QA-QC 3-1.xls]Scrub-elemental-anion

Table A-14. Percent recovery of the CEMS Condensate for the CMACT series.

Sample	Date	Time	COT	Description	IRC
					F
Second Test AAR 1.75					%Rec
585	22-Jan	1943	24	CEMS II Condensate	99.1

[CMACT QA-QC 3-1.xls]CEMS

Table A-15. Carbon bed samples for the CMACT test series.

Sample	Date	Description	SO4	Cl	Hg	S
			%RPD	%RPD	%RSD	%RPD
657	1/19	Virgin GAC Bed			5.5	
627	1/26	Center top 1-inch bed face			0.7	
628	1/26	Annulus top 1-inch bed face			1.0	
629	1/26	Wall top 1-inch bed face			2.0	0.500
629	1/26	Split 1 leach Wall top 1-inch bed face			0.6	
629	1/26	Split 2 leachWall top 1-inch bed face			0.8	
629	1/26	Split 3 leach Wall top 1-inch bed face			0.9	
629	1/26	Dupe 1 leach Wall top 1-inch bed face			0.6	
629	1/26	Dupe 2 leach Wall top 1-inch bed face			0.8	
629	1/26	Dupe 3 leach Wall top 1-inch bed face			0.7	
651A	1/26	3 -leach of Composite of top 1-inch bed face	4.100	4.700		
630	1/26	Center top 1-inch bed bottom plane			1.8	
631	1/26	Annulus top 1-inch bed bottom plane			1.5	
632	1/26	Wall top 1-inch bed bottom plane			1.0	
633	1/26	Center middle 2-inch bed face			0.8	
634	1/26	Annulus middle 2-inch bed face			0.9	
635	1/26	Wall middle 2-inch bed face			1.2	
636	1/26	Center middle 2-inch bed mid plane			1.3	
637	1/26	Annulus middle 2-inch bed mid plane			1.0	
638	1/26	Wall middle 2-inch bed mid plane			1.2	
639	1/26	Center middle 2-inch bottom plane			1.3	
640	1/26	Annulus middle 2-inch bottom plane			1.0	
641	1/26	Wall middle 2-inch bottom plane			1.3	
642	1/26	Center lower 9-inch Bed Face			1.2	
643	1/26	Annulus lower 9-inch Bed Face			1.3	
644	1/26	Wall lower 9-inch Bed Face			1.0	
645	1/26	Center lower 9-inch bed mid plane			2.0	
646	1/26	Annulus lower 9-inch bed mid plane			1.8	
647	1/26	Wall lower 9-inch bed mid plane			2.7	
648	1/26	Center lower 9-inch bottom plane			1.7	
648	1/26	Split 1 leachCenter lower 9-inch bottom plane			1.2	
648	1/26	Split 2 leach Center lower 9-inch bottom plane			1.7	
648	1/26	Split 3 leach Center lower 9-inch bottom plane			5.5	
648	1/26	Dupe 1 leach Center lower 9-inch bottom plane			7.2	
648	1/26	Dupe 2 leach Center lower 9-inch bottom plane			1.4	
648	1/26	Dupe 3 leach Center lower 9-inch bottom plane			5.0	
649	1/26	Annulus lower 9-inch bottom plane			5.3	
650	1/26	Wall lower 9-inch bottom plane			5.1	

[CMACT QA-QC 3-1.xls]C Bed