System Development And Automation - Task 1.1.10

Topical Report
October 1993 - January 1996

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Work Performed Under Contract No.: DE-AC21-93MC30171

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
Washington, DC

For

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
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1000 Independence Avenue
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Office of Fossil Energy
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P.O. Box 880
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1. System Development and Automation

This System Development and Automation Topical Report is submitted in accordance with Task 1.1.10 of the statement of work. It summarizes work performed under Tasks 1.1.6 through 1.1.9 of the statement of work.

2. System Development and Automation

2.1. Sensing and Monitoring Devices, and Control Methods

Development of advanced models and techniques to monitor and control key process parameters is crucial to robust, automated CEP operation. Specifications for methods, equipment, and procedures have been developed for QCEP™ reactor control strategies. These specifications are limited to the Q-CEP™ reactor only, which consists of the molten metal bath and its containment system. Key parameters to be monitored for reactor control include bath temperature, headspace temperature, bath composition, bath level, bath pressure, containment, tuyere injection, and visual observation. Other QCEP™ subsystems have been included to the extent that they may impact reactor control strategies. Commercial, off-the-shelf equipment has been utilized to the maximum extent possible. Emphasis has been placed on the use of non-invasive techniques in order to minimize both the potential for interruption in the flow of operations and potential delay opportunities for feedback to optimize process control. A list of vendors consulted by MMT for this effort is provided in Table 1.

Table 1
Vendors Contacted for Sensing and Monitoring Devices Studies.

Thermocouples: NANMAC Corporation Heraeus Sensor Heraeus Electro-Nite Hoskins HY-CAL Engineering	TV Camera J. M. Canty LENOX HITACHI IST Bass Electronics Metrovideo
Infrared Pyrometers Williamson Corporation IRCON Accufiber Mikron Omega Quantum Logic Corporation IMPAC	Ultrasonic Thermometry Thermosonics
IR Lightpipes Sapphire General Ruby and Sapphire Co. Crystal Systems Insaco Saphikon Valley Design Quartz glass Heraeus Amersil Fiber Optics Pro-Optical Technologies Schott CeramOptec	Analytical Extrel Fisons VTI Thermo Environmental Instruments
	Dust Loading Fireye Optimonitor Allen-Bradley Sensidyne MIE
	Spectroscopy American Holographics Ocean Optics Graseby ALG Hellma
High-Temperature Optical Fiber Thermometry Luxtron/ Accufiber	Level VEGA CASI Magnetron Dynavision Kay-Ray/Sensall
Suction Pyrometer John Zink NANMAC Corporation Land Combustion	

This report is submitted under Government Contract Number DE-AC21-93MC30171 and is releasable in accordance with the terms and conditions of that contract.

2.1.1. Bath Temperature

2.1.1.1. Requirements

The primary objective of the bath temperature control strategy is to keep the bath molten and above a minimum acceptable temperature. This minimum temperature depends on the liquidus temperature of the bath and on possible accretion growth effects. A secondary objective of the bath temperature control strategy is to minimize changes of the bath temperature and operate at the optimum temperature to minimize containment wear.

In general, temperature should be controlled to ± 50 °F. However, it may be important to be able to determine with a higher accuracy (e.g., ± 10 °F) if a low or high level limit has been reached.

The bath temperature is controlled by adjusting the power setting of the bath induction coil power supply. Closed-loop control is required, with the controlled variable being the bath temperature and the controller output the power supply setting. The primary concern is to obtain a continuous, accurate, and lag-free indication of the bath temperature.

2.1.1.2. Primary Sensing Method: IR Lightpipe

The infrared (IR) lightpipe sensor is an in-situ, continuous, lag-free, and non-invasive temperature sensing method to measure bath temperature. Unlike embedded thermocouples, this sensor is not affected by refractory wear. Bath temperature measurement using a lightpipe was first demonstrated at MMT during 10 lb unit run in May 1995, and was subsequently demonstrated in the 4-Ton demonstration Unit in June 1995. Since then, bath temperature sensing using a lightpipe has been successfully demonstrated in various MMT units.

The lightpipe provides a path for the IR radiation from the molten metal bath to a dual-wavelength pyrometer. The lightpipe is in direct contact with the bath, which prevents the changing intervening atmosphere from affecting the operation of the top-mounted, dual-wavelength pyrometer. A lightpipe is a solid rod of material with high IR transmission characteristics. Application of a lightpipe to CEP reactor control involves significant material science considerations including IR transmissivity, melting point, chemical stability, and coefficient of thermal expansion. Cost is also an important factor in the selection of the lightpipe material. After extensive consultations with various vendors, MMT developed a design compatible with CEP operations that is shown in Figure 1. One end of the lightpipe is in contact with the molten metal; the other end is outside of the containment system. IR emissions are collected by a reimaging lens or a terminated fiber optic cable and carried via a fiber-optic cable to a dual-wavelength pyrometer.

Figure 1
IR Lightpipe Schematic

The feasibility of MMT's lightpipe rod was demonstrated in May 1995. Lightpipes were installed in two locations: the throat and the tuyere block.

As a result of the demonstration of the technical and commercial feasibility of this sensing method concept, it was decided to include provisions to install a lightpipe in the castable bottom blocks of the QCEP™ containment system. The location for the lightpipe is between the tuyere pipe and the containment wall. A detailed lightpipe sensor package for QCEP™ has been designed and was successfully tested in the demo unit.

Figure 2 shows a 24-hour window of automatic bath temperature control using a lightpipe measurement of the bath temperature for the PID process variable: Table 2 summarizes the status of the IR lightpipe sensing technique.

Figure 2
IR Lightpipe and Auto Temperature Control Results

Table 2
Summary of IR Lightpipe Status

IR Lightpipe Status
<p>A lightpipe installed in the throat section of the demo unit has provided more than 220 hours of service in a molten metal environment, and has survived three full cooldown/warmup cycles.</p> <p>Automatic bath temperature control using the lag-free lightpipe bath temperature measurement as the process variable has performed very well, providing tight bath temperature control (± 50 °F from setpoint) for several days and under the presence of various perturbations (reaction ON/OFF, metal adds, etc.)</p> <p>A lightpipe package has been designed for QCEP and successfully tested in the tuyere block of the demo unit.</p> <p>The QCEP™ lightpipe package installed in bottom blocks will be tested after a redesign of the demo unit bottom plate system is finalized. This redesign was necessary to provide a straight path through the bottom plate for the lightpipe rod.</p>

2.1.1.3. Contingency Sensing Methods

2.1.1.3.1. Embedded thermocouples plus CET model

This is a proven sensing method for bath temperature prediction and has been used successfully several times in Fall River units. The bath temperature is estimated using a embedded thermocouples measurements and a temperature model (Compensated Embedded Thermocouple (CET)).

Figure 3 shows a 24-hour window comparison between the bath temperature predicted by the CET model and the bath temperature measured by an IR lightpipe (see section 3.2.1). The CET model prediction "lags behind" the bath temperature by approximately 20 minutes in this example.

Figure 3
CET Bath Temperature Results

Disadvantages of this method include the need for periodic calibration to compensate for refractory wear, reliability of individual thermocouples, and unavoidable lag between the predicted temperature and the actual bath temperature.

The design basis for QCEP includes two arrays of four thermocouples (B-type) each installed in the castable bottom blocks. Thermocouple spacing is a compromise between low lag and ability to maintain temperature control after 4" to 5" of refractory wear in the bottom block section. The arrays are 180 degrees from each other. The array radial location is between the tuyere and the crucible wall. This location is expected to minimize unwanted effects such as accretions and end effects. Thermocouples wires exit straight through the bottom plate to minimize failures.

Embedded Thermocouples Plus CET Model Status

The CET model has been tested successfully several times in the demo unit using throat and tuyere thermocouple arrays.

A CET software module of commercial quality has been developed. The module includes features such as easy configuration, digital filtering, sensor diagnosis, automatic rejection of bad sensors, self-tuning, and automatic refractory wear correction.

Closed-loop temperature control was successfully demonstrated in run 1T-95-001 using tuyere thermocouple arrays. Simulation and open-loop response test was used to tune the PID loop.

Embedded thermocouples arrays in bottom blocks will be tested after a redesign of the demo unit bottom plate system is finalized. This redesign is necessary to provide a straight path through the bottom plate for thermocouple wires.

2.1.1.3.1.1. Dual-Wavelength Pyrometer

A dual-wavelength IR pyrometer with a fiber optic cable and a reimaging lens installed on top of the reactor vessel, looking at the bath surface through the sightglass port, may be used as an independent measurement to calibrate the embedded thermocouple model. The presence of a ceramic phase and/or dust may affect this temperature sensing technique.

Dual-Wavelength Pyrometer Status
The concept has been demonstrated with an IRCON unit in the demo unit several times under no dust conditions. A dual-wavelength pyrometer from Williamson with a fiber optic cable and reimaging lens was tested in run 1T-95-004 ⁵² . The performance of this pyrometer was similar to the IRCON.
May provide a reference temperature to calibrate the CET model or the IR lightpipe under purge mode.

2.1.1.3.1.2. Temperature Sampler

Provisions for high accuracy, discrete temperature sampling system has been made in the QCEP design. The sampler is being designed and will be installed in a 8" penetration on the reactor headspace. This intrusive sensing method allows temperature sampling using a reusable temperature probe. The concept is similar to the Electronite temperature measurements routinely used in Fall River units.

The temperature sampler should provide an accurate reference temperature to calibrate the other continuous temperature sensing methods.

2.1.1.3.1.3. Energy Balance Model

An energy balance model provides a prediction of the bath temperature based on feed and power input measurements and an accurate estimate of heat losses. The energy balance model can be kept calibrated with the primary continuous temperature sensing method and used as a contingency.

2.1.1.3.1.4. Other Bath Temperature Sensing Methods Considered

A number of alternate bath temperature sensing methods were considered, including high temperature Optical Fiber Thermometry (OFT), side-wall thermocouple plugs, suction pyrometer, TV camera with image analyzer, millimeter wave pyrometer, ultrasonic thermometry, and optical fiber continuous feed. Evaluation of these technologies will continue as most show promise for potential application to CEP reactor control.

2.1.1.4. Control Strategy and Automation

2.1.1.4.1. Melt Control

The charge temperature during heatup can be monitored by embedded thermocouples arrays, the top-mounted dual-wavelength pyrometer, and the IR lightpipe. The

headspace temperature can be monitored by the headspace embedded thermocouple arrays and the upper susceptor dual-wavelength pyrometer. The pyrometers do not start reading until the target temperature exceeds 1700 °F. Below this temperature, the only instruments available are embedded thermocouples.

Power settings will be provided to operators. A melt model will be available to monitor progress of the melting procedure and compare predicted with actual temperatures.

A top-mounted color TV camera will provide images of the charge so operators can observe the onset of melting and perform power adjustments as appropriate to ensure a smooth melt.

As more experience is gained with QCEP™ melting, the melting procedure will be automated. An AUTO MELT module will automatically control the power supply with a pre-established power sequence and compare expected temperatures with measured temperatures. If the module detects a discrepancy, it will stop the AUTO MELT procedure and issue an alarm so the operator is notified that there could be a problem. The details of the AUTO MELT module are currently being defined.

2.1.1.4.2. Bath Temperature Control

The temperature of the molten bath can be monitored by the IR lightpipe, the CET model, and, when the system is not in reaction mode, by the top-mounted dual-wavelength pyrometer. It is assumed that the temperature sampler will be available to take periodic samples of the bath temperature.

The first choice to monitor bath temperature is the IR lightpipe. This sensor has no lag and requires no adjustment for refractory wear.

In the event that the IR lightpipe is not functional, the second choice is the CET model. This method has a lag and requires periodic adjustments to compensate for refractory wear. The CET model is designed to automatically reject bad thermocouples and for bumpless transfer when the lead model is no longer functional due to thermocouple loss. The reference temperature to periodically calibrate the CET model can be obtained from the temperature sampler. If the system is not in reaction mode, an additional reference temperature can be obtained from the top-mounted dual-wavelength pyrometer.

As demonstrated in the demo run, the bath temperature can be controlled automatically with a PID loop. One PID loop should be implemented in the PLC with the IR lightpipe output as the process variable, and another PID loop should be also implemented in the PLC with the CET model as the process variable. The tuning constants will be different for both PID loops, with the IR lightpipe loop providing tighter control due to its reduced lag.

The temperature setpoint will be established at a predetermined increment above the liquidus temperature. A simple control strategy is proposed, with only two temperature setpoints. The first setpoint corresponds to the liquidus temperature of the charge. The second setpoint corresponds to the liquidus temperature at saturation. This choice of temperature setpoints represents a conservative temperature control strategy.

2.1.2. Headspace Temperature

2.1.2.1. Requirements

The primary objective of the headspace temperature control strategy is to avoid skulling (i.e., solidification of molten metal in headspace walls.)

A secondary objective of the headspace temperature control strategy is to avoid condensation of volatile radionuclides present in the off-gas. However, the condensation temperature of these radionuclides is rather low.

The headspace temperature is controlled by the temperature of the upper section of the reactor crucible. This section heated by an inductive coil. The wall temperature is adjusted by manipulating the headspace inductive coil power supply setting.

2.1.2.2. Primary Sensing Method

2.1.2.2.1. Side-Mounted Pyrometer

A side mounted pyrometer with sight glass and sight tube through induction coil measures the outside wall temperature.

Side-Mounted Pyrometer Status
This sensing method was demonstrated using a dual-wavelength pyrometer and a single-wavelength pyrometer in a 10 lb. unit ¹⁷ .
A dual-wavelength pyrometer is recommended to minimize effects of changes in target conditions and intervening atmosphere.
A fiber optic link is recommended to minimize radiation damage to pyrometer electronics.

2.1.2.3. Contingency Sensing Methods

2.1.2.3.1. Embedded Headspace Thermocouples

One array of two type-B thermocouples embedded in headspace refractory. This system was designed to allow in-situ removal and replacement of the thermocouple array. This concept has been demonstrated in the 4 ton demo unit.

2.1.2.3.2. Thermal Model

Calculates the headspace temperature distribution based on the wall temperature, the bath temperature, and the bath spout. A preliminary model has been developed.

2.1.2.4. Control Strategy and Automation

The headspace temperature can be monitored by the susceptor temperature indication and the embedded thermocouple array. An on-line model will estimate the headspace surface temperature based on the embedded thermocouple readings. The upper susceptor power supply will be adjusted to maintain the desired headspace temperature. This process may be automated with a PID control loop.

2.1.3. Bath Composition

2.1.3.1. Requirements

Composition control in CEP reactors is typically used to maintain the desired off-gas quality, maintain the desired ceramic phase properties, and to ensure that the bath chemistry is compatible with the containment system.

In CEP reactors with a Fe-C molten bath, composition control is mainly achieved by carbon concentration control. Several non-invasive carbon control methods have been developed at MMT for this binary system and used in Fall River units

2.1.3.2. Primary Sensing Method

The bath composition is controlled mainly by off-gas characterization plus a thermodynamic model. Oxygen flow is adjusted to keep the bath composition within the desired range.

2.1.3.2.1. Off-gas Characterization: Mass Spectrometer

Initially the process gas analysis requirements for Q-CEP™ were defined as requiring only characterization of CO and CO₂ in the offgas. As the design progressed and various alternative operating strategies were introduced to accommodate new containment system designs, it was clear that increased flexibility was needed. This led to the conclusion that a design based on the use of discrete gas analyzers was neither

cost effective nor flexible enough to satisfy changing project requirements. As a result the use of a mass spectrometer was considered. A mass spectrometer provides the flexibility to adapt to changing design requirements, and it is therefore the recommended solution.

2.1.3.2.2. Thermodynamic Models: The CO/CO₂ Ratio Model

Conditions of high oxygen potential in the bath lead to FeO formation. To avoid FeO accumulation, enough carbon must be present in the melt so that oxygen will preferentially react with carbon to form CO and CO₂ instead of FeO. In other words, the bath oxygen potential must be kept below that required to form FeO.

The CO/CO₂ ratio model is based on the reaction:

At very low, relatively constant carbon mole fractions x_c , this ratio is directly proportional to bath carbon based on equilibrium at the bath surface:

$$\frac{P_{co}}{P_{co_2}} = \frac{K(T)\gamma_c^* x_c P_T}{P_{co}}$$

where P_{co} and P_{co_2} are the partial pressures of CO and CO₂, P_T is the total pressure, $K(T)$ is the equilibrium constant, and γ_c^* is the activity coefficient, assumed constant since operation is confined over a very short range of carbon concentrations. P_{co} is assumed constant, since $P_{co_2} \ll P_{co}$ and changes are below 10%. Assuming that all excess oxygen feed goes to CO, a material balance on carbon shows that the change in x_c is proportional to the excess oxygen flow rate. Combining these two effects, the change in the oxygen flow rate is found to be inversely proportional to the change in excess oxygen flow rate.

Assuming thermodynamic equilibrium, the predicted CO/CO₂ ratio or predicted dissolved oxygen depends on carbon percentage as shown in Figure 4. According to this thermodynamic relationship, the CO/CO₂ ratio could be used as an indicator of oxygen potential in the bath. As the CO/CO₂ ratio decreases, the likelihood of FeO accumulation increases. A bath composition control strategy could be based on maintaining the CO/CO₂ ratio above a certain value by adjusting the oxygen flow through the tuyere.

Figure 4
CO/CO₂ ratio and dissolved oxygen vs. %C in bath

A bath composition control strategy has been developed based on maintaining the CO/CO₂ ratio above a certain value by adjusting the oxygen flow through the tuyere. This control technique has been demonstrated and confirmed with a dissolved oxygen sensor. If at any point the CO/CO₂ falls below the setpoint, the O₂ flow is reduced by a predefined step (e.g., $\Delta O_2 = 1$ scfm). This action is repeated until the CO/CO₂ ratio exceeds the setpoint. A feedback loop controller for this system has been developed based on an estimate of the rate of change of CO/CO₂ and an estimate of the response time of the CO/CO₂ analyzer to changes in oxygen flow rate. For this system the response time is fast enough that a proportional controller is all that is necessary, with integral action included to avoid offset to disturbances. Figure 5 shows the effectiveness of the CO/CO₂ ratio model in maintaining a steady CO/CO₂ ratio. In this run, the bulk carbon concentration was maintained at a steady level of approximately 0.2% by continuous adjustment of the oxygen flow (not shown), leading to the steady off-gas composition shown.

Figure 5
CO/CO₂ Ratio at Low Bath Carbon

2.1.3.2.3. Thermodynamic Models: Total Hydrocarbons Content

In a Fe-C system, the Total Hydrocarbons Content (THC) Model has been implemented to use measurements of carbon-containing offgas species to infer the activity of carbon in the bath. It is based upon the following equilibrium relationship:

$$\Delta G = (-87.657) - T_{\text{bath}}(-0.108741)$$

$$\ln(K_{eq,CH_4}) \Delta G / (RT_{\text{bath}}) = \frac{\Delta G}{(RT_{\text{bath}})}$$

$$K_1(T) = \frac{P_{CH_4} P_T}{a_c P_{H_2}^2}$$

where K_1 is the equilibrium constant, P_i is the partial pressure of component i , P_T is the total pressure, and a_c is the activity of carbon. The activity of carbon can be determined based on the above relation given the partial pressure of the components are determined from the off-gas characterization and the equilibrium constant calculated

based on thermodynamics. The activity of carbon can then be mapped with the bath carbon concentration based on thermodynamics as shown in Figure 6. The THC levels can then be correlated with bath carbon composition as shown in Figure 7.

Figure 6
Carbon Activity (1500°C)

Figure 7
THC Readings vs. %C for Different Bath Temperatures

The use of the preceding relationship for the estimation of bath carbon is based on the following assumptions which apply to CEP operation:

- 1) The kinetics of these reactions are rapid enough to reach equilibrium at bath conditions and the residence time in the reactor is sufficient to raise the feed temperature to bath conditions.
- 2) After the gas stream leaves the bath, reactions involving the formation or destruction of the offgas trace products are negligible.

Experimental results had demonstrated the consistency of the predicted bath carbon concentration with the actual LECO measurements. Figure 8 shows the experimental results during a demo unit run, in which the bath carbon determined by LECO followed the thermodynamic behavior. This THC model demonstrates the sensitivity of bath carbon with the offgas quality at medium to high carbon concentrations. It thus can be used to set up the upper boundary of the bath carbon control operation.

Figure 8
Measured vs. Predicted THC Levels - 1T94-004

To apply this relation in the control scheme, the CH_4 level was predicted and compared with the actual measurements. The CH_4 level can be predicted based on the following equation:

$$y_{CH_4, measured} = y_{CH_4, bath} \frac{F_{T, bath}}{F_T}$$

Figure 9 demonstrates the CH₄ level determined by the model and the actual measurement based on THC analyzer. The THC analyzer reading is a function of the offgas CH₄ concentration (the concentration of C₂₊ hydrocarbons is negligible in comparison). The analyzer represents a fast and economical source of CH₄ measurements independent from the mass spectrometer, which can be used as a check of the THC analyzer. Note the consistency of the correlations.

Figure 9
Carbon Prediction via off Gas Correlation

The Total Hydrocarbon Model takes the advantage of the relationship between the equilibrium constant of hydrocarbon reactions and the carbon concentration in the bath. The input parameters included only off-gas characterization and bath T, P, independent of the feed composition. Further, no integration of systematic errors is present because the carbon concentration in the bath is calculated directly from off-gas measurements.

2.1.3.3. Contingency

2.1.3.3.1. Mass Balance Models

Mass balance models are based on balancing all the species going into the molten metal bath with all the species going out. There are two types of models: the Feed Forward Model and the Mass Spec Model³. Mass balance models require a specification of the

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feed composition and flow, as well as flow of natural gas, oxygen, and inerts into the system. This information is assumed to be available for the mass balance models input. In addition, the feed flow is measured and all flows going into the reactor are independently metered. The offgas flow is also metered, and the offgas composition is measured by a mass spectrometer. The Feed Forward Model predicts the offgas flow and composition from feed measurements plus thermodynamic models. It does not use the measurements of the offgas flow and composition. The Mass Spec Model uses offgas flow and composition measurements in addition to feed measurements.

The following discussion describes in detail the method of approach. The basis of the calculation is a general steady-state carbon balance on the reactor:

$$\frac{dN_c}{dt} = F_{c,in} - F_{c,out}$$

where $F_{c,in}$ is the carbon flow into the reactor, which is known from feed composition and manual additions, $F_{c,out}$ is the carbon leaving the reactor, which is estimated by the model, and dN_c/dt is the calculated accumulation term.

$F_{c,in}$ is determined by the following equation:

$$F_{c,in} = F_{c,feed} Y_{c,feed} + F_{c,hand\ add}$$

Two models were used to determine the value of $F_{c,out}$ (1) feed-forward model and (2) mass spec model.

In the feed-forward model, $F_{c,out}$ is estimated using partitioning and thermodynamic models as shown by the following equations:

$$F_{o,in} = F_{o,feed} + F_{o,other}$$

$$F_{c,out} = f(F_{o,in}, F_{ca,in}, F_{al,in}, F_{ss,in}, F_{c,in})$$

$$y_{c,bath(t)} = \frac{(M_{bath,T}(to)) \left(y_{c,bath}(to) + 12'_{to} \int N_{c,net} dt \right)}{M_{bath,T(t)}}$$

The output of carbon is determined based on the thermodynamic partitioning of feed material. Factors that affect the partitioning of carbon include the oxygen usage in the bath, the carbon input, etc. (see Equation (14)). The carbon concentration in the bath, (y) is thus the accumulation term between in and out and can be calculated based on the integration of the rate of change of bath conditions.

In the mass-spec model, $F_{c,out}$ is estimated using the mass-spec data as shown by the following equations:

$$F_{c,out} = T_{off,T} (y_{co,offgas} + y_{o2,offgas})$$

$$y_{c,bath(t)} = \frac{(M_{t,bath}(t_0))(y_{c,bath}(t_0)) + 12'_{10} \int N_c^{net} dt}{M_{t,bath(t)}}$$

The carbon exiting the system ($F_{C, out}$) is based on the off-gas concentration of carbon monoxide and carbon dioxide, assuming the total hydrocarbon trace levels were negligible to the overall carbon output. Again, the bath carbon concentration is the accumulation term between in and out and can be calculated based on the integration of the rate of change of bath conditions.

Figure 10 shows the performance of the mass balance models with self-tuning when compared with discrete bath carbon samples.

Figure 10
Carbon Models Prediction

Periodic calibration of model estimates is required due to the inherent integration of sensing errors by the model. Traditional LECO measurements are used to provide this calibration. These models are very useful for a short-term control, instantaneous measurement of bath carbon concentration, and coarse oxygen flow adjustment. The error raised from the model shift may be decreased in commercial applications in which fluctuations in conditions will be minimal.

Ongoing studies for improvements included:

- the application of techniques similar to temperature control, including filtering, self-tuning, and diagnostics control, aiming to improve the accuracy and minimize systematic errors.
- the application of procedural steps such as intermittent samples taking and metal tracing.

2.1.3.3.2. Other Bath Composition Sensing Methods Considered

A number of alternate bath composition sensing methods were considered, including opacity and turbidimetric dust loading sensors, oxygen sensor, laser-produced plasma spectroscopy, and molten metal emission spectrometry. Evaluation of these technologies will continue as most show promise for potential application to CEP reactor control.

2.1.3.4. Control Strategy and Automation

The mass balance models indicate the level of O₂ needed to maintain a stoichiometric feed, thus avoiding reaching a high O₂ limit (potential for FeO generation), or a low O₂ limit (potential for excessive offgas dust loading). Actual bath composition will drift over time; therefore, mass balance models are used as a coarse adjustment of the O₂ flow. Fine adjustments of the O₂ flow is provided by the CO/CO₂ ratio and THC models.

2.1.4. Bath Level

2.1.4.1. Requirements

The primary objective of bath level control is to determine whether the bath level has reached the maximum value. The maximum unexpanded bath level should be below the crucible joint to allow removal of this system. Bath growth can be minimized by selecting various compositions of the initial charge according to the type of feed materials.

2.1.4.2. Primary sensing method

2.1.4.2.1. Microwave switch

An off-the-shelf microwave level switch has been identified. It consists of a transmitter and a receiver which are mounted on the side walls of the vessel in two 5" penetrations 180 degrees from each other at a level a few inches above the final melt line. A clearance through the inactive coil section for the microwave beam has been provided for. The

microwave beam receiver detects the presence of the microwave beam. If the beam is interrupted by the bath, the receiver issues an alarm signal, indicating that the maximum level has been reached.

A bench-scale test confirmed that the microwave beam can penetrate the expected refractory thickness, and a water model test confirmed that under conditions of low flow the microwave switch can detect when the maximum level has been reached

2.1.4.2.2. Side-Mounted IR Lightpipe

This approach is currently under consideration. The total infrared energy collected by an IR lightpipe mounted in the side wall of the containment system is expected to depend on bath level for as long as the lightpipe is exposed. Once the lightpipe is totally submerged in the metal bath, the total IR energy should remain constant and represent the bath temperature.

Changes in injection flow rate should change the bath spout size, thereby changing the view factor of an un-submerged lightpipe. This change in view factor should be reflected as a change in IR energy. This relationship between injection flow and IR energy offers a simple way to detect whether the lightpipe is submerged or not: if the IR signal changes when changing the injection flow rate, it means that the lightpipe is not submerged. If it does not change, it means that the lightpipe is submerged.

Metal splashing is expected to add noise to the measurement. One way to determine when the lightpipe is totally submerged under conditions of a splashing bath is to observe the measurement noise and interpret noise suppression as level above the lightpipe location.

An experiment was conducted on a 10 LB unit to verify the feasibility of this method. Figure 11 shows the result. A sensitivity of more than 100 °F with bath level was observed.

Figure 11
IR lightpipe sensitivity to bath level

R013-95-069: Lightpipe sensitivity to bath level

2.1.4.3. Contingency

2.1.4.3.1. Side-Wall Thermocouple Plug ("Krowitz" array)

The concept of using embedded plugs with thermocouples in dry-vibe for temperature measurements was tested in the APU-10. The idea is to install thermocouples very close to the molten metal taking advantage of the excellent wear resistance of the high-density plugs. A sensitivity of the measurement to metal level indicated that the pressurization/depressurization of the reactor caused metal to uncover/cover the plug tip, resulting in temperature changes of 200 to 300 °F. Modeling confirmed the fact that radiation heat transfer generates lower surface temperatures with respect to the same surface in direct contact with the molten metal, and the difference is significant enough to be measurable.

2.1.4.3.2. Other Bath Level Sensing Methods Considered

A number of alternate bath level sensing methods were considered, including microwave radar, radiometric switch, laser, inductance, ultrasound, TV camera with image analyzer, axial temperature, load cells, and conductivity circuits. Evaluation of

these technologies will continue as most show promise for potential application to CEP reactor control.

2.1.4.4. Control Strategy and Automation

Level monitoring in the reactor is challenging due to the dynamics of the bath's surface, which reduces the accuracy of bath level measurements. Data provided by the microwave switch is the primary input for the bath level; however, the data is supplemented by thermocouple data and bath level models to compensate for potential measurement errors. The ability to accurately determine when the reactor level has reached its maximum setpoint will improve with the application of sensing technologies currently under evaluation.

2.1.5. Pressure Control

2.1.5.1. Requirements

The primary objective of bath pressure control is to maintain the bath at the desired pressure setpoint. Pressurized operation is desired to increase the system throughput.

2.1.5.2. Primary Sensing Method

Two reactor pressure transmitters are provided, one on process gas discharge and one on rupture disk penetration. PLC logic with operator override selects controlling signal. Chemical seals are used to protect sensor. Differential pressure transmitter measures the difference between process gas discharge line and rupture disk line to detect blockage. Pressurized operations have been demonstrated in the VPR and APU 10 units.

2.1.5.3. Contingency

Redundancy in pressure transmitters provide contingency.

2.1.5.4. Control Strategy and Automation

The reactor pressure is controlled automatically by a PID loop. Reactor inlet flows will be adjusted according to reactor pressure. An on-line control module is under development to provide automatic tracking of reactor flows with reactor pressure.

2.1.6. Containment Diagnosis

2.1.6.1. Requirements

The primary objective of the containment diagnosis is to provide the operator with an indication that conditions exists that could potentially develop into a potential containment breach in progress. A containment breach includes both permeation and

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cracking. This system will afford an orderly system shutdown prior to a breach in containment.

2.1.6.2. Primary Sensing Method

2.1.6.2.1. Grids

Detection grids, which are area sensors based on electrical behavior of the refractory lining, are expected to indicate either pointwise or uniform lining deterioration. Grids indicate the potential for a containment system breach by an increase in current.

The QCEP design includes three grids between the dry-vibe and the shell, and one grid outside of the shell. An additional bottom grid is under consideration. The concept of containment diagnosis using grids has been demonstrated several times in MMT units.

2.1.6.2.2. Tuyere Thermocouples

Thermocouples will be placed on the tuyere pipe which are inserted into drilled holes in a tuyere brick. These thermocouples will be potted with a high-temperature refractory cement. Three tuyere thermocouples have been incorporated in the QCEP design, at various depths from the hot face.

2.1.6.3. Contingency Sensing Method

2.1.6.3.1. Grid thermocouples

Three arrays of two thermocouples each are mounted between grids. Thermocouple indications may be used to differentiate between uniform permeation and metal fins. An increase in temperature or in temperature rate of change would indicate the potential for a containment breach.

2.1.6.3.2. Bottom plate thermocouple

One (1) type K thermocouple installed in the Q-CEP™ reactor bottom plate to detect failure of containment bottom blocks. Additional thermocouples may be added to provide a scanning system for bottom plate temperature.

2.1.6.4. Control Strategy and Automation

The major parameters to monitor are deviation and rate of change for both grid currents and thermocouple temperatures. An on-line software module is provided to calculate both values for each containment-related sensor, and to issue an alarm when corresponding setpoints are exceeded. Most indications will be treated as warnings, with a few providing shutdown indications.

2.1.6.4.1. Shutdown Indications (Preliminary)

When the indication of the last tuyere pipe thermocouple exceeds a setpoint, the outer grid exceeds a setpoint, or the bottom plate thermocouple(s) exceeds a setpoint.

As more experience is gained with this monitoring system, features to reject sensor failures and avoid nuisance alarms will be added to this module.

2.1.7. Tuyere Injection

2.1.7.1. Requirements

Injection of selected feed materials into melts with very little or no tuyere wear has been demonstrated. The major thrust of current efforts is to come up with a well defined start up procedure for iron melts that minimizes the initial accretion removal time with very little or no tuyere wear. Development of a strategy that minimizes injection startup time and provide an appropriate algorithm to automate the injection procedure is anticipated. Efforts are currently underway to automate commencement of feed injection during reinjection (i.e. feed injection after the initial accretion removal). This automation will be attempted in the next demo unit run as an advisory controller. Once fully tested, this model is expected to perform active control.

2.1.7.2. Primary sensing method

Tuyere injection control strategies require pressure and flow rate indication for each component flow in each passage, as well as reactor pressure and temperature indication.

2.1.7.3. Contingency Sensing Method

No contingency is provided for primary instrumentation associated with tuyere injection control strategies. It is assumed that the reliability of pressure transmitters and flow meters is adequate and that no redundancy is required. Enough instrumentation is available for the system to go to a safe-state injection condition after losing a primary instrument.

2.1.7.4. Control Strategy and Automation

Initially, tuyere injection control strategies will be manual procedures. A tuyere diagnostics module is available and predicts pressure drop in each passage. This information is expected facilitate injection control strategies decisions and tuyere wear assessment. Future in tuyere automation efforts include the development and testing of algorithms for an automatic injection start sequence and automatic feed flow tracking of reactor pressure.

2.1.8. Visual

2.1.8.1. Requirements

Visual observation of the bath conditions are required, particularly during the melting procedure. In addition, visual observation could be used during reaction mode to detect changes in the amount of dust loading, and in purge mode it could indicate presence of foam/ceramic and perhaps bath level.

2.1.8.2. Primary Sensing Method

A top-mounted compact TV camera with remote iris, zoom, and focus control will be provided. This camera will be mounted in a purged enclosure on top of one of the flange with sightglass.

2.1.9. On-line Control Models

2.1.9.1. Requirements

Some reactor control strategies require on-line computer models. These models are in-house FORTRAN modules which are interfaced to the control system via a C++ executive module. This executive, which facilitates the integration of FORTRAN modules with the control system.

The first package of on-line control models will provide basic monitoring and diagnostics information for the reactor. This package includes the following modules:

1. Model executive
2. Melt model
3. CET model
4. Mass balance model
5. Containment diagnosis model
6. Tuyere diagnosis model

The package will include operator interfaces and tagname database compatible with the system, and will be ready for integration with the rest of the control system. An improved control model package includes modules to enhance the control and automation of the reactor, and consists of:

- Enhancements to existing models

- Auto melt model
- Auto injection sequence
- Auto pressure tracking
- Any other on-line model needs identified

2.1.9.2. Primary on-line Models

2.1.9.2.1. Model Executive Module

Previous experience with on-line computer models at MMT Fall River indicates that it is very important to provide a flexible and robust environment for computer models and to minimize the number of interfaces for input/output to the control system. A contract with Bioprocess Automation, Inc. to develop a software executive that coordinates the execution of on-line FORTRAN modules and performs input/output with the control system was completed on July 1995. This software executive is expected to greatly facilitate the maintenance, robustness, and communication of on-line computer models for QCEP and other commercial units. Model developers will be able to modularize control models and concentrate on just the FORTRAN module development. Embedding the FORTRAN module into the control system will be an easy operation. The model has been tested and integrated into the APU-10 unit.

2.1.9.2.2. Melt Module

The melt module performs the following functions:

- Calculates the charge temperature based on available instrumentation input
- Trends the calculated charge temperature with the target temperature during heatup
- Trends future values of charge temperature based on current inputs
- Allows the operator to visualize the impact of changing current power settings on future charge temperatures.

2.1.9.2.3. Compensated Embedded Thermocouple (CET) Module

This CET module performs the following functions:

- Filters embedded thermocouple inputs.

- Calculates a smooth surface (bath) temperature and rate of change from user-specified pairs of embedded thermocouples, taking into account thermal conductivity dependence on temperature.
- Automatically selects one pair of embedded thermocouples as the lead predictor of bath temperature and rate of change. The lead predictor pair can also be selected manually.
- Optional self-tuning automatically adjust all other thermocouple pairs to follow the lead pair predicted temperature.
- Automatically rejects bad thermocouple inputs and issue high noise and/or rate of change alarms. Thermocouple inputs can also be rejected manually.
- If one thermocouple from the lead pair is rejected, it transfers to the next best predictor pair. The transfer is bumpless if the auto-tuning option has been previously selected.
- Automatic calibration for a user-specified reference bath temperature. Provides a set of thermocouple distances to match a user-specified reference bath temperature.

This module allows on-line configuration of models, and automatically rejects bad thermocouple readings for the calculation of the lead bath temperature.

2.1.9.2.4. Mass Balance Module

The mass balance module performs the following functions:

- Calculates the feed composition from lab analysis of feed and dust.
- Calculates stoichiometric O₂ per pound of feed.
- Calculates bath composition from species balance (feed forward and mass spec models)
- Calculates bath level based on bath composition
- Calculates expected offgas rates
- Performs What-if calculations

2.1.9.2.5. Tuyere Diagnosis Module

The tuyere diagnosis module calculates the expected pressure drop in tuyere passages. By comparing the predicted with the actual pressure drop, the operator can obtain useful information for control or tuyere wear assessment purposes.

2.1.9.2.6. Containment Diagnosis Module

This module calculates the rate of change of several containment-related instrumentation, and triggers alarms if deviation or rate of change setpoints are exceeded.

3. Particulate Characterization and Control

3.1. Dust Formation Studies

3.1.1. Summary

CEP has been identified as a technology whose robustness allows the processing of extremely heterogeneous wastes. The ability to partition volatile elements to the gas handling train dictates a need for a thorough understanding of the mechanisms for condensation and deposition of those elements.

An experimental unit was constructed to investigate condensation of zinc vapor in a test pipe. An argon stream saturated with zinc vapor was produced by bubbling a small portion of the hot gas (1200-1300°F) through a molten zinc bath at 1100-1200°F. Test piping of 1.00" to 1.25" nominal ID was used to condense the metal.

The test parameters studied were the wall temperature and the gas velocity. The wall temperature was varied by cooling the test pipe with either air or water. The effect of velocity was evaluated by reducing the pipe diameter at a constant gas flow rate. The effects of these two variables on the tenacity of the zinc deposition were evaluated by sectioning the test pipes and quantifying the weight of zinc deposited.

3.1.2. Introduction

Elemental partitioning in an iron bath has been quantified by previous experiments performed in the VPR. The VPR partitioning data for representative metal elements are summarized in Table 3. As the data indicate, most of the cobalt and sodium remain in the metal phase at 2500-2800°F. Cobalt stays in the bath because of its high boiling point, while sodium reacts with the sulfur in the feed to form non-volatile sodium sulfide. The majority of the zinc and the cesium partition to the gas phase as volatilized heavy metals which then enter the GHT.

Table 3
Volatile Metal Partitioning Data

Element	Boiling Point(°C)	% Retained in Bath
Zinc	907	<30
Cesium	671	<30
Cobalt	2879	>85
sodium	883	>85

Cesium and zinc that enter the reactor off-gas piping will condense if the pipe wall temperature is below the dewpoint of the off-gas. The condensed solids can either be swept away with the gas stream or accumulate on the wall of the pipe. In the latter situation, accumulation can lead to excessive pressure drop and eventual blockage of the off-gas piping.

In addition to physical blockage of the off-gas pipe, the accumulation of radioactive solids is an effect of Q-CEP operation that requires additional investigation, understanding and management.

The dewpoint for a particular element is a function of the system pressure, the vapor pressure of the element, and the concentration of the element in the off-gas stream.

The estimated dewpoints of cesium and zinc in the off-gas are summarized in Table 4 for the average and maximum concentration of the element expected in the feedstream. The dewpoint is calculated at 5 bar, assuming that all the metal in the feed is vaporized. The dewpoint calculations assume that for every pound of organic fed per minute, 60 SCFM of off-gas (40 SCFM process and 20 SCFM of dilution) is produced.

Table 4
Calculated Dewpoints

Element	PPM Dry Feed	Dewpoint at 5 bar (°F)
Cesium	800	<150
Zinc	800	824
Zinc	5000	950

To minimize the potential problem associated with the condensation of the heavy metals, two approaches can be considered:

- Maintain the pipe wall above the dewpoint, and
- Cool the pipe wall below the dewpoint and somehow prevent dust settling on the walls.

The objective of this study is to investigate the effect of wall temperature and gas velocity on zinc deposition and evaluate alternative cooling surfaces such as a sintered porous tube with radial flow.

3.1.3. Experimental Equipment

The equipment required to perform the zinc deposition experiment is shown in Figure 12. This equipment is designed to provide 10 SCFM of hot argon at 1200-1300°F with a maximum zinc dewpoint of 900°F. The modular design allows for a variety of test pipes and rapid changes in the equipment setup.

Figure 12
Zinc Dust Generator

The off-gas piping from the crucible is stainless steel tubing heated with electric heating tape to ensure that condensation does not occur in the off-gas piping or in the mixing tee. The tee was used to mix the saturated off-gas from the generator (0.1-0.5 SCFM) and the heated main argon stream (10 SCFM). The mixed stream is fed to the zinc deposition test pipe; the maximum design temperature of the mix gas is 1200°F.

The zinc deposition test section is stainless pipe that was air cooled by natural convection (no insulation) or water jacketed depending on the specific equipment. The pipe is either 1.0" or 1.25" ID and 10 feet long. Thermocouples were installed to measure the inlet and outlet temperatures and an I/R temperature indicator was used to measure the wall temperature along the length of the pipe for the uninsulated case.

After the test pipe, a high temperature Balston filter was used to collect and weigh the zinc particulate. The maximum gas temperature in the filter inlet is 900°F. A water-cooled heat exchanger or a direct water spray was used to cool the gas to 200°F. The gas flowed into a jet pump to maintain the generator at atmospheric pressure. Compressed air was used to provide the necessary flow to maintain pressure.

3.1.4. Theory

In Figure 13, the dewpoint of the mixed feed gas is shown as a function of generator temperature and flowrate at a total gas flowrate of 10 SCFM. The graph assumes the zinc generator off-gas is saturated with zinc. The maximum flowrate of the generator off-gas is estimated to be 0.5 SCFM. Assuming a generator temperature of 1200°F and a generator gas flowrate of 0.5 SCFM, this condition corresponds to a mixed gas dewpoint of 900°F with a zinc loading of 60 g/hr. If the generator flowrate is reduced to 0.1 SCFM at a constant temperature of 1200°F, the mixed gas dewpoint is reduced to about 800°F, lowering the zinc loading to 13 g/hr. It should be noted that the melting point of zinc is 788°F. If the dewpoint is higher than the melting point, the deposit may have more of a tendency to coat the wall because it will initially condense as a liquid and then solidify on the surface. If the dewpoint is below the melting point then the zinc will condense as discrete solid particles and have less tendency to coat the wall.

Figure 13
Dewpoint vs. Generator Temp and SCFM

Table 5
Zinc Vapor Pressure

Temp(°F)	Vapor Pressure (mmHg)	Normalized to P(800°F)
600	.0043	0.02
700	.0344	0.15
800	.1990	1.00

Table 5 shows the dependence of zinc vapor pressure with temperature. This data shows that cooling a gas with an 800°F dewpoint to 600°F condenses approximately 98% of the zinc vapor.

3.1.5. Experimental Plan

The initial set of runs is outlined in Table 6 below. Two parameters were varied: the wall temperature and the pipe diameter. The gas flowrate and the zinc loading were maintained constant. In the second pair of tests, the pipe diameter was decreased to 1.0 inch ID to increase the flow velocity by a factor of four.

Table 6
Experimental Runs

EXP #	FEEDGAS			ZINC GENERATOR			TEST PIPE			
	Dew Pt (°F)	SCFM	Inlet (°F)	gms/hr	TEMP (°F)	SCFM	L (FT)	ID (")	Inlet fps	Comment
1	800	10	1200	13	1200	0.1	10	1.25	42	Air Cooled
2	800	10	1200	13	1200	0.1	10	1.0	164	Air Cooled
3	800	10	1200	13	1200	0.1	10	1.0	164	Water Cooled 100F Wall
4	800	10	1200	13	1200	0.1	10	1.25	42	Water cooled 100F Wall

After each experiment, the test pipe was sectioned for microscopic examination. Zinc content of some sections was determined by soaking the test piece in acid and analyzing the zinc concentration.

3.2. Dust Formation Mechanisms - Chlorinated Feeds

Particulate control methods in the CEP system have been developed through an understanding of the basic mechanisms for generation of dust and particulates. Innovations in gas handling train technology and operation have led to both suppression of dust formation as well as recyclability of any dust that may form. The result is a system producing a clean gas product exceeding industrial specifications using proven, reliable technology.

Two different mechanisms exist for dust to enter the gas handling train. The first is by entrainment of particles due to the gas velocities exiting the bath. Typically, particles collected by this phenomenon are greater than 10 microns in size. The other mechanism involves vaporization of the material in the bath, primarily in the area surrounding the tuyere. These particles condense in the GHT and are typically smaller in size. Dust formation is therefore a function of the rate of gas generation from the feed and the surface velocity of the gas as it exits the condensed phases of the reactor. Studies have focused on several means of providing added control of dust generation.

High resolution electron microscopy indicates that most CEP dust samples are composed primarily of self-agglomerated submicron particles attached to each other. The mechanism is similar to sintering at high temperatures. Each of these submicron particles is either a single crystal or a single crystal with an external chloride shell. Some isolated alloy particles are also found, imbedded in graphitizing carbon platelets. Detailed chemical analyses and diffraction methods indicate that the composition and crystallography of CEP dusts is directly influenced by the type of injection and metal

addition during operation. Based on the structure of the CEP dusts, they are able to be recycled and recovered through engineering design.

Dust analysis has led to development of hypotheses for the mechanisms of dust formation (as shown in Figure 14). With a better understanding of the dust formation mechanism, the operating conditions can be adjusted to minimize it. Materials are injected into the melt from the bottom at high velocity. These materials decompose and continue with high kinetic energy up through the melt in a gaseous state. The gas passes through the molten iron, into the molten ceramic (if present), "dragging" the iron along. Because of the high viscosity of the ceramic, the gas and the metal punch through the ceramic. The chemical potential of the material at this peak is inversely proportional to the radius of the peak. The radius can be as low as $0.02\text{ }\mu\text{m}$, drastically increasing the chemical potential, μ . This reduces the melting point of the material at this peak, and the metal at this peak is "pinched" off, and escapes from the melt. This reaction can occur at numerous points on the surface of the melt simultaneously. The combination of these actions, as well as with "melt" bubbles at the surface can allow more particles to escape from the melt. The overall series of these separate events bring the melt into a turbulent state.

At very high temperature, this metal particle reacts with the HCl gas to form iron chloride which is a gas at these conditions. The particle, shown in Figure 15, shrinks in size as more of the iron reacts with chlorine to form the chloride. Eventually, the particle reaches an intermediate temperature zone where the iron chlorides are in a solid phase. In this temperature region, instead of the iron chlorides evaporating, a solid ash layer of iron chloride is formed around the metal particles. The gaseous chlorides formed in the high temperature zone also condense and are adsorbed to the surface of these particles.

Figure 14
Formation of an Iron or Alloy Droplet from Molten Metal Bath

Figure 15

Formation of an External Chloride Scale on Metal Particles Observed in Dust Samples

3.3. Dust Recyclability in Biosolids Processing

The MMT commercial design for a feed preparation system allows for solid particles (direct-fed or slurry-fed) up to 1000 microns (1 mm) in diameter. The data in Table 7 show that at least 98% of the dust analyzed was < 1 mm in diameter and would be acceptable for slurry recycling in a commercial CEP facility. At the Fall River facility, the nominal injection size of the solids feed system is 230 microns. This represents 80% of the dust analyzed. A sieve analysis and elemental composition was performed on biosolids process dust collected at the baghouse. The sieve results are listed in Table 7.

Table 7
Sieve Analysis of Baghouse Dust

Microns	Wt%
> 850	2.0
> 250	17.3
> 180	9.7
> 150	52.7
< 150	18.3
Total	100.0

3.4. Effect of Pressurized Operation - Fly Ash Processing

3.4.1. Experiment Summary

The following section describes experiments intended to investigate the effect of pressurized operation on the suppression of component volatilization. MMT has conducted a campaign to investigate the application of CEP to processing of fly-ash to produce synthesis gas and stable ceramic phase product. Several tests with fly-ash have been performed, from single variable investigations on small experimental units to large fully integrated processing runs. These results provided in-depth knowledge of the general characteristics of fly-ash processing including feeding methods, elemental partitioning, ceramic phase characteristics and properties, component volatilization, as well as environmental performance.

Recognizing the effect of secondary dust formation on fly-ash operations costs, MMT performed an experimental run operated entirely at elevated pressures to demonstrate the suppression of volatiles while processing fly-ash. This effect of pressure on dust suppression had already been observed by MMT during previous runs with different feed materials.

This elevated pressure test was performed with the following experimental conditions:

- operating temperature of $1320\text{ }^{\circ}\text{C} \pm 30\text{ }^{\circ}\text{C}$;
- operating pressure of 60 psig ($4.21\text{ kg/cm}^2\text{-g}$);
- starting metal bath of 36.32 kg of carbon-saturated iron;
- initial ceramic layer of 3.63 kg ($\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2\text{-B}_2\text{O}_3$).

A total of 2.8 kg of fly-ash was injected into the bath of a bench-scale reactor over a 5 hour period. No flux co-feed was used. The initial ceramic phase that was utilized in this run better simulates the continuous operation proposed for this type of feed.

The results have demonstrated the effects of pressurized operation on lowering dust formation by achieving a 52% reduction in dust formation. This result maps directly into reduced operating costs associated with secondary dust stabilization and disposal from previous atmospheric pressure results.

Minimization of secondary dust formation is accompanied by incorporating these volatile components (such as Na, K, and Cl) into a stable ceramic phase product. Pressurized test results have produced a ceramic phase composition showing an average composition of 6.95 wt% chlorine, a 107% increase over the previous fly-ash ceramic products that had 3.36 wt% chlorine. Alkali concentrations, represented as NaCl and KCl, in the ceramic phase product were 119% and 50% higher than previous atmospheric tests for NaCl and KCl, respectively. These results are indicative of the CEP ceramic phase's ability to capture increased levels of these volatiles into a stable, durable product.

3.4.2. Secondary Dust Formation

3.4.2.1. Effect of Pressure on Secondary Dust Formation

According to fundamental physical laws governing liquid/vapor phase equilibrium, an increase in pressure reduces the volatilization of a component within a mixture. This effect can be readily seen by analyzing Raoult's Law for ideal mixtures:

Raoult's Law

$$y_a = (P_{\text{sat}}/P_t) x_a$$

where: a = component a

y_a = mole fraction in vapor phase

P_{sat} = vapor pressure of component a

P_t = system total pressure

x_a = mole fraction in liquid phase

At a given temperature, the vapor pressure of component 'a' remains constant. However, as the pressure of the system is increased, the mole fraction of component 'a' in the vapor phase will be decreased, thus reducing volatilization. Also, reducing temperature will reduce the vapor pressure of component 'a', and Raoult's Law also predicts a reduction in volatilization.

This theory can be correlated to the *ceramic phase* formed in the CEP system. The gases evolving from the system will hold a given amount of component 'a' (i.e., NaCl or KCl) in accordance with the vapor pressure of the component, the mole fraction in the liquid phase, the pressure of the system, and also non-ideal interactions among system

components. While Raoult's Law does not account for the effects of non-ideal interactions, it is nevertheless useful for describing the impact of pressure on volatilization.

The results of previous fly ash runs at atmospheric pressure were analyzed to see how well Raoult's Law and ideal solution thermodynamics predicts the resulting volatilization. Utilizing defined run parameters of 1480 °C, effective atmospheric operating pressure, and reported material additions including carrier gas rate, the predicted volatilization of NaCl and KCl was analyzed and shown in Figure 16. The effect of increasing the system pressure would have is predicted in Figure 16. The actual run result was within 13% of the predicted value. Additional data points would be required to further confirm the correlation.

Figure 16
NaCl/KCl Volatilization for Atmospheric Pressure Test

The same analysis for the pressurized test at 1320°C and 60 psig was performed prior to the test and is shown in Figure 17. In Figure 17, the predicted volatilization for both NaCl and KCl combined and for total dust including other constituents is shown as a function of pressure. The predictions in both Figure 16 and Figure 17 support to a first approximation that pure component vapor pressure data and ideal solution

vapor/liquid equilibrium models can be used to characterize component volatilization (i.e., dust formation) in the processing of fly-ash.

Note: The values shown in Figure 16 and Figure 17 are not directly comparable to each other as carrier gas flow for fly-ash injection was significantly different between runs. This accounts for the higher volatilization predicted for NaCl/KCl even though the feeds were the same and operating temperatures were reduced from Figure 16 to Figure 17. These graphs also only predict the operation of the experimental runs and do not correlate to the proposed operation of commercial-scale facilities.

Figure 17
Dust Volatilization during Elevated Pressure Test

Because this model for predicting dust formation is based upon the physical properties of the fly-ash constituents, it should be valid not only for fly ash but also for other waste feeds. Operation at lower temperatures will reduce dust formation due to the reduction in component vapor pressure. However, CEP's ability to operate at increased pressure will allow even lower dust formation.

3.4.2.2. Dust Composition

Secondary dust, or volatile material that exits the bath in the gas phase, is collected in the experimental unit gas handling train filters. A small amount of dust was found in

the system piping prior to the filters that was collected and added to the filter-collected dust. The composition of the dust from the system lines and the filters was analyzed and the average values shown in Table 8.

Table 8
Average Secondary Dust Composition for
Processing Fly-Ash at Elevated Pressures (60 psig)

Element	wt%
Ca	6.26
Al	1.24
Si	0.61
Mg	0.23
Fe	2.48
Na	14.25
K	14.22
Cl	54.71
Zn	4.53
Pb	1.32
S	0.15
Total	100.00
These values were normalized to 100% due to the exclusion of C, H, and O. Prior to normalization the above elements constituted 98.03% of the dust composition.	

The material was a fine, gray dust with a consistent appearance to previous runs performed with fly-ash.

3.4.3. Ceramic Phase Composition

The final ceramic phase for the elevated pressure fly-ash tests was the product of 2.8 kg of fly-ash feed and 3.86 kg of an initial ceramic layer. A starting ceramic phase simulates a continuous operation where incoming fly-ash feed would see an established ceramic phase layer and thus benefit from the solution thermodynamics by producing less secondary dust formation. It is expected that after a suitable ceramic phase has been established, flux addition would have begun at approximately 35% of the fly-ash feed. This additional flux will maintain the composition of the ceramic layer and the fluidity of the phase.

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Operation at elevated pressure has shown its dramatic effects on reducing volatilization and thus secondary dust formation in Section 3.4.2. This correlates to higher levels of these "normally" volatilized materials (such as Na, K, Cl, etc.) remaining in the bath and partitioning into a stable ceramic product. The ceramic phase for the latest pressurized test has shown a significant increase in NaCl, KCl, and CaCl₂ concentrations in the ceramic product over previous ceramic product produced during atmospheric operations as shown in Table 9.

Table 9
Increased Volatile Capture in Ceramic Product
while Processing Fly-ash at Elevated Pressure

Constituent	Atmospheric Operation (wt% in ceramic)	Pressurized Operation at 60 psig (wt% in ceramic)	Net Increase in Ceramic Capture (%)
NaCl	0.43	0.94	219
KCl	0.22	0.33	150
CaCl ₂	4.82	10.00	207
Cl (total)	3.36	6.95	207

This increase in volatile capture due to increased pressure is indicative of CEP's ability to produce a stable ceramic phase product that can accommodate these components. These results confirm previous tests performed by MMT on alkali and chlorine capture in ceramic phases. The stable, durable ceramic phase products containing these components have always passed full TCLP tests. Table 10 shows the TCLP results for the ceramic phase product for the pressurized fly ash run with the increased levels of chlorine and alkalis.

Table 10
TCLP Results for Fly Ash Processing Ceramics

MMT Run	Sample ID							
	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
Fly-Ash Test Run (pressure = 60 psig)	ND	4.0	ND	ND	ND	0.01	ND	ND
Detection Limits (mg/l)	1.0	0.5	0.1	0.2	0.5	0.005	0.5	0.1
U.S. Regulatory Limits (mg/l)	5.0	100	1.0	5.0	5.0	0.2	1.0	5.0
ND = not detected.								

Table 11 shows the average composition of the ceramic product with chlorine represented as metal chlorides.

Table 11
Average Composition of the Ceramic Product

Constituent	wt%
CaO	38.87
Al ₂ O ₃	12.54
SiO ₂	31.84
MgO	3.12
NaCl	0.94
KCl	0.33
CaCl ₂	10.00
S	0.60
Total	100.00

The important result of this run is that the increased pressure was instrumental in suppressing the volatilization of the alkalis and chlorides and that the ceramic phase is capable of supporting increased levels of these constituents. Further demonstrations will only determine the limits of the system to optimize the superior performance of CEP in producing minimum secondary dust.

4. Volatile Heavy Metals Recovery

4.1. Introduction

Volatile heavy metals (VHMs) are present in varying degrees in DOE mixed waste streams being considered for CEP application. An understanding of volatile heavy metals partitioning in the CEP system is critical for effective processing of this waste. Developing the capability to characterize VHMs behavior under different reactor operating conditions will significantly enhance knowledge about VHMs accumulation in the GHT. This knowledge will be invaluable for the design of a gas handling train that ensures VHMs are fully recovered for re-injection or re-use.

Earlier bench- and pilot-scale VHMs partitioning studies, focused on lead, have indicated that at typical CEP temperatures of 1,500-1,550 °C, less than 15 wt% of the lead was recovered in the metal and ceramic phases. Sampling analysis has suggested significant volatility of lead and zinc and potential recovery in the GHT. Despite these findings, the preliminary nature of this early work accentuated the need for a more detailed and definitive study on VHMs behavior in CEP systems.

4.2. Objectives

To better understand the behavior of volatile heavy metals in a CEP system, demonstration-scale trial experiments were performed in which lead, zinc, and cesium were injected as co-reactants. In addition, thermodynamic modeling of the system under study was performed to predict VHMs partitioning and to examine the effect of different operating parameters. The primary goals of this study were as follows:

- 1) Validate earlier VHMs' partitioning data on a large scale unit;
- 2) Collect experimental data to fully account for VHMs accumulation and deposition in the gas handling train;
- 3) Improve sampling protocols to increase the level of confidence in the analytical data;
- 4) Examine the effect of a changing bath chemistry on VHMs final form;

4.3. Thermodynamic Analysis

To better explain the findings of the earlier studies, thermodynamic modeling of the system was performed. The components most favored to form were predicted and their volatilities determined for a given set of operating parameters. Phase stability diagrams, free energies of reaction, and vapor pressures were theoretically determined for a system containing the elements lead, zinc, iron, chlorine, and oxygen using thermodynamic analysis. Table 12 lists the boiling point for lead and zinc as well as for oxides and chlorides of both metals predicted to be encountered in the CPU. The vapor pressures, when available, of these components are also presented.

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Table 12
Boiling Points and Vapor Pressure Data

Compound	Normal Boiling Point (°C)	Vapor Pressure @ 1,500 °C (bar)
Lead (Pb)	1740	0.23
Zinc (Zn)	907	
PbCl ₂	950	
PbO	1482	0.16
ZnCl ₂	732	
ZnO		2.53E-5

Although the boiling point of lead (Pb) is quite high (1,740 °C), the high vapor pressures of Pb and PbO combined with the stripping action of the off-gas severely limit the amount of retention in the metal bath. This leads to significant volatilization and condensation in the gas handling train. To maximize VHMs recovery, areas of preferred deposition in the GHT must be identified.

To illustrate which compounds have the highest potential to form under CEP reactor conditions, phase stability diagrams for iron, lead, and zinc compounds as a function of oxygen and chlorine partial pressures have been determined, as shown in Figure 18, Figure 19, and Figure 20, respectively.

Figure 18
Phase Stability Diagram of Lead, Oxygen, and Chlorine at 1,500 °C

Figure 19
Phase Stability Diagram of Zinc, Oxygen, and Chlorine at 1,500 °C

Figure 20
Phase Stability Diagram of Iron, Oxygen, and Chlorine at 1,500 °C

Since iron is present in a molten stable phase, oxygen and chlorine partial pressures were predicted to be less than $10E-10$ and $10E-5$ atm, respectively, at a reactor temperature of 1,500 °C. However, both FeO and FeCl₂ were likely to be present in small amounts. Using a similar analysis, the phase diagrams indicate that PbO, PbCl₂, ZnO, and ZnCl₂, as well as a significant quantity of the pure elements are predicted to be present.

To substantiate these findings, the Gibbs Free Energy of formation per mole of gas (either chlorine or oxygen) for the above compounds was examined. The diagram is shown in Figure 21. As predicted, the components most favored have the lowest free energy of formation. For instance, ΔG_f of PbO at 1,500 °C is approximately -30 kcal/mole, versus -8 kcal/mole and 17 kcal/mole for PbO₂ and Pb₃O₄, respectively. It was also observed that oxides form more readily than chlorides. Therefore, if the partial pressure of oxygen and chlorine in the CPU were identical, volatile heavy metal oxides would be favored over the chlorides'. However, because CEP is operated under strongly reducing conditions, chlorine partial pressure exceeds that of oxygen when chlorine is present in the feed material.

Figure 21
Gibbs Free Energy of Formation of VHM's Compounds

Vapor pressure data for the pure metals (Fe, Pb, and Zn) as well as for their oxides and chlorides were determined in order to predict which compounds would be expected to volatilize. The relationship between vapor pressure and the equilibrium constant can be derived by starting with Raoult's Law, which is valid for ideal mixtures maintained at low total pressures and low vapor pressures. Raoult's Law states:

$$x_i P_i^{vap}(T) = y_i P$$

where x_i and y_i are the mole fraction of component i in the liquid and gas phase, respectively, $P_i^{vap}(T)$ is the vapor pressure of component i at the given temperature (T), and P is the total pressure. At atmospheric pressure, the relationship between vapor pressure and the equilibrium constant becomes:

$$\log P_i^{vap}(T) = \log \frac{y_i}{x_i} = \log K$$

The vapor pressure curves were generated by calculating the equilibrium constant (K) for component phase transformation from the liquid to the gas phase. The results are shown in Figure 22.

Examination of the relative volatilities of these compounds indicated that at a reactor temperature of 1,500 °C, significant amounts would be volatilized from the bath into the gas phase. At 1,500 °C, the vapor pressure of all compounds but Fe, FeO, and ZnO was found to be greater than 0.1 bar. Since the temperature of the off-gas is typically decreased from over 1,200 °C to approximately 550 °C before the inlet to the gas cooler, a significant reduction in the vapor pressure was predicted to occur, leading to materials condensation and deposition on the interior pipe surface. Over the length of the off-gas duct, the vapor pressure was expected to decrease by several orders of magnitude for all compounds. The vapor pressure of the most volatile compound, $ZnCl_2$, was predicted to drop below 0.05 bar at 550 °C. Although much of the condensed material is thought to be entrained in the off-gas flow to the gas cooler, thermodynamic analysis indicated that deposition of volatile heavy metal compounds on the pipe surface is plausible. Demonstration unit experiments should incorporate thorough pre-run and post-run inspection and sampling of the off-gas duct in order to account for VHM collection in this area.

To understand the effect of a changed bath chemistry on VHMs partitioning and final form, experiments were conducted during which zinc and cesium were injected in an Fe-C-S. To illustrate which compounds have the highest potential to form under CEP reactor conditions, phase stability diagrams for iron, zinc, and cesium compounds as a function of oxygen and sulfur partial pressures have been determined, as shown in Figure 23, Figure 24, and Figure 25, respectively.

Figure 22
Vapor Pressure of VHM's Compounds

Figure 23
Phase Stability Diagram of Iron, Oxygen, and Sulfur at 1,500 °C

Figure 24
Phase Stability Diagram of Zinc, Oxygen, and Sulfur at 1,500 °C

Figure 25
Phase Stability Diagram of Cesium, Oxygen, and Sulfur at 1,500 °C

When sulfur is incorporated into the bath, both iron and iron sulfide (FeS) were predicted to be present as stable molten phases. Based on Figure 23, the oxygen partial pressure would be less than $10E-10$ atm (at 1,500 °C), while that of sulfur would be between $10E-5$ atm and 1 atm. Using these limits, the phase diagrams of Figure 24 and Figure 25 indicate that ZnS as well as a significant quantity of the pure elements (primarily Cs and Zn) would be predicted to be favored.

To substantiate these findings, the Gibbs Free Energy of formation per mole of gas for FeS, PbS, and ZnS was examined. As predicted, FeS was found to be the most stable (has the lowest ΔG_f) compound, as shown in Figure 26.

Vapor pressure data for the pure metals (Fe, Pb, Zn, and Cs) as well as for their sulfides were determined in order to predict which compounds would be expected to volatilize under typical CEP operating temperatures. As shown in Figure 27, cesium and zinc had the highest volatility, while FeS showed the least tendency for volatilization.

Figure 26
Gibbs Free Energy of Formation of VHM's Compounds

Figure 27
Vapor Pressure of VHM's Compounds

4.4. Method of Approach

Volatile heavy metals were mixed with surrogate waste feed materials and injected at varying levels as co-addidants into the CPU. Lead, zinc, and cesium were presumed to represent volatile heavy metals behavior in the CEP system. Depending on the form of the feed stream to be processed, the metals were injected in solid or liquid-dissolved form. methods for VHMs sampling have evolved during the course of the study. For example, on-line isokinetic dust sampling protocols were not utilized initially. These protocols were later implemented in order to obtain on-line measured dust loading data for comparison with post-run analytical results. A new sampling method was used to collect samples from additional areas of the gas handling train.

Dust samples were taken from pre-specified sampling ports installed in various locations on the demonstration unit, as shown in Figure 28. Post-run samples were taken from the tapped metal, process baghouse dust, tap/ceramic baghouse dust, gas cooler dust, and tapped ceramic (if present).

Figure 28
CEP Demonstration Prototype Unit - Sampling Ports

Mass balance calculations were performed by analyzing pre-injection and post-run samples. The inlet mass was calculated from knowledge of the feed composition and total quantity injected. Outlet mass calculations were based on the total quantity and

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composition of post-run dust collected from the GHT and the tap/ceramic baghouse, and the quantity and composition of tapped metal and ceramic phases. Additional scraping samples were taken from the interior surface of the off-gas duct to assess the quantity and identity of dust deposition, if present.

4.5. Experimental Results

In the first set of experiments, lead and zinc were injected in an Fe-C metal bath. The quantity of metals injected was too small to ensure accurate partitioning data. During a second set of experiments, new methods have been added to the sampling protocol to improve mass balance closure data. The third set of experiments included injection of zinc and cesium in an Fe-C-S system.

4.6. Mass Balance Data (1)

The following tables summarize VHMs partitioning and mass balance closure data collected during demonstration-scale experiments. The experimental campaigns included R005-93-015, R005-93-017/018, R005-94-003/004, R005-94-005/006, and R005-94-008/009.

Table 13
R005-93-015: VHM's Partitioning

Sample Location	Pb (lb)	Pb Recovery (%)	Zn (lb)	Zn Recovery (%)
Total injected	7.79		7.79	
Tapped metal	ND	0	1.39	17.8
Tapped ceramic	ND	0	0.27	3.5
Gas cooler dust	0.008	0.11	0.01	0.12
Process baghouse dust	0.99	12.73	2.70	34.67
Tap/ceramic baghouse dust	0.0002	0.002	0.01	0.13
Cumulative	1.00	12.84	4.38	56.25
Scrubber - quench tank	0.31	3.98	0.28	3.60
Error - metal detection limits	0.13	1.67	0	0
Error - ceramic detection limits	0.02	0.26	0	0
Cumulative	1.46	18.75	4.66	59.85
Error - missing dust if dust recovery is 70%	1.43	18.33	3.88	49.88
Error - missing dust if dust recovery is 35%	2.85	36.67	7.77	99.77
Cumulative (with range for unaccounted dust)	2.89 - 4.31	37.08 - 55.42	8.54 - 12.43	109.73 - 159.62

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Table 14
R005-93-017/018: VHM's Partitioning

Sample Location	Pb - lbs	Pb - % recovery	Zn (lb)	Zn Recovery (%)
Total injected	7.616		7.616	
Tapped metal	ND	0	0.38	5.05
Tapped ceramic	ND	0	ND	0
Gas cooler dust	0.92	12.09	0.35	4.61
Process baghouse dust	0.21	2.81	0.24	3.18
Tap/ceramic baghouse dust	0.72	9.40	0.017	0.22
Cumulative	1.85	24.30	0.99	13.06
Scrubber - quench tank	0.10	1.31	0.03	0.40
Error - metal detection limits	0.16	2.14	0	0
Error - ceramic detection limits	0.004	0.05	0.001	0.01
Cumulative	2.11	27.80	1.02	13.47
Error - missing dust if dust recovery is 70%	2.64	34.72	0.87	11.44
Error - missing dust if dust recovery is 35%	5.29	69.44	1.74	22.88
Cumulative (with range for unaccounted dust)	4.75 - 7.40	62.52 - 97.24	1.89 - 2.76	24.91 - 36.35

Table 15
R005-94-003/004: VHM's Partitioning

Sample Location	Pb - lbs	Pb - % recovery	Zn - lbs	Zn - % recovery
Total injected	11.52		11.52	
Tapped metal	ND	0	ND	0
Tapped ceramic	0.02	0.21	0.007	0.06
Gas cooler dust	0.10	0.83	0.012	0.104
Process baghouse dust	1.53	13.28	0.84	7.29
Tap/ceramic baghouse dust	1.03	8.98	0.087	0.76
Cumulative	2.68	23.30	0.95	8.25
Scrubber - quench tank	1.87	16.23	1.09	9.46
Error - metal detection limits	0.13	1.12	0.32	2.78
Error - ceramic detection limits	0	0	0	0
Cumulative	4.68	40.65	2.36	20.49
Error - missing dust if dust recovery is 70%	3.80	32.97	1.34	11.65
Error - missing dust if dust recovery is 35%	7.59	65.95	2.68	23.30
Cumulative (with range for unaccounted dust)	8.48 - 12.27	73.62 - 106.60	2.70 - 5.04	32.14 - 43.79

Table 16
R005-94-005/006: VHMs Partitioning

Sample Location	Pb - lbs	Pb - % recovery	Zn - lbs	Zn - % recovery
Total injected	22.7		7.43	
Tapped metal	0.53	2.33	1.05	14.13
Tapped ceramic	0.01	0.04	0.02	0.27
Gas cooler dust	0.20	0.88	0.67	9.02
Process baghouse dust	0.38	1.67	0.87	11.71
Tap/ceramic baghouse dust	0.20	0.88	0.03	0.40
Cumulative	1.32	5.80	2.64	35.53
Scrubber - quench tank	0.28	1.25	0.24	3.23
Error - metal detection limits	0	0	0	0
Error - ceramic detection limits	0	0	0	0
Cumulative •	1.60	7.05	2.88	38.76
Error - missing dust if dust recovery is 70%	0.34	1.5	0.67	9.10
Error - missing dust if dust recovery is 35%	1.45	6.38	2.68	39.24
Cumulative (with range for unaccounted dust)	1.60 - 3.39	7.05 - 13.43	2.88 - 5.56	38.76 - 78.00

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Table 17
R005-94-008/009: VHMs Partitioning

Sample Location	Pb - lbs	Pb - % recovery	Zn - lbs	Zn - % recovery
Total injected	0.43		7.51	
Tapped metal	0.34	79.1	0.66	8.8
Tapped ceramic	0.01	2.3	0.01	0.13
Gas cooler dust	0.03	6.9	0.21	2.8
Process baghouse dust	10.06	2339	16.03	213
Tap/ceramic baghouse dust	0.05	11.5	0.01	0.13
Cumulative	10.48	2437	16.92	225
Error - metal detection limits	0	0	0	0
Error - ceramic detection limits	0	0	0	0
Cumulative	10.48	2437	16.92	225
Error - missing dust if dust recovery is 70%	4.31	1002	6.87	92
Cumulative (with range for unaccounted dust)	10.48 - 14.79	2437 - 3439	16.92 - 23.79	225 - 317

The recovery values for both Pb and Zn shown in Table 13 through Table 16 were low, averaging less than 35 wt% (discounting the low dust collection error assumption). This was caused by the inability to account for all the dust accumulation, either because of ineffective post-run dust collection or because additional areas in the GHT were not examined for dust deposition. A thorough cleaning of the process baghouse following run R005-94-009 (see Table 17) revealed the presence of dust and VHMs contributed from earlier experiments. The quantity of dust collected from the gas handling train was estimated to comprise 35 to 70 wt% of accumulated dust. These estimates were used to calculate a range of VHMs recovery values (error in dust collection measurement). In addition, the estimated error due to equipment detection limits in the metal and ceramic layers was included in the mass balance calculations.

The lack of retention of Pb and Zn in the metal or ceramic phase was in-agreement with results from earlier heavy metal partitioning studies. In general, the majority of zinc and lead was collected in the form of dust. Figure 29 and Figure 30 show the

cumulative percent recovery of Pb and Zn observed in the CEP system. It was also observed that for a given component, the percent recovery in each location in the gas handling train (e.g., process baghouse vs. gas cooler) was not consistent. The chemical form of the volatilized metal was thought to affect its condensation profile in the gas handling train. During processing of feed containing a relatively higher concentration of chlorinated components, VHM chlorides were preferentially formed (e.g., ZnCl_2). Because the volatility of ZnCl_2 is higher than that of ZnO (see Figure 22), zinc chloride was expected to travel farther down the GHT, and hence accounting for the difficulty in determining all the areas of deposition.

Figure 29
Cumulative Pb Recovery in the Demonstration Unit

Figure 30
Cumulative Zn Recovery in the Demonstration Unit

Additional samples were obtained from the off-gas duct in order to determine the extent of VHMs deposition upstream of the gas cooler. Results of the analytical analysis are shown in Table 18.

Table 18
Off-gas Duct Sampling Analysis

Element	South portion of disconnect flange (Wt%)	6" Downstream of south portion of disconnect joint (Wt%)
Lead	<0.010	<0.010
Zinc	<0.010	<0.010
Iron	56.87	61.25
Sulfur	2.81	2.45
Chlorine	<2.44	3.82
Phosphorus	0.26	0.39
Chromium	0.61	0.69
Sodium	3.31	1.56

No significant quantities of lead and zinc were detected. Although thermodynamic analysis predicted VHMs deposition in the off-gas duct, physical entrainment of dust particulates by the off-gas flow was believed to preclude any significant deposition.

The scrubber material contribution to the mass balance was thought to contain a high degree of error inherent in the measurement techniques. The post-run sampling method of the scrubber/quencher solution did not provide a representative sample of the materials captured in the scrubber. To address this deficiency, a new sampling protocol was used during R005-94-008/009 involving diverting a slipstream from the inlet to the scrubber and sending it through a set of impingers designed specifically for VHMs capture. No difference between the baseline (inert purge mode) concentrations and the majority of the impinger samples, indicating that only trace amounts of VHMs were present upstream of the scrubber. However, the feed concentration of Pb and Zn was very low for this run, which might have contributed to the lack of any detectable concentrations. Sampling from this location was continued in later runs.

4.7. Mass Balance Data (2)

To improve VHMs material balance closure, additional injection experiments were performed. Previous sampling protocols had limitations which contributed to some degree of uncertainty in the experimental results. Modifications to the sampling protocol and sampling devices were implemented in order to improve the quality of data collected. Isokinetic dust samples were taken in order to correlate the amount of dust generated with that actually collected. An attempt was made to improve post-run dust removal from the process baghouse and the gas cooler to reduce error associated with incomplete recovery.

A new sampling method was implemented downstream of the process baghouse by diverting a slipstream from the inlet stream to the scrubber and sending it through a set of impingers designed specifically for VHMs capture. The impinger set-up followed standard method 5 (M5) protocol for volatile heavy metal (lead) capture. The impinger train was comprised of 2 impingers filled with 0.1N nitric acid, one knockout impinger (empty), and one impinger filled with silica gel. The nitric acid solutions were analyzed for Pb and Zn. Preliminary impinger samples indicated that the quantity of VHMs present downstream of the process baghouse was negligible. Analysis of samples taken during VHM-enriched feed injection were used to confirm these findings.

Table 19 outlines the samples taken during the experimental campaigns (R005-94-010 and R005-94-011) and their purpose.

Table 19
VHM Samples During R005-94-010 and R005-94-011

Sample Location	Type of Sample	Purpose
Dutchman	non-isokinetic dust	Determine ratio of VHMs to other species to see if VHMs drop out in lines preferentially relative to other species
Baghouse inlet	isokinetic dust	Determine dust loading and VHM levels
Scrubber inlet	slipstream to impingers	Determine quantity of VHMs that remains in dust stream
Reactor bath	metal	Identify amount of VHMs which remain in reactor

Table 20 and Table 21 show a summary of the mass balance calculations for lead and zinc.

Table 20
R005-94-010: Volatile Heavy Metal Partitioning

Sample Location	Quantity Pb (lb)	Pb Recovery (%)	Quantity Zn (lb)	Zn Recovery (%)
Total injected	20.26		19.45	
Tapped metal	1.04	5.1	1.6	8.22
Tapped ceramic	0	0	0	0
Gas cooler dust	0.34	1.68	1.36	6.99
Process baghouse dust	20.51	101.23	9.51	48.89
Tap/ceramic baghouse dust	0	0	0	0
Cumulative	21.89	108.05	12.47	64.10
Error - metal detection limits	0	0	0	0
Error - ceramic detection limits	0.025	0.15	0.005	0.02
Cumulative	21.92	108.20	12.48	64.12

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Table 21
R005-94-011: Volatile Heavy Metal Partitioning

Sample Location	Quantity Pb (lb)	Pb Recovery (%)	Quantity Zn (lb)	Zn Recovery (%)
Total injected	3.37		11.34	
Tapped metal	0.38	11.27	0.08	0.67
Tapped ceramic	0.001	0.03	0.0009	0.01
Gas cooler dust	0.039	1.15	0.386	3.41
Process baghouse dust	9.87	292.92	11.09	97.76
Tap/ceramic baghouse dust	0	0	0	0
Cumulative	10.29	305.39	11.55	101.84

Table 21 shows lead recovery was close to 100 wt% while zinc recovery was 64 wt%. In R005-94-011, calculated lead recovery was approximately 300 wt% and the zinc recovery was close to 100 wt%. These recovery values are relatively high compared with 25-30 wt% recoveries that were calculated in the earlier runs. The dramatic improvement in the relative recovery values for lead and zinc was attributed to effective cleaning and collection of dust from the process baghouse and other locations in the GHT. The large amount of lead collected from the gas handling train following R005-94-011 may have been contributed by earlier runs, hence accounting for a theoretically unplausible recovery value.

Impinger sampling was also performed at the baghouse outlet to determine the extent of VHMs which were present downstream of the baghouse. The results are summarized in Table 22 and Table 23.

Table 22
R005-94-010: VHM Impinger Baghouse Outlet Sampling

Feed (lb/min)	g Zn/SCF	g Pb/SCF	g Zn/g Zn fed (%)	g Pb/g Pb fed (%)
0	0.0012	0.0012		
1.2	9.69E-06	2.42E-05	0.02	0.06
1.4	0.0028	0.0029	6.91	6.73
1.9	0.0002	0.0001	0.37	0.23
Average	0.0011	0.0011	1.82	1.76

Table 23
R005-94-011: VHM Impinger Baghouse Outlet Sampling

Feed Rate (lb/min)	g Zn/SCF	g Pb/SCF	g Zn/g Zn fed (%)	g Pb/g Pb fed (%)
0	0.0007	0.0002		
1.3	0.0003	0.0002	0.77	0.38
2.1	0.0001	3.7E-05	0.19	0.06
Average	0.0002	0.0001	0.48	0.22

The average amount of each element collected at the baghouse outlet per amount fed was less than two percent in run R005-94-010, and less than half a percent in run R005-94-011, indicating that most VHMs were captured upstream of the scrubber.

4.8. Mass Balance Data (3)

Mass balance calculations were performed for zinc and cesium injected in an Fe-C-S bath containing varying levels of sulfur. Dust samples were taken from pre-specified sampling ports and analyzed for Zn and Cs, as outlined in Table 24.

Table 24
VHMs Sampling Protocol

Sample Location	Type of Sample	Purpose
Hot dust port	isokinetic dust	Determine dust loading and VHMs levels downstream of reactor
Baghouse inlet	isokinetic dust	Determine dust loading and VHMs levels upstream of baghouse
Reactor bath	metal	Identify amount of VHMs which remain in reactor

The partitioning data for Zn and Cs for runs R005-95-004/005, R005-95-006, and R005-95-007 are summarized in Table 25, Table 26, and Table 27, respectively.

Table 25
R005-95-004/005: Partitioning Data for Zn and Cs

Location	Quantity (lb)	Wt% Cs	Wt% Zn	Quantity Cs (lb)	Quantity Zn (lb)	Wt% Cs Recovery	Wt% Zn Recovery
Final Tapped Metal (run 005) ¹	4463	0.001	0.007	0.045	0.321	0.49	2.66
Gas Cooler	12	0.53	2.24	0.06	0.27	0.69	2.23
Process Baghouse	292	0.80	1.73	2.34	5.05	25.39	41.86
Total Recovery						26.57	46.75

¹ No final metal sample was taken from run 004

Table 26
R005-95-006: Partitioning Data for Zn and Cs

Location	Quantity (lb)	Wt% Cs	Wt% Zn	Quantity Cs (lb)	Quantity Zn (lb)	Wt% Cs Recovery	Wt% Zn Recovery
Final tapped metal	3642	0.005	0.0012	0.182	0.044	1.3	0.31
Process baghouse	40	0.67	1.99	0.268	0.796	1.91	5.69
Tap/ceramic baghouse	28.3	0.01	0.03	0.003	0.08	0.02	0.06
Gas cooler	0						
Total recovery						3.23	6.06

Table 27
R005-95-007: Partitioning Data for Zn and Cs

Location	Quantity (lb)	Wt% Cs	Wt% Zn	Quantity Cs (lb)	Quantity Zn (lb)	Wt% Cs Recovery	Wt% Zn Recovery
Partial tapped metal	3035	0.021	0.0077	0.637	0.234	2.10	0.77
Final tapped metal	2000	0.022	0.0072	0.44	0.144	1.45	0.47
Gas cooler dust	31	4.84	6.4	1.50	1.984	4.94	6.53
Process baghouse dust	426	4.27	6.24	18.19	26.582	59.84	87.44
Tap/ceramic baghouse dust	28	0.01	0.04	0.003	0.011	0.009	0.037
Total recovery						68.32	95.25

There was a wide variation in the recovery values for zinc and cesium (6, 47, and 95 wt% for Zn, and 3, 27, and 68 wt% for Cs), primarily due to inconsistent post-run dust collection from the gas handling train. Consistent with earlier findings, the majority of dust was collected from the process baghouse. On-line isokinetic dust samples were taken to gain a better understanding of VHMs loading in the gas handling train. The results are summarized in Table 28 through Table 31.

Table 28
R005-95-004: VHM Loadings during Solids Injection

Solids Feed Rate (lb/min)	Hot Dust Port: g Cs/g Cs fed	Hot Dust Port: g Zn/g Zn fed
1.3	0.47	0.30
1.6	0.31	0.25
1.3	0.36	0.26
1.2	0.16	0.14
Average	0.33	0.24

Table 29
R005-95-005: VHM Loadings during Liquid Injection

Location	Wt% Zn	g Zn/g Zn fed
Hot dust port	12.07	0.10
Baghouse inlet	2.37	0.07

Table 30
R005-95-006: VHM Loadings during Feed Injection

Solids Feed Rate (lb/min)	Hot Dust Port: g Cs/g Cs fed	Baghouse Inlet: g Cs/g Cs fed	Hot Dust Port: g Zn/g Zn fed	Baghouse Inlet: g Zn/g Zn fed
2.2	0.44		0.36	
1.9	0.30	0.26	0.34	0.27
1.5	0.41	0.45	0.51	0.50
2.0	0.37	0.33	0.39	0.40
1.9	0.40	0.38	0.49	0.41
2.4		0.21		0.23
Average	0.38	0.33	0.42	0.36

Table 31
R005-95-007: VHM Loadings during Feed Injection

Solids Feed Rate (lb/min)	Hot Dust Port: g Cs/g Cs fed	Baghouse Inlet: g Cs/g Cs fed	Hot Dust Port: g Zn/g Zn fed	Baghouse Inlet: g Zn/g Zn fed
1.6		0.57		1.02
1.8		0.70		1.01
2.3	0.25	0.30	0.38	0.52
2.3	0.96	0.20	1.11	0.30
2.4		0.11		0.20
2.5		0.19		0.21
2.4		0.36		0.43
Average	0.61	0.35	0.75	0.53

Typical loading (wt element/wt element fed) values for Zn and Cs ranged from 0.3 to 0.5 at both the hot dust port (gas cooler inlet) and the baghouse inlet. The metals' loadings in the baghouse inlet were only slightly less than those in the inlet to the gas cooler, indicating that only a small percentage of the volatile metals was deposited in the gas cooler. This is consistent with the fact that the majority of post-run dust was found in the process baghouse.

furthermore, the calculated loading values (wt element/wt element fed) of Zn and Cs indicated deposition of significant quantities of these elements in the off-gas piping upstream of the hot dust port. When samples were scraped off the piping surface and analyzed, small concentrations of zinc and cesium were detected. It was postulated that the observed loading was affected by the amount of time required for dissolution of Zn and Cs in the bath and subsequent volatilization. The isokinetic samples did not capture all the zinc and cesium added to the bath due to insufficient volatilization time.

The relatively small magnitude of the loading values calculated for both zinc and cesium indicate deposition of significant quantities of these elements in the off-gas piping upstream of the hot dust port. When samples were scraped off the piping surface and analyzed, only small concentrations of zinc and cesium were detected. It was postulated that the observed loading was affected by the amount of time required for dissolution of Zn and Cs in the bath before subsequent volatilization. The rates of

VHMs incorporation and volatilization are normally determined by the operating conditions such as bath temperature and the components' vapor pressures. The lower than predicted loadings were derived from the on-line isokinetic samples, which did not capture all the zinc and the cesium added to the bath due to insufficient volatilization time.

To compare with the actual amount of post-run dust collected, the total amount of dust predicted to be generated was calculated using average dust loadings, VHMs concentrations in the dust, and feed injection times. The predictions reflected dust and VHMs generation during feed injection only, and did not account for volatilization occurring during inerts injection or during post-injection operations. Therefore, it was believed that the amount of dust calculated would underestimate the actual amount of dust expected to accumulate in the gas handling train, assuming that dust collection was complete. Estimated dust and VHMs generation for runs R005-95-006 and R005-95-007 are shown in Table 32 and Table 33. The amount of material collected in the gas cooler was based on the difference between the dust loading entering the gas cooler and the dust loading entering the baghouse.

Table 32
R005-95-006: Estimated Dust Generation and VHMs Recovery

	Gas Cooler	Baghouse
Average off-gas rate (scfm)	161	161
Total injection time (min)	820	820
Total dust collected (lb)	11.85	62.17
Avg Cs concentration (Wt%)	7.30	7.46
Avg Zn concentration (Wt%)	8.03	8.21
Wt% Cs recovery (based on dust generated)	6.18	33.11
Wt% Zn recovery (based on dust generated)	6.80	36.48

Table 33
R005-95-007: Estimated Dust Generation and VHM's Recovery

	Gas Cooler	Baghouse
Average off-gas rate (scfm)	146	146
Total injection time (min)	1764	1764
Total dust collected (lb)	20.3	117.2
Avg Cs concentration (Wt%)	7.65	7.13
Avg Zn concentration (Wt%)	8.71	10.58
Wt% Cs recovery (based on dust generated)	5.11	27.51
Wt% Zn recovery (based on dust generated)	5.71	40.01
¹ Problems with sample equipment prevented isokinetic sampling. This number was generated assuming a similar difference in dust loading between hot dust port and baghouse inlet as observed in run R005-95-006.		

The projected recovery values for zinc and cesium in run R005-95-006 were significantly higher than the actual recoveries (see Table 33) calculated based on the amount of dust collected. In addition, the projected dust generation during feed injection was 50% higher than the actual amount of dust recovered from the process baghouse. These findings are consistent with the conclusion that post-run dust collection was incomplete. In run R005-95-007, the projected recovery values for Zn and Cs were less than the actual recoveries by approximately 50%, and the projected dust generation was one third that of the actual dust removed from the process baghouse. The dust loading projections were based on isokinetic dust samples taken during feed injection only, and did not account for dust and VHM's generation during inert injection.

4.9. Conclusions

- Volatile heavy metals (Pb, Zn, and Cs) partitioned almost completely to the gas phase, with very little retained in the tapped metal or ceramic phase;
- Mass balance closure for VHM compounds varied significantly with the extent of post-run dust removal from the process baghouse. Materials mass balance closure approached 100 wt% for Pb and Zn in some experiments. The highest Cs recovery was 68 wt%;
- VHM loadings typically varied between 0.3-0.5 g/g fed at both the hot dust port and the baghouse inlet, based on isokinetic dual sampling. There was only a

slight drop in dust loading observed between the two locations, indicating that deposition of VHMs in the gas cooler was much less than in the baghouse;

- Calculations of projected dust and VHMs generation was consistent with the fact that the majority of dust accumulation occurred in the process baghouse. The projections also confirmed that the mass balance closure was strongly dependent on the extent of dust collection;
- Thermodynamic analysis predicted a large degree of VHM deposition in the off-gas duct between the CPU and the gas cooler. However, sampling analysis showed very little VHM concentration in the line, primarily due to entrainment by the high gas velocities exiting the CPU;
- Impinger sampling indicated that the quantity of VHMs present downstream of the baghouse was negligible.

4.10. Addition of Lead Chromate - Part 1

4.11. Objective

In earlier volatile heavy metal partitioning studies, VHMs were injected through the bottom tuyere in a fine solid form and in a dissolved liquid form. The amount of VHMs injected comprised 1-3 wt% of the total feed stream. Processing of waste feed materials can also be accomplished by top addition of materials on the metal bath surface. In this experiment, lead-containing feed was top-added below the surface of a molten metal bath, and data was collected on the partitioning of its elemental components.

4.12. Experimental Set-up

The test material for the trial consisted of lead chromate contained in 2 1/2" x 2 1/2" x 7.25" ceramic shell. Each shell, containing 1 lb of lead chromate powder, was packed in an open ended 3 1/2" x 3 1/2" x 8" metal container made from 1/16" steel plate. Steel balls were used to fill up some of the enclosed spare volume of the container and the contents were held in place by expanded metal mesh tacked over the open end. Vent holes near the closed end of the container were covered with mineral wool to prevent the lead chromate powder from being ejected by gases vented from the container. A 2" diameter solid steel bar 24" long was welded to the closed end of each container to counter buoyancy forces from the submerged container. The overall length, 32", was chosen to prevent the container assembly from lying horizontally in the metal bath.

A 36" long feeding pipe 6" in diameter was mounted on a pneumatically actuated gate valve sighted immediately above the molten metal bath of the CEP reactor. An isolating valve on top of the pipe allowed loading of individual shell container assemblies. Nitrogen purge and vent connections on the pipe enabled air and furnace gases to be swept from the loading tube as required.

The ceramic shells were enclosed in steel containers in order to force the containers to be submerged beneath the metal bath, hence ensuring that disposal of the powder over the bath and its possible entrainment in the off-gas was effectively minimized. This procedure was deemed necessary because the CEP demonstration unit used for this experiment consists of one chamber only and, therefore, does not facilitate pre-processing of the feed while maintaining the quality of the off-gas.

4.13. Method of Approach

Prior to lead chromate addition, five metal samples were taken in quick succession to determine average chromium and lead baseline concentrations in the metal bath. An isokinetic gas probe was operated for 30 minutes at the baghouse inlet in order to collect a baseline dust sample.

One shell-container assembly was loaded into the feeding tube which was then isolated and purged. The lower gate valve was activated and the assembly with the round bar uppermost was dropped vertically into the bath. A slight darkening of the TV monitor display provided visual evidence of the container's drop into the bath. Five more markers were loaded and dropped in succession over a period of 21 minutes.

Dust sampling at the baghouse inlet was initiated at the start of feed addition and was continued for 30 minutes after the last shell was added. Five more post-injection metal samples were taken 60 minutes after the last shell was added to the bath to determine metals' retention in the bath. In addition, post-run metal and dust samples were taken from the tapped metal and the GHT, respectively, for analysis. The metal and dust samples were analyzed by an independent third party laboratory. Table 34 shows the sampling protocol followed during the experiment.

Table 35 shows chromium and lead levels detected in the metal samples during the experiment.

Table 34
Sampling Protocol

Timing	Sample Type	Purpose
Baseline (prior to lead chromate addition)	Metal samples (5)	Obtain average Cr and Pb baseline concentrations in the metal
Baseline (prior to lead chromate addition)	Isokinetic dust at the baghouse inlet port	Determine Cr and Pb baseline concentrations in the dust
During addition of lead chromate (start 5 minutes before first addition and finish 30 minutes after final addition)	Isokinetic dust at the baghouse inlet port	Determine Cr and Pb concentrations and loading in the dust during injection
30 minutes after final addition	Isokinetic dust at the baghouse inlet port	Determine residual Cr and Pb concentrations in the dust
60 minutes after final addition	Metal samples (5)	Obtain average final Cr and Pb concentrations in the metal
Post-run (after metal tapping)	Tapped metal sample	Obtain post-run Cr and Pb concentrations in the metal
Post-run	Collected dust from GHT	Obtain post-run Cr and Pb amounts in the GHT

Table 35 Concentration of Cr and Pb in the Metal Bath

Sample	Pb (ppm)	Cr (ppm)
Pre-Injection Metal (Avg)	< 25	380±11
Post-Injection Metal (Avg)	1264±80	692±43
Post-Run Metal	< 25	830

4.14. Discussion

In a CEP system, reaction thermodynamics and solution equilibria drive feed conversion and product synthesis. When a feed is injected into the CEP reactor, it dissociates into its elemental constituents. Reducible metals will readily dissolve in the molten metal solvent, as predicted by the Gibbs Free Energy diagram (Figure 31), under

the given reaction conditions. Therefore, at a reaction temperature of 1260-1345 °C, chromium will be recovered as an alloy in the iron solvent.

Figure 31
Gibbs Free Energies of Oxidation

Source: Moore, J.J., *Chemical Metallurgy*, 2nd Edition Butterworth & Co., London, 1990

Lead partitioning, on the other hand, is dependent on a number of factors and hence cannot be predicted simply. Although the boiling point of lead (1740 °C) is higher than normal CEP operating temperatures, the vapor pressure of lead is high enough that it can severely limit the capture of lead in the metal phase. When lead (or lead compounds) is added to the metal bath, it will dissolve until it reaches its solubility limit as determined thermodynamically. The amount of time needed for lead concentration in the bath to reach steady-state depends on the operating conditions. In addition, the stripping action of the evolving gas stream can also cause entrainment of

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lead into the gas handling train. Earlier work (see 3.7.1) had suggested that at temperatures of 1480-1540 °C, less than 15% of the lead was recovered in the metal phase indicating significant lead volatility.

Post-run partitioning data for chromium and lead were calculated. In order to maximize the amount of Cr and Pb accounted for, post-run dust and liquid samples were collected from the various process units in the gas handling train including the process baghouse, the gas cooler, the quencher, the scrubber, and the tap/ceramic baghouse. Mass balance closure data and recovery values for Cr and Pb are summarized in Table 36.

Table 36 Post-run Partitioning and Recovery data for Cr and Pb

	Qty (lbs)	Pb (ppm)	Cr (ppm)	Pb (lbs)	Cr (lbs)	Pb (%) recovery)	Cr (%) recovery)
Gas cooler average	31	1920	163	0.060	0.005	1.575	0.6737
Tap/ceramic baghouse	28	760	510	0.021	0.014	0.563	1.904
Process baghouse	426	3888	140	1.656	0.060	43.817	7.952
Scrubber (gals)	100	92	6	0.077	0.005	2.031	0.668
Quencher (gals)	100	32	14	0.027	0.012	0.706	1.558
Metal (post-addition sample)	2000	1239 ¹	312 ²	2.478	0.624	65.556 ³	83.20 ⁴
Metal ⁵ (tapped sample)	2000	25	450 ⁶	0.050	0.900	1.323 ⁷	120 ⁸
Total recovery (based on tapped metal samples)						50.02	132.76
^{1,2} (post-addition concentration) - (pre-addition concentration)							
^{3,4} Recovery % values in the metal bath based on post-addition samples							
⁵ Post-run sample							
⁶ (post-run concentration) - (pre-addition concentration)							
^{7,8} Recovery % values in the metal bath based on post-run samples							

Recovery in the metal phase was calculated from the difference in average initial and final concentrations, based on a bath weight of 2,000 lb. This bath weight was determined as the average of the initial pre-melting metal charge to the reactor and the amount of metal tapped out (rather than just using the final tap weight). The lead chromate powder material was determined to contain 63 wt% Pb and 12.5 wt% Cr. The weight of the powder material was approximately 1 lb per shell.

As predicted, chromium was almost completely partitioned to the metal phase. Only trace levels were detected throughout the gas handling train, as shown in Table 37. The high chromium recovery (greater than 100%) was due to uncertainty in estimating the final metal bath weight and to the fact that the total amount of chromium (0.75 lb) added to the reactor was small relative to the total bath weight (2,000 lb).

Post-run analysis of the tapped metal samples (see Table 35) shows that changes in pre- and post-run lead levels were not detectable, indicating complete partitioning of lead to the gas phase. These results are consistent with data observed during earlier lead partitioning experiments. The partitioning of significant quantity of Pb to the metal phase observed shortly after lead chromate addition was due to insufficient volatilization time.

Volatilization rates for lead were calculated during different time periods in order to compare with the known quantities of Pb collected in the dust. A summary of these calculations is shown in Table 37.

Table 37
Pb Volatilization Calculations

	During markers addition	Post markers addition (1 hour)	Inert injection prior to tapping	Total Pb (lbs)
Initial Pb in bath (lbs)	3.78	2.52 ¹	2.06	
Total Off-gas flow (scfm)	90	85	100	
Time (min)	102	60	160	
Total Pb volatilized (lbs)	0.47	0.18	0.46	1.11
¹ based on post-addition metal samples				

Based on the amount of volatilized Pb calculated for each time period, the high concentration of Pb in the metal bath analytically observed 60 minutes after the last feed addition is reasonable. The total amount removed from the bath based on the volatilization calculations was less than observed by the tapped metal analysis. However, these calculations did not include any removal by entrainment, which can be quite significant at the observed off-gas rates. The combination of the volatilization and the entrainment over a sufficient time period resulted in approximately 100% partitioning of Pb to the gas phase.

The majority of lead was collected from the process baghouse dust. The overall recovery of Pb was 50%, which is slightly higher than typical Pb recovery data from previous experimental runs on the demonstration unit. The incomplete closure is attributed to difficulty in accounting for the small amounts of lead injected and to the incomplete recovery of dust from the gas handling train.

4.15. Conclusions

- The injection method ensured dissolution of the marine markers in the bath without allowing bypassing of lead chromate;
- Chromium partitioned almost completely to the metal bath. Only trace levels were detected in the dust entering the baghouse;
- Based on post-run samples, lead partitioned almost completely to the gas phase and was condensed and captured in the GHT. Volatilization calculations supported the higher Pb concentrations observed shortly following lead chromate addition.

4.16. Addition of Lead Chromate - Part 2

4.17. Objective

During an earlier experiment, ceramic containers of lead chromate were added to the top of the metal surface. To ensure complete submersion upon addition, the ceramic shells were enclosed in steel containers. The metal components (Cr and Pb) partitioning was evaluated and documented (see 3.7.2). The primary goal of this experiment was to examine the metals' dissolution and partitioning patterns through addition of lead chromate shells on top of the metal bath without submerging. In addition, comparisons were made with submerged top addition of the feed material.

4.18. Experimental Procedure

Prior to lead chromate addition, the CEP demonstration unit was maintained at steady-state conditions during inert gas injection through the tuyere to induce bath agitation. The liquid metal temperature was 2,750 °F. The metal bath carbon content was 3 wt%.

4.18.1. Base Line

Five metal samples were taken in quick succession prior to feed addition to provide a base line metal analysis in the bath. Fifteen pounds of nickel was added as a tracer so that a more accurate determination of the metal bath weight could be calculated through subsequent bath meta sampling. Off-gas dust sample were also taken prior to lead chromate charging to determine base line conditions.

4.18.2. Single Addition of Containers

Twenty ceramic shell containers were added individually through the double lock and hopper system to the bath over a period of 40 minutes. Off-gas dust sampling was performed throughout the addition period and was concluded only 30 minutes after the last container was added. Five metal samples were taken from the bath after addition was completed.

4.18.2.1. Multiple Addition of Containers

An additional twelve lead chromate containers were added to the bath in quick succession. Two batches each containing five shells and one batch of two shells were all added through the double lock and hopper feeding system within three minutes. Five metal samples were taken from the bath 10 minutes after the bulk addition of markers was completed. Samples were taken at an approximately two minute intervals. Single metal samples were taken at hourly intervals for another three hours to examine short and long term bath compositions.

4.19. Results And Discussion

4.19.1.1. Base Case

The initial five metal samples were analyzed by X-ray fluorescence (XRF) in house. A summary of metal sampling analysis is shown in Table 38. Prior to lead chromate addition, bath chromium, lead, and nickel content was 0.0435 wt%, < 0.003 wt%, and 0.032 wt%, respectively. The lead content was picked up merely as a trace. Fifteen pounds of nickel were added to the bath. The nickel content rose to 0.480 wt% indicating a bath weight of 3,330 lb.

Table 38
Metal Sampling Analysis: Base Case

Sample No	Concentration Cr (Wt%)	Pb (Wt%)	Ni (Wt%)
M1	0.042	<0.001	0.033
M3	0.043	<0.004	0.034
M4	0.043	<0.001	0.030
M5	0.044	<0.004	0.030
M7	0.044	<0.001	0.033
Average	0.0435	<0.003	0.032

4.19.1.2. Single Additions

Five samples (M9 through M13) were taken after the sequential addition of 20 individual ceramic containers of lead chromate. The average chromium content of the bath rose to 0.14 wt%. The bath nickel content of 0.488 wt% indicated a bath weight of 3,290 lb. Based on this close correspondence, a bath weight of 3330 pounds was used throughout the analysis.

Lead remained at a trace level in the bath despite the addition of approximately 13.8 lb Pb contained in the 20 containers, indicating complete partitioning to the gas phase. The average bath concentration of chromium was 0.14 wt%, resulting in an overall recovery of 127 wt% (mass Cr out/mass Cr in).

Table 39
Single Additions of Lead Chromate Ceramic Containers

Sample No	Concentration Cr (Wt%)	Pb (Wt%)	Ni (Wt%)
M9	0.13	<0.001	0.50
M10	0.18	<0.001	0.49
M11	0.13	<0.001	0.49
M12	0.13	<0.001	0.49
M13	0.13	<0.004	0.49
Average	0.14	<0.002	0.049

4.19.1.3. Multiple Additions

Twelve lead chromate containers were added batchwise (batches of 5, 5, and 2 containers). Samples M14 through M18 were taken at timed intervals of approximately 2 minutes. Sampling began ten minutes after the last batch was added.

It was observed that dust loading in the off-gas stream increased shortly after the addition of the containers before gradually declining. Lead volatilization from the bath occurred upon addition which diminished as the lead content in the bath was reduced. The bath lead content remained at trace levels throughout the sampling period, indicating rapid dissolution in the bath followed by evaporation into the gas phase. Alternatively, lead sublimation could have occurred without dissolution in the metal bath prior to departing the CPU.

Bath metal sampling revealed an average chromium content of 0.176 wt%, resulting in a recovery value of 77 wt%. The overall (single and multiple addition sequences) mass balance closure for chromium was 107.5 wt%. Table 40 is a summary of metal sampling analysis.

Table 40
Multiple Additions of Lead Chromate Ceramic Containers

Sample No	Concentration Cr (Wt%)	Pb (Wt%)	Ni (Wt%)
M14	0.16	<0.001	0.51
M15	0.17	<0.001	0.50
M16	0.18	<0.004	0.50
M17	0.20	<0.004	0.49
M18	0.17	<0.004	0.51
Average	0.18	<0.003	0.502

4.19.1.4. Isokinetic Sampling

Isokinetic dust sampling was performed at the baghouse inlet prior to, during, and after lead chromate containers were added. Pre-addition samples were taken to determine baseline Pb and Cr concentrations. Post-addition samples were taken to determine if lead volatilization was complete. Both the pre- and post-addition samples showed negligible accumulation of dust. The samples taken during feed addition were analyzed for Pb and Cr by an independent third party laboratory. Lead and chromium loadings in the process off-gas measured at the hot dust port and the process baghouse inlet are shown in Table 4.

Table 41
Pb and Cr Loading in the Off-gas during Lead Chromate Addition

Baghouse Inlet Samples	Addition Sequence	Pb Wt%	Cr Wt%	Pb Loading (g/scf)	Cr Loading (g/scf)
Hot dust port	Single	90.69	0.14	0.059	9.14E-05
Baghouse inlet	Single	9.38	0.07	0.238	1.78E-03
Hot dust port	Multiple	69.59	0.15	0.291	6.27E-05
Baghouse inlet	Multiple	3.96	0.01	0.004	1.0E-05
Run R005-95-007		1.40	0.07	0.0018	8.8E-05

During the addition of multiple containers, lead and chromium component loading decreased from the hot dust port to the baghouse inlet, due to condensation. The baghouse inlet loading during the single addition sequence appeared unreasonably high compared to the loading calculated during multiple additions. Moreover, the loading observed at the baghouse inlet was higher than that calculated at the hot dust port. It is most likely high due to inaccuracies with the sample weight or a large amount of dust clogging the filter and reducing the flow, resulting in non-isokinetic flows through the sample device. The loading values for Pb and Cr at the baghouse inlet were comparable to those calculated during the submerged addition of lead chromate. There was not an appreciable effect of using different charging methods on Cr and Pb concentration in the off-gas.

A standard EPA Method 5 impinger train was used to sample the process off-gas at the baghouse outlet (upstream of scrubber), to determine the amount of Pb remaining in the gas during lead chromate addition. No visible particulates accumulated on the filter, and Pb levels were non-detectable in the impinger solutions. This result is consistent with earlier findings indicating that very little, if any, VMHs existed downstream of the process baghouse.

4.20. Conclusions

- Top addition of lead chromate contained in ceramic shells to the metal bath achieved complete decomposition of the compound into its elemental components;
- Chromium partitioned to the metal bath, with negligible amounts detected in the gas phase. Lead was not retained in the metal phase leading to complete separation of the two metals;
- The method of feed addition (submerged, top-charging, singly, or batchwise) did not have an appreciable effect on the ability to effectively separate and recover chromium and lead metals.

5. System Development and Automation Conclusions

MMT has successfully a robust reactor control system which utilizes commercial off-the-shelf equipment to the maximum possible extent to monitor critical reactor parameters including bath temperature, headspace temperature, bath composition, bath level, bath pressure, containment system, tuyere injection, and visual observation. Emphasis was placed on the use of non-invasive techniques to minimize both the potential for interruption in the flow of operations and potential delay opportunities for feedback to optimize process control. Similarly, sensors for the remaining critical reactor parameters and control system hardware/software which integrates the data provided by these diverse sensors into a robust reactor control system have also been successfully demonstrated. Further, these sensors and their control system have been successfully implemented into the two commercial CEP facilities which are currently processing mixed low level wastes.

MMT has successfully developed and demonstrated particulate control methods based on the basic mechanisms for dust and particulate generation. Innovations in gas handling train technology and operation have led to both the suppression of dust formation, the recyclability of any dust that may form during processing, and the recovery of volatile heavy metals. Research and development efforts directed at particulate suppression indicate that with the exception of species predicted to volatilize in our system (e.g. lead, mercury), less than 2% will be carried over as dust and can be recycled to the bath (e.g. FeO). Further, the distribution in the particle size is skewed heavily towards the large end of the scale (i.e. greater than 10 microns), which makes them relatively easy to separate from the gas stream. The result is a system which produces a clean gas product that exceeds industrial specifications using proven, reliable technology.