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Final Report

Separation of Mercury from Flue Gas Desulfurization Scrubber Produced Gypsum

Prepared for the Department of Energy
Report DOE/ER/84669-1
Grant Number DE-FG02-07ER84669
By Frontier GeoSciences, Inc.
June 16, 2008

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1. Executive Summary

Frontier Geosciences (Frontier; FGS) proposed for DOE Grant No. DE-FG02-07ER84669 that mercury control could be achieved in a wet scrubber by the addition of an amendment to the wet-FGD scrubber. To demonstrate this, a bench-scale scrubber and synthetic flue-gas supply was designed to simulate the limestone fed, wet-desulfurization units utilized by coal-fired power plants. Frontier maintains that the mercury released from these utilities can be controlled and reduced by modifying the existing equipment at installations where wet flue-gas desulfurization (FGD) systems are employed. A key element of the proposal was FGS-PWN, a liquid-based mercury chelating agent, which can be employed as the amendment for removal of all mercury species which enter the wet-FGD scrubber. However, the equipment design presented in the proposal was inadequate to demonstrate these functions and no significant progress was made to substantiate these claims. As a result, funding for a Phase II continuation of this work will not be pursued.

The key to implementing the technology as described in the proposal and report appears to be a high liquid-to-gas ratio (L/G) between the flue-gas and the scrubber liquor, a requirement not currently implemented in existing wet-FGD designs. It may be that this constraint can be reduced through parametric studies, but that was not apparent in this work. Unfortunately, the bench-scale system constructed for this project did not function as intended and the funds and time requested were exhausted before the separation studies could occur.

2. Introduction and Intent

Over half of the U.S. energy requirement is supplied by coal-fired electrical utilities. Given the current technology and the diminished availability of “clean” coal, these plants are responsible for approximately one third of the anthropogenic mercury emitted in the U.S. annually.

Frontier GeoSciences, Inc. (Frontier; FGS) maintains that the mercury released from these utilities can be controlled and reduced by modifying the existing equipment at installations where wet flue-gas desulfurization (FGD) systems are employed. Wet-FGD technology is used to remove sulfur dioxide (SO_2) from the combustion gas (flue-gas) which is produced from burning coal. Sulfur dioxide is a precursor to acid rain and is already regulated by the Clean Air Interstate Rule (CAIR). As a pollution control device, the wet-FGD system converts hazardous SO_2 to synthetic gypsum. This process utilizes equipment that affords the utility an advantageous opportunity to add technology for mercury control.

Currently, approximately 30% of the existing coal-fired utilities have wet-FGD systems. This number is expected to increase as the supply of economical, low-sulfur coal declines. Wet-FGD systems can be effective at removing ionic mercury (Hg^{II}) from the flue-gas as the inorganic mercury salts are highly soluble in water. Elemental mercury (Hg^0), which is also present in the flue-gas, is only slightly soluble in aqueous solutions and is not typically retained by the wet-FGD system; rather, it is expelled to the atmosphere where it enters the ecosystem as a pollutant. The amount of Hg^0 and Hg^{II} in flue-gasses varies, but in many installations, Hg^0 is typically the predominant species. Consequently, promoting the formation of Hg^{II} is an active area of research among the scientific community. The major efforts to date being the use of additives to the coal feedstock (most often halides), modification or addition of selective catalytic reactors, and the implementation of plasma fields in the flue-gas transfer line. The aim of these efforts is to increase the amount of mercury, as Hg^{II}, retained in the wet-FGD liquor. It is Frontier's position that Hg^0 and Hg^{II} can be captured, without oxidation, by simply adding an amendment to the scrubber liquor which will capture both Hg^0 and Hg^{II} from the flue-gas using the wet-FGD system.

It was the intent of this proposal to demonstrate that the addition of an amendment in a simulated, wet-FGD scrubber is able to achieve this mercury capture, with added benefits. However, due to time constraints, this goal was not achieved.

3. Benefits of Technology

The use of an amendment for mercury capture in the wet-FGD system presents numerous benefits to the coal-fired utility in both terms of performance and ease of use.

Given that inorganic Hg^{II} is readily captured by the scrubber liquor and efforts are underway by others to convert elemental Hg^0 to Hg^{II} in the flue-gas stream, the wet-FGD system is a logical choice for mercury control. Metal-chelating agents have been used in the wastewater treatment industry with great success for many years. With this in mind, Frontier has developed a technology that can achieve greater-than 99% removal of Hg^{II} in aqueous solutions: FGS-PWN. Moreover, with this technology the oxidation of Hg^0 to Hg^{II} is not necessary as FGS-PWN is able to complex elemental Hg^0 that dissolves in the scrubber waters (albeit the solubility of elemental Hg^0 in these waters is low). Both forms of mercury, ionic Hg^{II} and elemental Hg^0, react with FGS-PWN to form a water-insoluble precipitate.

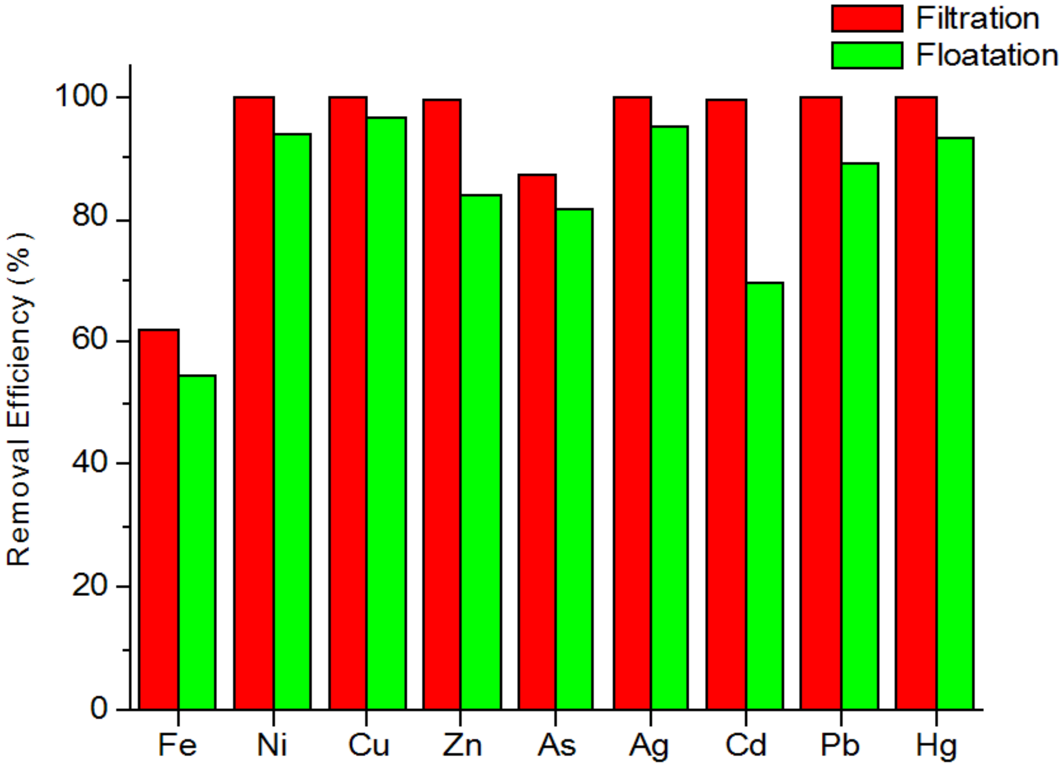
This precipitate is light-weight with a low specific density and is easily suspended in solution. It was proposed that these properties would allow it to be separated from the heavier, wet-FGD solids by gravimetric methods. An additional benefit was that owing to its low specific density, the precipitate also has a low physical volume, beneficial to handling and disposal.

FGS-PWN had been demonstrated to work over a wide range of pH and also form stable complexes other dissolved metallic species, including nickel, arsenic, selenium, cadmium, and lead.

Table 2.1 – Removal efficiency of select trace metals from 0.1% NaCl using FGS-PWN. Removal efficiency is determined using a 0.45 µm filter.

Trace Metal	**Ag**	**As**	**Cd**	**Co**	**Cu**	**Fe**
% Removed	>99	>99	>99	>99.9	>99	>95
Trace Metal	**Pb**	**Hg**	**Ni**	**Se**	**V**	**Zn**
% Removed	>99	>99.999	>95	>99	>99	>96

Figure 2.1 – Bench-scale comparison of the floatation potential of FGS-PWN verses filtration (0.45 mm filter) for the removal of select trace metals from 0.1% NaCl.



FGS-PWN is a liquid product and as such, the capital expenditure required of a utility to implement this technology is minimized. The product is added directly to the liquor of an existing wet-FGD scrubber. These systems are already liquid based and require no modification of existing designs and very little additional equipment.

The final benefit associated to the technology is that the FGS-PWN/Hg complex has been determined to be non-toxic and passes TCLP and CAL-WET tests. Therefore, under RCRA guidelines, it may be disposed of in a non-hazardous landfill.

The utility and innovation of adding an amendment to the wet-FGD scrubber was clear when the challenge set forth in the DOE SBIR 2007 solicitation was considered: *"More effective strategies are needed to concentrate and sequester Hg in FGD solids so that it is not released to the environment either during disposal or through re-use."*

Frontier believed that using an amendment, such as FGS-PWN, to achieve mercury control in the wet-FGD scrubber took the DOE premise one step further. It was Frontier's intention to demonstrate that FGS-PWN would capture mercury in a manner that allowed easy separation from the gypsum. The goal was to show that not only could mercury be sequestered and converted to a form that is easily and safely disposed, but gypsum free of mercury would be generated by this approach. This would be achieved by comparing the performance of FGS-PWN to other metal-chelating agents in commonly used in the wastewater treatment industry in a simulated, bench-scale wet-FGD scrubber. To this end, Frontier selected examples of four classes of metal-chelating agents with the intent of comparing their performance to FGS-PWN.

Table 2.2 – Selected amendments for testing.

Classification	**Examples**	**Manufacturer**
Organo-thiol	FGS-PWN	CCI (under agreement with Frontier)
Dithiocarbamate	Aquamet M DTC Perkacit SDMC WST_P2	ALCO Ecologix Flexsys WST
Polythiocarbonate	PTR_1 Perkacit SMEC Thio Red	Ecologix Flexsys WST
Sulfide	PSB 1 METALSORB SPX	Ecologix SNF FLOERGER WST

4. Technical Objectives

The proposal contended that the key to reducing mercury in the slurry is to capture the mercury in the flue-gas as it enters the scrubber. To achieve this, a chelating agent would be added to the liquor which is expected to bind Hg^0 and Hg^{II}. The mercury must be sequestered immediately as it enters the scrubber and the reaction must thermodynamically and kinetically out-compete any other reaction where the mercury might become included in the formation of other solids in the FGD reservoir.

Because Hg^0 is only sparingly soluble in aqueous solutions, amendment technology requires that the scrubber design incorporates a large liquid-to-gas (L/G) ratio. The desulfurization reaction occurs rapidly as SO_2 is readily soluble in aqueous solutions and the neutralization product is an insoluble precipitate. The chelation reaction is also kinetically fast, however it is rate-limited by the solubility of gaseous Hg^0. To drive this reaction, a small amount of gas must be permitted to contact a large amount of liquid.

To demonstrate the effective use of amendments for mercury capture in the wet-FGD scrubber, the project was divided into four important milestones/technical objectives. Each successive objective required the successful completion of the previous:

1. **Construction of the FGD Apparatus.** To simulate the wet-FGD scrubber, a bench-scale apparatus would be constructed which allows wet-scrubber chemistry to be duplicated and permits Hg^0 to be continuously monitored in the treated gas.
2. **Baseline Performance.** The apparatus would be operated using a limestone-slurry and forced-air oxidation to treat the simulated flue-gas. Sulfur dioxide would be captured and converted to gypsum from the simulated flue-gas which contains Hg^0. In addition, Hg^{II} would be added via a chemical addition pump to simulate the accumulation of the inorganic mercury species.
3. **Amendment Optimization**. The performance (ie: ability to capture mercury) of the metal-chelating agents selected would be evaluated at several different concentrations to determine the optimum dosing level. This was expected to differ for each amendment. In addition, it was believed that the optimum concentration might have a negative effect on the scrubber's baseline performance.
4. **Separation Comparisons.** With the optimum conditions for each amendment, the scrubber would be operated to generate gypsum in the presence of Hg^0 and Hg^{II}. Several different gravitational methods would be employed to separate this gypsum from unreacted limestone. The mercury content of the isolated gypsum would be determined.

4.1. Phase I Performance Schedule

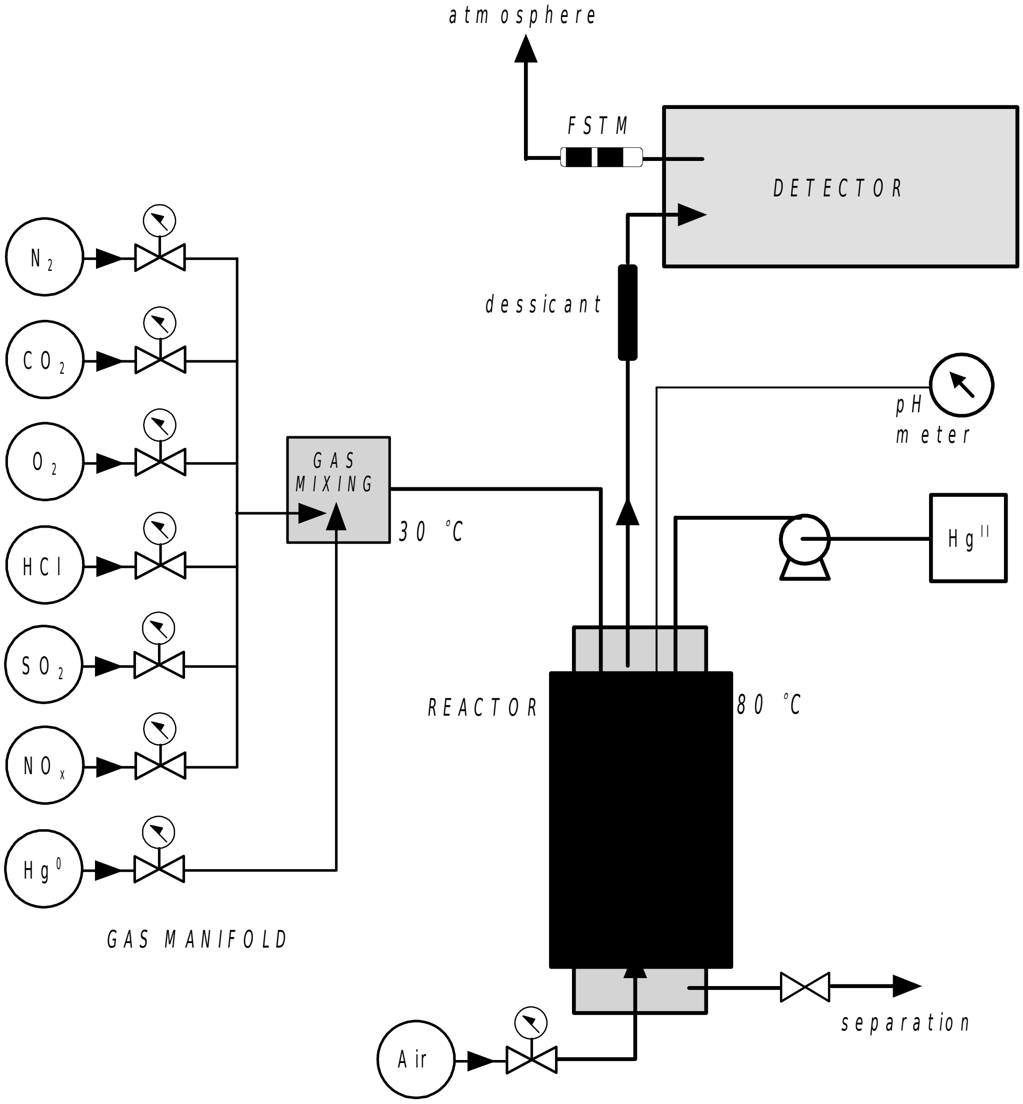
The following table summarizes the progress achieved on each technical objective.

Task	Descriptions	Result
1	Construction of the FGD Apparatus	Success
2	Baseline Performance	Failure
3	Amendment Optimization	Not Achieved
4	Separation Comparisons	Not Achieved

4.2. Task 1 – Construction of the FGD Apparatus

An apparatus was constructed to simulate a wet-FGD scrubber. The major components of the apparatus are a gas manifold, a gas mixer, a reactor, and a Hg^0 detector. The gas manifold and mixer are used to generate a simulated flue-gas containing a known quantity of Hg^0. The reactor simulates the scrubber. In this case, synthetic flue-gas is introduced to the simulated scrubber liquor through an impinger. The gas reacts with the slurry and liquor as it bubbles to the top of the reactor where it exits through a port. The treated gas is conveyed through a detector where Hg^0 is monitored by Zeeman-AAS (Lumex-915+).

Figure 3.1 – FGD Apparatus, schematic.



The apparatus consists of the following elements:

- **Gas manifold**. Stock gasses are combined proportionally using a suite of rotameters which allow the flow rate of each gas to be set individually. The rotameters were selected based on the required flow rate necessary to achieve the concentrations as specified in Table 3.1. The regulator pressure for each gas was kept at 5 psig as the apparatus attains the pressure of the highest regulator setting. Excessive system pressure was a major contributor to the lack of progress on this project. Hydrogen chloride gas (HCl) was not used as it promotes the oxidation of Hg^0 to Hg^{II}.

- **Gas mixing**. The gasses were to be homogenized and mixed with Hg^0 at 30 °C by passing them through a packed U-tube One side of a U-tube was packed with glass beads; the other side held a permeation cell containing a Hg^0 source. Given a flow rate of 5 lpm, a Hg^0 concentration of 10 ugm^{-3} would be possible. However, the water bath containing the U-tube was not stable at this temperature setting and the lowest temperature for this unit was 50 °C. This resulted in a Hg^0 concentration of 40 ugm^{-3}.
- **Reactor**. A jacketed, glass cylinder was used to simulate the wet-FGD liquor tank. A temperature of 80 °C was maintained by circulating heated water through the external jacket. The mixed, synthetic flue-gas was distributed into the reactor liquid by an impinger placed just above the bottom of the reactor. A pH probe was installed to monitor the pH of the scrubber liquor, which contained an excess of limestone. Ionic mercury, as a pH neutral solution of mercury chloride, could be added incrementally by means of a mechanical pump. Air was not added for forced oxidation, rather the percentage of oxygen was increased over that specified in Table 3.1 to promote gypsum formation. Two problems were continuously encountered with the reactor: gypsum would form in the impinger reducing the orifice size and causing an overpressure in the gas mixer; and, foaming caused the reactor contents to evacuate through the gas exit.
- **Detector**. An Ohio Lumex RA-915+ Zeeman-CVAAS portable mercury detector equipped with the side cell option was used to monitor Hg^0 in the gas stream during the reaction. The synthetic flue-gas exiting the reactor was conveyed to the detector inlet. Data from the lumex was collected electronically by a computer to record the Hg^0 exiting the FGD apparatus. A trap containing activated carbon (FSTM) was connected to the detector exit line to prevent atmospheric mercury discharge. Preventing condensation in the optical cell was a significant challenge. Figures 3.3 and 3.4 show typical data collected.

Figure 3.2 – FGD Apparatus, actual.

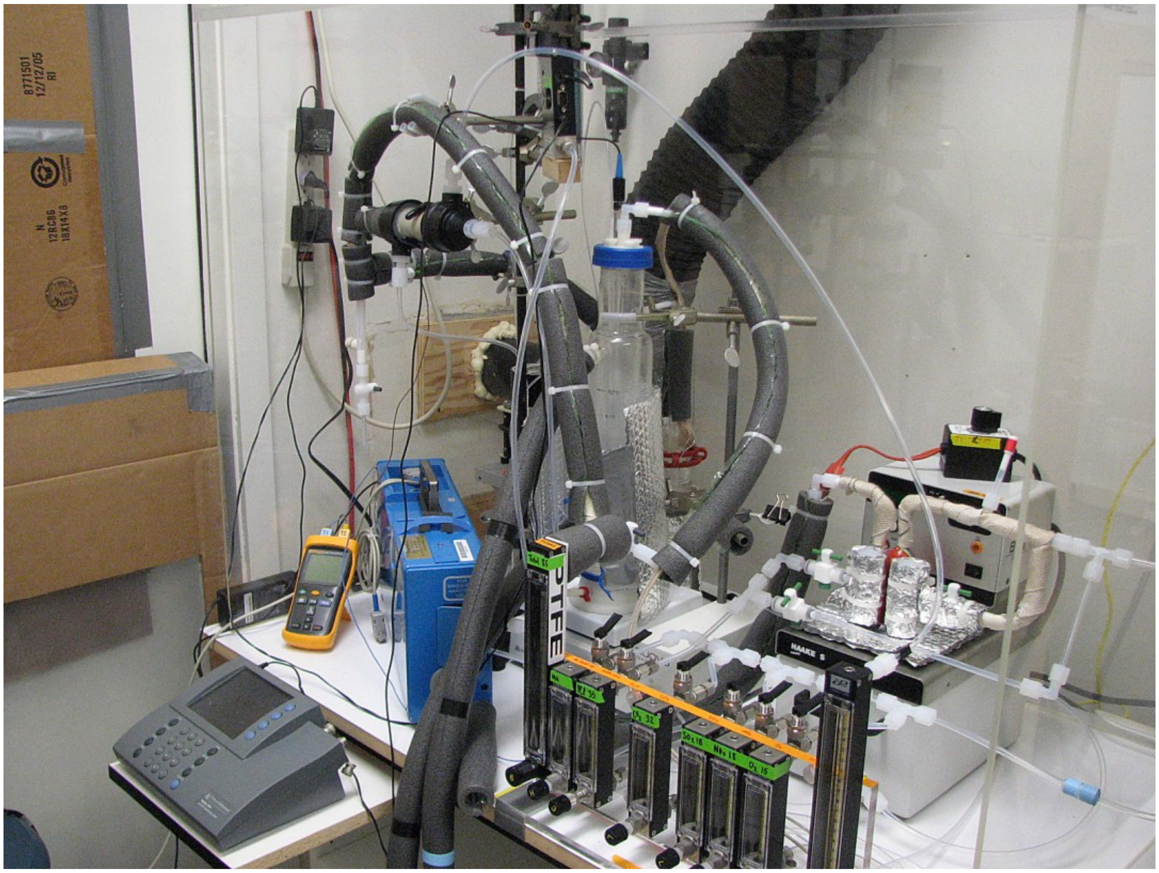


Table 3.1 – Simulated flue-gas concentrations and parameters.

Component	Flue-gas Concentration
Total N_2	78 %
O_2	5 %
CO_2	15 %
SO_2	1000 ppmv
HCl	0 ppmv
NO_X	500 ppmv
Hg^0	10 ugm^{-3}
Flow rate	5 $Lmin^{-1}$

Table 3.2 – Reactor concentrations and parameters.

Ionic Components	**Concentration**
Mg^{2+}	1,000 ppm (mgL^{-1})
Ca^{2+}	650 ppm
Na^{+}	650 ppm
Hg^{2+}	36 ppt
Cl^{-}	1,500 ppm
SO_3^{2-}	0 ppm
S_2O_3	0 ppm
SO_4^{-2}	5,000 ppm
Initial pH	5 – 6
pH Control Reagent	Limestone
Reaction Tank Temperature	80 °C
Oxidation Mode	Forced
Initial Weight % Limestone	15 grams
Solution Volume	0.5 liters
Amendment Concentration	1, 10, 50, or 100 ppm

Using these parameters, data can be generated by the detector and captured via a serial link to a computer. The data collected is concentration of Hg^0 vs. time. Depicted in Figures 3.3 and 3.4 are plots typical of the system.

The data in Figure 3.3 shows Hg^0 vs. time for a typical run. At T_0, the mercury permeation cell is opened which results in a large release of Hg^0. While the cell sits at 50 °C with no gas flow, mercury is evaporated from the source which collects on the glass walls of the cell. When the cell is opened and gas flows through, this mercury is swept out of the cell, through the apparatus and detector, and is captured on the FSTM trap. After the initial cell purge, mercury is evolved at the rate of 40 ugm^{-3}. This results in a flat line, unless something occurs to disturb the rate of emission.

In Figure 3.4, the area of the plot after the initial permeation cell purge has been enlarged. The data shows an increase and decrease in Hg^0 as the increase and decrease in the line of Hg signal vs. time. Instantaneous events are typically not captured, unless they are catastrophic. Instead, the detector is designed to show the system operating at steady state.

Figure 3.3 – Typical detector response of mercury vs. time.

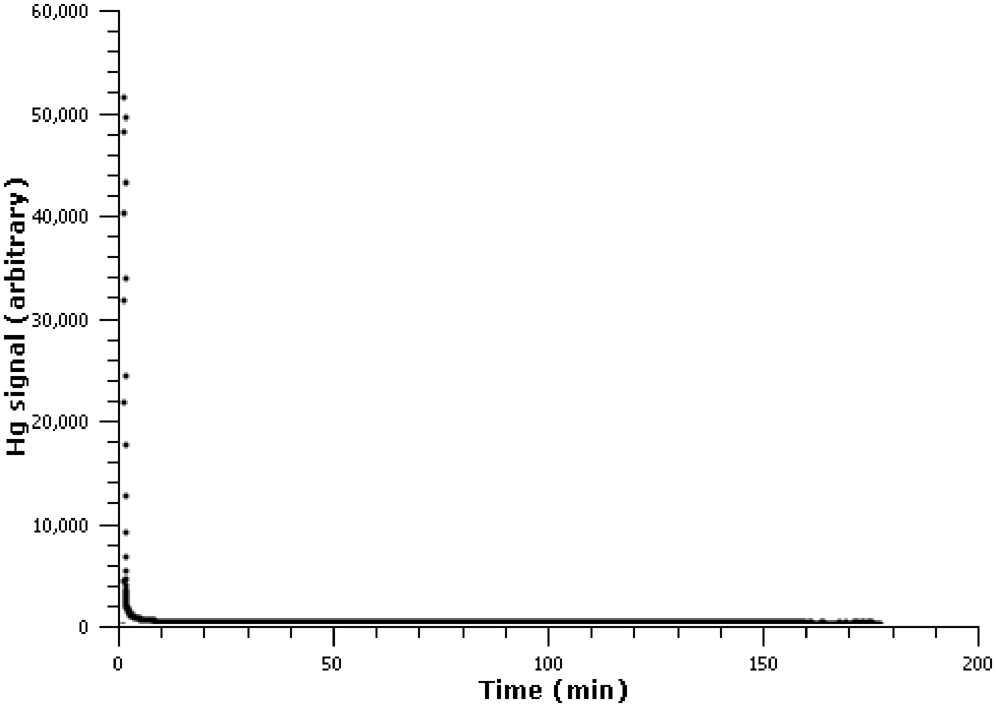
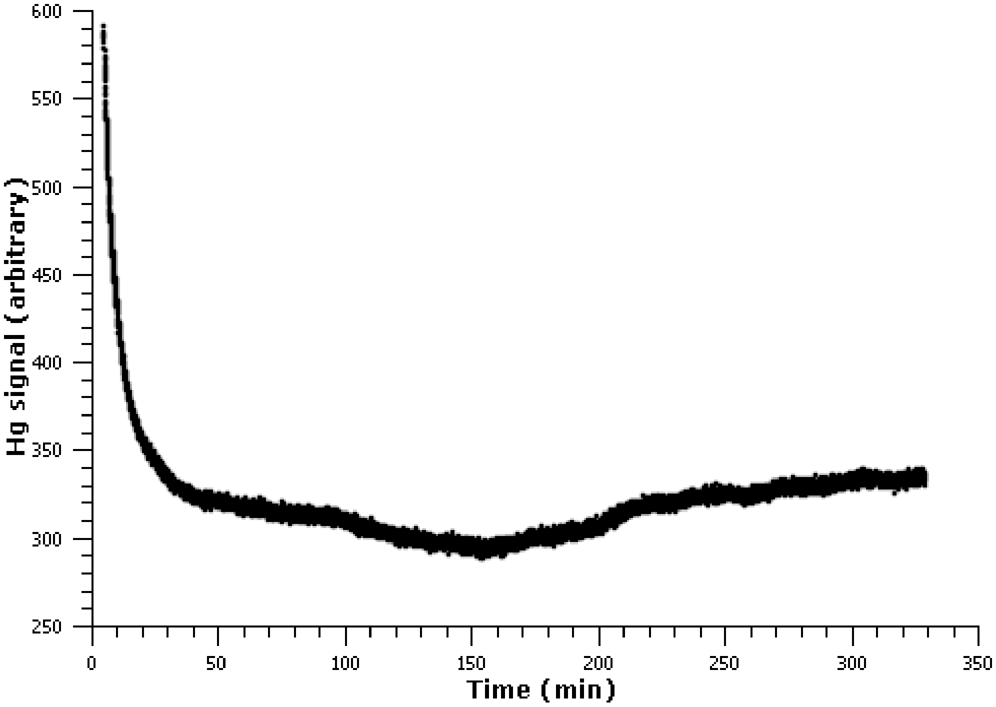


Figure 3.4 – Typical detector response with system perturbation.



4.3. Task 2 – Baseline Performance.

The purpose of the limestone fed, wet-FGD scrubber is to remove SO_2 from flue-gas. Sulfur dioxide is formed when sulfur, ubiquitous in coal, is oxidized via the combustion process. The SO_2 enters the scrubber and is dissolved in an aqueous solution saturated with limestone ($CaCO_3$). Limestone is only partially soluble in water and results in a slightly basic solution. This solution reacts with the acidic, dissolved SO_2 forming insoluble calcium sulfite. An excess of limestone is maintained with more added as it is consumed. Thus, SO_2 is removed from the flue-gas and converted to calcium sulfite ($CaSO_3{\cdot}2H_2O$) through the following reactions:

$$SO_2\ (g) + 2H_2O \rightarrow HSO_3^- + H_3O^+ \tag{1}$$

$$CaCO_3\ (s) + H_3O^+ \rightarrow Ca^{2+} + HCO_3^- \tag{2}$$

$$H_3O^+ + HCO_3^- \rightarrow CO_2\ (g) + 2H_2O \tag{3}$$

$$Ca^{2+} + HSO_3^- + 3H_2O \rightarrow CaSO_3{\cdot}2H_2O\ (s) + H_3O^+ \tag{4}$$

If sufficient oxygen is present, the calcium sulfite can be converted to calcium sulfate (gypsum). In forced oxidation scrubbers, this is accomplished by injecting air into the slurry.

$$CaSO_3{\cdot}2H_2O\ (s) + \tfrac{1}{2}O_2 \rightarrow CaSO_4{\cdot}2H_2O\ (s) \tag{5}$$

The design of the wet scrubber and the composition of the liquor vary according to the installation and the operating parameters of the utility. The process is steady-state and is optimized to ensure SO_2 capture. Any amendment added to the scrubber must not interfere with the scrubber's basic function, or SO_2 may be released and the utility may be out of compliance.

To determine whether the amendments chosen will affect the operation of the bench-scale scrubber, the baseline performance (without amendment) was to be determined. By determining the rate of limestone consumption, and thus, the rate of gypsum production, a standard level of performance for the apparatus would be established. Any deviation from this performance with an amendment in place would be an indication that the amendment is not be suitable for use in the scrubber, regardless of its performance with respect to mercury capture.

It was not possible to determine the baseline performance for a number of reasons. Principally, these had to do with operational difficulties which were not anticipated in the design. Many of these problems were solved but resulted in undesired modifications of the equipment. This generally introduced new problems with the result that additional compromises were necessary. Ultimately, it was impossible to complete the project as addressing and correcting these issues consumed the time and budget allocated for the entire project. Therefore, the optimal premise of this technology, a favourable L/G ratio was compromised as the project moved forward in a non-ideal manner.

The apparatus has two weak links: the detector cell, and the gas impinger. Both devices are linked to numerous difficulties.

The detector itself, a Lumex-915+, is perfectly suitable to detecting mercury in the synthetic flue-gas; however it must be used with its external, optical cell. Owing to the size of the cell's entrance and exit connections, a backpressure condition of 1-2 psig was imposed on the apparatus at a 5 lpm flow rate. The apparatus is constructed of glass and Teflon and is not intended to be pressurized. To alleviate this, a flow rate of 4 lpm was adopted. In addition, the optical cell cannot be heated and proved an excellent location for moisture to condense. As condensation accumulated on the cell windows, artefacts were introduced into the mercury signal. To reduce the amount of humidity in the synthetic gas, the reactor temperature was reduced to 75 °C, which negatively affected gypsum production. Initially, a desiccant was used to absorb moisture from the gas exiting the reactor; however it would become wet if the reactor was run for over 2 hours. The wet desiccant acted as a flow restrictor and the system would pressurize to 10 psig at which point the safety valve would actuate, venting at the gas mixer. The desiccant was replaced by a nafion dryer, which worked well to reduce condensation in the optical cell. However, when synthetic scrubber liquor was prepared (Table 3.2) and used in the reactor, considerable foaming occurred which would foul the dryer and enter the optical cell. An anti-foaming agent had little effect and the only effective solution was to reduce the volume of the simulated scrubber liquor by half (from 500 mL to 250 mL). Reducing the volume of liquor reduces the intended L/G ratio.

The impinger was also a source of difficulty. To achieve the intended, favorable L/G ratio, the gas must be distributed into the liquor as small bubbles. To accomplish this, a glass frit is used to disperse the synthetic flue-gas. As the reactor was operated, gypsum would form in the frit causing it to become less and less porous. As this became more pronounced, the system pressure would increase until it reached 10 psig, triggering the safety relief valve. Initially, a very fine frit was used and the reactor could be operated for 2 hours before clogging and over-pressurizing. As a partial solution, the impinger was substituted for one with a coarser frit (larger pore size). This allowed for 4 hour runs; an amount of time insufficient to produce a quantity of gypsum conducive to analysis. Ultimately, the frit was abandoned and a hollow tube with an inner diameter of $^1/_8$ inches was used. This was resistant to the scaling which clogged the fritted impingers, however it generated large bubbles with vigorous "bumping". When synthetic scrubber liquor was used, this resulted in significant losses through the gas exit-port, even when the reactor was half-filled to accommodate foaming.

With these changes, a benchmark check was made on the efficiency of the scrubber with an addition of FGS-PWN. In previous work, FGS-PWN had effectively complexed the target mercury species. The expected mercury capture did not occur; in fact no mercury capture was observed. This is due to the unfavourable operating conditions introduced with the modified equipment design, as described above.

More specifically, it is speculated that the result of a half-filled reactor with large bubbles resulted in a complete departure from the initial, controlled L/G ratio. As described, any attempt to improve the L/G interaction through greater bubble surface area resulted in equipment failure. Increasing the scrubber liquid volume resulted in the volume losses and obscured, usable data.

At this point the timeline and funds of the project were exhausted.

4.4. Task 3 – Amendment Optimization.

This task was not achieved due to failure of Task 2.

4.5. Task 4 – Separation Comparisons.

This task was not achieved due to failure of Task 2.