Novel Process for Removal and Recovery of Vapor-Phase Mercury

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Novel Process for Removal and Recovery of Vapor-Phase Mercury

The purpose of this project is to investigate the application of a sorbent-based process for removing and recovering mercury in the flue gas of coal-fired power plants. The process is based on the sorption of mercury by noble metals and the regeneration of the sorbent by thermal means, recovering the desorbed mercury for recycling. ADA Technologies holds a patent on this process (US 5,409,522) and has tested it under conditions typical of municipal waste incinerators. In this process, the noble metal sorbent is thermally regenerated, and the mercury is recovered for commercial recycle or disposal. ADA has adopted the name "Mercu-RE" to describe its process.

ADA has been testing its process under conditions typical of coal-fired power plants where the mercury concentration is low (below $10 \mu\text{g}/\text{m}^3$) and little pressure drop can be tolerated. The objective of this program is to develop the Mercu-RE process as a suitable mercury emission control technology for use at coal-fired power plants.

Overview of Progress

Phase I tasks 1 through 5 were completed as of October 1997. No additional activities have occurred under those tasks. Current period activities are summarized by task:

II-6 Modify 20-acfm Skid

ADA initiated some modifications to our continuous mercury analyzer to enhance its performance on flue gas. The instrument has worked under some conditions but continues to be hampered by signal drift and reliability issues. The changes are designed to improve signal to noise ratio, eliminate thermal drift, and simplify operation. The revised unit will be tested on the skid at Hudson. Successful operation of the analyzer will enhance out data tracking ability during the field test.

II-7 Establish Routine Operation at Pilot Combustor

At the end of the last quarter we had obtained conflicted data regarding the effectiveness of the sorbent. Iodated-carbon traps (IC traps) indicated 65% removal across each of the two sorbent vessels, whereas Ontario-Hydro sampling indicated no removal. These samples were pulled simultaneously during the last weeks of operation on the CONSOL pilot combustor. At the start of this quarter we removed a sample of the sorbent from the skid in order to perform standard laboratory tests with the material.

The first indication of a change in the sorbent was the disappearance of the characteristic pale purple color. Whereas the fresh material is uniformly purplish, the used

sorbent was white. The used materials had a coating of brown ash on the surface, but washing this layer off revealed a white sorbent underneath. Crushing the sorbent pellets revealed them to be white throughout. Samples of fresh sorbent and the used pellet form of the sorbent (from R-102) were sent to local laboratories for analysis. We examined the sorbent for the accumulation of chlorine, nitrogen and sulfur species that might indicate sorbent poisoning or fouling. We also assayed for the amount of active noble metal on the sorbent. These findings are provided in Table 1.

Table 1. Results from analysis of fresh and used sorbent.

Sample ID	Total Chloride (mg/kg)	Total Nitrate (mg/kg)	Total Sulfate (mg/kg)	Total Noble Metal (mg/kg)
F101/4	720	ND	98	480
F102/5	590	0.73	98	720
F103/6	590	8.30	200	740
Average	633±75	5±5	131±59	647±145
U101/4	24	ND	93,000	510
U102/5	18	ND	93,000	360
U103/6	29	ND	84,000	440
Average	24±6	ND	90,000±5200	437±75

Two items are apparent from the Table 1 findings – a large amount of sulfate was recovered from the used samples and there was a loss of approximately 1/3 of the noble metal. Assuming the sulfate originated as SO₂, the amount recovered equals a roughly 20% coverage of the sorbent surface area. It is unknown if the SO₂ covered the sorbent uniformly or was localized to the noble metal sites. Certainly this amount of SO₂ could completely cover the noble metal sites; however, it is more likely that the SO₂ would favor adsorption onto the alumina support.

The loss of noble metal was a more serious finding. While loss of metal would by itself lead to a drop in sorbent capacity, it also indicates that the metal achieved some mobility during the operation of the skid. Thus, it is possible that metal crystallite size was altered. This is consistent with the loss of purple color. The color loss suggests the crystallites are no longer of colloidal size. We attempted to ascertain crystallite size of the fresh and used sorbent with X-ray Diffraction Spectroscopy (XRD) and Scanning Electron Microscopy (SEM). The metal line in the XRD samples was difficult to distinguish from the background noise in both the fresh and used samples so these tests were inconclusive. Results from the initial SEM tests were not high enough resolution to identify the metal crystallites. Both the XRD and SEM tests are being repeated with higher resolution instruments.

Standard tests in ADA's sorbent test apparatus indicated that the spent sorbent had lost roughly 70% to 80% of its capacity for mercury. These tests, typical runs are depicted in Figures 1 and 2, were run with elemental mercury in air at temperatures of

280°F. Superficial velocities during these lab tests were higher than that in the 20-acfm skid in order to accelerate the testing times.

Figure 1. Sorbent capacity test of fresh sorbent. Complete breakthrough occurs at about 12 hours. Test number 021099.

Figure 2. Sorbent capacity test of used sorbent. Complete breakthrough occurs at about 2 hours. Used sorbent air test #2, 021999.

The noble metal is known to be stable to flue gas at 300°F and in inert atmospheres at much higher temperatures. It is possible to remove the metal under aqueous acidic conditions. This led to the theory that acid attack on the metal may have generated volatile metal salts that were subsequently lost from the alumina surface. The chloride salt, in particular, has a measurable vapor pressure at temperatures over 180°C (355°F), well within our regeneration temperature. The key in this scenario is generating the acids necessary to dissolve the metal. To ascertain if this was possible, we re-examined the time/temperature profile of the skid. As operated, one bed was on line for 24 hours, then cycles off-line for an 8-hour regeneration, then waits to return online (see Figure 3). After the regeneration cycle, the bed cools to roughly 90°F. When this cool bed cycles back online it is rapidly warmed by the hot, moist flue gas. The bed takes about 30 to 60 minutes to reach flue gas temperature. The flue gas composition is 5% water vapor, giving a dew point temperature of slightly over 100°F. Therefore it is possible that moisture condenses within the pores of the sorbent as the flue gas initially contacts the cool sorbent. Acid gases within the flue gas (HCl, NO_x, and SO₂) could react with this water to form an acid mixture capable of attacking the noble metal. Although this attack would be brief (the moisture will quickly evaporate as the sorbent heats up), over the course of several months it may be sufficient to degrade the metal crystallites.

Figure 3. Sorbent bed temperatures as a function of cycle time.

II-8 Install and Shakedown Pilot System at Utility Site

At the end of March the equipment skid was relocated to Hudson Station in Jersey City, NJ. ADA prepared a 30 ft by 8 ft office trailer to serve as equipment enclosure and office for work at Hudson Station. The skid was loaded and anchored within the trailer at CONSOL's facility and then shipped to Hudson Station. Installation at Hudson went smoothly and all piping and utilities were connected. Final checkouts of the equipment will be completed in late April and operation will begin at that time.

II-9 Test Long-Term Performance at Utility Site

No work on this task.

II-10 Prepare Economic Assessment for Full-Scale System

No work on this task.

II-11 Prepare Documents

Monthly reports for December through February (status, summary, cost management, milestone schedule) were submitted during the quarter. In March ADA

submitted a manuscript for presentation at the June Air and Waste Management Association Meeting in St. Louis.

Project Plan for Next Quarter

The analysis of the spent sorbent suggested coalescence and loss of noble metal from the material. This led to the observed drop in sorbing capacity. Although the first laboratory analyses were suggestive they were not conclusive. Further studies with higher resolution instruments are to be run to ascertain the metal crystallite size on the spent material.

The regeneration cycle of the skid will be modified to prevent the off-line bed from cooling to the point where condensation may occur when the bed is brought back online. Skin heaters may also be added to the vessels. This change should prevent liquid acid attack on the noble metal crystallites. Once the new ceramic monoliths are installed and the revised regeneration cycle implemented, operation of the skid will begin at the power plant. Hudson Station already has a facility where pilot work is being undertaken by ADA; consequently, the site has slip-stream ducting, and plant personnel are familiar with having a small pilot facility on site. Hudson burns a low-sulfur, bituminous coal. ADA has contracted with PSE&G's testing division (Maplewood Testing Services, Maplewood, NJ) to pull samples while the equipment is at the New Jersey site. At the outset of the testing at the power plant we will pull both IC Traps and O-H samples for comparison. This should indicate any discrepancy between the sampling methods. Operation at the power plant will continue at least through the end of the calendar year.