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Mercury Removal at Idaho National Engineering and Environmental Laboratory's New Waste Calciner Facility

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ABSTRACT

Technologies were investigated to determine viable processes for removing mercury from the calciner (NWCF) offgas system at the Idaho National Engineering and Environmental Laboratory. Technologies for gas phase and aqueous phase treatment were evaluated. The technologies determined are intended to meet EPA Maximum Achievable Control Technology (MACT) requirements under the Clean Air Act and Resource Conservation and Recovery Act (RCRA). Currently, mercury accumulation in the calciner off-gas scrubbing system is transferred to the tank farm. These transfers lead to accumulation in the liquid heels of the tanks. The principal objective for aqueous phase mercury removal is heel mercury reduction. The system presents a challenge to traditional methods because of the presence of nitrogen oxides in the gas phase and high nitric acid in the aqueous scrubbing solution. Many old and new technologies were evaluated including sorbents and absorption in the gas phase and ion exchange, membranes/sorption, galvanic methods, and UV reduction in the aqueous phase. Process modifications and feed pre-treatment were also evaluated. Various properties of mercury and its compounds were summarized and speciation was predicted based on thermodynamics. Three systems (process modification, NOxidizer combustor, and electrochemical aqueous phase treatment) and additional technology testing were recommended.

OBJECTIVE

The overall objective of this study was to provide a set of potential technologies and alternatives for meeting the Maximum Achievable Control Technology (MACT) gaseous emissions standard for mercury at the New Waste Calcining Facility (NWCF). MACT may govern future operations at the NWCF as well as other thermal processes at the Idaho National Engineering and Environmental Laboratory (INEEL). Efforts are in progress by several groups at the INEEL, other national laboratories, and private industry to determine the best mercury removal technologies for various processes and media.

BACKGROUND

The DOE, in its past mission of reprocessing nuclear fuel at the INEEL has generated large quantities of HLW that have been in storage at the Idaho Nuclear Technology and Engineering Center (INTEC) for many years. The DOE must dispose of the stored wastes in accordance with regulations and to fulfill agreements with the State of Idaho. The DOE is preparing a HLW Environmental Impact Statement (EIS) to identify alternative management strategies for the HLW. If a decision is made to treat the stored wastes (i.e., calcine and stored liquid wastes) for off-site disposal, high temperature immobilization is the primary processes in consideration.

The sodium-bearing liquid waste stored at the INEEL's INTEC is DOE mixed waste. Mixed waste is defined as waste materials having hazardous contaminants regulated under the Resource Conservation and Recovery Act (RCRA) and radioactive contaminants regulated under the Atomic Energy Act. The sodium-bearing liquid waste will likely be converted to a more stable waste form (e.g., calcine) in the near future. The calcination process would be performed at the NWCF located at INTEC. The calcination process may generate an offgas stream containing MACT-regulated contaminants, including mercury and its compounds, acid gases (HCl/Cl_2), volatile organics (VOCs) and dioxins/furans (D/F).

At the NWCF, the calciner operates at 500-600°C. A schematic is shown in Figure 1. The feed from the tank farm to the calciner has significant amounts of mercury present from past operations in which mercuric nitrate was used as a catalyst to help dissolve aluminum clad fuels. The offgas from the calciner is scrubbed/quenched in a spray tower using recirculated nitric acid. The nitric acid is used to dissolve solids entrained from the calciner. The quench tower operates at 73°C (164 °F). The scrub liquid containing particulates, condensibles, and nitric acid enters a scrubber collection tank. Some entrainment occurs that carries small particles from the calciner to the scrub solution. Entrainment likely brings in actinides, aluminum, iron, chlorides, and others. The scrub liquid is subsequently recycled to the quench system, and a much smaller amount is intermittently recycled to the calciner feed. The scrub liquid is sent back to the tank farm when the chloride level increases to approximately 5,000 ppm. The quenched offgas is treated in a venturi scrubber for particle removal and then through a demister and a HEPA filter. There are ruthenium adsorbers downstream consisting of beds packed with silica gel that were installed to remove radioactive ruthenium. The mercury accumulates in the scrub tank to concentrations up to approximately 30 g/L. Volatile mercury components, likely $HgCl_2$ and metallic Hg, are emitted into the offgas. The mercury emission concentration from the stack is estimated to be in excess of 1,000 $\mu g/m^3$.

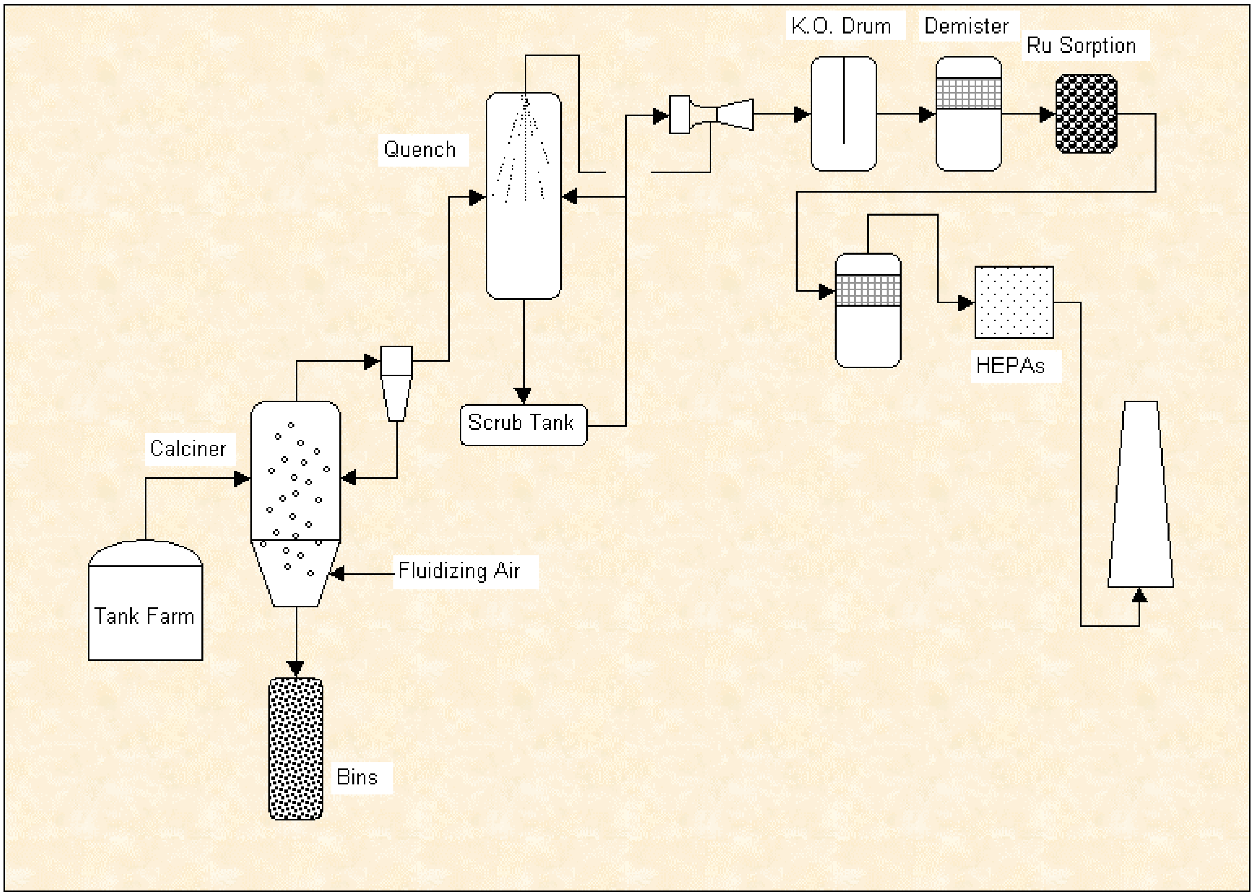

Figure 1, Current NWCF Schematic

MERCURY SPECIATION AND PROPERTIES

Mercury speciation is complex. However, some simplifications can be made. Considering gas removal, only the information concerning the volatile species present is required. Hg metal and $HgCl_2$ have fairly well known properties. The oxide (HgO) does not have a measurable vapor pressure as it breaks down to Hg and oxygen upon heating (1) but it does exist as an aerosol. Therefore, there are only two gaseous chemical species to deal with in the vapor phase with large differences in properties. While their vapor pressures are similar, the solubilities are very different as well as other thermodynamic properties.

Tank Farms Species. The speciation was determined by hand but this is more difficult for the Hg:Cl ratio observed in the tank farms. Therefore, the HSC Chemistry equilibrium program was used to estimate the speciation. The results indicate most as $HgCl_2$ with lesser amounts of $HgCl_3^-$ and $HgCl_4^{-2}$.

Scrub Collection Tank. For the scrub observed Hg:Cl ratio of 1-2, there is a mixture of $HgCl_2$, $HgCl^+$, and Hg^{+2}. The following equations are considered the most important, assuming that the vapor pressure of $HgCl_2$ does not impact the equilibria**:**

$$Hg^{+2} + Cl^- = HgCl^+ \quad K_1 = 5.8x10^6$$
$$HgCl^+ + Cl^- = HgCl_2 \quad K_2 = 2.5x10^6$$
$$HgCl_2 + Cl^- = HgCl_3^- \quad K_3 = 6.7$$
$$HgCl_3^- + Cl^- = HgCl_4^{-2} \quad K_4 = 13$$

To determine speciation over the entire expected range, the HSC chemistry package was used. Small amounts of $HgCl_3^-$ and $HgCl_4^{-2}$ were predicted but with increasing $HgCl^+$ at higher [Hg]/[Cl] .

Gas Phase

In the gas phase, the temperature and NO_x composition impacts the speciation of mercury. It is well known that the decomposition temperature of HgO is close to the calciner operating temperature. The following thermodynamic analysis is used to estimate what will happen to mercury at different temperatures and NO_x compositions.

$$NO_2 = NO + \frac{1}{2}O_2 \qquad K_2$$
$$Hg + \frac{1}{2}O_2 = HgO \qquad 1/K_1$$

Adding these two together

$$NO_2 + Hg = NO + HgO \qquad K_2/K_1$$

$$\frac{[HgO]}{[Hg]} = \frac{K_2}{K_1}\frac{[NO_2]}{[NO]}$$

The K_1 and K_2 were determined from published references for free energy as a function of temperature (1, 2). The results of this indicate that lower temperatures favor the oxide as NO_2 is oxidizing while NO is reducing. The mercury speciation depends on the $[NO_2]/[NO]$ ratio, but the converse is not true. It has been determined (3) that this oxidation is rapid so the indication is that the mercury metal converts to HgO as it flows through the offgas system. This has also been verified by recent testing of wetted silica gel by INEEL personnel (4).

The offgas speciation is predicted to be $HgCl_2$ not removed in the wet processes and HgO solids that are removed by other equipment. The other species present in the offgas (e.g., CO) might also impact gas-phase speciation. HSC Chemistry was used to predict the predominance of Hg or HgO in this at various temperatures. The results indicate predominance of HgO at the cooler temperatures downstream of the calciner.

The kinetics of the reaction

$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

has the rate equation (5) with the rate constant units of $s^{-1}atm^{-2}$ (the back reaction is insignificant at lower temperature).

$$\log_{10} k = \frac{652.1}{T°K} - 0.7356$$

This lends itself to the following kinetic model

$$-\frac{dC_{NO}}{dt} = kC_{O_2}(RT)^2 C_{NO}^2$$

Using a plug flow model for a vent pipe, the following NO disappearance as a function of residence time was determined.

$$C_{NO}(t) = \frac{C_{NO_i}}{1 + k' t_R C_{NO_i}}$$

Assuming a constant temperature of 70°C, the following Figure 2 was constructed showing disappearance of NO and conversion to NO_2.

Figure 2, Kinetics of NOxidation

Properties

HgO does not have a measurable vapor pressure but decomposes as temperature is increased (6). It is expected to exist as fine particles in the gas phase (however, some researchers indicate HgO is a gas at T > 200°C).

$$HgO = Hg + \frac{1}{2}O_2$$

The decomposition temperature is approximately 500°C (1) where K=1 (it also takes higher temperature to form the HgO from Hg in the first place, i.e., it doesn't occur appreciably at ambient conditions).

- **Water Solubility** 2.37x10^{-4} mol/dm^3 @298.2 °K 3.47x10^{-4} @ 308.2 °K (7)

$$HgO_s + H_2O = Hg(OH)_2 \qquad K = 2.4x10^{-4}\, mol/dm^3$$

- **Acid (298.2 °K) Solubility** – HgO is highly soluble in acid but is complicated by the presence of anions, particularly Cl$^-$ Also, these reactions take significant time (7).

$$HgO_{(s)} + H^+ = HgOH^+ \qquad K = 0.17$$

$$HgO_{(s)} + 2H^+ = Hg^{+2} + H_2O \qquad K = 53$$

The solubility chart derived from the solubility of HgO as a function of acidity-alkalinity from the solubility data series (8) is shown in the reference. If chloride is present, it has a major impact on this curve with much more being soluble (as $HgCl_2$).

The metal has low solubility in air-free water as shown in Table I (also includes Henry's Law Constant). However, this solubility increases by a factor of 700 in aerated water (9).

Table I, Hg Solubility

Temperature, °K	Solubility, mole/kg	Henry's Constant, Atm
273.15	1.36E-07	108
298.15	3.03E-07	495
328.15	6.82E-07	1980
358.15	1.59E-06	5560
373.15	2.40E-06	8390

To extrapolate to lower temperatures for the vapor pressure of $HgCl_2$, an Antoine type equation was used to fit the data and extrapolate.

$$\ln p = A - \frac{B}{T}$$

Where p = vapor pressure, mm Hg
T = Temperature °K
A = 10.094
B = 4170

Although the vapor pressure of $HgCl_2$ is similar to the metal, the solubility is far different. The main portion of solubility is as a molecular species (similar to ammonia) as shown below:

$$HgCl_2(s) = Hg^{+2}(aq) + 2Cl^-(aq) \qquad K = 7.1x10^{-15}$$

$$HgCl_2(s) = HgCl_2(aq) \qquad K = 0.11$$

The solubility ranges from 0.163 mole/kg at 273.15 °K to 2.128 at 373.15 °K.

Vapor-Liquid

To estimate the vapor quantities of $HgCl_2$, the activity coefficient is needed. The activity coefficient, γ, is a function of temperature and composition and for electrolytes, ionic strength and other factors.

$$\varphi y_i P = \gamma x_i P^0$$

Assuming the fugacity coefficient is one (φ =1, ideal gas assumption), the activity coefficient was determined at 70 and 100°C from ESP .

$$\gamma = \frac{y}{x} * \frac{P}{P^0} = 0.015 * \frac{1}{0.000167} = 90 \quad @\, 70°C$$

$$\gamma = \frac{y}{x} * \frac{P}{P^0} = 0.02 * \frac{1}{0.000444} = 45 \quad @\, 100°C$$

MACT STANDARD

The proposed, revised technical standards would limit emissions of D/F, mercury, semi-volatile metals (cadmium and lead), low-volatile metals (arsenic, beryllium, chromium, and antimony), particulate matter, acid gas emissions (hydrochloric acid and chlorine), hydrocarbons, and carbon monoxide. The standards are based on MACTs, an approach required by the CAA. MACT reflects the maximum degree of hazardous air pollution reduction that can be achieved considering the availability, current use, costs, benefits, and impacts of emissions control technologies.

This proposed rule would apply to hazardous waste incinerators, cement kilns, and lightweight aggregate kilns that burn hazardous waste as fuel. Hazardous waste incinerators are enclosed, controlled flame combustion devices used primarily to treat organic and/or aqueous wastes. Table II provides the proposed standards for existing incinerators (10).

Table II. MACT Standards[1]

Compound	Proposed Standards
D/F	0.20 ng/dscm
Particulate Matter (PM)	69 mg/dscm
Mercury	50 μg/dscm
SVM (Cd, Pb)	270 μg/dscm
LVM (As, Be, Cr, Sb)	210 μg/dscm
$HCl+Cl_2$	280 ppm_v
CO	100 ppm_v
HC	12 ppm_v

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[1] Modeling and analysis based on the MACT for Hg, 50 μg/dscm. The results will change if a different value is used (e.g., 130 μg/dscm for existing facilities).

REMOVAL OF NITROGEN OXIDES

Although nitrogen oxides (NO_x) emitted from the NWCF are currently within the INEEL air emissions permit, there are several reasons that removal would be beneficial. NO_x impacts sampling and monitoring of the gases emitted. The EPA methods and protocols require modification due to the NO_x presence. Gas phase mercury removal via activated carbon and other sorbents is impacted by NO_x. Systems to remove NO_x have been investigated. The John Zink, multi-chamber NO_xidizer® was selected for further study. The NO_xidizer® has a reduction section that reduces NO_x to nitrogen and oxygen and a re-oxidation section that can oxidize CO and organic compounds. This system is currently being installed for testing by MSE Technology Applications of Butte, Montana.

INEEL Tank Farm Mercury

INEEL wastes contain more mercury than other DOE Sites as mercury was used as a catalyst in reprocessing of aluminum fuels. Table III includes information on tank farm mercury, vapor concentrations (assuming none removed and all vaporized from the feed), and the required DF to meet MACT.

Table III. Tank Farm Mercury

Waste tank	Mercury, Molar (g/L)	Vapor Conc., µg/dscm	DF Required
WM-180	0.00098 (0.196)	1.30E+04	2.60E+02
WM-181	0.0005 (0.1)	6.62E+03	1.32E+02
WM-184	0.0018 (0.36)	2.38E+04	4.76E+02
WM-185	0.004 (0.8)	5.30E+04	1.06E+03
WM-186	0.0013 (0.26)	1.72E+04	3.44E+02
WM-189	0.0051 (1.02)	6.76E+04	1.35E+03
WM-182 (heel)	0.001 (0.2)	1.32E+04	2.64E+02
WM-183 (heel)	0.0029 (0.58)	3.84E+04	7.68E+02
WM-187 (heel)	0.0027 (0.54)	3.58E+04	7.16E+02
WM-188 (heel)	0.0077 (1.54)	1.02E+05	2.04E+03

Quench Model 1. This models the current system with a continuous sidestream. Figure 3 indicates the amount of Hg projected exiting the venturi scrubber versus the sidestream rate. This is assuming an 84 percent scrubbable fraction and that Hg:Cl is 1:1. This model assumes the quench tower and the venturi scrubber are one equilibrium stage each and hence the exiting liquors are in equilibrium with the exiting vapors.

Quench Model 2. This models the current system with a change such that the quench and venturi systems have separate liquors. Each is treated with an independent recirculating scrub stream with the liquors mixed for aqueous phase mercury removal. Implementing this modification reduces scrubbable mercury in the venturi effluent at the same sidestream treatment rate as shown in Figure 3. With this modification and a continuous sidestream rate of 2-5 gpm, the effluent is about four times MACT at worst case assumptions and feed concentrations, at least for the fraction that is $HgCl_2$.

New Scrubber. A multi-stage absorber (scrubber) unit using plates or packing could be installed. Recirculation can be used only if most of the mercury is removed (DF varies depending on the scrub loop recirculation rate). This can reduce the scrubbable mercury to less than 50 µg/scm with approximately10 theoretical transfer units.

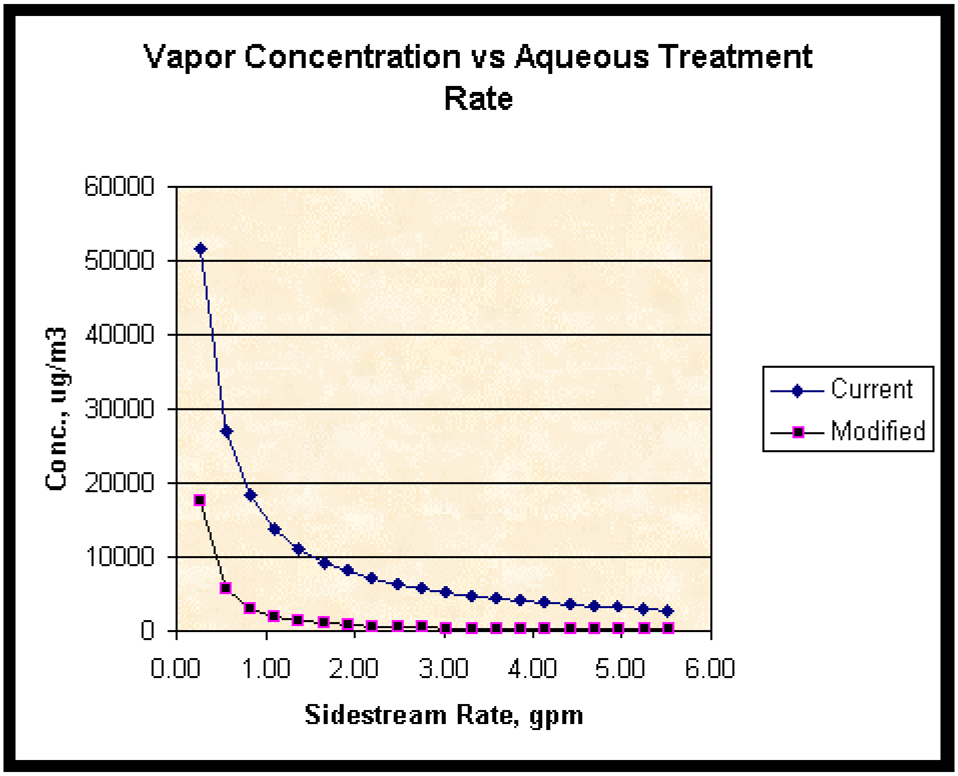

Figure 3. Current System, Sidestream Flow vs. Vapor Concentration

TECHNOLOGY ASSESSMENT

These technologies range from laboratory experiments to operating facilities. In the aqueous phase scrub liquor, removal is a serious challenge as mercury exists in several speciated forms. Therefore, many of the potential technologies may not be effective (e.g., Ion Exchange and Adsorption). This is compounded by likely problems with gelatinous solids (presumed to be $Al(OH)_3$) if the quench scrub liquors are partially neutralized, a requirement for most aqueous phase technologies. Likewise, in the gaseous phase, the presence of NO_x in large concentrations impacts gas-phase adsorption. Even if most of the NO_x is removed via a NO_xidizer, the remaining NO_x may still impact adsorption.

ADSORPTION

Activated Carbons

Several municipal incinerators are using PAC systems to remove mercury from the offgas system. The PAC systems require baghouses and other major equipment. Mercury concentrations are usually much lower than at the NWCF for these types of facilities (540-9,503 µg/dscm) and removal efficiencies range from 78-98 percent. Three facilities that use this technology are Burnaby, British Columbia; Camden, New Jersey; and Stanislaus, California (11).

While being able to adsorb dissolved mercury, the GAC also adsorbs other metals and radionuclides. The limitation is a pH of about 4 so that treatment of the quench receiver tank via GAC requires pH adjustment. There is some evidence that the efficiency of mercury removal is increased at lower pH, but nitric acid attack of the matrix also occurs.

Vapor phase adsorption of mercury using activated carbon is considered one of the best technology applications for removing gas phase mercury. Additional testing is required for adsorption as NO_x gases appear to interfere with adsorption and breakthrough. It can also result in a fire hazard.

Sulfur/Iodine-Impregnated Activated Carbon
The impregnated carbons include chemical reactions (chemi-sorption) with the impregnated working best on metallic mercury (Hg^o) and the plain activated carbon working best for speciated mercury (via physi-sorption). Most of the impregnated carbons are being used and/or tested in Europe (12).

Selenium Filters
Selenium filters were first developed in Sweden in the 1970s for use on smelter flue gas streams and others (13). There are several selenium filters installed for mercury removal in Sweden. Vendors indicate they meet the MACT standard of 40 $\mu g/m^3$. The EPA was contacted to obtain more information but have yet to respond.

Selenium filters are a potentially viable technology for NWCF vapors. However, it is not known how the NO_x gases may impact the efficiency or breakthrough time. Also, they can not be regenerated and would require disposal. However, they may pass the TCLP due to the affinity of mercury for selenium (and other sulfur family elements).

Noble Metal
No existing thermal unit is using a noble metal based process. However, ADA technologies have been testing one called Mercu-RE at various facilities, including INTEC and MSE in Butte, Montana. Results using metallic mercury indicate interference from NO_2 gases where the mercury is oxidized in the gas phase. Metallic Hg would not desorb in the presence of NO_2. Other testing indicates $HgCl_2$ is also removed but with reduced capacity (i.e., reduced sorption capacity before breakthrough) in the presence of NO_2 (3).

Other Adsorption
As a control (for Mercsorbent testing), regular GAC was used to test for elemental mercury sorption as a function of temperature and humidity (ranges: 280-400°F, 40 $\mu g/m^3$, gas face velocity of 0.61 m/s). With dry air, the GAC could sorb 60 percent at 400°F (14). However, with moisture the sorption dropped to zero at this temperature. At reduced temperatures, the GAC would again sorb the mercury. Testing with the Mercsorbent indicated 95 percent removal at 230°F and 100 percent at 300°F indicating a good high temperature sorbent. Some $HgCl_2$ is also removed but testing is still in progress. Exfoliated, chemically treated vermiculites were tested. The one treated with a proprietary chemical showed especially promising mercury-capture abilities (15). In a 70-hour run, 95 percent removal was observed with no diminution (55-115°C range). The vermiculite also passed the TCLP (0.2 mg Hg/L) at 0.08 mg Hg/L. At 230 °C approximately 85 percent removal was realized. In-plant slipstream testing was conducted at R.E. Burger Station near Shadyside, Ohio. The removal varied between 75-97 percent.

MEMBRANES

Pervaporation
In the pervaporation process, a membrane is used to selectively separate solvents by reducing the vapor pressure on the permeate side of the membrane. Components in the stream being treated must permeate through the membrane by first dissolving into and then diffusing through the membrane (16). Evaporation occurs on the permeate side via vacuum. The driving force is the difference in chemical potentials or fugacity (i.e., vapor pressure) across the membrane similar to membrane distillation. The rate is also determined by a solvent's solubility and diffusivity in the membrane. It differs in this respect from membrane distillation.

Artisan Industries have standard units available for separating water from organics based on size difference. Artisan's membrane consists of a zeolite on a porous ceramic substrate. This material has apparently provided better stability than the organic polymer pervaporation membranes.

This technology would require that water and NO_x be soluble and permeable while excluding mercury or vice versa. At present, there are no known membranes that can be used in pervaporation for this process (17). However, it is believed that one could be developed but it would require extensive research.

Reverse Osmosis and Nano-Filtration

There are no known RO/NF processes treating water for mercury removal or solutions similar to tank farm feed. There is potential for treating the scrub solution using RO/NF. It would be required to cool this solution to approximately 60°C , the membrane material limit (18). Tests are required to determine the percentage of mercury compounds rejected and to determine if the material can maintain its properties under the 5 molar nitric acid concentration. The Koch membrane considered has been tested in 10 percent nitric acid. The concentrate would require further treatment via an aqueous phase process.

The pressure required is on the order of the osmotic pressure of the solution, which is approximated by

$$\pi = CRT$$

Where C=TDS, molar
R= Gas constant, 0.082 L-atm/gmole/°K
T= Temperature, °K

Applying this to feed that has a TDS of approximately 240,000 mg/L (a typical scrub liquor) results in an osmotic pressure of approximately 3,000 psi, which is not considered practical for this application. Further, ROSA (RO program provided by Dow Chemical) was used to try and establish an RO array for feeds with high TDS. The program would not converge under any configuration exceeding the manufacturers' membrane pressure limitations. Therefore, RO/NF are not considered for further analysis.

Membrane Distillation

Hot feedwater flows past a microporous, hydrophobic membrane. Surface tension prevents the feed, while in a liquid state, from penetrating the membrane. In the vapor phase, however, water molecules will pass through and condense on a cooling surface, while non-volatile matter remains completely withheld by water's surface tension. The driving force is the difference in vapor pressure, created by the temperature difference between the hot feed and the cooling surface. When it condenses, this vapor water has substantial purity; in fact, only other volatile compounds may pass through at the same time as water. The technology and the theory for it were developed in several countries chiefly in the 1980s, and the term "membrane distillation" was adopted at a conference in the Netherlands in 1989.

This technology has potential applicability to treating the scrub solution sidestream. The HNO_3 chiefly stays with the concentrate, but small amounts transmit through the membrane. Further treatment of the reject stream, and possibly the permeate, are likely required. The process would concentrate the reject stream and require upstream filtration to remove particles.

ABSORPTION

The reference process is the existing NWCF quench and venturi system that is known to scrub most of the mercury from the calciner gas. Scrubbing is applicable to the vapor phase for $HgCl_2$ but not for Hg^o. However, a scrubber, at lower temperatures can act as a contact condenser. Low soluble candidates[2] (i.e., Hg^o) are poor candidates for this technology based on the mass transfer relations and material balance:

$$Vy_i - K_L a(x_s - x) = Vy_o$$

$$K_L a(x_s - x) - kx = 0$$

Where k = First order reaction coefficient (e.g., $Hg + 2H^+ = Hg^{+2} + H_2$)
$K_L a$ = Liquid phase mass transfer coefficient
x = Liquid phase mercury concentration (x_s is solubility)
y = gas phase mercury concentration

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[2] Although references (Perry 1985) indicate solubility of Hg^0 in nitric acid, this is believed to be as an ionic compound that requires significant time to produce.

V = Rate of gas flow to quench

Combining the above two equations, the following significant prediction results:

$$y_o = y_i - \frac{K_L a}{V} * x_s (1 - \frac{K_L a}{K_L a + k})$$

This shows that scrubbing does little for Hg^o as x_s is small ($x_s < 1x10^{-6}$)[3]. Similar results can be determined using the Kremser equation (19), which shows that as Henry's constant increases (for scrubbing), exceedingly high scrub liquid flowrate is required. Henry's constant for Hg^o at the operating conditions is about 7,300 atm and decreases to 495 atm at 298°K (20), both too high for scrubbing mercury metal as a practical technology. However, if a fast oxidizing reagent were available that could be used in large quantities, the reaction would be concentrated at the interface. For this case, the gas phase is the controlling resistance and the metal could possibly be removed. Nitric acid is an oxidizing reagent but the reaction is not adequately fast. $KMnO_4$ may provide the oxidizing power to do this but would require testing.

PRECIPITATION

Tests were performed in a pilot unit at Rotterdam, Holland using water from a gas scrubber. The analyses were performed by three independent laboratories using Na_2S, trimercapto-S-triazine (T-S-T), and the polythiocarbonate (MP7). The results are provided below in Table IV and indicate that any of these reagents are successful in meeting the proposed Dutch limit of 1 ppb. All of the testing used a flocculating agent.

Table IV. Precipitation Tests, Holland

Metal	Average Influent (ppb)	Average Effluent (ppb)		
		T-S-T	Na_2S	MP7
Hg	230	0.2	0.2	0.2

Degussa Corporation has tested the trimercapto-s-triazine (TMT 15) in high nitric acid concentration with good results. Degussa achieved 99.9 percent removal (DF=1,000) during testing of TMT 15 starting with 1,000 ppm Hg and 3.5 M HNO_3 initially simulated nitric acid scrubber solution with a 25-minute stirred residence time.

A precipitation process would require installation of a sidestream process on the quench scrub collection tank. However, it may require pH adjustment as toxic H_2S gas is formed under the acidic conditions, at least when using sulfide. If using TMT 15, no pH adjustment is required and it can be used directly in the acid. It would also require flocculation if based on the Dutch experience (alum may be beneficial in this respect). The precipitate will require filtration and the solid passes the TCLP.

ION EXCHANGE

The Treated Effluent Disposal Facility (TEDF) at Hanford uses mercury specific ion exchange as one of their unit processes. The water is high chloride so significant $HgCl_2$ is likely present. The resin functional group is thiol. The columns are regenerated with HCl. However, the water has been pre-treated at this point using precipitation at a pH of 10 and a $FeCl_3$ flocculating agent and contains much less dissolved solids than the NWCF scrub solution.

Several IX/sorption resins were tested on INEEL tank simulants at ORNL (21). The tank waste simulated was that of a high-sodium tank waste with HNO_3 at 1.66 M, 0.02 M HCl, 0.002 M Hg $(NO_3)_2$ and various nitrates and other

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[3] Higher levels of metallic Hg are possible than predicted by this as Hg metal solubility is ~ 700 times higher in aerated waters (9).

salts. The results of this testing indicate limited capacity (during sorbent tests, column testing was not conducted) likely due to high acid but also impacted by chlorides as shown in Table V below. However, these were sorbent capacity tests and column testing indicates that most of the resins/sorbents will work. High acid concentration attacks some of these resins, which likely leads to early breakthrough.

Table V. IX with Acid-Type Solution

Resin	Functional Group	Final Hg Conc., mg/L[4]	% Removed
Ionac SR-4	Thiol	205	25.6
SuperLig 618	Proprietary	213	25.2
Durasil 70	Proprietary	265	3.6
Ionac SR-3	Isothiouronium	267	3.0
Mersorb[5]	Sulfur (S-GAC)	273	0.5
Filtersorb	GAC	274	0.4
IRC-718	Iminodiacetate	278	0.0

Testing at higher pH with chlorides present indicate better efficiency. The following results in Table VI are for SRS simulant that had 1.33 M NaOH, 0.22 M NaCl, 0.002 $HgCl_2$, and various nitrates and other salts.

Table VI. IX With Basic-Type Solution

Resin	Functional Group	Final Hg Conc., mg/L[6]	%Removed
Mersorb	Sulfur (S-GAC)	0.8	99.3
Durasil 70	Proprietary	21.9	79.7
Ionac SR-3	Isothiouronium	22.4	79.2
SuperLig 608	Proprietary	24.1	75.1
Filtersorb	GAC	60.2	44.1
Ionac SR-4	Thiol	66.6	38.2
IRC-718	Iminodiacetate	68.4	36.5

The HSC Chemistry speciation equilibrium program was used to understand the above results. The mercury in both of the simulants was virtually all as $HgCl_2$ due to the high chloride according to the program results (it is believed there is also significant $HgCl_3^-$ and $HgCl_4^{-2}$). The acid interferes with Mersorb sorption of $HgCl_2$ by oxidizing the sulfur on the granules, but the removal efficiency is excellent in the absence of acid indicating good affinity for $HgCl_2$ and S-GAC in aqueous solution (lower limit of pH~4).

There are also newer type IX/sorption resins that are specific to mercury. Mesoporous silica materials containing functionalized organic monolayers (thiol groups) have been developed to remove heavy metals from wastewater. The distribution coefficient for Hg ranges from 56,000 to 340,000 using SRS simulants (22). Also known as self-assembled monolayers on mesoporous supports (SAMMS), the material has good potential but would require testing. Previous testing was conducted in the pH range of 3 to 9.

This technology has potential applicability to a scrub sidestream. However, IX resins are normally not designed for high acid conditions so pH adjustment (or water scrub) is likely required. Also, the presence of chloride in this stream complicates IX possibilities. Cation exchangers prefer other cations to Hg^{+2} if chloride is present (23). The use of this technology would require the installation of IX columns and associated regeneration and/or replacement/removal equipment. Even with pH adjustment, it is questionable whether some of the resins can apply to this type of waste as the speciation indicates a significant amount of mercury bound up as $HgCl_2$. While the

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[4] Initial Hg was 278 mg/L

[5] Mersorb is a S-Impregnated GAC made by NUCON

[6] Initial concentration of 108 mg/L Hg

Mersorb may sorb this, Hg^{+2} and $HgCl^{+}$ are also significant in the scrub at the Hg:Cl ratios observed. Additional testing with partially neutralized solutions would be required.

CHEMICAL REDUCTION

Reference Process

SRS has developed a process that uses formic acid to chemically reduce mercury oxide (SRS has no $HgCl_2$) in sludge feeds to the DWPF melter (24). Formic and nitric acids are added to sludges that result from treatment of SRS high-activity wastes that contain 0.2-2 weight percent mercury. The mixture is heated to 95°C for six to 12 hours, then steam-stripped to remove the reduced mercury. The pH is limited to 4.5 to prevent reoxidation.

$$Hg^{+2} + HCOOH = Hg + CO_2 + 2H^{+}$$

Based on thermodynamics, the other expected mercury species can also be reduced.

$$HgCl_2 + HCOOH = Hg + CO_2 + 2HCl$$

$$HgCl^{+} + HCOOH = Hg + CO_2 + H^{+} + HCl$$

SRS (25) indicates the second reaction, above, does not go to completion forming HgCl. However, recent discussions (26) indicate that the reaction does go to completion in caustic solution and depends somewhat on the initial speciation.

POLYMERS

Polymer Filtration

Specialized polymers are added to contaminated water where they create a bond with the targeted metals. This bonded complex forms a much larger compound that can then be separated from the waste stream. An acid-resistant thiacrown polymer has been developed as a cost-effective mercury extractant (27).

Testing indicates mercury (as Hg^{+2}) is removed ranging from 95-99 percent depending on concentration and time (27). This process was selective even in the presence of competing cations. The bound Hg^{+2} can be stripped from the polymer allowing reuse. This technology has been shown to be effective for Hg^{+2} in the presence of lead and other competing cations. It is also possible to use this material in a column/sorption unit.

This process is applicable and designed for treating aqueous liquids. It will require testing for this particular application on a sidestream treatment of the scrub collection tank liquors. Testing has been conducted in the pH range of 1.5 to 6.2. Although it was designed for acidic conditions, it is not known how higher acid concentrations would impact material integrity and sorption efficiency. Also, the fact that there are mercury chlorides may impact this technology negatively. Since NWCF scrub solution contains other species of mercury, this technology by itself may not remove all of the mercury.

Polyelectrolyte Enhanced Removal

This technology uses water soluble chelating polymers (WSCP) that have been designed for mercury ion selectivity in the presence of dilute acid and mild oxidant (7). The technology was developed to assist in the oxidation of elemental mercury to mercuric cation (Hg^{+2}) and remove the mercury via chelation. The solution is chemically adjusted removing the mercury while the polyelectrolyte and solution is recycled. The concentrated mercury is treated via sulfide precipitation.

The process was developed at Los Alamos National Laboratories (LANL) for treating debris that is chiefly metallic contaminated. A number of different WSCPs were evaluated for their ability to bind Hg(II) as a function of pH.

Their research shows that all of the polymers bound well in the pH range >3. Most of the polymers bound well even to pH 1 with two polymers, WAB-100 and WABOH-30, showing some release starting to occur below pH 2 Hg(II) can be stripped from the WSCP by using a diafiltration process (28) at a lower pH range. Some of the polymers studied thus far have poor solubility in the < pH 0.2 ranges. Only WABOH-30 had reasonable solubility at low pH values. A number of the polymers were able to reach the target limit in the higher pH ranges (7).

This process was developed for solubilizing and binding metallic mercury from waste debris. However, it may be possible to adapt the process for the scrub liquor but will require further testing to determine if the speciated mercury will bind to the polymer. This will also require ultra-filtration and a form of mercury recovery, presumably sulfide precipitation.

PHOTOCATALYTIC

Photocatalysis, an athermal process, uses ultraviolet (UV) light with a wavelength < 385 nm to excite an electron of solid particles of TiO_2 to a higher energy level. This leaves holes in the semi-conductor that oxidize organic compounds. While most research has focused on the oxidation of organics, the free electrons generated reduce metals in solution. The technology has the potential of removing hazardous metals from solution, including mercury (29).

ADA Technologies has received funding from the DOE to perform treatability testing for mercury removal from selected surrogates using this technology. There has been previous research using this method (30, 31, 32). ADA has completed some Phase I testing that indicates that this is a good potential process for treating non-acidic liquid streams. Table VII summarizes some of the recent testing using TiO_2 with finely dispersed noble metal on the surface.

Table VII. Photocatalytic Results

Mercury Species	Organic source	Post-Treatment Conc.	Removal Efficiency
$HgCl_2$, 10 mg/L as Hg	Citric Acid	13 μg/L	99.9%
$HgCl_2$, 10 mg/L as Hg	Na-EDTA	46 μg/L	99.6%
HgI_2, 10 mg/L as Hg	Na-EDTA	10 μg/L	99.9%

The TiO_2 with noble metal was found to adsorb 230 percent of its own weight while plain TiO_2 is able to adsorb 160 percent of its own weight. Recent testing conducted by ADA on scrub surrogate indicates feasibility in nitric acid.

This process is applicable to treating scrub liquors. The process can reduce all of the potential species of mercury and operate in nitric acid. This technology requires addition of an organic compound to provide electrons that may be perceived as a safety issue.

GALVANIC TYPE TECHNOLOGIES

Electrochemical

A method using a mercury pool cathode is potentially feasible to remove dissolved mercury from acid solutions. The process can be batch or continuous. The process is more efficient at higher concentrations.

There are no known industrial processes using this technology for a similar application. However, testing has been conducted indicating the feasiblity. One method, using a graphite felt cathode proved infeasible, at least at nitrate concentrations greater than 2M. The other uses a liquid pool of mercury metal for the cathode and a platinum foil anode. Removal rates ranged from 0.8 to 9.8 g/hr. The mercury pool cathode requires sparging or agitation to obtain significant reduction rates. Three tests with an average cell voltage of 3.7 volts averaged 99 percent Hg removal and average removal rate of 9.6 grams of Hg/hour. Also, future tests will focus on determining the effects of waste solution components on Hg removal rates. Further testing has demonstrated this as a viable technology.

Metal Displacement/REDOX

REDOX media (copper and zinc) remove up to 98 percent of water soluble cations of lead, mercury, copper, nickel, chrome, and other metals.

$$Zn^{0} + Hg^{+2} \rightarrow Zn^{+2} + Hg^{0}$$

The zinc goes into solution while the mercury plates out on the copper. KDF Fluid Treatment, Inc. process media are high-purity copper-zinc granules used in a number of pretreatment, primary treatment, and wastewater treatment applications (33).

KDF informed us that the reference process they have is the New Jersey Department of Environment, which recommends the KDF 55 media for reduction of mercury. It performed a two-year study in 1992 on treating the Kirkwood-Cohansey aquifer that has an average pH of 4.5.

Galvanocoagulation

Hydrated iron oxides are generated from internal processes of galvanic couples. This process is the physi/chemi-sorption of metals on the ferrohydroxides. The following might represent the removal of the three main species of mercury:

$$Fe(OH)_3 + HgCl_2 \rightarrow Fe(OH)O_2Hg + 2HCl$$

$$Fe(OH)_3 + Hg^{+2} \rightarrow Fe(OH)O_2Hg + 2H^{+}$$

$$Fe(OH)_3 + HgCl^{+} \rightarrow Fe(OH)O_2Hg + H^{+} + HCl$$

This technology also removes some radionuclides and other metals. These are concentrated in the solid phase. The information provided (34) indicates a pH range of 2-14 and high turbidity operation. Borsekov Institute of Catalysis (Novosibirsk, Russia) has tested this at the Siberian Chemical complex in Seversk. No data were available for mercury but the process is very efficient for actinides.

Electrocoagulation

This technology uses electric fields to coagulate metals, i.e. it facilitates chemical coagulation. Contaminant-laden water moves through an electric field where destabilization, ionization, and electrolysis influence treatment. The mechanism for electrocoagulation is based on reduction of the zeta potential, i.e. the repulsive charges between colloidal particles are reduced so that larger particles can form and drop out of solution. This process was an EPA superfund project to stabilize oil reprocessing on acidic sludge. Mercury was non-detectable in bench-scale TCLP results. The influent mercury was 0.06 mg/kg.

TECHNOLOGY SELECTION CRITERIA

The following criteria are used to qualitatively rank mercury removal technologies:

- Minimization of secondary waste
- Simplicity of installation and operation
- Effectiveness in presence of NO_x (gas phase)
- Contact-handled waste form preferred
- Practical final waste form dispositioning and disposal
- Ability to remove all species of mercury present
- Technical maturity
- Minimal research and development
- Compatibility with current process and any proposed upgrades
- Negligible safety issues

No ranking has yet been conducted for gas phase mercury removal. Further testing is required for both adsorption and absorption (scrubbing).

Ranking of the aqueous phase technologies based on the above criteria leads to three unit processes for consideration; electrochemical reduction, UV/Ti photocatalysis, and TMT 15 precipitation. All three of these have been tested in simulated scrub liquors. The TMT 15 precipitation process was not able to efficiently remove mercury under scrub liquor conditions. The UV/Ti process removes significant mercury but requires addition of sugar or other organic compounds as electron donors. The requirement of an organic additive renders this technology as unacceptable based on safety issues. If an inorganic electron donor can be determined, this technology can be considered.

DISCUSSION OF PREFERRED TECHNOLOGIES

It is assumed that the ionic/molecular diffusion/mass transport of mercury compounds is much smaller than the reaction rate at the cathode. Hence, this becomes a mass transfer problem.

Plug Flow Reactor

$$-QdC - KW(C - C_s)dx = 0$$

With C >>Cs,

$$Wx = A_c = \frac{Q \ln DF}{K}$$

For a stagnant film, K = Diffusivity/Stagnant film boundary layer (D/δ), so the mass transfer coefficient K is:

$$K = \frac{D}{\delta} = \frac{5x10^{-5}\ cm^2/s}{0.05\,cm} = 0.001\,cm/s\,(10^{-5}\ m/s)$$

Where C=Hg concentration
D=Diffusivity, 10^{-5} cm^2/s (for most ions @25°C)
K_L=Mass Transfer Coefficient (~D/δ)
Q=Flowrate (2 gpm)
Wx=Cathode area
δ=Concentration Boundary layer, 0.05 cm (stagnant solution)

The required mass transfer area for a DF = 10 is then

$$A_c = \frac{2\,gpm * 3.785\,L/gal * \ln 10 * 10^3\ cm^3\ /L * m^2\ /10^4\ cm^2}{0.001\,cm/s * 60\,s/\min} = 29.1\,m^2$$

Based on this large area, the mass transfer coefficient needs to be larger via some type of mixing of the stagnant boundary layer while ensuring minimal entrainment of liquid mercury metal. Fortunately, recent testing has provided this. The data indicate that the mass transfer coefficient is a function of concentration or reactions are not instantaneous as assumed. In either case, the model can blindly assume one or the other. Assuming that the mass transfer coefficient is a power function of concentration ($K = K'C^n$), n was found to be ½ from the data. This leads to:

BATCH

$$-V\frac{dC}{dt}-K'A_cC^{3/2}=0$$

$$\frac{1}{C^{1/2}}=\frac{1}{C_0^{1/2}}+\frac{K'A_c}{2V}t$$

For these results to be true, a plot of $1/C^{1/2}$ versus t should give a straight line with a slope of $K'A_c/2V$ and an intercept of $1/C_0^{1/2}$. The plot below indicates that this is a fair representation.

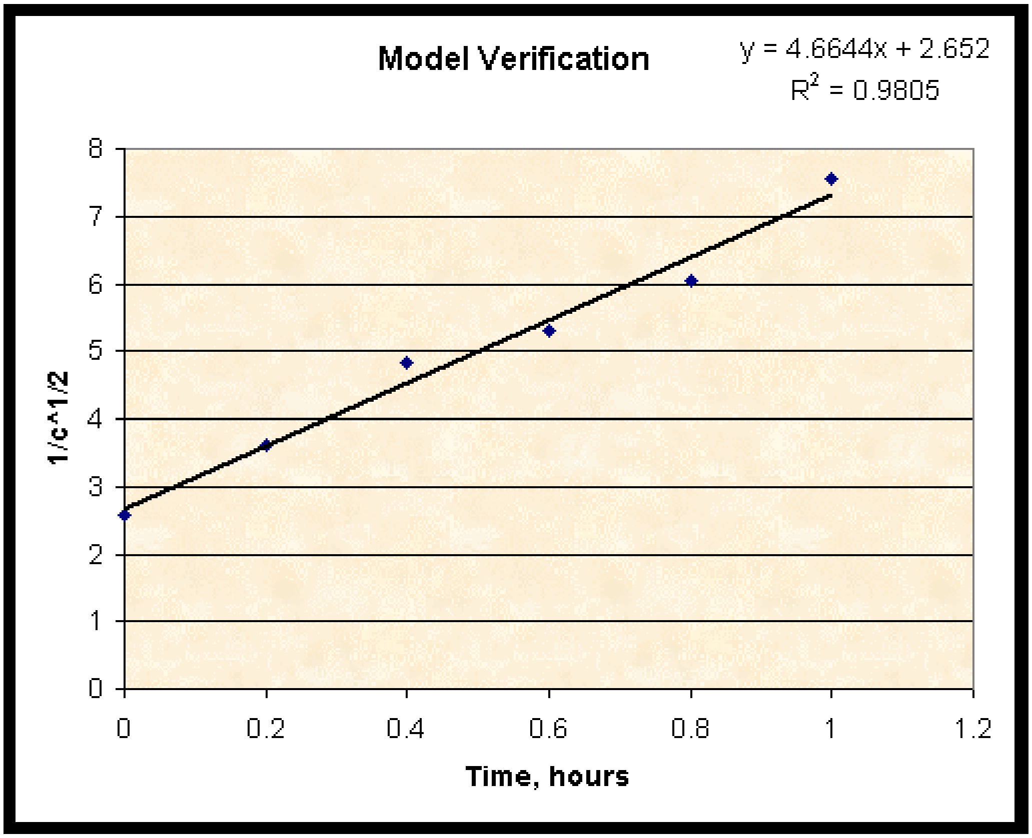

Figure 4, Model Verification

K' is then

$$K'=4.66\ \frac{(L/mole)^{1/2}}{hr}*\frac{2*0.004\,m^3}{0.0155\,m^2}*hr/3600\,s=6.68x10^{-4}\ (L/mole)^{1/2}\,m/s$$

The K value at a starting concentration of 0.15 M is

$$K = 6.68x10^{-4} * 0.15^{1/2} = 2.59x10^{-4}\ m/s$$

and declines thereafter. This result is quite favorable compared to the stagnant film results and literature values.

PFR

The results for the PFR are analogous to the batch:

$$\frac{1}{C^{1/2}} = \frac{1}{C_0^{1/2}} + \frac{K' A_c}{2Q} = \frac{1}{C_0^{1/2}} + \frac{K' A_c}{2V}\tau$$

Scale up for this process should make use of the Sherwood number (Sh) as the K' will change with Reynolds number and the entrance orientation (hydraulic diameter). Based on these results, an electrochemical system is a reasonable technology.

PATH FORWARD

Additional testing is required prior to a complete design and subsequent upgrades to remove mercury. The following testing is planned to implement the upgrades:

Electrochemical Reduction. The unique nature of the scrub solution dictates that a mercury removal process operate effectively in strong nitric acid at ≈ 70°C. Previous studies and laboratory work have shown that electrochemical reduction is the only available method at this time. The only other alternatives determined to be viable needed a higher pH and thus require either neutralization or a water scrub. Neutralization was not considered due to problems with precipitation and a water scrub would require a filter system to remove solids. Therefore, demonstration of the electrochemical process is required. Previous testing indicates that this is a viable technology. However, information is required prior to scale-up to a pilot or full scale system including

- Hg Surface Regeneration/Stagnant Film Mixing. This testing determines the best method of agitating the mercury surface and adjacent stagnant electrolyte. Mass transfer is very limited if a stagnant solution persists. The objective of this testing is to find the optimum surface regeneration/agitation method by trying different methods including nitrogen sparge, scrub solution sparge, ultrasonic agitation and gas sparge orientation.
- Anode Design Investigation. This testing investigates different anode designs and materials. The current anode is platinum that oxidizes under test conditions leading to reduction in removal rates over time.
- Simulated Scrub Testing. This is a major testing activity that uses simulated scrub (including cold calcine) to do a cold test on the system. The main objectives are to evaluate filters, observe co-reduction of other projected metals, and overall operation with the simulated scrub.

Vapor-Liquid Equilibria (VLE). Mercury is expected in three speciated forms (gaseous) at the NWCF; $HgCl_2$, Hg, and HgO (aerosol). The VLE for Hg is well known in water and is expected to be similar in HNO_3 solutions (the Hg solubility can be higher in highly aerated water). HgO exists in aerosol/particle form so no VLE is needed for it. $HgCl_2$ VLE has been calculated in previous evaluations using ESP computer modeling. Actual data is mandatory to evaluate current and proposed absorption (scrubbing) scenarios including a new scrubber, the current quench/venturi configuration, and modifications. The objective of this testing is to provide aqueous and gas phase equilibrium concentrations of $HgCl_2$ over the range of several concentrations and temperatures. This will provide activity coefficients and/or Henry's Law constants to use in design and modeling.

Absorption Testing. Partially based on the VLE, absorption scenarios can be modeled and designed. However, actual laboratory or pilot scale testing is required for demonstration. Mercury metal vapor (Hg) cannot be scrubbed efficiently largely due to the low solubility (instantaneous) in water and water solutions. However, $HgCl_2$ can be scrubbed (interphase mass transfer) and HgO can be removed by inertial processes (including scrubbing). The following are test objectives for this testing:

- Hg to HgO Oxidation. Hg appears to rapidly oxidize in the presence of NOx (NO_2). If this can be determined, modeling can be done to predict speciation in the offgas system at the NWCF and subsequent design. The rate constants need to be determined by introducing metallic Hg vapor into a batch reactor of NOx and obtaining concentrations over time.
- Particle Size. The HgO produced above will have a particle size distribution (PSD). This PSD will allow evaluation and design of HgO processes.
- Scrubber Lab/Pilot Scale. Removal effciencies for HgO and $HgCl_2$ will be determined in a larger scale, counter-current absorber (scrubber). The system L/G will be varied and compared to the VLE.

REFERENCES

1. ICT 1930, *International Critical Tables of Numerical Data*, Physics, Chemistry and Technology, National Research Council, McGraw-Hill 1930.
2. Lide, D.R., and Kehiaian, H.V., *CRC Handbook of Thermophysical and Thermochemical Data*, CRC 1994.
3. ADA 1998, *Investigation on the Removal of Elemental mercury and Mercuric Chloride from a Highly Oxidizing Gas Stream*, ADA Technologies, November, 30, 1998.
4. Siemer, D., Personal Conversation (email), September 23, 1999.
5. Zamencik, J., Personal Conversation, September 1999.
6. Chase, M., National Institute of Standards, personal conversations (email), January 6, 1999.
7. Smith, B. F. et al, *Polyelectrolyte Enhanced Removal of Mercury from Mixed Waste Debris*, Waste Management 1999, Tucson, Arizona, 1999.
8. IUPAC 1983, *Solubility Data Series*, Vol 23, Pergamon Press.
9. Bailar, J.C., *Comprehensive Inorganic Chemistry*, Pergamon Press, 1973.
10. Federal Register/Vol. 61, No. 77/Friday, April 19, 1996/
11. Proposed Rules. EPA 1992, *EPA Research and Development Report*, EPA-600/R-92-192.
12. Restor, D., Personal Converstion with Dennis Restor, Norit Americas, Inc., January 26, 1999.
13. EPA 1997, *Mercury Study Report to Congress* (Vol. VIII), EPA-452/R-97-003, December 1997.
14. Nelson, S. Jr., Wang, A, *Recoverable-Mercury Sorbents*, 96-WP64B.04, Air & Waste Management Association, Nashville, Tennessee, June 8-13, 1997.
15. Nelson, S., Jr., Miller, J., Summanen, D., *Innovative Mercury Emission Control*, Air & Waste Management Association, Toronto, Ontario, June 23-28, 1996.
16. AWWA 1996, Mallevialle, J, et al, *Water Treatment Membrane Processes*, McGraw-Hill, 1996.
17. Giberti, Richard, Personal Communications with Artisan Industries, December, 1998.
18. Koch 1999, personal communications with Koch Membranes, January 4, 1999.
19. Treybal, R. E., *Mass Transfer Operations*, McGraw-Hill, 1987.
20. Clever, L.H., Johnson, S.A., Derrick, M.E., *Solubility of Mercury and Some Sparingly Soluble Mercury Salts in Water and Aqueous Electrolyte Solutions*, J. Phys. Chem. Ref. Data, Vol. 14, No. 3, 1985.
21. Taylor, P.A., et al, *Mercury Separation From Mixed Wastes*: Annual Report, ORNL/TM-13121, November, 1995.
22. Fryxell, G.E., et al, *Functionalized Monolayers on Ordered Mesoporous Supports*, Science Vol. 276, May 9, 1997.
23. Helfferich, F., *Ion Exchange* (republication), Dover Publications, 1995.
24. Coleman, C.J., et al, *Reaction of Formic Acid and Nitric Acid with Sanannah River Site Radioactive HLW Sludge in the DWPF Pretreatment Steps*, WSRC-MS-93-563, 1994.
25. Eibling, R.E., *Results of Mercury Reduction with Formic Acid*, Savannah River Plant Internal Memo DPST-83-1047, December 1, 1983.
26. Eibling, R.E., Personal Communicationss with Russ Eibling, July 19, 1999.
27. Baumann, T.F., Reynolds, J.G., Fox, G.A., *Polymer Pendant Crown Thioethers for Removal of Mercury from Acidic Wastes*.
28. Cheryan, M., *Ultrafiltration Handbook,* 1986, Technomic, Lancaster, United Kingdom, see also Winston, W. S. and Sirkar, K. K. *Membrane Handbook*, Van Nostrand Reinhold: N.Y., 1992.
29. Serpone, N., Heterogeneous *Photocatalysis at Work, Selective Separations and Recovery of Metals from Industrial Waste Streams*, AIChE Annual Meeting, New York, November, 1987.
30. Aguado, M.A., et al, *Continuous Photocatalytic Treatment of Mercury (II) on Titania Powders*, Kinetics and Catalyst Activity, Chem. Eng. Sci., 50, 1561-1569, 1995.

31. Lau, L.D., et al, *Photoreduction of Mercuric Salt Solutions at High pH*, Environ, Sci. Technol., 32, 670-675, 1998. Prairie, M.R.,
32. *Practical Aspects of Aqueous Photocatalysis*, Photocatalytic Oxidation Research Review Meeting, NREL/CP-471-20577, Copper Mountain, Colorado, October 4-6, 1995.
33. KDF 1999, http://kdfft.com/html/metals/. htm
34. MSE 1998, Tradeoff Study: *Air Pollution Control Scrubber Blowdown Mercury Removal System*, MSE Technology Applications, Inc., Butte, MT, June 1998.