Trace Mercury Removal from Flue Gas Desulfurization Wastewater

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ABSTRACT: Discharges from Wet FGD Systems are facing new, very stringent, effluent limitations for mercury. To comply with these new limitations, an end-of-pipe system to remove trace mercury contamination to <12 parts per trillion was developed. This report will present the results of a successful pilot test performed in 2008.

INTRODUCTION

Many coal-fired power plants have installed or plan to install wet flue gas desulfurization (FGD) scrubbers in response to increasing pressure to control air emissions. The blowdown from these units contains elevated levels of solids, chlorides, sulfates, and heavy metals as well as nutrients (nitrates and/or ammonia)

This wastewater is generally treated in a physical/chemical system including desaturation of sulfates and chemical precipitation. These systems may or may not include filtration depending on effluent requirements. Physical/chemical treatment with sand filtration can remove mercury from FGD wastewater to concentrations as low as 2-10 parts per billion (ppb).

In general, physical/chemical treatment of FGD blowdown wastewater has been sufficient to achieve discharge standards for many years. Many installations in the US have been operating from the early 1990s. However, new and more stringent *water quality based* standards are being introduced, which require additional removal of specific contaminants such as mercury, selenium, boron, or nutrients. These standards are set based on the ability of the receiving water to accept the discharge without significant impact. They are not set based on any available technology.

Mercury is of particular interest and concern because of its toxicity as well as the fact that it bio-accumulates. Due to water quality based standards such as the Great Lakes Initiative (GLI), some states are setting effluent mercury standards as low as 1-10 parts per trillion (ppt).

The information discussed in this paper is the result of collaborative research studies conducted by the Dow Chemical Company and Degremont Technologies in an effort to achieve trace mercury removal down to these new regulatory standards. The pilot test was performed at a power station in the eastern United States.

Prior to pilot testing, a bench-scale treatability test was performed by Degremont's North American R&D Center (DENARD) in Richmond, Virginia using the mercury selective resins. With preliminary treatability data in hand, the treatment train was developed and the necessary pilot equipment was assembled.

The pilot treatment train included:

- Addition of organosulfide
- Sand Filtration
- Cartridge Filtration (5 micron)
- Ultrafiltration (0.03 micron)
- Selective Ion Exchange

It is important to note that all of these technologies are well established and can be implemented commercially. The novel part of this system is the selective resin itself.

The goals of the pilot study included:

- The determination of the lowest achievable effluent mercury concentration
- The determination of the most effective mercury-selective resin
- The determination of the effectiveness of differing levels of filtration
- The identification of potential operations and maintenance issues

The pilot operated from July through December 2008 and achieved all of the above goals.

A number of interesting observations have been made during the course of these investigations. A patent disclosure has been filed on these observations.

DEVELOPMENT OF MERCURY SELECTIVE RESINS

Modern ion exchange resins are made from styrene divinylbenzene plastic. This material is a tough and proven base for attachment of a variety of functional chemistries. Liquid styrene and divinyl benzene are combined with diluents, solvents, catalysts and stabilizers and formed into organic phase droplets by suspension polymerization processes. The suspension is heated to polymerize the styrene and DVB into a solid plastic sphere.

The functional groups are added by first activating the benzyl rings of the plastic by chloromethylation with chloromethyl, methyl ether that adds a $-CH_2-Cl$ functional group. It is through this group that a wide variety of nucleophiles can be reacted to create the wide variety of selective media that are enjoyed today.

For selective mercury removal, the chemical form of the mercury is a primary concern. Mercury is a very reactive molecule, often referred to as "sticky" in

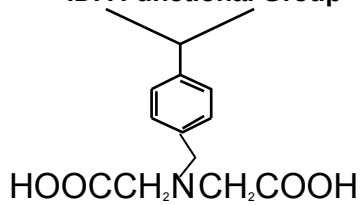
that it associates with a wide range of other molecules, forming a wide variety of complexes. In addition, mercury can exist in various forms such as Hg^0 the zero valence or metallic form, Hg^{+2} the ionic form and organo-mercury such as methylmercury. Each of these forms of mercury has different physical and chemical properties that must be taken into account in the design of a selective media.

A speciation study of the form of mercury that is present is recommended so that the right media is used for the right form of the molecule. Speciation studies are difficult to perform, as relatively few laboratories are capable of this kind of study at these very low levels. Speciation studies are subject to interpretation as the error in the analysis can be significant. In this case, the ionic form of the mercury was identified as the primary target for treatment.

Since ionic mercury is a cation, removal with a cation exchange resin is logical. In the case of FGD wastewater, this treatment has not been successful, presumably due to the high salt background of the wastewater matrix.

The literature describes Iminodiacetic acid (IDA) functionalized resins as having very high affinities for mercury.

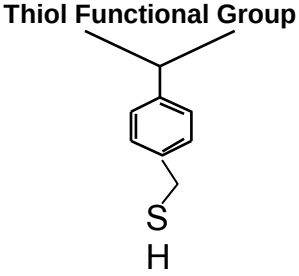
Figure 1A
IDA Functional Group



While this may be true for neat solutions, the high salt background of FGD wastewater likely causes interference with the IDA group causing lower affinity in testing.

Another chemistry of interest is the Thiol functional group. The interactions of sulfur and mercury are used for mercury removal from vapor phase treatment of natural gas.

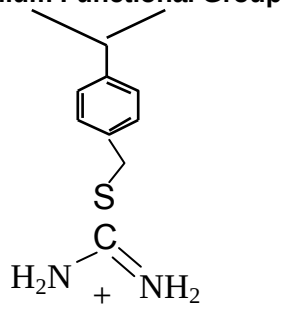
Figure 1B
Thiol Functional Group



Other Thiol chemistries attach the S-H directly to the benzyl ring changing the chemical properties of the functional group.

Yet another functional group of interest is the Thiouronium chemistry. Here a thiourea moiety is the active group that forms an attractive charge transfer interaction.

Figure 1C
Thiouronium Functional Group



A final note on selective media is that for removal of contaminants like mercury at parts per trillion levels, the total loading capacity of the media may not be the limiting factor. These media, when challenged with mercury at high levels (mg/L range) will load metal to wt/wt% levels. To even come close to approaching this level of loading, the media would need to be exposed to billions of bed volumes of solution. Thus the media is less likely to become fully loaded with the trace contaminant and more likely to fail due to fouling. Thus the issues of concern are fouling resistance of the

media, an open pore structure of the media creating easy access and allowing fast flow rates and short contact times for cost effective system design.

BENCH-SCALE TREATABILITY STUDY

Prior to performing on-site pilot testing, a bench-scale study was performed to screen various ion exchange resins for performance evaluation.

Bench-scale treatability for mercury with selective ion exchange resin was determined using a „shake flask' technique. This method includes adding a measured mass of resin to a flask containing the wastewater to be treated. The flasks are left on a flask shaker for 24 hours. After the 24-hour shake period, the resin is allowed to settle and the supernatant is analyzed.

The purpose of this test was not to determine the achievable mercury concentration, but to determine which resin achieved the best relative result.

Table 1
Shake Flask Results

Resin Type	Ratio (g/mL)	Hg (ppt)	Percent Removal
Blank	---	---	
Raw	---	126	
Thiol Resin	0.01	7.98	94%
	0.005	10.7	92%
Thiouronium	0.01	5.45	96%
Resin	0.005	8.61	93%
Silver Impregnated	0.01	73.8	41%
Alumina Resin A	0.005	101	20%
Silver Impregnated	0.01	87.9	30%
Alumina Resin B	0.005	89.4	29%

The above results clearly indicated the superior performance delivered by the Thiol and Thiouronium resins.

PILOT EQUIPMENT AND PROCESS FLOW DIAGRAMS

For the purposes of this study, the mercury present was loosely classified as „colloidal' or „soluble.' On this basis, the pilot equipment was divided into a chemical precipitation and filtration portion designed to remove the colloidal mercury followed by the selective ion exchange step to remove the remaining soluble mercury.

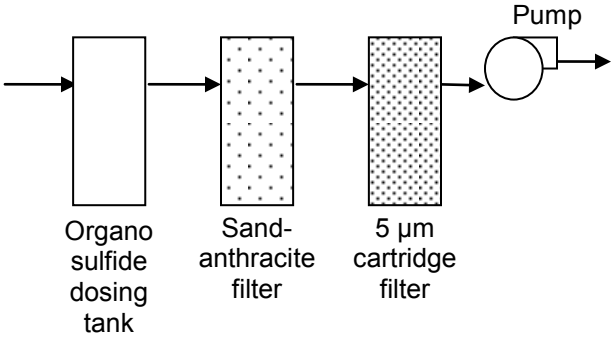
Chemical Precipitation

Prior to filtration, the wastewater is dosed with an organosulfide precipitant. The purpose of this chemical is to coagulate mercury as a sulfide complex prior to filtration.

Filtration Removal of colloidal mercury by filtration is dependent on particle size. Accordingly, the pilot system was designed with serial filtration using decreasing pore size. In this way, the particle distribution could be loosely determined.

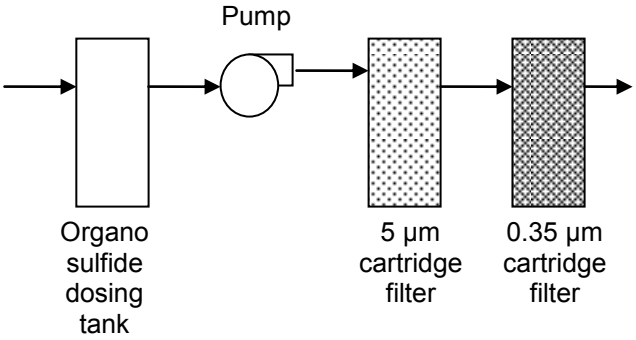
Initially, the filtration sequence included a sand/anthracite filter followed by a 5-micron cartridge filter as represented below.

Figure 2A
Initial Treatment Train



However, initial analytical data suggested that colloidal mercury was passing through the 5-micron filter and contaminating the resin downstream. To eliminate the remaining colloidal mercury, a second cartridge filter rated at 0.35 microns was added as represented below. At this time, the sand filtration step was bypassed as redundant with the downstream filtration.

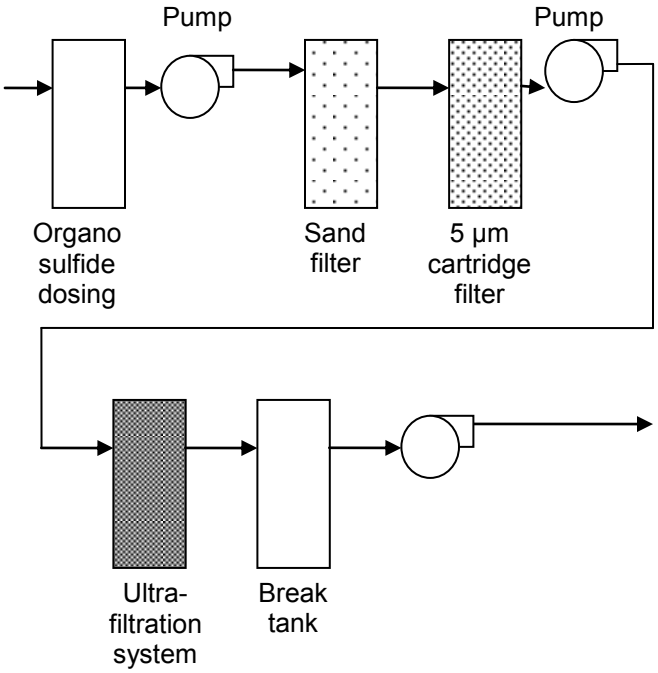
Figure 2B
Revised Treatment Train



Even with this change, ongoing analytical data indicated that colloidal mercury was still passing through filtration to contaminate the resins. At this early stage of the pilot study it was decided to add an ultrafiltration step to replace the 0.35-micron filter in order to completely remove the colloidal mercury.

The UF membrane module was a hollow fiber, PVDF design, employing an outside-in flow configuration, with an effective pore size of 0.03 microns. The new pilot configuration is represented below:

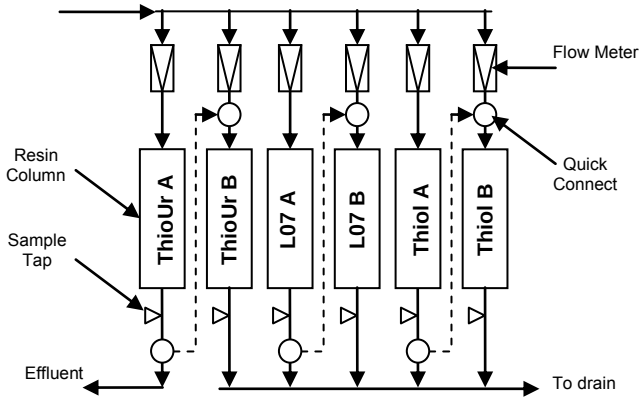
Figure 2C
Final Treatment Train



Selective Ion Exchange

The selective ion exchange skid was comprised of six columns housing three different resins. The resin columns employed a packed-bed, down-flow design and were pump fed from a tank through a common distribution header. Each pair of columns could be connected in series allowing for evaluation of an effective resin depth of either 48” or 96”.

Figure 3
Ion Exchange Beds



Based on this setup, the effluent from any individual column could be collected for analysis.

PILOT PLANT OPERATION

The operation of the pilot proceeded without any major operational issues. The sand filter required periodic backwashing as expected. The cartridge filters also required periodic changeout. A clean in place system was included with the ultrafiltration skid and weekly chemical cleanings were performed.

The resins were kept in place for the remainder of the test. Some compaction of the resin did occur within the columns.

The one operational issue that was observed was a significant fouling of the ultrafiltration membranes. Even after physical/chemical treatment, the FGD wastewater remains very high in dissolved solids and makes a difficult matrix for ultrafiltration. Several different cleaning regimes were used before the appropriate cleaning regime was determined.

SAMPLING AND ANALYTICAL METHODS

To obtain reliable data in the single digit part per trillion range, sampling and analytical analysis are extremely important. All sampling collection followed EPA's "Sampling Guidance" (EPA Method 1669) to reduce or eliminate contamination. Using this method, samples were collected using the "clean hands/dirty hands" technique in fluoropolymer (FLPE) and glass sample collection bottles. Samples were shipped unpreserved via overnight delivery and then acid-preserved upon receipt by the analytical lab.

EPA developed Method 1631 specifically to address the need for reliable measurement of mercury to concentrations in the range of 0.5 to 100 ng/L. Method 1631 supports technology-based and water quality-based monitoring programs authorized under the Clean Water Act for mercury. Following EPA Method 1631, measurement of mercury is accomplished via the oxidation of mercury with bromine monochloride (BrCl), sequential reduction with ammonium hydroxide and stannous chloride to convert Hg(II) to volatile Hg(0) for ultimate detection via cold-vapor atomic fluorescence spectrometry (CVAFS).

PILOT TEST RESULTS

The initial results revealed limited removal (approximately 40%) of the total mercury through the treatment train. Subsequently, this hydraulic loading rate was considered too high for the influent pollutant load, which during that time ranged from 800 to 1,700 ppt as highlighted in the table below.

Lowering the hydraulic loading rate produced an immediate and significant improvement in treatment performance, yielding 65 to 80% removal of influent mercury for a similar influent concentration range. However, the effluent mercury

concentration remained well above the ultimate objective of 12 ppt.

It was suspected that the resin performance was being hindered by non-specific fouling with particulate or colloidal mercury. A serial filtration study was conducted to characterize the form of mercury present. These results illustrated that a significant fraction of mercury thought to be soluble was in fact removed via filtration through a 0.2-micron filter, demonstrating the presence of a significant colloidal mercury fraction smaller than 0.2 microns.

Accordingly, the ultrafiltration stage was added to the pilot treatment train. The new configuration showed immediate improvement.

Using this configuration, the results continued to show significant variability, presumably due to colloidal mercury remaining on the resin. However, the system performance improved over the next few weeks. Results are presented below:

Table 2
Microfiltration & Ion Exchange Results

Sample Date	Results				
	Influent	Influent Flow	Effluent	Resin/ Depth	Column Flow
	ppt	gpm	ppt		gpm
07/23/08	825	2.33	530	Thiol/96"	0.5
08/06/08	647	1.11	221	Thiol/96"	0.2
08/13/08	1640	2.59	337	Thiol/96"	0.2
08/19/08	375	2.50	56.8	ThioUr/48"	0.1
08/20/08	337	2.38	47.9	ThioUr/48"	0.2
08/20/08	385	2.38	42.3	ThioUr/48"	0.2
08/27/08	816	2.55	333	ThioUr/48"	0.2
09/03/08	1670	2.31	112	ThioUr/48"	0.2
09/10/08	2030	2.42	30.4	ThioUr/48"	0.2
09/17/08	1460	1.92	494*	ThioUr/48"	0.2
09/24/08	1080	2.42	88.7	ThioUr/48"	0.2
10/01/08	553	2.51	45.6	ThioUr/48"	0.2
Min	337	1.11	30.4		0.1
Max	2030	2.59	530		0.5
Average	**985**	**2**	**168**		**0.2**

Table 3
Ultrafiltration & Ion Exchange

Sample Date	Results				
	Influent	Influent Flow	Effluent	Resin/ Depth	Flow
	ppt	gpm	ppt		gpm
10/22/08	421	2.48	< 5	ThioUr/48"	0.2
10/29/08	167	2.6	< 5	ThioUr/48"	0.2
11/05/08	168	2.47	< 5	ThioUr/48"	0.2
11/12/08	588	2.22	< 5	ThioUr/48"	0.2
11/19/08	372	2.24	< 5	ThioUr/48"	0.2
12/09/08	130	2.09	< 5	ThioUr/48"	0.2
12/10/08	189	1.69	< 5	ThioUr/48"	0.2
Min	130	1.7	< 5		0.2
Max	588	2.6	< 5		0.2
Average	**291**	**2.3**	**< 5**		**0.2**

RESIN LOADING AND DISPOSITION

As mentioned earlier in the paper, bulk loading of the mercury was not the primary challenge for the media tested here. Both the Thiol and the Thiouronium functionalized resins were capable of removing mercury to the desired limits. Post mortem analysis of the resin showed that loading of other metals via the selective functional groups or non-selectively via inorganic precipitation or fouling may be a more important consideration for the long term application of these media. Since variation in coal sources, variations in station operations and variations in pretreatment processes all affect the type and level of potentially interfering ions, pilot evaluation of the various media options is likely to be needed to sort through these issues.

PILOT STUDY CONCLUSIONS

Achievable Effluent Mercury

The pilot was successful in removing trace mercury from FGD wastewater to concentrations below 5 ppt . Thus the most important goal of the study was achieved.

Most Effective Resin

The most effective resin was the thiouronium functional group. While the Thiol resin was also very effective, the performance of the Thiouronium resin was slightly more consistent. Only minimal/ incidental removal was achieved by the silver impregnated resin.

Effect of Filtration

The majority of the mercury removal (on a mass basis) was via filtration. While sand and cartridge filters removed the mercury to some degree, they did not remove all of the colloidal mercury. Complete removal of colloidal mercury was only achieved upon incorporation of the ultrafiltration treatment stage. It must be noted that the observed results are based upon the distribution and form of mercury present

within the FGD wastewater at the specific facility tested.

In any application where selective ion-exchange is to be used downstream, it is necessary to remove ALL of the colloidal mercury to avoid its deposition on the resin.

The form and concentration of mercury is known to vary widely in FGD wastewater based on a number of variables such as coal composition and wet scrubber operational practices. Limited data from other pilot testing show removal of mercury to single-digit ppt concentrations without the use of ultrafiltration. Because of this, a bench scale analysis of particle size distribution is recommended prior to pilot or full-scale testing of any trace mercury removal application.

Operational Difficulties

As previously mentioned, the only significant operational difficulty encountered during the pilot study involved scaling of the ultrafiltration membrane. This issue was resolved by optimizing the chemical cleaning regime including reagent chemistry and dosage, length of cleaning cycle and cleaning frequency.

Technology Status

All of the technologies included in the pilot test are well established and can be implemented commercially. With the proper application of the selective ion resin, it is possible to achieve mercury concentrations below 5 ppt in FGD Wastewater. With proper design work (including treatability testing), this technology is ready for commercial application.

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