# Meeting Part-per-Trillion Mercury Limits for Power Plant Wastewater

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ABSTRACT

This paper reviews options available to power plants to comply with low part per trillion mercury limits on wastewater discharge.  Such limits are being driven by both water quality-based effluent limits (especially in the Great Lakes region), as well as technology-based limits (proposed Effluent Limitation Guidelines for the industry). These limits pose a challenge to most commercially available treatment technologies. This paper documents results of full-scale testing of treatment technologies to remove mercury to low part per trillion levels from flue gas desulfurization (FGD) wastewater. This paper also describes lessons learned from case studies of plants that have reported improved mercury removal over time through treatment plant optimization. This includes a discussion of the mercury-removal levels achieved, factors that affect mercury removal, and design and operations issues and lessons learned in optimizing treatment for mercury removal. Technologies evaluated include physical/chemical treatment including organosulfide addition and anaerobic biological treatment. The effect of mercury particle size on removal is evaluated. This provides insights on whether removal performance is due to mercury solubility or the ability to remove particulate mercury (either mercury in particulate matter that is formed in the FGD absorber or precipitated in treatment).

# INTRODUCTION

Regulatory agencies are increasingly tightening mercury limits in wastewater discharges for power plants. The Great Lakes Initiative has limited mercury discharged into the Great Lakes to 1.3 nanograms per liter (ng/L). Recently, the United States Environmental Protection Agency has proposed to amend the effluent limitations guidelines (ELGs) and standards for the Steam Electric Power Generating category (Environmental Protection Agency, 2013). The proposed rule would establish new or additional requirements for the following wastewater streams at steam electric power plants: flue gas desulfurization (FGD), fly ash, bottom ash, flue gas mercury control, leachate, and gasification of fuels.  Mercury limits for FGD wastewater are set in the proposed ELG as 119 ng/L monthly average limit and 242 ng/L daily maximum.

# SOURCES OF MERCURY WITHIN A POWER PLANT

The primary source of mercury at power plants is from coal burned, with a smaller contribution from the limestone slurry used in the FGD (EPRI, 2008) and the plant's source water. At plants with flue gas desulfurization (FGD) scrubbers, mercury partitions primarily to the FGD with smaller fractions to fly ash and stack emissions (EPRI, 2009). The mercury captured in the FGD systems is discharged from the FGD in byproduct streams (FGD solids and FGD wastewater or blowdown). The wastewater stream includes both mercury in fine particles and mercury in dissolved form.
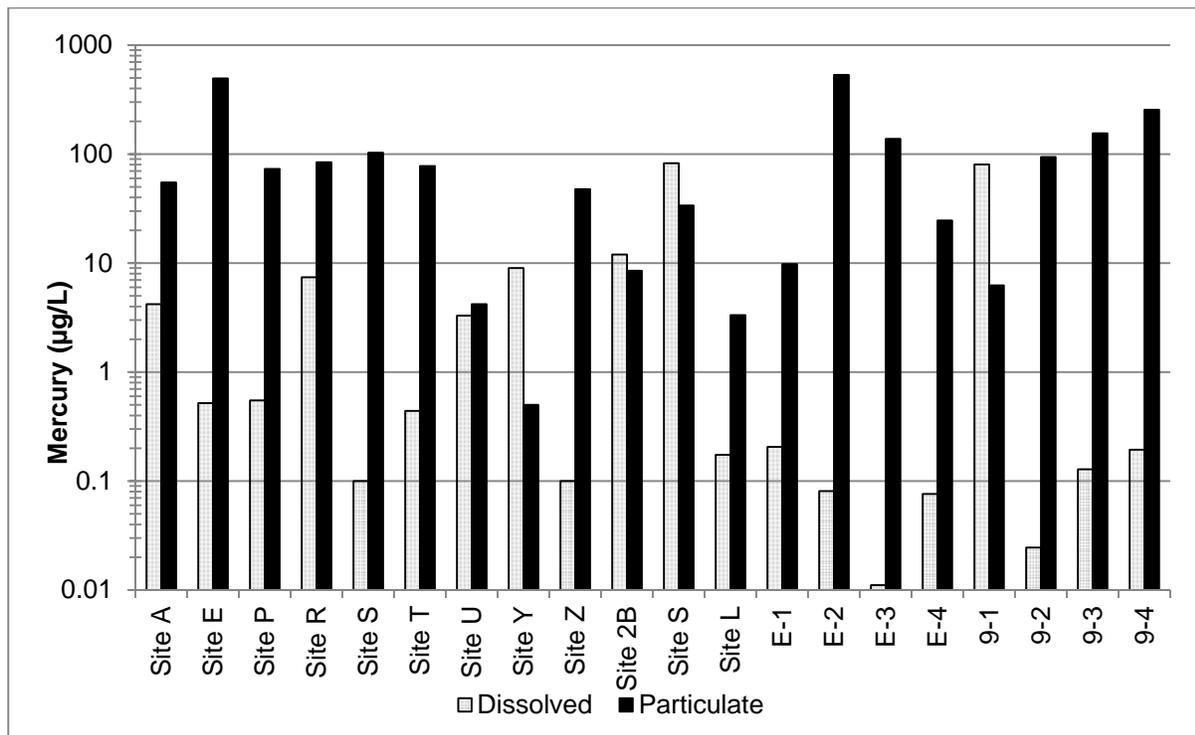


Figure 1. Untreated FGD Wastewater: Dissolved versus Particulate Mercury (EPRI, 2010)

## MERCURY IN FGD WATERS IS DISSOLVED AND PARTICULATE

The removal of mercury in FGD wastewater treatment plants is strongly affected by the amount of mercury present as dissolved mercury versus mercury present in particulate matter. The concentration of mercury in untreated FGD wastewater varies widely, as is seen in Figure 1 (EPRI, 2009 and EPRI, 2010). The majority of mercury in untreated FGD wastewater is typically present as particles passing through 0.45 micron filters.

The dissolved fraction is somewhat arbitrarily defined based on typical use of a 0.45-micron pore size filter. Thus what is typically referred to as soluble consists of those species that are present as single ions or molecules that are truly dissolved, as well as colloidal

particles that are smaller than 0.45 microns.

As can be seen from data in Figure 1, both particulate and dissolved mercury concentrations in untreated FGD wastewater are typically above the ELG limits of 100 to 200 ng/L. Therefore, to reach low ng/L levels, generally particulate and dissolved mercury must be significantly removed by treatment.

## OVERVIEW OF FGD WASTEWATER TREATMENT

Figure 2 shows a typical FGD wastewater physical/chemical treatment system. Typically, a FGD wastewater treatment plant designed to remove suspended solids that employs chemical precipitation includes the following unit processes: equalization, desaturation, chemical precipitation and clarification. Plants that require additional metals
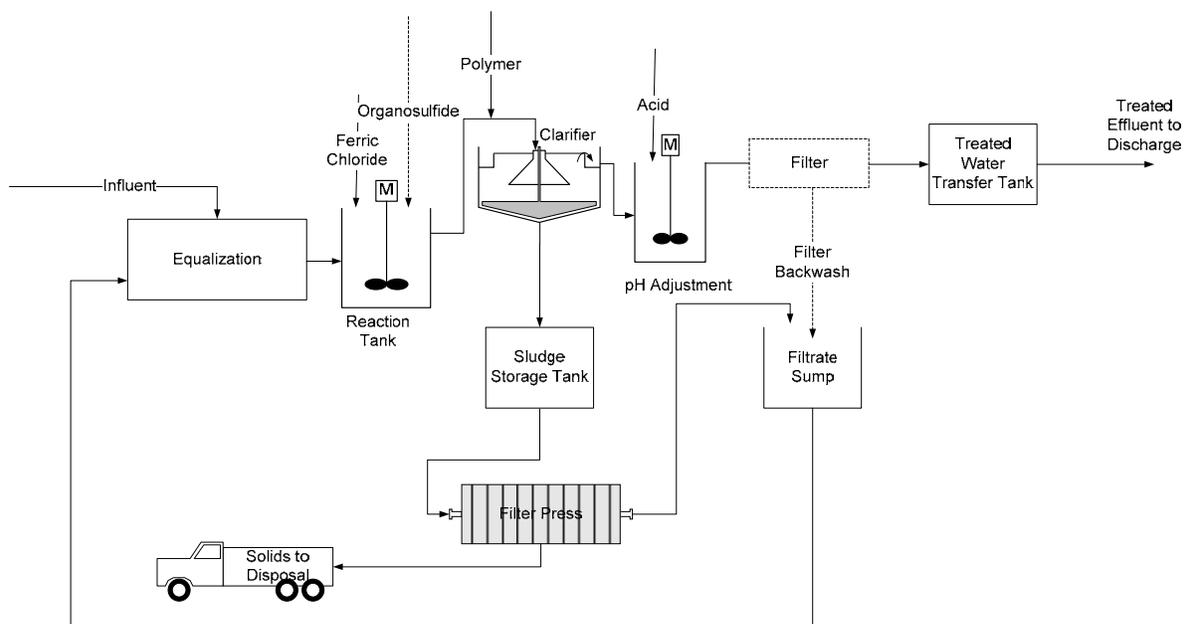


Figure 2. Typical Chemical Precipitation FGD Wastewater Treatment System

polishing may also include filtration to remove solids that pass through the clarifier. Chemical precipitation may include addition of iron, polymers, acids or bases and sulfide compounds to improve precipitation.

IRON CO-PRECIPITATION - In the iron co-precipitation process, a ferric salt such as ferric chloride is added. The iron precipitates as iron hydroxide. (Figure 3). Other metals precipitate as hydroxides and are included in the ferric hydroxide precipitate.  When iron is added in excess of the other metals, the ferric hydroxide covers over the other metals, preventing them from dissolving,
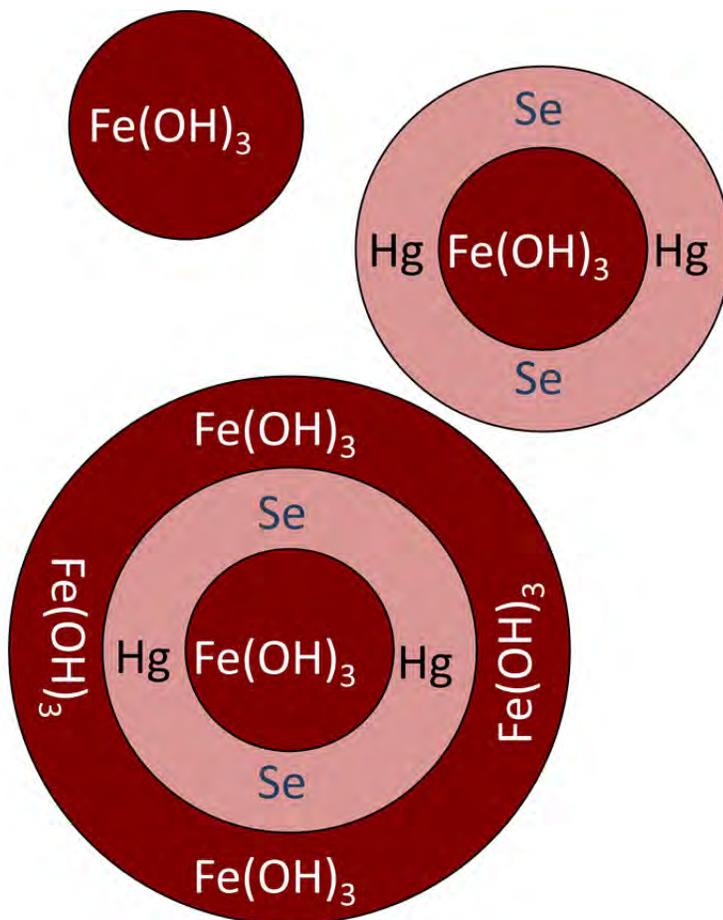
allowing these other metals to continue to precipitate to concentrations lower than they would if precipitating by themselves.

## MERCURY TREATMENT MECHANISMS

Iron co-precipitation alone is generally not effective at removing mercury to low ng/L levels. Mercury removal from FGD wastewater to low levels generally requires addition of sulfide chemistry.

SULFIDE CHEMISTRY - Both particulate and dissolved mercury require removal from FGD wastewater to achieve low ng/L levels. Dissolved mercury can be precipitated into a solid by addition of sulfides. The most insoluble metal sulfide is mercury sulfide, one mineral form of which is cinnabar. The theoretical solubility of mercury sulfide is so low that it would take over 300 liters of water to dissolve one molecule. However, direct use is not practical because it precipitates so fast that it forms a colloid that is difficult to remove from water. Therefore much work has been done to develop organic molecules with sulfide or thiofunctional groups that can form larger particles that are easier to remove. Sulfide chemistry has evolved over the years from straight sulfides, to simple organosulfides, to the larger molecular weight polymers with



Figure 3. Iron Co-precipitation.

sulfide functional groups (Figures 4 and 5), and to solids with sulfide-impregnated granular activated carbon and silicates with sulfides, as well as others.
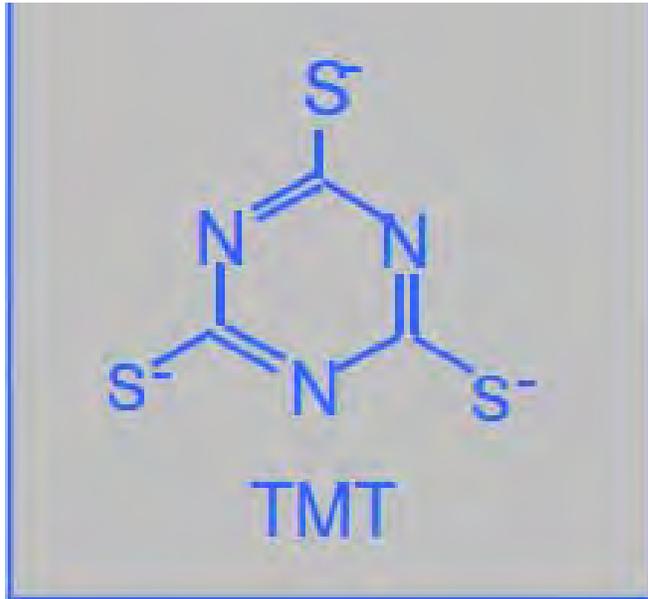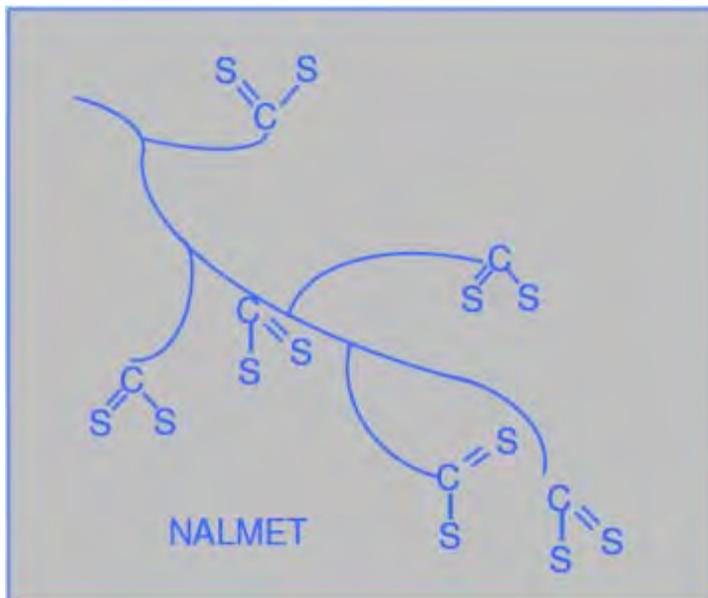


Figure 4. TMT-15



Figure 5. Nalmet-1689

ORGANOSULFIDE ADDITION FOR DISSOLVED MERCURY REMOVAL-

Organosulfide addition is typically used to enhance mercury removal in power plant wastewater. Organosulfide compounds are polymers that bond with cationic metals and are used to counter the solubility of mercury and other cationic metal chloride complexes, and form precipitates of mercury that can be removed.

Polymer addition may be needed after organosulfide precipitation to enhance flocculation. Various organosulfides are available from numerous vendors (e.g. Nalco's Nalmet-1689 and Evonik's TMT-15). Organosulfides are used at numerous power plants for mercury removal from FGD wastewater. Organosulfides are typically only effective at removal of divalent and some monovalent cationic metals.

Table 1 shows results of jar testing for the addition of coagulant (ferric chloride) and organosulfide to remove mercury from a FGD scrubber at a power plant in the midwest. The results of this jar testing shows removal of mercury, to single digit ng/L levels for one sample.

Table 1. Organosulfide Treatability Test Results

| Jar Test ID | Coagulant (ppm) | Organo-sulfide (ppm) | pH | Mercury (ng/L) |
|---|---|---|---|---|
| Jar Test #1 | | | | |
| Starting Point* | 0 | 0 | 6.5 | 39700 |
| Treated Sample 1a | 50 | 0 | 6.5 | 38400 |
| Treated Sample 1b | 50 | 10 | 6.5 | 180 |
| Treated Sample 1c | 50 | 20 | 6.5 | 20 |
| Treated Sample 1d | 50 | 40 | 6.5 | 5.6 |
| Jar Test #2 | | | | |
| Starting Point* | 0 | 0 | 8.5 | 20100 |
| Treated Sample 2a | 50 | 0 | 8.5 | 27100 |
| Treated Sample 2b | 50 | 10 | 8.5 | 490 |
| Treated Sample 2c | 50 | 20 | 8.5 | 360 |
| Treated Sample 2d | 50 | 40 | 8.5 | 280 |
| *- Treated concentrations due to pH adjustment and filtering | | | | |

Another example of mercury removal using various organosulfides is shown in Table 2 from a FGD scrubber at a power plant in Appalachia . Jar testing was conducted on various organosulfides, including Nalmet-1691, TMT-15, Nalmet-1689, and MetClear MR2403. In general, performances between the organosulfide alternatives (1691, 1689, and MR2403) were fairly similar to one another. All of the organosulfides tested within this study were effective at removal of mercury to low ng/L levels. Mercury solubility in FGD wastewater is related to the cycling up of the FGD absorbers to minimize effluent flows. Figure 6 shows soluble mercury concentrations in four different power plants with increasing hydraulic

Table 2. Organosulfide Treatability Testing

| | Mercury (ng/L) | | | | | |
|---|---|---|---|---|---|---|
| Dose | Raw Water (2/26/13) | Raw Water (2/28/13) | TMT, pH 8.5 (2/27/13) | Nalmet 1689, pH 8.5 (2/28/13) | Nalmet 1691, pH 8.5 (2/28/13) | MetClear MR2403, pH 8.5 (2/28/13) |
| 0 | 32.0 | 18.0 | 35.9 | -- | -- | -- |
| 20 | -- | -- | 21.0 | 1.5 | 0.4 | 1.3 |
| 40 | -- | -- | 5.5 | 0.9 | 1.5 | 0.8 |
| 60 | -- | -- | 5.6 | 0.6 | 1.4 | 0.7 |
| 80 | -- | -- | 4.6 | 0.3 | 1.3 | 0.5 |
| 100 | -- | -- | 0.4 | 0.3 | 1.1 | 0.4 |

retention times, as measured by ratio of chloride in blowdown to chloride in the coal. This indicates that longer
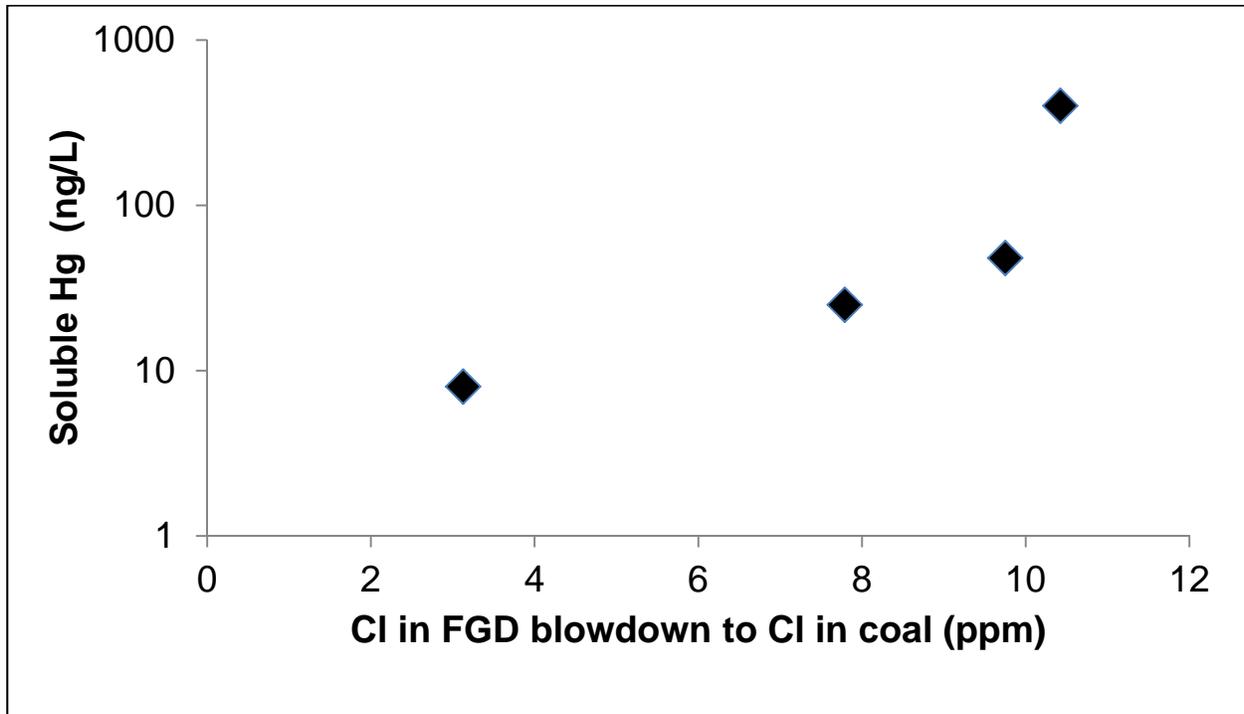
Figure 6.  Effect of Absorber Residence Time of Soluble Mercury in Blowdown

hydraulic residence times increase the solubility of mercury. In addition, these waters were treated with organosulfides, coagulated with ferric salt and filtered in a standardized jar test procedure. Figure 7 illustrates that increased hydraulic detention time in the absorbers significantly affected the ability to remove the mercury, more than taking away any advantage of reduced flow in reducing mass discharge of mercury to the environment. One of our clients reduced the hydraulic detention time in their absorbers by about half and reduced their typical mercury concentrations by about 90%. This is not solely due to reduced hydraulic retention time, as other optimization changes were made at the same time, but a significant part of the improvement was attributable to reducing the hydraulic detention time.
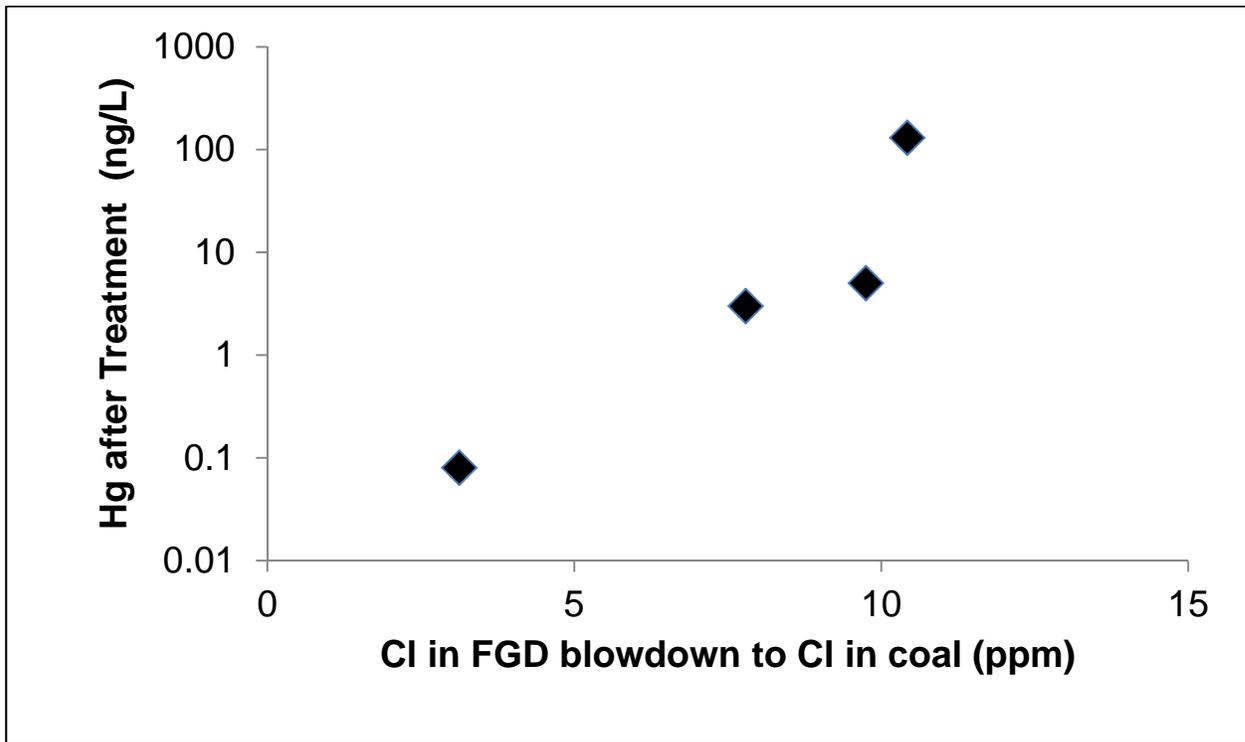
Figure 7.  Effect of Absorber Hydraulic Retention Time on Mercury post-Treatment

PARTICULATE MERCURY REMOVAL- In FGD wastewater treatment systems that use physical and chemical processes, particulate mercury is removed by settling, in either a clarifier or pond. Particulate mercury removal is improved by addition of a coagulant such as ferric chloride or a polymer to combine small particles into larger ones that can be removed in a clarifier or pond.

Media filtration can be used to further remove mercury particulate. However, small particles of mercury can pass through sand filtration mercury. Figure 8 shows mercury removal within a treated FGD wastewater treatment sample.

Typical media filters remove particulates greater than 5 microns. Most of the mercury particles within this treated sample are less than 5 microns. The total mercury is similar between the secondary effluent sample and the sample taken after filtration, showing little further removal of mercury using a media filter.

The colloidal mercury was attributable to the high shear mixers used in mixing of the organosulfide and coagulants with the wastewater, resulting in small particulate mercury that was not removed by either the clarifier or sand filter.
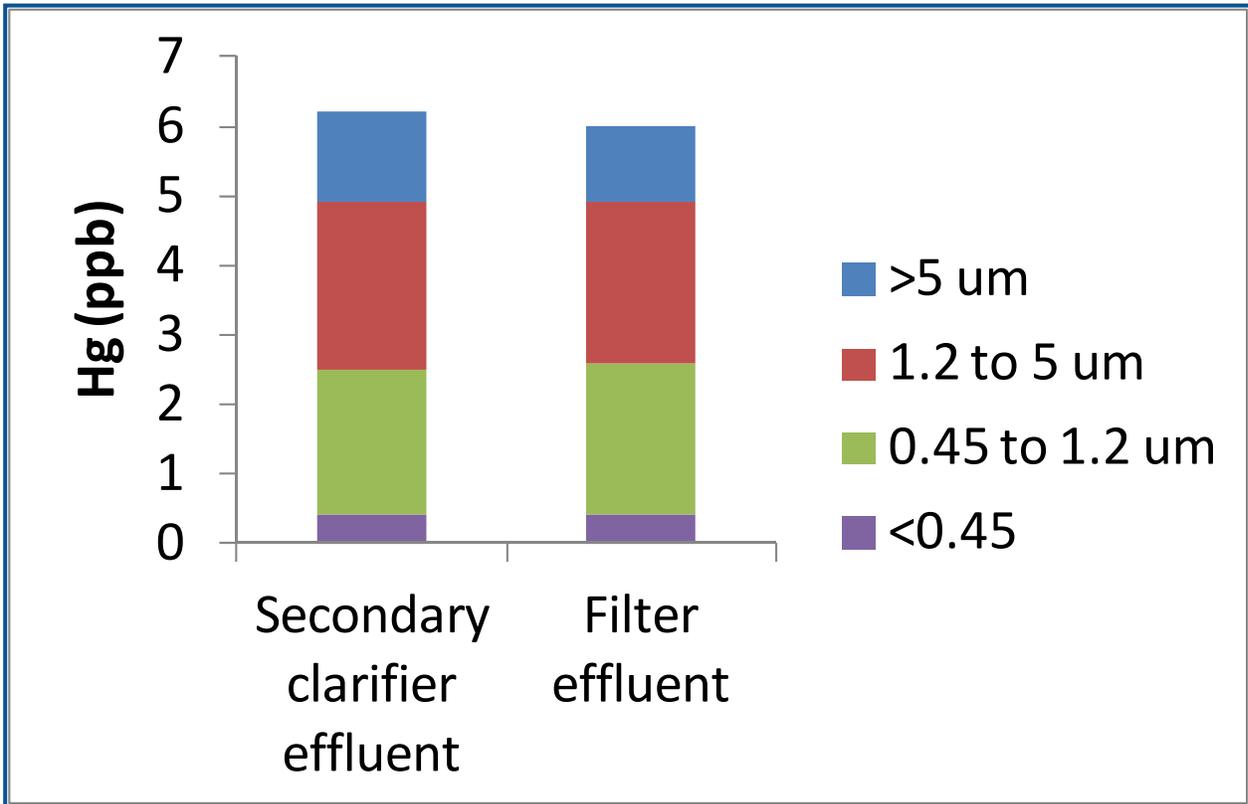
Figure 8. Mercury particle size distribution within a treated FGD wastewater sample

The plant tested use of cartridge filters to improve capture of the particulate mercury passing through the sand filter. They tested different pore size filters in a laboratory using a vacuum filter apparatus. After selecting cartridge filters based on the lab testing, they found the pore size selected was ineffective. Cartridge filters with smaller pore size were effective. The full size system used pumps with high shear to push the water through the filters, resulting in finer particles being produced compared to the particles treated using the laboratory vacuum filters. The vacuum did not impart shear, while the pumping did, causing the mercury particle size to change, requiring cartridge filters of much lower pore size than predicted in lab tests. Effective mercury removal depends on use of low shear mixing and pumping.

Table 3 shows mercury particle size for FGD wastewater treated using iron coagulation, high shear mixing, and settling. Adding organosulfide to the treatment system by itself was not effective, as a significant portion of the mercury was present as colloidal particles which were already precipitated. Jar testing with organosulfide and iron coagulant along with use of low shear mixing resulted in producing a filtered effluent as low as 1 ng/L.

Table 3. Results of particle size distribution of treated FGD wastewater sample

| Description | Mercury (ng/L) |
|---|---|
| PWTS Clarifier Effluent | 4,200 |
| 0.45 micron filtrate | 1,300 |
| 0.10 micron filtrate | 860 |
| 30,000 MW[1] filtrate | 410 |
| 10,000 MW filtrate | 300 |

1. MW = Molecular Weight

Particle size and settling characteristics can also be enhanced by recirculating sludge from the clarifier to the ferric mix tank, but only if a low-shear pump and flocculator mixers are employed. Otherwise, any recirculated solids will only be sheared to a small size, thereby negating the benefits of recirculation. CH2M HILL has employed this type of "iron pearl" approach to treat to low levels of trace metals at several systems.

BIOLOGICAL TREATMENT-
Bioreactors have been used to date on FGD water for removal of selenium. Because the bacterial reduction of selenium utilizes sulfate reducing bacteria, these reactor produce sulfides resulting in the precipitation of mercury and other cationic metals as sulfides.

Additionally, mercury can be removed through settling (of particulate mercury) or uptake into bacteria cells. As the substrate used for these biological processes is course (granular activated carbon), the beds are not effective at removal of colloidal particles. As a result, they are only effective at removing soluble mercury and larger mercury solids, and are not effective at removal of colloidal mercury precipitates.

Figure 9 shows the relative performance of two systems that use iron co-precipitation and anaerobic biological treatment to remove mercury. Both sites show improved mercury removal with the anaerobic biological reactors of roughly an order of magnitude (from median values of around 80 ng/L to median of around 5 ng/L).
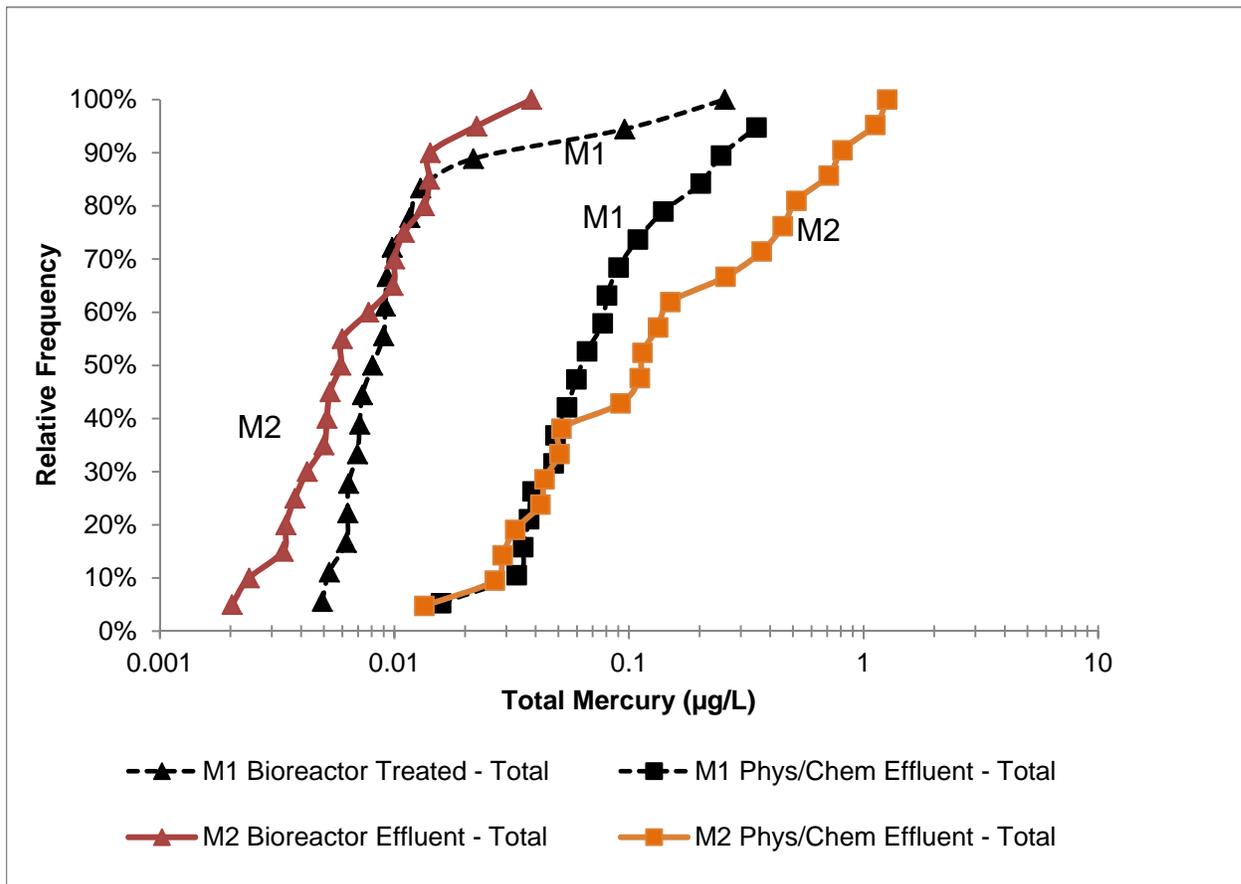
Figure 9. FGD Wastewater Total Mercury Removal by Bioreactors (EPRI, 2010)

## LESSONS LEARNED IN MERCURY REMOVAL OPTIMIZATION: CASE STUDIES

The following are case studies of mercury treatment for three FGD wastewater treatment plants. The following three case studies detail lessons learned from facilities working to improve mercury removal within their FGD wastewater treatment systems.

CASE STUDY 1 -Site 1 has performed optimization testing with ferric chloride

and three types of organosulfides. The following additional changes also appear to have improved treatment of mercury: keeping the FGD absorber aerated during shut-downs; reducing retention time of FGD absorber liquor in the scrubber by lowering the target chloride concentration of the liquor; and recycling secondary clarifier sludge in order to build precipitate solids that can be better removed by clarification. The fact that the plant is over-sized for actual flow allows for improved solids removal during clarification.  The plant also uses onsite analysis of mercury by collecting

grab samples of treated FGD wastewater, which allows the plant to go into a recirculation mode rather than discharging when mercury levels are elevated.

Site 1 has previously experienced periodic incidents of poor mercury removal. This seemed to be associated with periods of treatment following shutdown of the FGD absorber, and was associated with a yellow color in the FGD wastewater after solids removal. When the water was filtered through a 0.45-micron filter the filtrate was still yellow. During shutdown, the aeration in the absorber was turned off, and the absorber slurry may have become anaerobic. Also, the utility had problems removing mercury using the organosulfide when operating at high chloride concentrations (long liquid residence times) in the absorber. They switched organosulfides to an alternate having a larger molecular weight, reduced the chloride level (reduced residence time) in the absorber, and have reduced the levels of mercury in the effluent. Testing was also done using a granular activated carbon supplemented with sulfides to improve mercury removal. This did not result in removal of additional mercury, showing that if a wastewater mercury is resistant to organosulfide precipitation, it is likely to be resistant to absorption technologies that are based on sulfide chemistries.

CASE STUDY 2 - Site 2 employs physical/chemical FGD wastewater treatment. Iron is added as a coagulant.

The treatment plant was not designed for mercury removal. However, by April 2010, two process changes were made to improve mercury removal. First, a cationic polymer feed was added to the primary clarifier. Also, an organosulfide polymer (Nalmet® 1689) feed was added just upstream of the secondary clarifier. These changes were made to help ensure compliance with mercury effluent limitations applicable to the main plant discharge (EPRI, 2010).

To further reduce the levels of particulate and dissolved mercury of the main plant discharge, the same organosulfide chemicals are added to the inlet of the plant's bottom ash pond, which receives treated FGD wastewater as well as other process waste streams. It is important to note that this in-pond "polishing step" has proven to be needed to successfully comply with the mercury effluent limitations that became effective in May 2010 (12 ng/L [average] and 18 ng/L [maximum]).

Site 2 personnel evaluating these new treatment methods find that the addition of organosulfides for FGD wastewater treatment is not sufficient to meet the final discharge limits, but is viewed as a means to decrease the cost of the in-pond treatment chemicals. Based on success at this site, a combined strategy of organosulfide polymer feed in the FGD wastewater treatment plant, coupled with subsequent in-pond mercury removal using cationic and organosulfide polymers, is being used at other power plant sites fitted with wet

FGD systems owned by the same company that owns Site 2 (EPRI, 2010).

CASE STUDY 3- Treatment of mercury across the FGD wastewater system is shown in Figure 10. Mercury is removed to between 50 and 600 ng/L. The treated FGD wastewater flows to an ash pond. Mercury concentrations in the pond effluent are typically below 10 ng/L.

In 2007 and 2008, the site conducted bench-scale and full-scale testing of various organosulfides to optimize mercury removal. Although Site 3 has previously employed the use of ferric

chloride, they have recently switched to only using NALMET® 1689 as they can reduce chemical costs by eliminating the need for ferric chloride. Site 3 continues to test alternative dosages to fine-tune the dosage needed to optimize mercury removal. Optimization efforts have focused on mercury.

Figure 11 shows a comparison of mercury removal across the three case study sites. The treated FGD wastewater results shown on this figure show that even for plants who have experimented to optimize their FGD wastewater treatment systems, it is difficult to meet low ng/L levels on a continual basis including the proposed
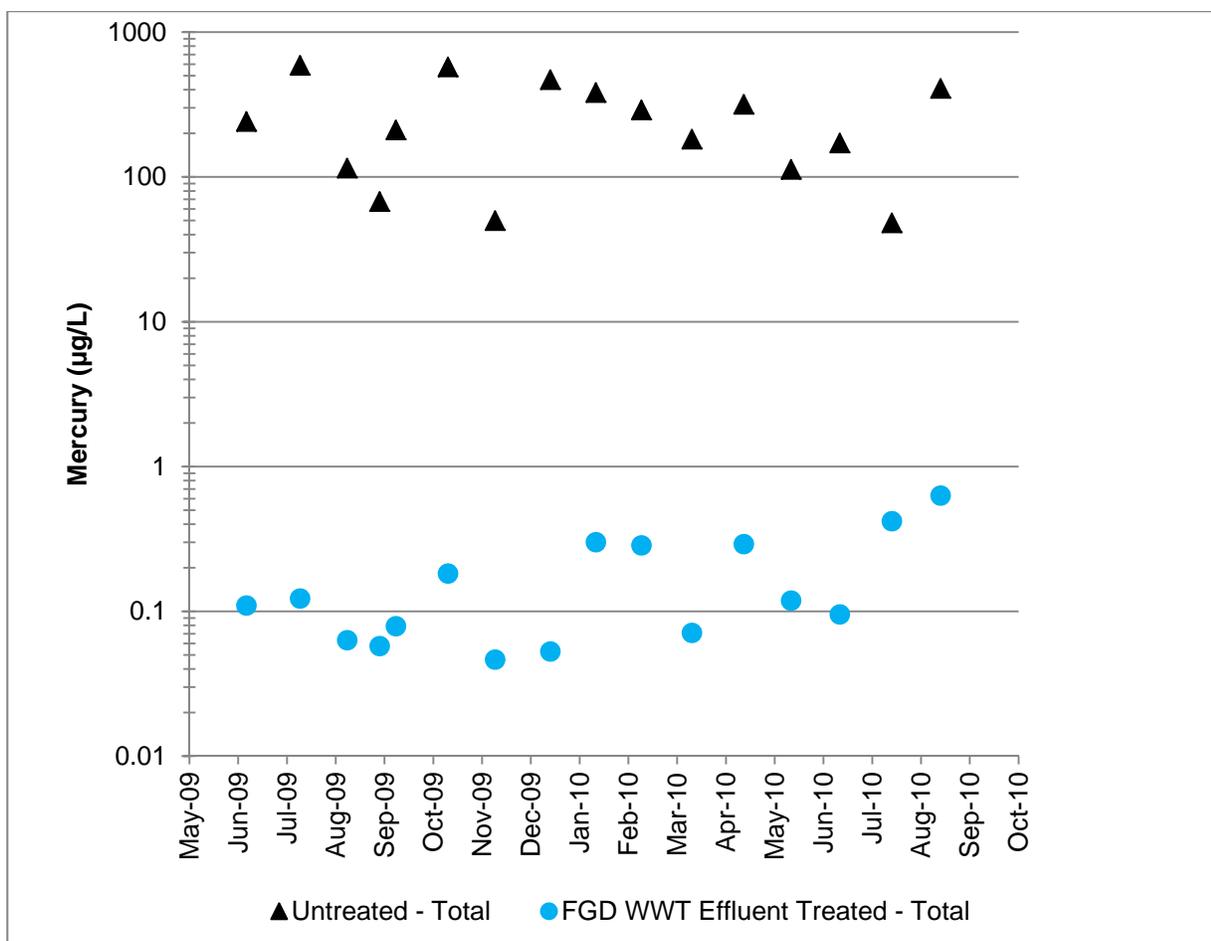


Figure 10. Site 3 Mercury Across FGD Wastewater Treatment (EPRI, 2010)

monthly limit for mercury within the ELG
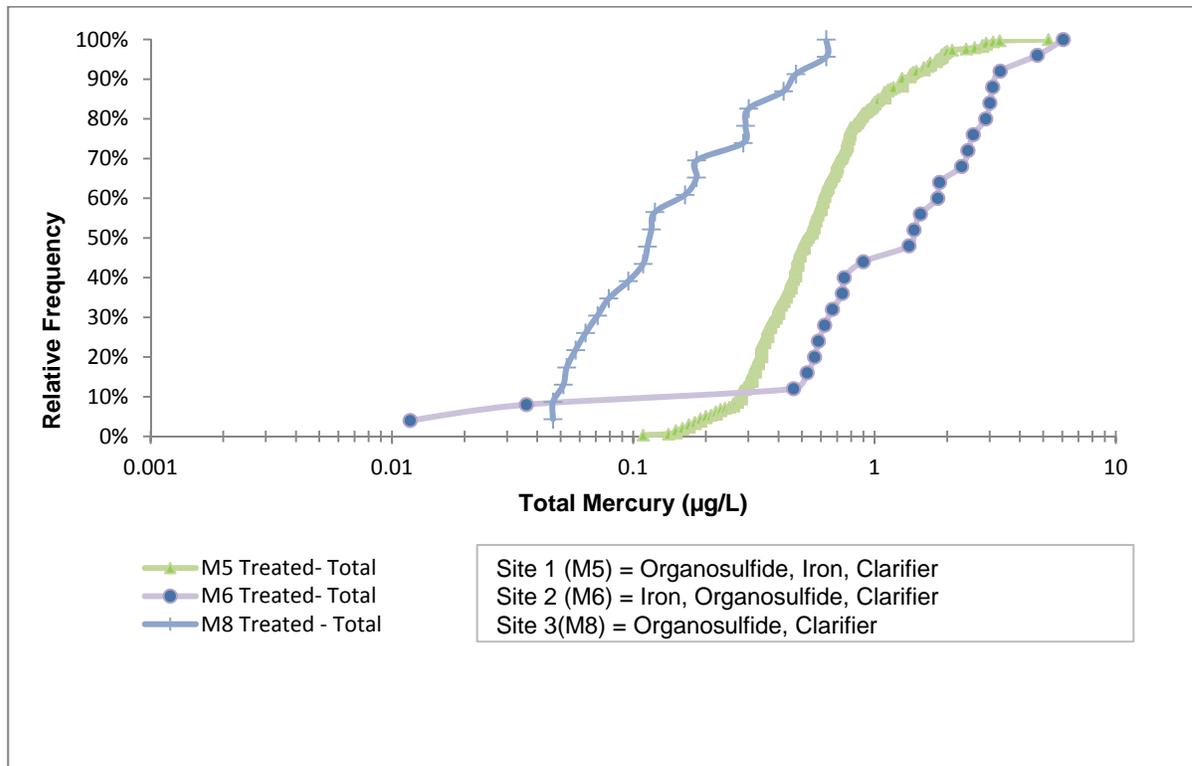of 119 mg/L.



Figure 11. FGD Wastewater Total Mercury Removal by Physical/Chemical Treatment
(EPRI, 2010)

## CONCLUSIONS

1. Treatment of mercury to low
   levels depends on sulfide
   chemistry.
2. Sulfide precipitation can result in
   formation of colloidal particles.
3. Colloidal mercury precipitates
   cannot be removed by
   precipitation or absorption
   processes.
4. Use of low shear mixing and
   pumping is required to preventing
   formation of colloidal precipitates
   and instead produce particles
   that can be removed by settling
   or media filtration.
5. Some FGD wastewaters, such as
   produced in absorbers with long
   hydraulic retention times, have
   mercury compounds that are
   resistant to sulfide chemistry,
   making them difficult to treat.
6. As a result, increasing recycle in
   an FGD system to reduce
   wastewater flow can be counter-
   productive and increase mass
   discharge of mercury from a
   treatment plant.

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