



# Fate of Oxidized Mercury in Biologically Regenerated NO<sub>x</sub> Scrubber Liquor



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## Abstract

A process is under consideration that achieves treatment and regeneration of spent scrubber water from a NO<sub>x</sub> wet scrubbing process using a mixed-culture bioreactor. Preliminary prototype bioreactor operation suggests that, in addition to other desired reactions, a small concentration of dissolved sulfide (less than 5 mg/l) can be generated and maintained in the reactive process water. Presence of dissolved sulfide will allow precipitation of oxidized mercury that has passed from the flue gas into the scrubber solution. In addition, iron mono-sulfide precipitate in the reactive process stream will contribute to dissolved mercury removal as a result of rapid displacement of ferrous iron to form the more stable mercury sulfide. Metal sulfide would then be separated from bulk solution in a relatively small and concentrated stream using available solid/liquid separation technology. Concerns remain with regard to potential for methylation of mercury in the anoxic/anaerobic bioreactor. It is hypothesized that this can be avoided by prompt removal and pasteurization of metal sulfide precipitate. Further investigation of this phenomenon will be required.

## Background

Mercury that is released into the atmosphere as a result of combustion is deposited onto the land and into water bodies. There, it can be converted to methyl mercury under anaerobic conditions by sulfate reducing bacteria. Methyl mercury is readily absorbed into living organisms, and is biomagnified through the food chain, especially in aquatic systems. By this mechanism, methyl mercury can reach concentrations that are toxic to humans and other vertebrates.

In humans, low exposure to methyl mercury (greater than 0.1 µg/kg of body weight/day) is believed to cause neurological damage. Higher doses (0.1-0.5 µg/kg of body weight/day) have been shown to result in tremors, loss of motor function, and death in lab animals. Tragic events like the fish contamination and poisoning deaths of 439 at Minamata Bay, Japan and the death of Dr. Karen E. Wetterhahn, Professor of Chemistry at Dartmouth University, bring to our attention the extreme toxicity of methylated mercury.

The United States Environmental Protection Agency (US EPA) recently proposed regulation designed to curtail emission of mercury from coal fired utility boiler flue gas, the largest source of airborne anthropogenic mercury in the United States. Because it has a relatively low boiling point (357 °C), mercury present in coal is vaporized during combustion. Elemental mercury vapor in the flue gas is not soluble in aqueous streams and does not readily precipitate onto flyash particles. As a result, conventional APCDs do not remove elemental mercury from flue gas.

Most control technologies under development for mercury fall into two general categories: sorbent technologies and mercury oxidizing technologies. Sorbents are typically either injected into the flue gas as a powder, or configured as a granular, packed, fixed-bed reactor. Sorbents that are currently being considered include activated carbon, sulfur impregnated activated carbon, sulfur impregnated activated alumina, cristobalite, and diatomaceous earth, among others. In many cases, mass transfer limitations prevent sufficient removal of elemental mercury through adsorption.

Oxidation of elemental mercury in flue gas is also under consideration. Several mechanisms for mercury oxidation are being studied, including: chlorine addition, corona discharge, and exposure to ultraviolet light. In addition, some work has been done on catalysis of oxidation reactions via titanium oxide, iron oxide, or copper oxide catalysts.

However, oxidized mercury typically adsorbs onto fly ash or dissolves in wet scrubber solution and can be removed using conventional APCDs. As a result, mercury oxidation will result in increased concentration of mercury in fly ash, spent wet scrubber solutions, and gypsum product. As the effort to curtail gaseous release of mercury from coal-fired utility boilers intensifies the importance of mercury content in solid and liquid streams also increases.

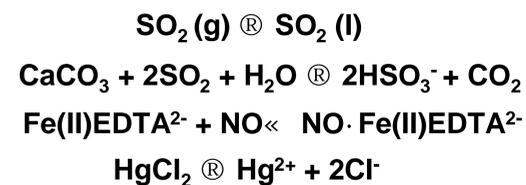
## Objective

The objective of ongoing research is to evaluate a NO<sub>x</sub> scrubbing process with biologically catalyzed treatment and regeneration of spent scrubber solution. There is particular interest in fate of mercury in such biologically active systems and opportunities to selectively remove mercury from liquid and solid process streams.

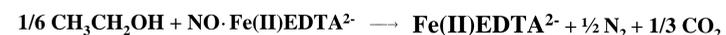
## Process Description

The process being evaluated involves the scrubbing of nitric oxide from the gas phase, biological treatment of spent scrubber solution and subsequent recycle of treated solution. The scrubbing of nitric oxide from the gas phase is based on the reaction of dissolved nitric oxide with ferrous ethylenediaminetetraacetic acid (Fe(II)EDTA<sup>2-</sup>) to form the reversible adduct NO•Fe(II)EDTA<sup>2-</sup>. The resulting spent scrubber solution is then treated biologically to remove the nitrosyl adduct (bound nitric oxide) from the ferrous EDTA and to reduce the oxidized ferric EDTA (Fe(III)EDTA<sup>2-</sup>) to the ferrous form that is active for NO<sub>x</sub> scrubbing. In addition, the process water can be amended with limestone to make the scrubber function as a combined SO<sub>x</sub>/NO<sub>x</sub> scrubbing process. The scrubbing reactions of interest are as follows:

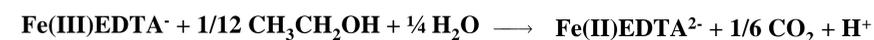
### Simplified Scrubber Reactions



### Microbially Catalyzed Reduction of Nitric Oxide



### Microbially Catalyzed Regeneration of Fe(II)EDTA<sup>2-</sup>



## Prototype Scale Apparatus

A prototype scale scrubber/bioreactor system was operated at the Pittsburgh campus of the United States Department of Energy's National Energy Technology Laboratory. The system consisted of a small packed bed scrubbing tower (effective height of 21", diameter of 8", 1" pall ring packing), a 42.5 liter upflow anaerobic bioreactor, and a 50 liter aerobic upflow reactor that served as a forced air oxidation chamber. In addition, one slanted plate settler was positioned after the anaerobic bioreactor and two arranged in series after the aerobic reactor. These were located for the removal of anaerobic biomass/metal sulfide precipitate, and gypsum, respectively. Ethanol was used as the primary electron donor in the microbially mediated reduction of NO•Fe(II)EDTA<sup>2-</sup> and Fe(III)EDTA<sup>2-</sup>. Figure ## provides a simplified schematic of the prototype process configuration.

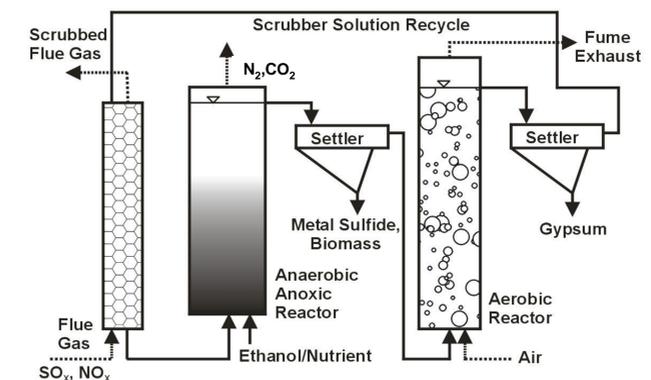


Figure 1. Simplified schematic of prototype apparatus

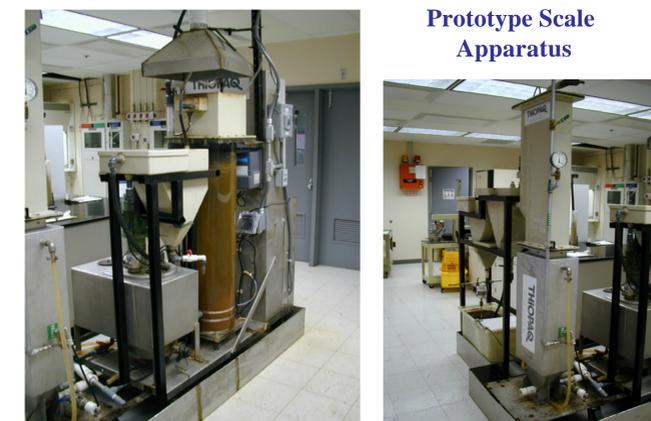
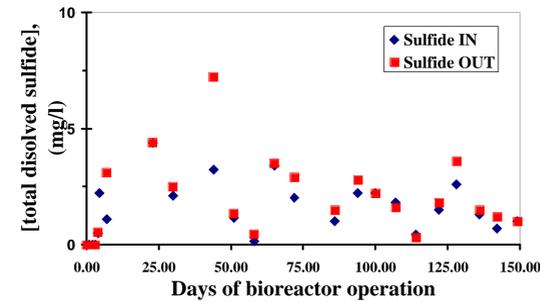


Figure 2. Upflow anaerobic bioreactor with subsequent slanted plate settler (left) and upflow aerobic reactor employed for gypsum production (right)

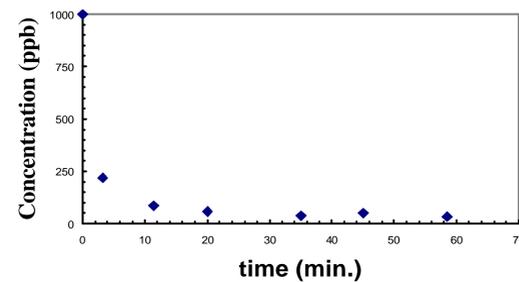
## Possible Selective Precipitation of Hg

Initially, cultivation of a small SRB population in the mixed culture present in the bioreactor was seen as an opportunity to convert free mercury in solution to a highly insoluble metal sulfide precipitate. To that end, the prototype system was operated under the following conditions:

- Operate bioreactor at a lower oxidation reduction potential to promote a small amount of sulfate reduction (approximately -170 mV with hydrogen reference electrode)
- Maintain a low concentration of dissolved sulfide in solution (around three ppm)
- Maintain a low concentration of iron sulfide particulate that allows mercury capture through iron displacement
- Separate relatively concentrated metal sulfide precipitate following anaerobic bioreactor



**Figure 3. Over 150 days of operation, it was demonstrated that the bioreactor could be controlled to maintain a small concentration of dissolved sulfide.**



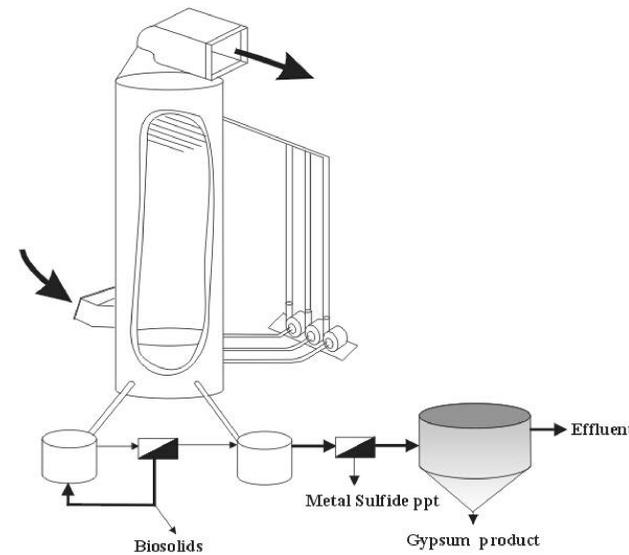
**Figure 4. Dissolved copper was used as a surrogate for mercury to demonstrate that more reactive metals will rapidly replace iron present in iron sulfide, in addition to sulfide formation through reaction with free dissolved sulfide.**

## Potential for Methylation

In this configuration, it would be unadvisable to promote sulfate reducing conditions, since it will not be possible to sufficiently separate mercury sulfide precipitate from the sulfate reducing bacteria that are responsible both for sulfide production and methylation of mercury. As a result of this realization, preliminary consideration has been given to an alternative configuration that would allow formation of mercury sulfide while preventing contact between sulfide precipitate and SRB responsible for methylation. Figure 5 illustrates a configuration in which a small bioreactor is employed to produce biologically generated sulfide.

Characteristics of the alternative configuration include:

- Generation of a relatively concentrated stream of sulfide as a result of microbially catalyzed sulfate reduction in a high-rate bioreactor
- Separation of sulfide from SRB by membrane filtration
- Introduction of abiotic sulfide stream to spent scrubber solution before forced air oxidation
- Separation of concentrated metal sulfide precipitate by membrane filtration
- Sterilization of metal sulfide precipitate to prevent methylation
- Production of essentially mercury free gypsum product
- Configuration can be applied to most wet scrubbing processes



**Figure 5. Schematic of modified configuration for selective removal of dissolved mercury from scrubber process water**

## Future Work

Future investigation along these lines should include:

- Study of methylation rates in biologically active wet scrubber systems
- Evaluation of membrane separation technologies for separation of dissolved sulfide from sulfate reducing bacteria
- Evaluation of membrane filtration technologies for separation of fine suspended metal sulfide precipitate from spent scrubber process water

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