Wastewater Treatment for Flue Gas Desulfurization (FGD) at Electric Power Plants

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1. Abstract

A study of coal-fired power plant Flue Gas Desulfurization (FGD) Wastewater Treatment Systems (FGD-WTS) identified options for sustainable and cost-effective compliance with low selenium and other metal NPDES discharge limits. Sulfur is removed in a plant's emissions stack by application of an oxidized lime slurry spray, capturing airborne sulfur and converting the airborne sulfur to calcium sulfate (gypsum), which is then used to manufacture drywall. Flows from the blowdown of a FGD control system reduce corrosion causing TDS and other corrosion causing constituents in the recycled lime solution. The FGD-WTS discharge flow rate is typically small compared to an overall facility effluent discharge that combines with the larger Cooling Water (CW) discharge flow and several other plant flows. The FGD-WTS selenium discharge concentration is higher than the CW discharge, and is significantly higher during process upsets, low river flows, or due to a change in the facility's fuel source. The potential for discharge exceedances increases when the speciation of selenium fluctuates to a ratio as high as 80% to 90% selenate to selenite from changes in the fuel source, as selenate is more difficult to remove by precipitation in an aqueous environment. There is, however, an opportunity for a significant cost advantage in mitigating selenium excursions by focusing on enhanced selenium removal within the FGD-WTS rather than focusing on treating the entire wastewater stream.

In this testing program, sustainable compliance options were identified and verified, incorporating alternative chemical treatments for both selenium and mercury removals, with a focus on more stringent future limits. The alternative treatments included ferrous reducing agents, a sulfide agent, optimized co-precipitation, double precipitation, and sequential combinations of a dozen alternative treatments. Cost savings are predicted by incorporating sludge recycle to minimize chemical addition and also to minimize sludge production. The result of this program recommended both process modifications as well as an additional evaluation to reduce effluent metal concentrations, lower operating costs, and minimizes sludge production.

2. Keywords

FGD
Flue Gas Desulfurization
Mercury
Selenate
Selenite
Selenium
AB Met
ICB
LFSO
PWTS

3. Introduction

Flue gas desulfurization ("FGD") treatment is incorporated in most coal burning power generation plants to remove sulfur dioxide ("SO_2") by either wet scrubbing, dry scrubbing, or dry sorbent injection. The majority of plants in the US use wet scrubbing technology, where acidic gases contact alkaline slurries in absorbers. These slurries are generally lime, sodium hydroxide, or limestone, or a mixture of these. The SO_2 is converted to a calcium sulfite in older systems. Wet scrubbing systems use a limestone forced air oxidation system (or "LSFO"). This process converts calcium sulfite to calcium sulfate. The calcium sulfate solution flows to a clarifier, where the calcium sulfate precipitates. Frequently, a wallboard production facility is co-located at or near the power plant to use the calcium sulfate, or gypsum, as the raw material for producing wallboard. If no wallboard facility is available, the gypsum is land filled. Rejects from the gypsum production are also landfilled. Chlorides and other impurities are removed from the gypsum by washing before wallboard manufacturing. The FGD clarifier effluent is returned to the FGD process where more alkaline compounds are added and SO_2 removal cycle resumes. The coal combustion process added ions such as chloride, fluorides, sulfates, as well as selenium, mercury, iron, and others to the FGD recycle. As the ions increase in the FGD system, a smaller volume of the FGD flow is directed to either lagoons or a FGD blowdown treatment system to reduce these ions to prevent corrosion, scaling, and process inefficiencies.

Selenium is increasingly a constituent of interest, and physical-chemical alternatives were evaluated to reduce selenium concentrations in a FGD blowdown treatment system. Additionally, cyano compounds are of interest, not only in their total loading, but how they may complex with selenium to impact the total removal operation. A number of alternative treatments not specifically targeted by this study are noteworthy, including biological removal. These options are in use for selenium removal in coal-fired power plants or for mining wastes include:

- Settling Ponds
- Physical Chemical Precipitation
- Biological Treatment
  AB Met™ System (several operating systems)
  Immobilized Cell Bioreactor (ICB) (Used on mining selenium system) ™
  Passive Biochemical Reactors
- Constructed Wetlands
- Innovative Processes
  - Vapor-Compression Evaporation Systems
  - Zero Liquid Discharge (ZLD)

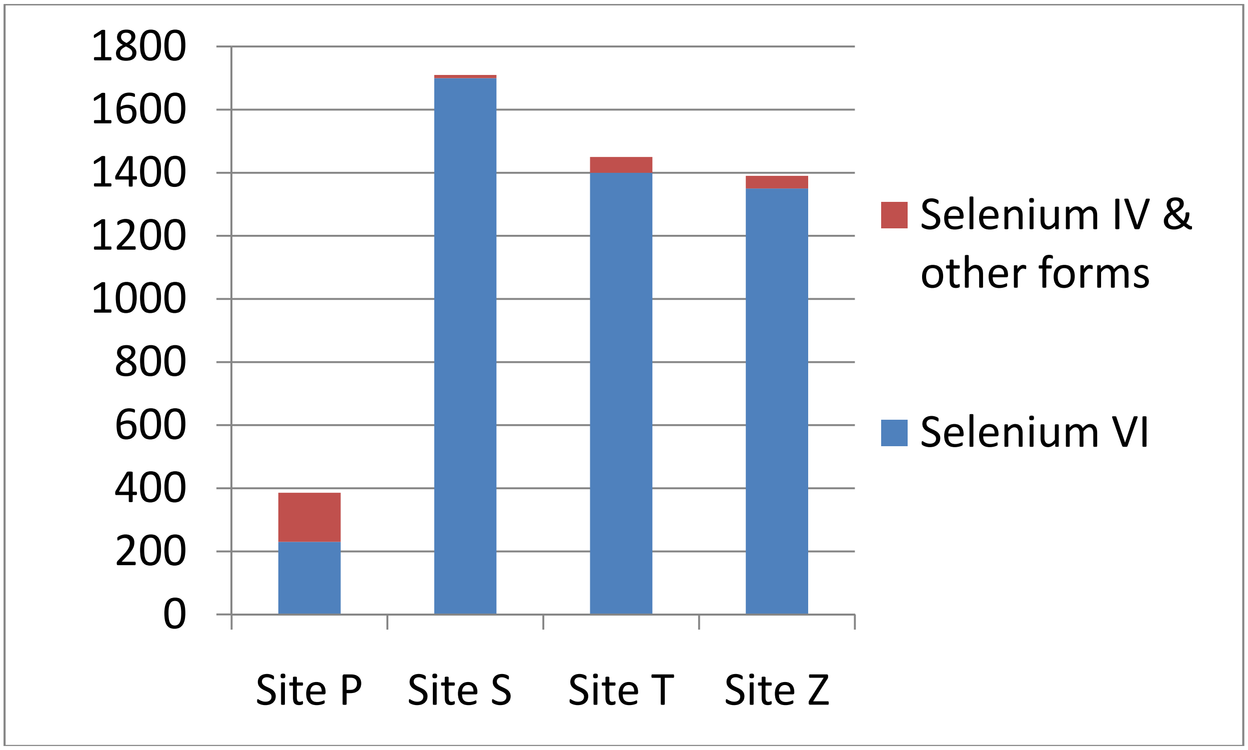
FIGURE 1. AN ICB SYSTEM REMOVING SELENIUM IN THE BLACK HILLS OF SOUTH DAKOTA

Reverse Osmosis and ZLD systems may also be effective treatment options, but at a significant capital premium and parasitic electrical load over biological methods.

This study identified several physical – chemical treatment scenarios with varying cost implications that can reliably decrease effluent constituent concentrations, sludge production volumes, and other implementation issues to meet effluent requirements.

Since the FGD scrubber blowdown is the lowest volume wastewater stream with the highest concentration of contaminants, improvements or modifications can be focused more economically and efficiently in this area verses other larger volume streams such as cooling tower blowdown. Typically, at FGD operations, the bulk of the selenium that enters the scrubber system leaves in the blowdown water. Scrubber cycling, organic dibasic acid (DBA) addition, and trace metal catalyzation all increase the relative ratio of selenate to selenite in the purge stream. Dissolved selenium compounds that are captured in the gypsum are typically washed out when rinsing the gypsum for chloride removal before the gypsum is processed for wallboard manufacture. The chart below shows some selected power plant FGD blowdown total and speciated selenium concentrations in parts per billion. NPDES limits can be as low as 10-20 ppb, identifying a need for reliable technologies to remove selenium prior to a coal-burning power plant's effluent discharge.

FIGURE 2. SELECTED FGD BLOWDOWN SELENIUM CONCENTRATIONS, ppb



a. Process Considerations

pH Considerations

The purpose of bringing the system pH up to an alkaline environment is to form metal hydroxides that readily co-precipitate. Although there are a number of alternative physical chemical treatment scenarios consisting of iron salts (ferrous as well as ferric sulfate), organo-sulfide, lime, and polymer addition, this study initially reviewed a ferrous chloride, lime, and polymer treatment scenario as an initial treatment, based on an operating system under investigation. Once an alkaline environment is generated, the addition of ferrous ions is intended to form iron hydroxide amorphous precipitate particles that aid in the co-precipitation of other metal hydroxides. For the co-precipitation step to effectively work, particle formation and growth is important, along with reaction kinetics. Other metals may be concurrently precipitated as hydroxides. Selenium adsorption on a particle surface may be a removal mechanism and would be heavily dependent on pH due to the influence of pH on the surface charge of an adsorbent. Selenite adsorption is most effective in the pH range of 4 to 6.5 s.u. (Tidwell, L.G., J. McCloskey, P. Miranda and M. Gale. 2000). By adding the ferrous early and allowing the system to go acidic, existing crystals and other suspended nucleating seeds may be dissolved. A chemical treatment system of this type would normally be operated in a continuous fashion with multiple tanks. Lime, reducing agent, and/or sulfide would be added into a first tank or in sequential tanks, along with some sludge recycle to begin metal hydroxide formation and crystal growth. The lime and sludge would enter through a flash mixer or a reaction well for intimate contact and mixing. The tank size and design flow would determine minimum residence time. A second tank, gravity fed out of the first, would typically be where a co-precipitant would be added. Again, this tank should be sized to provide the reaction time required for treatment. Finally the flow would proceed, continuously, via gravity, to a flocculation stage for solids agglomeration, and then to a clarifier for settling and solids separation. A filtration system would remove remaining particulates. Some systems follow this physical chemical treatment with a biological treatment scenario using systems such as the AB Met technology for further selenium removal in an anaerobic environment by conversion of a portion of the remaining selenium concentration to neutral valent selenium and incorporation of the converted selenium into a retained biomass.

ORP

In the investigation conducted in this study, the dosage rate of ferrous chloride, in varying concentrations, to achieve selenate reduction at a target ORP may be achieved by automatic control of both pH as well as ORP. Ferrous chemicals offer the potential to reduce selenate to selenite. Selenite has a lower solubility product than selenate. By allowing the ferrous to drive the reaction tank acidic initially, more of the selenite may shift to selenate, reversing the desired effect. The reaction kinetics of a low ORP on selenium speciation has some merit, but conversion equilibrium is also a function of pH. A low ORP is typically an effective reducing environment which may result in the formation of classical anoxic compounds such as H_2S and HCN, given the presence of sulfates and organic and NOX compounds in the water. After chemical addition, the water has a unique dark blue green appearance, which may be attributed to the high ferrous and calcium ion loadings.

Fuel Variability

Coal source variability has a notable impact on FGD blowdown water selenium concentration. The total selenium, sulfur, and chloride concentrations in the coal impact selenium concentrations in the FGD units. The higher the sulfur content of the coal, the more gypsum is formed in the FGD units and then subsequently purged. Increasing chloride concentrations necessitate less cycling in the scrubber and a greater purge volume is required to reduce the potential for corrosion.

4. Methodology

Several physical-chemical technologies were evaluated in this testing program. Technologies compared selenium removal with ferrous chloride and lime at various pH levels; a double stage treatment, where the process was repeated in a second stage; a process that included organosulfide, ferric chloride, and polymer, as well as several other chemical precipitants in over a dozen variations of concentration, sequences, and reaction times. Additional treatment technologies including evaluating an oxidation step for cyanide removal as well as an additional nitrification process for nitrogen control were evaluated, but are not the subject of this paper. Those process evaluations included the investigation of macro-porous synthetic polymer beads that were reported to remove ammonia, nitrites, and nitrates by removing nitrogenous organic waste from the wastewater; however, no significant removal of ammonia, nitrite, or nitrate was observed.

The FGD blowdown treatment systems using ferrous salts provide a reducing environment, often with an ORP of -600 to -700mV which forces the selenium speciation from the selenate form (valence of +6) to a selenite (valence of +4). Speciation identification and modification is critical, as selenate has a significantly higher solubility than selenite, thus is more difficult to remove. Coagulant aids, such as polymer, help minimize floc carryover in clarifiers.

Bench scale results for the selenium removal technologies were obtained for conductivity, ORP, pH, turbidity, settleable solids (45 minutes), and long term settleable solids, (15 hours) as well as removal efficiencies for metals, speciated cyanide, nitrogen series, and typical ions such as chlorides and sulfates.

The chemical addition scenarios and the concentrations of treatment chemicals consisted of various combinations and sequences of addition of lime, ferrous chloride, organosulfide, ferric chloride, and polymer in one or two stage treatments. The most optimum results showing the minimum concentration obtained in the treated flow are presented below for ferrous chloride, lime, and polymer from a where the blowdown flow was subjected to two stages of chemical precipitation. The tests were conducted on a batch rather than continuous flow basis with sample volumes of 100 – 1,000 ml.

TABLE 1: SUMMARY OF TREATMENT SIMULATIONS

Parameter	Initial Sample	Single Stage Precipitation	Double Stage Precipitation
Selenium ppb	386	15.8	4.28
Mercury ppb	9.75	2.15	1.03
Boron, ppm	316	249	299
Iron, ppm	0.45	283	72.9
NO_3-N, ppm	15.7	10.1	9.3
Cyanide, ppb	53	17	<10
TDS, ppm	35,300	37,700	38,100
NH_3-N, ppm	9.5	8.1	9.6
SS, ml/l	NT	270	250

NT = Not Tested

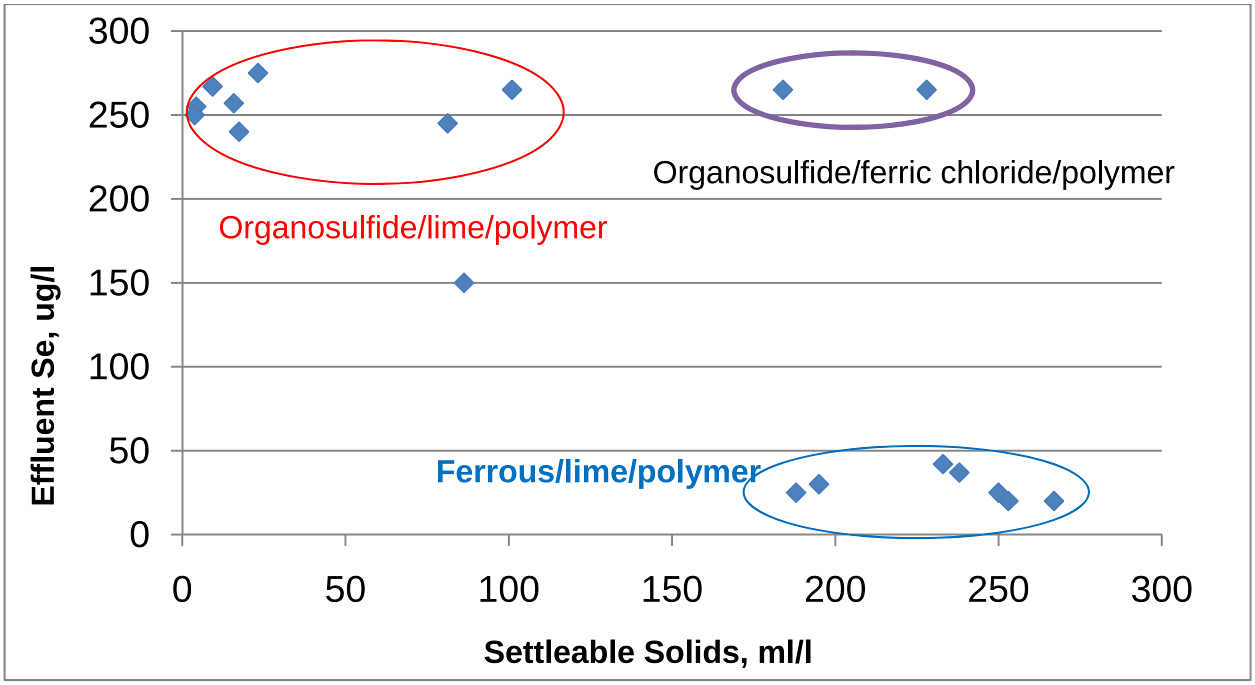
The feed rates for the optimum chemistries are 1,445 ppm ferrous chloride and 40 ppm anionic polymer. Hydrated lime was added to adjust the pH to 8.0 s.u. Chemical feed rates may vary based on coal consistency, FGD cycling rates, blowdown percentage of the entire FGD flow, and other variables. (Se removal looks promising!)

5. Discussion

The findings of this FGD blowdown treatment system study are critical in implementing a plan to confirm compliance with a low ppb discharge selenium limit. The treatment system discharge flow rate is typically small compared to an overall facility discharge that combines with the cooling water discharge flow rate which is much larger. The potential for an effluent discharge exceedance increases when the speciation of selenium fluctuates to a ratio of 80% to 90% selenate to selenite from changes in the fuel source. There is, however, an opportunity for a significant cost advantage in mitigating the potential of a future selenium excursion by focusing on enhancing selenium removal within the blowdown treatment system compared to treating the entire wastewater flow from a generating station.

The graph below shows the general chemical precipitation performance with various blends of process chemistry. The approach generally shows that the best performance for selenium removal occurs with ferrous chloride, lime and polymer at this particular coal usage, FGD cycling rate, blowdown percentage of the entire FGD flow trace contaminants in the treatment chemicals, and other considerations. While this particular chemistry resulted in the lowest selenium concentrations and the densest sludge, it performed poorest for mercury removal. The organosulfide precipitation performed poorer for selenium removal, but was quite effective for mercury removal. The initial concentration of the FGD blowdown was 386 ug/l.

FIGURE 3. RELATIVE PERFORMANCE OF ALTERNATE CHEMCIAL TRIALS COMPARING SELENIUM REDUCTION TO SOLIDS SETTLING



The results of trials, comparison tests, and investigations conducted over the course of this study suggest that physical chemical treatment systems may be able to meet the goal of selenium compliance. The metals acting as catalysts may be a unique feature of the ferrous chloride reduction of selenate to selenite for subsequent removal by precipitation.

The treatment trials suggest that better than 95% removal of total selenium is possible. The double stage treatment suggests that an additional 60% removal of total selenium in the first stage effluent is possible, for a total of 98% removal. The double stage precipitation trials used twice the amount of reagents for both treatment steps. In order to minimize reagent additions, counterflow sludge recycle should be evaluated. Additional testing is recommended to confirm the minimum dosage rate for reagent addition as well as the maximum rate for sludge recycle. The goal of sustainable compliance requires sufficient safety factors, component duplications, and other engineered controls along with the necessary operational and management controls to minimize the potential for effluent exceedances.

Additional trials using organosulfide treatment suggest that better than 97% removal of mercury is possible. The two stage organosulfide treatment suggests that an additional 50% removal of mercury is possible for a total of 98.5% removal. Additionally, the double precipitation process used double the concentration of reagents for both treatment steps. In order to minimize reagent additions, counterflow sludge recycle should be evaluated. Additional testing is recommended to confirm the minimum dosage rate for reagent additions as well as the maximum dosage rate for sludge recycle.

6. Conclusions

The major conclusions of this study were:

- Low effluent concentration Se is possible by chemical treatment chemical treatment, but sludge volume is significant;
- There is a need to understand process chemistry;
- Analytical labs may be challenged when presented with low levels of constituents, speciation, and matrix interference;
- Low level sampling protocols are mandatory;
- All sites must be evaluated individually;
- Paper designs are risky and bench scale and pilot scale testing is critical for success;
- Consistency of treatment chemicals and coal variability impact treatment;
- There are many ways to achieve effluent concentration reduction;
- Detailed cost evaluations are necessary as a component of a design to achieve optimum cost efficiency; and
- Selenium can be removed to <10 µg/l

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