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Environmental compliance issues and treatment options for FGD wastewater

In today's environmentally conscious world, coal-fired power plant owners and operators are encountering challenges never experienced before. Tough air emissions standards coupled with stringent water discharge permits have created the need for a balancing act that demands coordination and synchronization between dealing with pollutants in the plant flue gas stream and dealing with pollutants in the plant wastewater streams.

Wet flue gas desulfurization (FGD) systems are considered by many to be today's technology of choice for reduction of SO2 emissions from coal-fired power plants. These systems typically operate by spraying alkaline reagent slurry such as limestone slurry into the boiler flue gases to remove sulfur compounds. Figure 1 presents a schematic of a typical wet FGD system. In addition to removing sulfur compounds, the slurry will also absorb other contaminants from the flue gas including particulates, chlorides, heavy metals, and organics. Chlorides from the coal form hydrochloric acid in the furnace during combustion; this acid is then readily absorbed by the FGD slurry. The chloride concentration of the FGD slurry must be controlled through a routine wastewater purge to minimize corrosion of the absorber vessel materials. Heavy metals such as mercury, selenium and arsenic are also transferred to the slurry from the coal gases. Organics may be present in the FGD makeup water and may be introduced into the system through the use of performance enhancing additives, such as dibasic acid (DBA) in the FGD absorber vessel. The concentrations of these various contaminants in the FGD purge wastewater are heavily dependent on the concentrations of the contaminants in the fuel, in the FGD reagent and in the FGD makeup water. Table 1 contains a brief summary of the chemistry of a typical wet FGD purge wastewater.

Discharge Permit Limits and Challenges

Even though most National Pollutant Discharge Elimination System (NPDES) permits today are heavily restricted on the quality and quantity of wastewaters allowed for discharge, having the ability to discharge the FGD wastewater in some fashion from the facility opens up a wider range of options. This discharge may be via a dedicated outfall or via a combined outfall with other plant wastewater streams. If the owner/operator is successful in obtaining a discharge permit, the very low discharge limits of certain parameters commonly being enforced present treatment challenges. Chlorides, total dissolved solids (TDS), heavy metals and organics are typically the parameters of interest in most recent NPDES permits regulating FGD wastewater. Of the various heavy metals present in the stream, mercury and selenium are generally the two that are most heavily regulated, although arsenic, cobalt, cadmium and thallium have also drawn the interest of some permitting authorities.

New Environmental Protection Agency (EPA) test methods permitting very low level detection of mercury in water streams have helped to spark the regulation of very tight mercury limits in recently issued discharge permits. EPA Method 1631E, approved for use in 2002, allows for detection of mercury in water down to 0.5 ng/l utilizing cold vapor atomic fluorescence spectrometry methods. Recently, a Midwestern U.S. power plant has received a permit limiting mercury discharged from its facility to a maximum concentration of 1.3 ng/l. The plant NPDES permit does, however, allow for measurement of mercury to be performed at a combined outfall location enabling the plant to combine the FGD wastewater treatment system effluent with the condenser once-through cooling water return stream. At another facility operating in the Northeastern U.S., a mercury limit of 12 ng/l has been mentioned by the state regulators as a potential future restriction, although it has not yet been imposed. Selenium, another strictly regulated heavy metal common in FGD wastewater, is regulated by the EPA drinking water standards to 0.05 mg/l in bodies of water that supply drinking water to the public. Due to the toxic effects that high levels of selenium have been demonstrated to have on both humans and wildlife, proposals have been made in some areas to restrict selenium discharges to 0.3 mg/l or lower. Presently, NPDES permit limits on selenium of 0.2 mg/l or less are quite common.

The addition of organic compounds into the FGD absorber to improve system performance complicates the treatment of FGD wastewater for discharge. Some FGD equipment manufacturers are promoting the injection of DBA into their scrubber vessels touting SO2 capture rates greater than 99 percent. DBA is a biodegradable organic additive which has been shown to reduce FGD reagent consumption, reduce flue gas exit corrosion, improve SO2 reduction through over-scrubbing and reduce vessel scale and pluggage. The product is a blend of adipic, glutaric and succinic acids. It degrades in the absorber vessel and is measured as biological oxygen demand (BOD) in the FGD wastewater stream. Many facilities are restricted on BOD in their NPDES discharge permit; therefore, usage of DBA complicates and increases the cost of the FGD wastewater treatment system by necessitating that the treatment system includes biological steps for organics removal. DBA may also complicate the removal of some heavy metals from the stream via physical/chemical precipitation processes. While laboratory studies have shown that DBA addition has little effect on mercury removal, it has been observed to impact selenium removal from the wastewater. The addition of DBA promotes the transformation of selenium into selenate compounds, which are not readily precipitated in physical/chemical treatment processes. If the power plant is subject to low level selenium restrictions in its NPDES permit, biological processes may be required as part of the wastewater treatment system design to not only remove the organics, but also to convert the selenium into a form which can be precipitated.

Treatment for Discharge Options

Presently physical/chemical precipitation systems are the most widely utilized treatment methods for FGD wastewater. These treatment systems use a combination of hydroxide, carbonate and sulfide precipitation processes with coagulant addition to precipitate metals from the wastewater. Metal effluent concentrations achieved by these processes vary depending on the solubility of the metal species that are targeted for reduction. The lower the solubility product of the metal compound, the more readily the compound will precipitate; that is, remove the dissolved metal from the water as a settable solid. Lowest concentrations are typically achieved by precipitating metals in the sulfide form. For example, the mercury hydroxide Hg(OH)2 has a solubility product of 3.2 x 10-26 while mercuric sulfide Hg2S has a solubility product of 1.0 x 10-47. Physical/chemical precipitation, when used as the primary treatment method for FGD wastewater, typically is employed as one of two process combinations: hydroxide/carbonate precipitation or hydroxide/sulfide precipitation. Both combinations usually include the addition of a coagulant such as ferric chloride to promote adsorption of metals onto the bulk clarifier sludge improving overall metals reduction. Two clarification steps are utilized in each scheme with primary TSS reduction and hydroxide precipitation occurring in the first clarifier and sulfide or carbonate precipitation occurring in the second. This sequence optimizes chemical consumption and reduces the utilization of expensive chemicals, such as organic sulfide products. Media filtration usually follows as a final step to remove any remaining fine suspended particles. Figure 2 provides a schematic diagram of a typical FGD wastewater treatment system employing a physical/chemical treatment.

Aerobic and anaerobic biological processes may be utilized in an FGD wastewater treatment system for the removal of BOD and heavy metals from the FGD wastewater. Presently, selenium is the most frequently targeted metal in design of FGD wastewater treatment systems employing biological processes. The biological processes are typically preceded by treatment for reduction of suspended solids to permit more effective utilization of the microorganisms. The system design may include aerobic units, anaerobic units or a combination of both depending on the compounds targeted for reduction. Aerobic bacteria are utilized to remove organics such as BOD due to DBA addition from the FGD wastewater. Anaerobic bacteria such as sulfate reducing bacteria can be utilized to remove selenium, bound in the form of difficult to precipitate selenates, from the FGD wastewater. The anaerobic bacteria utilize the oxygen present in the selenate forms and sulfates in the wastewater stream for respiration, reducing the selenates to elemental selenium which can be easily precipitated in a clarifier. Figure 3 provides a schematic diagram of a typical FGD wastewater treatment system employing biological components.

Constructed wetlands treatment systems (CWTS) offer an option for treatment of FGD wastewater that is natural and environmentally friendly. CWTS are designed to utilize specific microorganisms and plants to remove pollutants from the FGD wastewater. A typical CWTS treatment train includes a clarifier as a pretreatment step to remove suspended solids. The clarifier is followed by a series of wetland cells and aeration cells. The wetland cells are designed with plants and microorganisms to accomplish targeted metals reduction; for instance, bulrush is commonly added to target mercury and selenium removal. The aeration cells, usually rock filters, add dissolved oxygen to the wastewater promoting oxidization of iron species in the wastewater. These oxidized iron species help with the removal of heavy metals from the wastewater through co-precipitation processes. CWTS, however, require that the power plant have significant land acreage available for the treatment system. The FGD wastewater may also need to be diluted with water from a low TDS source, prior to treatment in the CWTS, as high chloride concentrations, which are typical of this wastewater, can be toxic to certain plants and wildlife.

Alternative Licensing Approaches

If a plant is unable to obtain an NPDES permit to discharge the FGD wastewater, other options for ultimate disposal include recycle within the plant, deep well injection and crystallization into a landfill-suitable cake in a zero liquid discharge system (ZLD). Due to the high TDS content of this wastewater stream, recycling this stream for reuse internally within the power plant even after treatment can be quite difficult. The most common reuse application for this wastewater is ash stabilization water, which is a limited volume application.

Deep well injection of treated FGD wastewater is a disposal option that has been gaining popularity in recent years in certain areas of the country. This scenario involves treating the wastewater for the reduction of TSS prior to injecting it into wells thousands of feet below the earth's surface. Standard criteria for most deep well injection facilities require that the treated wastewater have TSS content less than 100 mg/l consisting of particles smaller than 5 microns only. For FGD wastewater, this generally requires pretreatment of the wastewater in a clarifier for suspended solids reduction followed by two stages of filtration: a roughing media filter followed by fine filtration through a 5 micron cartridge filter.

ZLD is generally the last option analyzed for disposal of wastewater due to the high costs associated with the installation and operation of the equipment. This design includes pretreatment of the wastewater stream in a clarifier/softener for TSS and hardness reduction followed by concentration in a brine concentrator and a crystallizer. Since the FGD wastewater is high in calcium and magnesium as well as chlorides, the calcium and magnesium chloride salts present in this wastewater stream could result in a very high scaling potential within the ZLD concentrator vessels. The clarifier/softener reduces the scaling potential in the brine concentrator and crystallizer by reducing the levels of calcium and magnesium. The brine concentrators and crystallizers must be constructed from expensive metals and alloys such as titanium, CD4MCu, 254 SMO, and AL6XN to prevent scaling and plugging of the vessel internals. Operation of this equipment may also require low pressure steam for startup and/or continuous service or medium-voltage motors that contribute to a high plant auxiliary load.

The design of a FGD wastewater treatment system for a power plant is essentially a custom design based on that plant's particular characteristics. When choosing a treatment and disposal plan, one needs to carefully consider the various treatment options available given the local attitudes towards wastewater of this nature and anticipate future changes in regulations particularly in the areas of heavy metals limits. Despite the strict environmental discharge regulations that are coming into play in many areas of the country, numerous environmentally viable options are available to successfully deal with this wastewater stream.

Author: Colleen Layman is a Senior Engineering Specialist and Manager of Water Treatment for Bechtel Power

Corporation located in Frederick, MD.

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