A Fall in Mercury

Optimizing mercury removal processes for industrial wastewater

By Larry Smith & Gerald Walterick Jr.

Mercury removal from both air emissions and industrial wastewater, especially from coal-fired power plants in the U.S., has been a topic of extensive study for the past decade. Much of the initial focus was on controlling air emissions of mercury contaminants from coal-burning power plants, which were identified as the single largest source of airborne mercury emissions in the U.S. and were specifically targeted by the U.S. Environmental Protection Agency's (EPA) Clean Air Mercury Rule. This problem was addressed by the installation of wet flue gas desulfurization (FGD) systems at many coal-burning facilities. The FGD process has resulted in a significant reduction in air emission of mercury, but it does this by transferring the mercury to wastewater streams. Petroleum refining, natural gas recovery, and other light and heavy industries also generate mercury-contaminated wastewater. Much of the recent research has focused on removing mercury from this wastewater.

Mercury typically occurs at low parts-per-billion levels in industrial wastewater. The severe toxicity of some mercury compounds and the tendency of these compounds to bioaccumulate in aquatic ecosystems have led to stringent wastewater discharge regulations to keep it out of the environment. The Ohio River Valley Sanitation Commission mercury discharge limit of 12 parts per trillion (ppt) into the Ohio River, and the Great Lakes Water Quality Initiative standard of 1.3 ppt for mercury discharges into bodies of water in the Great Lakes basin are examples of U.S. mercury limit guidelines.

Meeting these limits presents a significant challenge to many industries.

Wastewater Treatment Processes

A significant portion of the airborne mercury contaminants removed from flue gas is transferred to aqueous waste streams that must be treated prior to discharge. The mercury species of most concern in wastewater are soluble mercury and particulate mercury. Treatment processes to handle these contaminants can be as simple as settling ponds.

More complex wastewater treatment systems, specifically designed to incorporate the chemical precipitation reactions required for adequate treatment of highly contaminated FGD wastewater streams, typically include several separate unit operations, including desaturation (addition of lime to precipitate sulfate as gypsum), equalization (to stabilize influent pH and water chemistry), metals precipitation, coagulation, clarification and filtration. Biological waste treatment processes also may be included to remove organics, nitrogen compounds and selenium.

Chemical Additives

Proper selection and application of chemical additives is critical to the success of a wastewater treatment program for mercury removal. Additives used to enhance the removal of contaminants in conjunction with the unit operations described above may include lime, coagulants, flocculants and heavy metal precipitants. Use of an appropriate precipitant is critical to ensuring that soluble mercury contaminants are reduced to low parts-per-trillion concentrations. Several years of lab, pilot and full-scale testing have determined that the most effective mercury precipitants are types like GE's MetClear MR2405, which has a strong affinity for mercury and also precipitates other heavy metals such as silver, cadmium, copper, lead, zinc, cobalt and nickel.

Experimental Studies

Bench-scale mercury removal studies (jar tests) were conducted in a laboratory on samples of mercury-contaminated wastewater from several industrial sources. Because of the extremely low concentrations of mercury typically found in this wastewater, great care was taken to ensure that the test apparatus and sample bottles were meticulously clean. The procedures used for the studies reported here are summarized below:

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- ***Test apparatus.*** Mercury removal studies were conducted in a dedicated clean laboratory using customized apparatus to eliminate the potential for sample contamination.
- ***Clean lab.*** Samples for low-level mercury analysis were processed in a dedicated clean lab using EPA protocols.
- ***Personal protective equipment.*** Safety gloves and protective eyewear and clothing were worn by lab personnel at all times.

The jar test procedures used for the mercury removal studies were customized for each application using a proprietary computer program to design mixing protocols that simulated the mixing conditions and reaction times of the full-scale wastewater treatment process. The use of this program improved the accuracy of the bench tests and facilitated scale-up to full-scale processes.

A variety of wastewater was evaluated, including power plant and refinery wastewater. The range of chemical compositions varied widely.

Study results with various contaminated wastewater demonstrated that the low parts-per-trillion mercury discharge concentrations required for each wastewater could be achieved with proper application of chemical additives. In many cases, the target discharge concentrations were achieved using existing plant unit operations.

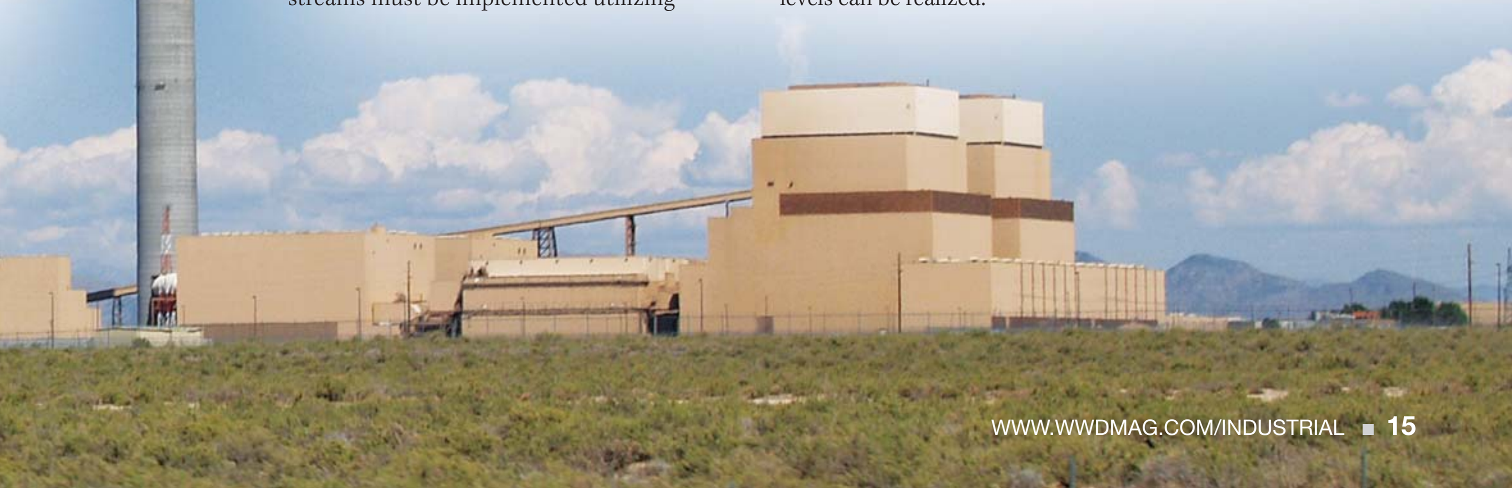
Key Treatment Considerations

When a mercury-contaminated wastewater stream is identified as a candidate for mercury removal studies, several key steps must be followed to determine the potential for successful treatment. Periodic, routine and historical sampling, and analysis of mercury-contributing wastewater streams must be implemented utilizing EPA-approved protocols for sampling, handling and analysis. EPA has published guidelines for proper procedures. Method 1669, titled "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels" is commonly used as a guide for sampling techniques. Analytical techniques to measure low parts-per-trillion levels were evaluated, and, in a 2007 memorandum, guidelines for use of these analytical techniques were disclosed. Analytical method 1631E is currently the method of choice for low-level mercury analyses.

Common power plant FGD and ash pond systems have a variety of incoming water quality characteristics. This variability is one reason why it is so important to routinely analyze and conduct evaluations in the laboratory and on site to ensure optimum removal is maintained.

Pilot Studies

Actual application of the treatment programs developed in the laboratory jar testing commonly is conducted through plant trials or pilot studies, leading to extended or continuous treatment. Several applications are outlined below to demonstrate the effectiveness of the MerCURxE program for removal of total mercury. Often, the requirements for meeting final discharge permit limits are accomplished by treating each candidate stream individually. Treated water may either be combined or discharged separately. In many cases, immediately after the precipitation process, results show excellent removal, even though the final discharge limits are not met at that point in the system. Depending on the downstream design, further removal can be achieved and lower mercury levels can be realized.



FGD System No. 1. This coal-fired power plant FGD system has a traditional design with equalization, reaction tanks and a circular clarifier. The treatment program includes the use of a coagulant, MetClear MR2405 and a GE flocculant to remove total suspended solids (TSS) and mercury. Specific regulatory discharge limits for mercury have not yet been established at this site. Mercury removal of more than 99% on average has been accomplished, from approximately 30 ppb to less than 0.2 ppb. The inlet loading of most other heavy metals is not significant (less than 1 ppb), compared with iron and mercury. Results indicate that boron, selenium and arsenic also are removed by the combined treatment approach.

FGD System No. 2. This FGD system includes equalization, desaturation, a primary clarifier, a chemical reaction tank, a secondary clarifier and a continuous backwash sand filter. This filtered effluent is discharged through ash ponds. In this system, only the secondary clarifier is treated with chemicals. Additives include lime for pH adjustment, MetClear MR2405, a coagulant and a GE flocculant. Target levels for mercury are less than 200 ppt out of the treated clarifier. Results have shown that mercury can be removed from an inlet range of 230 to 350 ppt down to 65 ppt after the clarifier, and as low as 45 ppt after the filters—well below the target goal of 200 ppt.

FGD System No. 3. This FGD wastewater treatment system includes equalization, reaction tanks and a clarifier prior to discharge. This system also utilizes a coagulant, MetClear MR2405 and a GE flocculant to remove mercury, other heavy metals and TSS. Mercury removal in excess of 99.91% was achieved with treatment. Average influent mercury of 84,800 ppt was reduced to 78 ppt across the clarifier, and then to 18 ppt through the sand filter. This site also is not currently regulated for mercury removal.

Incorporating Treatment

The use of MerCURxE chemical technology for the removal of both soluble mercury and particulate mercury has been shown to be effective for a wide variety of industrial wastewater. Incorporating this type of treatment into an overall wastewater treatment program can improve mercury removal significantly. The industry generating the wastewater, the design of the wastewater treatment plant, the operating conditions of the plant, and the mercury concentration and speciation in the influent wastewater are all factors that have an impact on the efficacy of a treatment program. Understanding the unique characteristics of each system and the variability of the contaminant loading is vital to the successful removal of mercury from industrial wastewater. iWWD

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