

Cleaning Mercury & Selenium

**FROM SCRUBBER
WASTEWATER**



Nearly two decades ago, Congress amended the Clean Air Act to limit sulfur dioxide emissions from the smokestacks of coal-fired power plants. Subsequent rulemakings by the U.S. Environmental Protection Agency (EPA) and the states have resulted in significant further reductions through utilities' installation of emissions controls. While these regulations have helped reduce acidic deposition, formation of secondary particulates, and ozone concentrations, they have created new challenges for the electric power industry.

Flue gas desulfurization (FGD) systems—called wet scrubbers—use a slurry of water and an alkaline material (such as lime or limestone) to absorb as much as 95–99% of a plant's sulfur dioxide emissions. However, wet scrubbers generate wastewater containing mercury, selenium, and other trace elements that may necessitate treatment of the wastewater before discharge. With sulfur restrictions being continually tightened, many more FGD systems are being installed, according to Paul Chu, an EPRI project manager.

While federal water discharge limits for the electricity industry (referred to as effluent guidelines) don't yet exist for selenium and mercury, the EPA recently announced plans to revise its technology-based effluent guidelines for power plants under the Clean Water Act. The agency's revisions may include limits on selenium and mercury in FGD wastewater, given concerns over their potential impacts on aquatic species. Many states already regulate selenium and mercury discharges through water quality standards. For example, states bordering the Great Lakes and the Ohio River have set goals of mercury levels between 1.3 and 12 parts per trillion. To date, however, no one has demonstrated a technology that is able to reduce concentrations to these extremely low levels.

To meet anticipated future limits, the industry will need new, cost-effective technologies, and EPRI is evaluating an array of technologies to remove mercury, selenium, and other trace elements from wastewater

THE STORY IN BRIEF

With revisions of federal effluent guidelines expected to include new discharge limits for mercury and selenium, power companies are looking for wastewater treatment options that can meet increasingly stringent requirements. EPRI is evaluating an array of technologies for boosting the removal of such trace elements from scrubber wastewater, including vertical flow wetlands, which use anaerobic bacteria to help remove contaminants in a passive treatment system.

discharges. "We see EPRI's primary role as being an independent, third-party evaluator," said Chu, who heads the project to evaluate FGD wastewater treatment solutions.

EPRI researchers also are working to understand how trace elements such as selenium behave chemically in FGD wastewater. The hope is that greater understanding will lead to new ways of dealing with these contaminants.

A Focus on Mercury and Selenium

Like sulfur, mercury and selenium occur naturally in coal. When the coal is burned, these constituents vaporize and can end up in the fly ash and be removed in the scrubber or be released up the stack. In the scrubber, some portion ends up in the solids (e.g., gypsum), with the remainder in the wastewater.

Selenium and mercury are both difficult to remove from wastewater, but for different reasons. "What makes selenium so difficult to treat is that it can be present in different chemical forms," Chu said. The two forms most common in wastewater are selenate and selenite. While selenite is relatively easy to remove, selenate is quite difficult.

Other forms of selenium exist as well, some easier to remove than others. Naomi

Goodman, a chemist at EPRI, has spent the past several years trying to figure out what forms of selenium FGD wastewaters contain. "If we don't know what we are trying to treat, that makes it harder," she said.

To remove mercury from wastewater, power companies typically use compounds known as organosulfides. Sulfide reacts with mercury to form insoluble cinnabar. The problem, Chu said, is that the reaction happens so fast that the cinnabar particles are minuscule and difficult to collect. Some companies have tried to combine sulfide with other compounds to make bigger molecules that are easier to filter. The lowest mercury levels that can be achieved by using this method are typically in the range of hundreds of parts per trillion.

In 2008, EPRI began to search for new technologies to remove mercury and selenium. Depending on the developmental status of the individual technologies, EPRI's objective is to conduct laboratory evaluations followed by field testing of the most promising options.

Vertical Flow Wetlands

On North Carolina's Lake Norman, Duke Energy operates a 2,000-megawatt coal-fired power plant that relies on several acres of man-made wetlands to filter the

plant's FGD wastewater. To boost selenium reductions, EPRI project manager John Goodrich-Mahoney recommended, and Duke agreed, to construct a pilot-scale vertical flow wetland. In this system, the water travels down through the substrate rather than horizontally across the wetland surface, as in traditional treatment wetlands. The anaerobic bacteria that live inside a vertical flow wetland remove selenium more effectively than the aerobic bacteria in the horizontal flow counterpart.

The pilot-scale wetland uses a 3,000-gallon plastic tank, at the bottom of which lies a drainage bed composed of 1 foot of aggregate covered with a woven organic-mesh fabric. Above the mesh is a 4-foot layer of compost, a by-product of local mushroom cultivation. "The water enters from the top and percolates down through the system and out," Goodrich-Mahoney said. As the water travels through the compost, anaerobic bacteria reduce selenium to its elemental form or to selenium precipitates. "We build wetland treatment systems because they're very cost-effective," he said. "The up-front capital costs can be similar to those of more traditional physical or chemical treatments, but the operation and maintenance costs are always significantly lower."

Passive treatment systems such as this have been used to treat other kinds of wastewater, but this is the first study to evaluate the treatment of FGD wastewater. And it seems to be working. Weekly water sampling began in May 2008. Mercury and selenium levels in the influent were already low, but the wetland treatment system brought levels even lower. "It seems to do the trick as far as reducing our effluent to acceptable levels," said Ron Lewis, an environmental scientist at Duke Energy.

In fact, the system worked so well that Duke is planning to build a full-scale system of six wetland cells to handle all the wastewater generated by its FGD system. Each cell will cover roughly half an acre; the complete system, with access roads and piping, will occupy 5.6 acres and, like a

natural wetland, will be covered with vegetation. Costs are projected to be \$3.3 million for construction and roughly \$32,000 a year for operation and maintenance. The plan is to have the new wetland up and running before 2012.

"Not every power company has enough space to build a wetland treatment system. That's one of the real constraints," Goodrich-Mahoney said. "We are looking at how to minimize the footprint."

Other Approaches

One biological option with a potentially smaller footprint is a bioreactor. "Chemically, the technologies appear to be quite similar," Chu said. Both use anaerobic conditions and microbiology to remove selenium and mercury. But there are differences: In a vertical flow wetland, bacteria colonize the substrate naturally. In a bioreactor, various bacteria are selected to optimize selenium and mercury removal for each specific water matrix. Also, the bioreactor is a constructed treatment system with traditional tanks, pumps, and piping and with precise process control. The vertical flow wetland is more passive. Chu pointed out that the underlying chemistry of these systems is not well understood. EPRI has launched a project to characterize the specific reactions that are taking place inside the compost beds.

EPRI began testing a full-scale bioreactor at another Duke power plant in North Carolina last December. The bioreactor is more intensively managed than the vertical flow wetland. "They're constantly feeding and monitoring the bacteria within that bed to optimize selenium removal," Lewis said. At this plant, too, mercury and selenium levels in the wastewater are already low, but the bioreactor lowers them further. "This is a very promising technology," Chu said.

EPRI also is testing technologies that rely on chemical precipitation and adsorption to remove trace elements. "We tried to evaluate and screen as many technologies as are out there," Chu said. "We threw the net as wide as possible." Some of the



Pilot-scale vertical flow wetland

most promising technologies were tested in a series of pilot studies at a power plant in the Midwest.

The current technology to deal with selenium involves iron coprecipitation, where dissolved metals are adsorbed onto the surface of iron particles, which are then removed. This process is limited because iron reacts preferentially with selenite, leaving much of the selenate in solution. EPRI is investigating an advanced technique, called iron cementation, to help chemically reduce the selenate species to selenite, which can be dealt with more easily.

At one test site, iron cementation brought selenium levels down from roughly 6,000 parts per billion to, in the best case, under 200 parts per billion. "It shows that this technology has promise," Chu said, "but it didn't get down to the very low levels we had hoped to see."

EPRI also evaluated several technologies designed to address mercury. One technology relies on the standard technique of using sulfides to trap mercury in tiny particles that can then be captured by a microfilter. This approach brought mercury levels down from several hundred parts per trillion to about 90 parts per trillion. The potential benefits of microfiltration for mercury removal may vary with FGD water makeup, however, because of differences in the mercury particle-size



Duke Energy plans to modify an existing FGD wastewater treatment system in North Carolina with six full-scale vertical flow wetland cells.

distribution. More important, long-term operation of microfiltration has not been demonstrated for FGD waters, which may have high scaling potential; thus further evaluation is required.

Two technologies use advanced filtration combined with adsorption media designed specifically to capture mercury. One system demonstrated potential for reducing mercury levels to below 100 parts per trillion, while the other adsorption medium did not effectively remove mercury in the pilot study. Both technologies will need much more study and development before any commercial use.

Mysterious Molecules

One of the most puzzling aspects of this research is the wide variation in the makeup and treatability of FGD wastewater. At the two Duke test sites in North Carolina, much of the mercury and selenium from the flue gas ends up in the FGD solids. At other plants, however, the mercury and selenium stay dissolved in the FGD wastewater, making treatment more difficult.

EPRI will test the most promising technologies at various sites to see how they perform with different kinds of wastewater. “Every FGD wastewater is different, so removal performance for any technology will likely vary,” Chu pointed out. “Until we truly understand the chemistry behind mercury and selenium, it will be difficult to predict removals from individual wastewaters.

“We think there are a number of different things that affect the fate of mercury and selenium,” Chu said. Research shows that mercury is more likely to form particles when iron levels are higher in the wastewater. With respect to selenium, oxygen could be a factor. In most new FGD systems, air is blown into the FGD slurry to convert the solids to gypsum, a form that’s more easily managed and can be sold as wallboard. “We think that in that process selenium is oxidized to selenate—the more difficult form to treat,” Chu said. But even similar systems can generate widely varying wastewaters. “Different metals in the FGD water may facilitate

that chemical reaction, and other compounds may slow it down,” Chu said. Variations in the power plants themselves and in the coal they burn also may influence the makeup of FGD wastewaters.

Once scientists understand the chemistry, plant managers might be able to manage the conditions in the FGD system itself to favor the development of selenite over selenate or to ensure that more mercury and selenium fall out with the solid particles. “If we can do that, we can potentially avoid the wastewater treatment needs,” Chu said. “That will be the way of doing it in the future.”

This article was written by Cassandra Willyard. For more information, contact Paul Chu, pchu@epri.com, 650.855.2362, or John Goodrich-Mahoney, jmahoney@epri.com, 202.293.7516.



Paul Chu is a senior project manager in the Land and Groundwater program area of the Environment Sector. His current research activities focus

on air and water toxics. Before joining EPRI in 1992, he worked at Babcock & Wilcox, where he was involved in various development projects related to flue gas cleanup of SO₂, NO_x, and particulates. Chu received a B.S. in chemical engineering from the University of Arkansas in Fayetteville and an M.S., also in chemical engineering, from the University of Texas at Austin.



John Goodrich-Mahoney is a senior project manager in the Water and Waste Management program area of the Environment Sector. He manages research on toxic metals in the aquatic environment and on ecological issues associated with transmission and distribution systems. Before joining EPRI in 1990, Goodrich-Mahoney worked at the U.S. Environmental Protection Agency in Washington, D.C., the University of Wisconsin-Madison Water Resources Center, and the Woods Hole Oceanographic Institution. Goodrich-Mahoney received a B.S. in geology from St. Lawrence University and an M.S. in geochemistry from Brown University.

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