



Big Market for Chemicals to Capture Mercury

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The McIlvaine Company provides market and technical analysis on environmental subjects

New standards limiting discharges of mercury from power plants, cement kilns and incinerators in the U.S. will boost the market for treatment chemicals.

Until recently, it appeared that the bulk of the business would be captured by activated carbon manufacturers. Now, it appears that brominated product and technology suppliers will be carving out a significant share.

When halogens such as bromine and chlorine react with elemental mercury in the combustion zone or in the flue gas, they convert the mercury to forms (e.g., mercury chloride) which can be absorbed in conventional FGD scrubbers. Furthermore, when activated carbon is impregnated with halogens, it is considerably more effective in capturing the elemental mercury. Bromine has proven to be considerably more effective than chlorine due to its reactivity and efficiency to convert mercury to a form that can be captured.

Calcium bromide can be added to the coal and at various points in the air pollution control system prior to the wet scrubber. The SO₂ wet scrubber has proven effective in removing more than 90% of the mercury in the ionic form. Therefore, the calcium bromide-wet scrubber combination offers an alternative to the activated carbon-dry injection approach. However, not all power plants will want to make the investment in the wet scrubbers and will consider alternatives for SO₂ removal.

The Market

The U.S. represents more than 90 percent of the current total market for capture of mercury from stack gases. The U.S. electricity generators will be making most of the purchases. However, there will be significant markets in cement and industrial boilers. There is already a market in waste incinerators.

Most of the non-U.S. market is presently in the waste incineration markets. This includes both municipal and hazardous waste. There are additional markets in sewage sludge incineration, crematories, and mining.

One reason that European, Japanese and Korean power generators are not specifically regulated for mercury emissions is that nearly all the plants have wet scrubbing systems and are already removing most of the mercury. These plants, however, can increase mercury removal with bromide additions.

China is seriously investigating mercury removal technologies. There are more coal fired boilers operated in China than all the countries of Europe combined making it the largest mercury emitter. Most plants there are equipped with SO₂ wet scrubbers, thus making bromide-based chemical additives to improve scrubber capture an attractive solution for Chinese power generation facilities.

In the U.S., the market for removal of mercury has now been quantified by the new proposed Utility Toxic Rules (MATS), the final Industrial Boiler Rules and the final Cement MACT Rules. The Utility Rules will have most of the impact on the mercury control market. The original rule, the Clean Air Mercury Rule (CAMR), covered just mercury but was struck down. The rule which is in place covers air toxics including metals other than mercury and toxic gases such as hydrogen chloride.

If the U.S. EPA assumptions are correct, the activated carbon market for power plants will rise to over \$500 million/yr. This represents demand in sales for both plain activated carbon and brominated activated carbon producers. The 2010 market was around \$50 million, and the 2011 market was not much larger due to the fact that the rule was withdrawn and then re-promulgated thus changing the timelines for use of activated carbon. Brominated carbons have been shown to reduce carbon usage and improve control efficiencies.

The present U.S. market for chemicals is primarily in the States that have implemented their own regulations and utilities benefiting from a tax credit for refined coal. There is also an ongoing market in waste incineration. However, the U.S. landfills most of its waste. In contrast, the rest of the world believes waste-to-energy is the answer and regulates accordingly, making the market for chemicals for waste incinerators much bigger outside the U.S.

Although utilities, cement plants and industrial boilers should be finalizing their choices for mercury

reduction, most have not done so. This creates a great deal of uncertainty. A supplier of activated carbon or halogen compounds has to consider the following possibilities:

- Another compound, such as silicates, will capture the majority of the market.
- The combination of wet scrubbers, SCR, and chemical additives will achieve the required efficiency.
- The use of fabric filters and halogenated carbons will minimize the total activated carbon requirements to achieve the needed efficiency.
- A higher percentage of older plants will be retired rather than install equipment.
- Dry lime injection is used to capture HCl and it is found that less carbon is needed for mercury.

There are some possibilities which would increase the use of activated carbon beyond EPA projections:

- Brominated carbons in conjunction with precipitators prove adequate and utilities opt to use more carbon rather than make the large investment in fabric filters.
- The ability to capture selenium and avoid contamination of the scrubber wastewater results in the use of A-C on many plants with scrubbers and adequate mercury removal.
- Wet scrubbers are less efficient than anticipated, and there is a supplemental need for activated carbon injected ahead of the scrubber.

Given all these variables, McIlvaine Company predicts that substantial quantities of bromide additives or specifically, Calcium bromide will be utilized and that the use of activated carbon falls well below EPA expectations.

Proposed Mercury and Air Toxics Standards

On March 16, 2011, the EPA issued a proposed 946 page rule that would reduce emissions of Hazardous Air Pollutants (HAP) from power plants. Specifically, the proposal would reduce emissions from new and existing coal- and oil-fired electric utility steam generating units (EGUs). EPA is also proposing to revise the new source performance standards (NSPS) for fossil fuel-fired EGUs. This NSPS would revise the standards new coal- and oil-fired power plants must meet for PM, SO₂, and NO_x. Existing sources have up to four years to comply with these standards. All existing sources must comply in three years, but individual sources can obtain an additional year if technology cannot otherwise be installed in time.

The proposed toxics rule would reduce emissions of heavy metals, including mercury (Hg), arsenic, chromium, and nickel, and acid gases, including hydrogen chloride (HCl) and hydrogen fluoride (HF). The proposed rule would:

- Prevent 91 percent of the mercury in coal burned in power plants from being emitted to the air;
- Reduce acid gas emissions from power plants by 91 percent; and
- Reduce SO₂ emissions from power plants by 55 percent.

A major source of HAP emissions is generally a stationary source that emits or has the potential to emit 10 tons per year or more of any single HAP or 25 tons per year or more of any combination of HAP. CAA section 112(a)(8) defines an EGU as: A fossil fuel-fired combustion unit of more than 25 MWe that serves a generator that produces electricity for sale. A unit that cogenerates steam and electricity and supplies more than one-third of its potential electric output capacity and more than 25 MWe output to any utility power distribution system for sale is also an electric utility steam generating unit.

EPA estimates that there are approximately 1,350 units affected by this action; approximately 1,200 existing coal-fired units and 150 oil-fired units at about 525 power plants. EPA has divided coal- and oil-fired EGUs into the following subcategories:

- Coal-fired units designed for coal \geq 8,300 Btu/lb
- Coal-fired units designed for coal $<$ 8,300 Btu/lb
- IGCC units
- Liquid oil-fired units
- Solid oil-derived fuel-fired units (e.g. petcoke)

The numerical emission standards that are being proposed for existing coal- and oil-fired electric utility steam generating units are shown below.

Table 2-1. EMISSION LIMITATIONS FOR COAL-FIRED AND SOLID OIL-DERIVED FUEL-FIRED EGUs

SUBCATEGORY	MERCURY
Existing coal-fired unit designed for coal $\geq 8,300$ Btu/lb	1 lb/TBtu (0.02 lb/GWh)
Existing coal-fired unit designed for coal $< 8,300$ Btu/lb	11 lb/TBtu (0.2 lb/GWh) 4 lb/TBtu* (0.04 lb/GWh*)
Existing: IGCC	3 lb/TBtu (0.02 lb/GWh)
Existing: Solid oil-derived	0.2 lb/TBtu (0.002 lb/GWh)
New coal-fired unit designed for coal $\geq 8,300$ Btu/lb	0.00001 lb/GWh
New coal-fired unit designed for coal $< 8,300$ Btu/lb	0.04 lb/GWh

* Beyond-the-floor limit

Note: lb/MMBtu = pounds pollutant per million British thermal units fuel input

lb/TBu = pounds pollutant per trillion British thermal units fuel input

lb/MWh = pounds pollutant per megawatt-electric output

lb/GWh = pounds pollutant per gigawatt-electric output

Bromide Additive Technologies

There has been considerable experience with bromide addition already. It is being utilized in several different forms and results have been impressive in Section 45 tax credit projects that have been operational now for approximately 2 years and utilize Calcium Bromide to assist with mercury oxidation. Mostly, these projects are utilizing a technology from Chem Mod and its licensees, but ADA has reported technology as well for tax credit approved facilities.

Shaw is using bromide compounds (HBr) at various injection points to enhance mercury capture but at the same time to improve particulate capture. Shaw has successfully demonstrated greater than 90 percent mercury removal and reduction of mercury to levels to meet the new MATS standard. For some applications some combination of the bromide compounds and PAC may be required. HBr as a strong acid would require some additional handling and storage considerations.

A combined total of approximately 8,000 MW of U.S. utility coal-fired boilers use Alstom's KNX™ technology to control mercury emissions. KNX™ processes use calcium bromide (CaBr₂). In addition, Alstom offers two alternatives. Mer-Cure™ is designed to process and inject activated carbon into targeted regions that are critical for maximum mercury oxidation and capture. Filsorption™ is a simple dry sorbent injection process driven upstream of air quality control system equipment. Removal of more than 90 percent of total mercury in the flue gas, Filsorption™ systems have been installed and operated on waste-to-energy (WtE) facilities since the 1990s, and more recently on both utility wet and dry flue gas desulfurization applications.

Nalco Mobotec has been marketing its Mercontrol™ 7895 oxidant (bromide additive) as part of its

technology offering which includes mercury reemission products for Wet FGD scrubbers and control for metals from wastewater streams.

Bromine and bromide derivatives are being extensively used to impregnate activated carbon. The impregnated carbon is proving to provide cost-effective improvements in capture efficiency.

Bromine Suppliers

Chemtura Corporation [CHMT], Albemarle and ICL are the major suppliers of bromide compounds. Elemental Bromine has many uses from water treatment to use in the production of flame retardant products and bromide additives such as Calcium Bromide.

Chemtura's Great Lakes Solutions business is a leading manufacturer in the USA that has been operating bromine and bromine derivative units in South Arkansas for more than 35 years. The business is positioning itself to meet the significant demand for this new application for bromine in its home market by making investments of more than \$100 million to optimize its bromine production facilities in Arkansas. In 2011, Chemtura signed a letter of intent with India-based Archean Group to establish a strategic alliance, including a joint venture, in bromine and brominated derivatives. This venture will help to support the growing global demand for bromine and will allow Great Lakes Solutions to focus its U.S. based production on the domestic demand for mercury control. These investments are part of its strategy to optimize its manufacturing footprint to best serve growing markets.

"Chemtura is heavily investing in the Great Lakes Solutions business' strategic program of "greener" innovation. Investment in GeoBrom™, our product line for mercury control in coal-fired electricity generation, fits within this program. We have made significant investments in our U.S. facilities in the form of brine infrastructure upgrades including the acquisition of certain brine leases in 2009. These investments, along with the strength of our existing brine field rights, ensure the long-term viability of our existing brine wells and enhances our already solid position to sustainably deliver bromine and brominated derivatives from South Arkansas for decades to come," said Anne Noonan, president of the Great Lakes Solutions business.

Craig Rogerson, CEO of Chemtura, added that "the addition of a strategic supply position in India, coupled with our current long-term supply strengths in the U.S. and from the Dead Sea, provides us with a unique supply footprint to market globally."

Albemarle has positioned itself to compete as a supplier of both activated carbon and bromine additives, as well as on-site services. In April 2008, it purchased Sorbent Technologies for \$20 million. Sorbent Technologies had been supplying brominated activated carbon.

Headquartered in Beer-Sheva, Israel, ICL-IP manages its bromine resources from the Dead Sea, and supports the demand for this market from material imported into the United States.

Summary

There is a rapidly growing market for chemicals to reduce mercury emissions in the U.S. which will undoubtedly include bromine derivative products to meet the regulatory requirements. In the longer term, the market will expand to other countries, including China. The injection of activated carbon and calcium bromide addition to the coal or directly to the combustion zone have been the technologies. It now appears that the use of bromine activated carbon or calcium bromide addition to the coal or combustion zone will play a substantial role in solutions to meet more stringent mercury emissions restrictions. The major world suppliers of bromine will be able to meet the demand.