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OPPORTUNITIES FOR IMPROVED ENVIRONMENTAL CONTROL IN THE ALUMINA INDUSTRY

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Abstract

Alumina production from bauxite offers a unique set of environmental concerns that affect air, water, and solids. Governments and industry have recognized that reductions in plant emissions and environmental impacts are necessary. The alumina industry is not the only industry that has been subjected to, and responded to, such regulatory scrutiny over the past decade. A number of industry sectors are actively developing innovative ways to control a broad range of potential environmental hazards. Several of these technologies may have direct application in alumina refineries. Methods to significantly reduce mercury emissions in both air and water have recently been developed for use in a range of industries. This paper reviews some of these new technologies now in commercial use in non-alumina plants and considers how they may be applicable within the alumina industry.

Introduction

The emissions to air and water from alumina refineries are coming under increasing scrutiny by both the industry itself and the communities in which they operate. Such environmental concerns are common to a variety of industries[1-6] and alumina producers can learn much by looking outside the industry to other industrial processes where emissions problems are being successfully addressed. In recent years, Nalco has developed a number of strategies designed to reduce air and water emissions of a variety of hazardous contaminants. These technologies have been initially targeted at processes unrelated to alumina refining. Nonetheless, the issues that many of these technologies address – emissions of mercury, sulfur oxides (SOx), and nitrogen oxides (NOx) – are also commonly found as issues in the alumina industry.

This paper focuses on the issue of mercury in the alumina industry and then considers a number of recent developments in the area of mercury emissions control and reviews the benefits and downsides of their implementation in the coal-fired power industry. Consideration is also given to how some of these technologies, which are based on both chemical and engineering solutions, might be applied or adapted within the alumina industry to resolve specific problems associated with mercury in the Bayer process.

Sources of Mercury in the Bayer Process

The major source of mercury in Bayer process operations is the bauxite ore used. While trace levels of mercury are distributed throughout the geosphere in soils, ores, and mineral deposits at concentrations typically in the range from 20 to 150 ppb,[7] mercury levels in bauxite can vary quite drastically between different sources and even between different deposits from a single source. Mercury levels as low as 20-100 ppb have been found in Boke bauxite, 500-700 ppb levels are common in Jamaican bauxites, and mercury levels as high as 1200 to 2000 ppb have been reported in some bauxites in Suriname.[8] Regardless of the initial level, due to the large volumes of bauxite that are processed in the production of alumina, significant quantities of mercury can accumulate at various points in the Bayer process, ultimately resulting in mercury emissions to air and water of up to several tons per year.[9] Additionally, depending on the source of the lime and raw caustic that are also added to the Bayer process, these too can contribute significant inputs of mercury to the system.

Fate of Mercury in the Bayer Process

Figure 1 outlines the major sources of mercury input and output in a typical Bayer plant. It is interesting to note that the potential output streams are dominated by gas phase emissions. While clearly there are some differences, emission to air is also the predominant issue in most coal-fired power plants. As a result, the potential for the use or adaptation to Bayer plant operations of the existing control technologies used in coal-fired power plants is apparent.

The mercury contained in bauxite exists as a mixture of different inorganic and organic compounds and oxidation states. Regardless of its initial form, virtually all of the mercury is converted to elemental mercury (Hg^0) by the highly reducing environment of the digestion phase of the Bayer process.[10] A portion of this mercury can then be emitted to the air via digestion vent gases, especially within the first few stages of flash cooling, and some mercury may be collected in the downstream condensate systems, Figure 1.

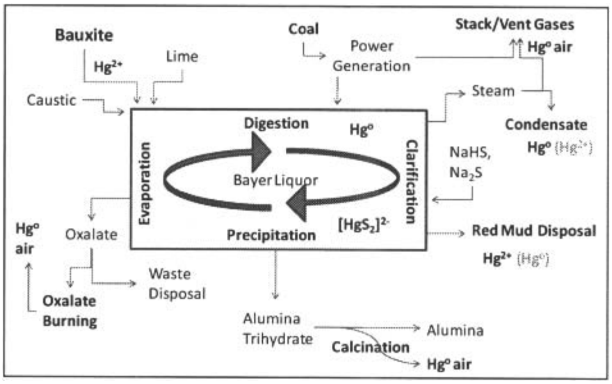

Figure 1. Potential Hg Inputs and Outputs in the Bayer Process

Following digestion, a large portion of the mercury may be carried within the red mud slurry. The extent to which the mercury will partition to the red mud solids or to the liquor will be influenced by many factors such as the digestion conditions used, the liquor chemistry and the extent to which mercury oxidation will occur, and the type and quantity of process additives used. These will ultimately influence the concentration of the mercury present in the pregnant liquor. Mercury losses to red mud residues have been estimated to be as high as 0.5 lb/day or more, and these losses may account for 15-60% of the mercury input to the process.[7]

Upon precipitation of the alumina trihydrate from the liquor, trace levels of mercury can become incorporated in the trihydrate crystals which will be vaporized and emitted into the air during the downstream calcination process. Similarly, trace levels of mercury may be incorporated into oxalate solids that are either co-precipitated with the trihydrate or precipitated by side-stream oxalate removal. Thus, depending on the oxalate removal operations in a specific refinery, additional mercury can exit the process through residue disposal or potentially via air emissions if the oxalate residues are sent to a downstream furnace for lime recovery. The oxalate cake at one refinery was reported to have as much as 2000 ppb mercury and it contributed to a loss of 15% of the input mercury.[7]

Completing the cycle, small amounts of the mercury may be stabilized in the liquor, which will then be recirculated to evaporation and then back to digestion where it can be lost via air emissions through the barometric condensers or, as mentioned before, it may become a contaminant in the process condensate streams. Digestion condensates have been reported to have soluble elemental mercury concentrations in the order of 20 μg/L.[11]

Mercury Control Options in the Bayer Process

In the course of processing the very high volumes of vent gases and or condensate that are produced from evaporation and digestion at a typical refinery, elemental mercury often accumulates in the traps on condensers and heat exchangers to the point where it can be drained off and collected. This can yield several hundred grams of metallic mercury (Hg^0) per day which can be collected and isolated for proper disposal.

In addition, gas volumes from digestion vents tend to be much smaller than those from calciners and oxalate furnaces, such that these can potentially be much more readily treated by standard techniques to remove mercury. For example, the vent gases can be chilled to further condense mercury vapors and then passed through an appropriate adsorbent, such as activated carbon columns to remove the mercury.[7-9] Indeed, the removal of elemental mercury from digestion condensates by passage through a column containing mercury sorbents has already been demonstrated on a lab scale.[11]

With respect to mercury in Bayer process liquors, it has been discovered that the use of sodium hydrogen sulfide to precipitate problematic zinc salts can dramatically affect the partitioning behavior of the mercury in the red mud and liquor.[10] If a sufficiently high concentration of sulfide ion is maintained in the liquor, the mercury will remain in solution, presumably in the form of $[HgS_2]^{2-}$,[12] which will help to prevent it from precipitating with the alumina and the oxalate residues. While this can potentially reduce mercury emissions in calcination or in oxalate removal, the stabilization of mercury in solution decreases as excess sulfide is slowly converted to sulfate in spent liquor and residual mercury species will be reduced back to the elemental form in digestion.

Zinc, mercury, and other heavy metals may also be precipitated from digestion condensates or pregnant liquor by treatment with a series of Nalco dithiocarbamate or dithiocarbonate products.[13] For example, the additive(s) could be added just prior to mud filtration and the resulting residues may be removed from the process with the filter cake through the red mud disposal operations. This is similar to current practice in power plants for the control of mercury levels in industrial wastewater as outlined below. Furthermore, the use of these additives could substantially reduce or eliminate the need for sulfide addition and the corresponding large quantities of organics (and often liquor poisons) that are introduced to the process as a result of their use.

There also exists the potential to treat calciner stack gases with the injection of mercury sorbents in between the point where the alumina is collected and the final particulate control device. In addition, the co-injection of a mercury oxidant product, again such as currently used in other industries, could also be considered as a means to lower the sorbent feed rate. The mercury sorbents would of course become mixed with the alumina fines and this would prohibit the recycling of the fines back into the calcination cycle as is usually done. However, such a strategy could still prove to be the most economically and technically feasible, especially for refineries where the mercury tends to partition to the alumina.

Some of these control options may likely require consideration of the overall needs of the Bayer process to enable appropriate implementation. They may also require modification for specific plant conditions. However, the successful implementation of such strategies in other industries indicates the potential for improved control using these techniques. In particular, a number of these strategies have been successfully implemented within coal-fired power plants and the lessons learned from this industry can provide useful insights for alumina producers looking to reduce emissions.

Mercury Control in Coal-Fired Power Plants

Mercury is naturally found in coal in concentrations ranging from 20 to 1000 ppb and coal-fired power plants account for 30% of the global anthropogenic mercury emissions.[14] All forms of mercury present in the coal decompose during combustion into the highly volatile elemental form (Hg^0) which can readily evade capture by existing air quality control devices typically found at power plants. However, in contrast to alumina refineries where mercury is emitted almost exclusively in the elemental form, in coal-fired power plants a significant portion of the mercury can subsequently become oxidized to an ionic form (Hg^{2+}) depending on the coal type and process conditions. In this oxidized state mercury is more readily captured by fly ash and sorbents and/or scrubber liquors. As a result, it is advantageous to maximize the conversion of elemental mercury to the oxidized form to enhance capture. However, this is not the only strategy. The extent to which the mercury becomes oxidized and is removed from the flue gas is highly dependent both on the type of coal being fired, and the operational conditions employed at the plant.[15] This means that mercury emission rates can be highly plant specific and an intimate understanding of the factors that affect mercury transformations and partitioning is crucial to developing a successful control strategy for any given plant.

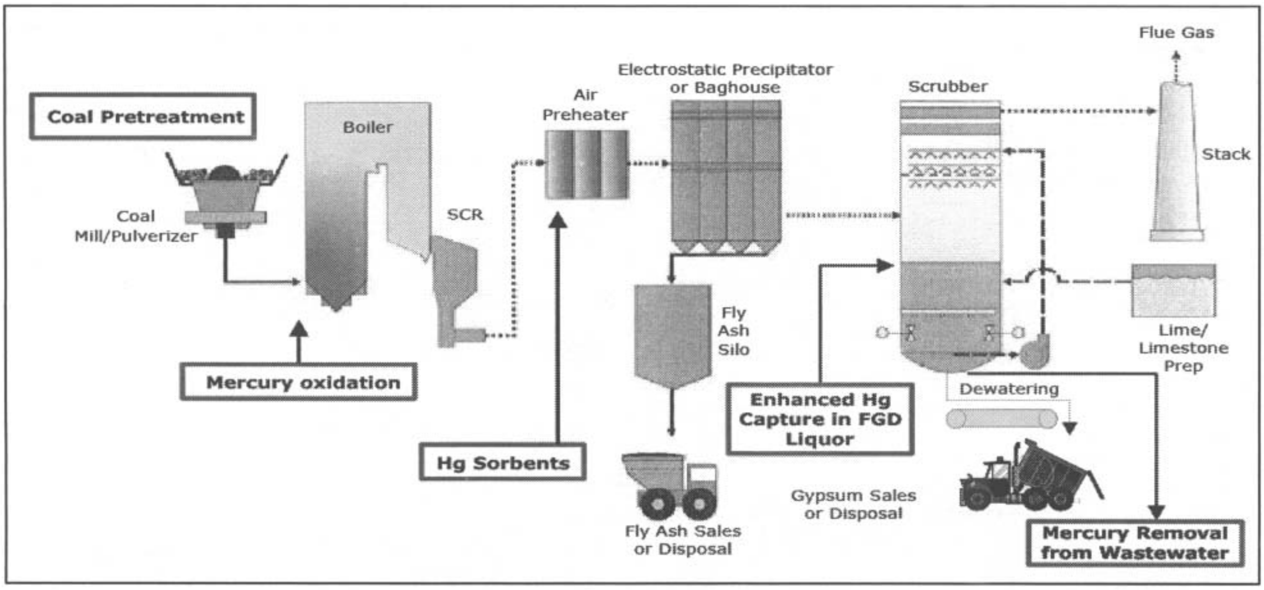

Figure 2. Mercury control technologies and their respective points of application for the control of mercury emissions from coal-fired power plants.

As a result, like alumina refineries, there is no single, universal solution for controlling mercury emissions from coal-fired power plants. Rather, a wide range of complementary control technologies can be employed to cater to the broad range of process conditions and plant operations in facilities where better control of mercury emissions is required. By understanding the process, where the problems are and what form they take, a suite of various control measures can be selected and employed together, as necessary, to effectively target the needs of each specific site (Figure 2).

While the details of the various control strategies can be complex, a brief overview of some of the key technologies that have been developed by Nalco and are now in use within the industry are presented below.

Coal pretreatment

One option to limit the emission of mercury and other contaminants from a power plant is to prevent them from entering the process in the first place. While beneficiation of coal to enhance thermal output has been long practiced, the removal of minor elements such as mercury is more problematic. Nalco has developed a technology known as MagMill™ which can remove a large fraction of many of the heavy metals (e.g. Hg, Se, As) present in coal. This is completed in a dry process before the coal is burned. A combination of crushing, belt separation, and high powered magnets removes abrasive minerals like pyrites. By targeting the removal of pyrites, a high degree of mercury removal can be achieved since mercury in coal is known to be associated with pyrite occurrence.[16] The result of processing the coal with MagMill is a product that is a cleaner, less abrasive coal with lower sulfur and heavy metal content.

Mercury oxidation / speciation control

Capture of mercury in downstream particulate control devices and/or scrubbers can be enhanced if the mercury is in the oxidized state (Hg^{2+}) rather than the elemental form (Hg^0). To facilitate the conversion to the oxidized state, boiler additives can be applied to increase the relative proportion of oxidized mercury in the flue gas. For example, Nalco has developed a solution product that can be applied directly to the coal prior to combustion. It can be added to the coal at the pulverizers, or injected directly into the furnace. In numerous commercial trials, the fraction of mercury in the oxidized state has been increased to as high as 90%.[17] By using such mercury oxidants the performance of mercury sorbents, including activated carbons, is significantly enhanced. This can be a major benefit to plant operations since, by using this technology, a reduction in sorbent feed rates (and thereby operating costs) can be achieved.

In addition to reducing sorbent costs, this can also result in the preservation of a plant's ash sales since high carbon feed rates will render the fly ash unsuitable for use as a pozzolan in concrete manufacture.[18] By reducing sorbent feed rates or eliminating the need for sorbents entirely, the value and quality of the fly ash sold by the plant to the concrete market can be maintained.

While the fly ash is nominally a "waste product", the value can be quite substantial for those plants that are able to sell their fly ash. For example, a typical 500 MW plant generating 150,000 tons of fly ash annually that can be sold for $20/ton, risks $3 million per year in lost revenue by injecting activated carbon as a sorbent to control mercury emissions. In addition, the plant may incur an additional fly ash disposal cost of at least $1.5 million per year as a result.

Mercury sorbents

One of the most promising technologies to recently emerge for the control of flue gas mercury emissions is the use of mercury sorbents. Powdered sorbents such as activated carbon or engineered inorganic sorbents can be injected into the ductwork upstream of a plant's particulate control device to capture mercury.[19] In this way, mercury is removed from the flue gas and becomes commingled with the fly ash which can then be safely disposed of or, depending upon the quality of the ash, used in various applications including concrete, pavement, structural backfill, and brick manufacture. Activated carbon injection (ACI) is by far the most established technology in this area with over 60,000 MW of commercial bookings at over 150 coal-fired plants in North America as of June of 2010.[20]

Enhanced mercury capture in FGD liquor

The application of mercury oxidation technology as described above is especially well suited to those plants that have wet flue gas desulfurization (FGD) units installed for SOx control, where the ionic form of mercury readily dissolves in the aqueous liquor phase. With the bulk of the mercury shifted from the gas phase to the aqueous phase, a coagulant product can be applied to sequester and precipitate the mercury from FGD liquors without any concomitant measurable increase in the mercury content of FGD byproducts. This also has the effect of suppressing the phenomenon of FGD mercury re-emission whereby oxidized mercury in the aqueous phase is reduced back to the elemental form and emitted from the stack.[21]

Mercury removal from wastewater

In order to meet challenging industrial wastewater mercury discharge limitations, companies often turn to precipitation aids. For this application Nalco has developed polymeric chelants with an exceptionally high affinity for mercury. Upon binding mercury from solution, it forms large precipitates that flocculate, settle, and are readily filtered to consistently attain extremely low mercury levels in the parts-per-trillion range.

Case Studies

The various technologies outlined above can be applied, either individually or in many cases in concert, to reduce and control mercury emissions. These strategies have been applied in a number of commercial power plant operations with excellent results. Two examples of how these technologies have been applied, each outlining how different control strategies can be used to achieve the desired results, are presented as case studies.

Case study #1:

Site description: 600 MWe pulverized coal-fired boiler firing sub-bituminous coal with low NOx burners, overfire air, and cold-side electrostatic precipitator (ESP).

The overall aim of the operation was to increase mercury capture without impacting plant operations. Therefore, simply increasing the activated carbon injection (ACI) rate was not an option, as this would have compromised the quality of the fly ash produced at the plant, which was being sold for use in concrete. Thus, a 90% mercury capture with an ACI rate of less than 2 lb/MMacf was sought.

The "normal" operation involved use of a halogenated carbon added to the outlet of the air pre-heater. Under such an operating mode, using an ACI rate of 2 lb/MMacf, the reduction in mercury was less than 80% (Figure 3). Increasing the ACI rate improved mercury capture, however the target of 90% capture was only reached using an ACI rate well above 3 lb/MMacf.

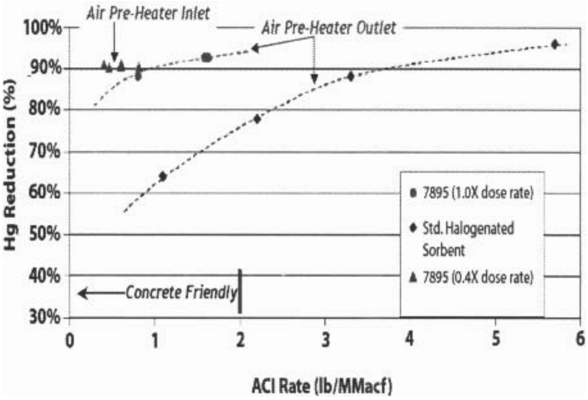

Figure 3. Percent total mercury capture as measured from air heater inlet to stack plotted as a function of ACI rate.

Two separate strategies were employed to try and achieve the desired goals. In the first, a solution of the oxidant, MerControl™ 7895 was applied (at a 1.0X dose rate) while the ACI rate to the pre-heater outlet was maintained using a non-halogenated carbon sorbent. This treatment resulted in a significant increase in mercury capture as shown in Figure 3. Greater than 90% capture was achieved well below the target ACI rate of 2 lb/MMacf.

While this was an excellent outcome, a review of the operation in total indicated that further efficiencies could be obtained by a slight change in operating conditions. By injecting the non-halogenated carbon sorbent to the air pre-heater inlet instead of the outlet, and then applying the MerControl 7895 product at a significantly lower rate (0.4X dose rate), a 90% capture rate of mercury could be maintained with an ACI rate of less than 0.5 lb/MMacf.

Case study #2:

Site description: 192 MWe pulverized coal-fired power plant firing high chlorine bituminous coal with selective catalytic reduction (SCR), cold-side ESP, and wet FGD.

The goal at this utility was to achieve greater than 85% mercury capture to reach an emissions target of 0.008 lb Hg/GWh *and* meet mercury water discharge regulations.

In this case, two separate issues needed to be addressed. First, improved capture of the mercury from the gas phase was required. Similar to the previous example, MerControl 7895 was applied to the coal feed to help achieve this. Additionally, the discharge of mercury in the plants wastewater was strictly controlled. While the improved capture from gas could be achieved, further containment and control of the mercury from the aqueous environment was required. For this purpose, a polymer chelant product (e.g., Nalmet® 1689) was used to treat the FGD wastewater.

Figure 4 shows the stack emissions of total mercury (in both elemental and oxidized forms) plotted across a range of dose regimes of the MerControl 7895 product. The same data are plotted as a percent of mercury capture. Application of MerControl 7895 at a rate of 265 mg/kg of coal resulted in greater than 85% mercury capture and achieved the target of 0.008 lb Hg/GWh. The net result of this treatment was that the bulk of the mercury reported to the FGD liquor.

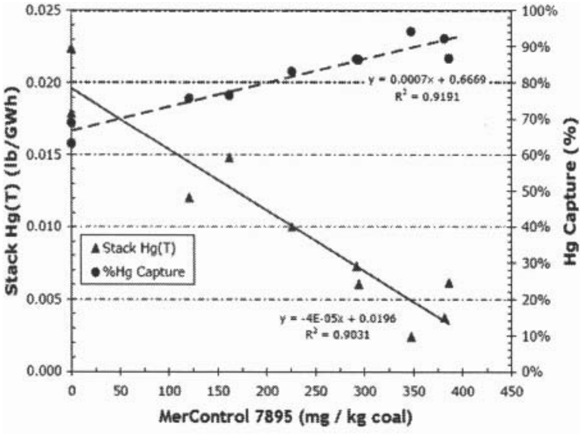

Figure 4. Stack emissions of total mercury and percent mercury capture plotted as a function of MerControl 7895 dose.

Without treatment, the mercury concentration in the FGD wastewater was historically observed to be in the range of 10,000 – 30,000 ppt. Treatment of the FGD wastewater with the polymer chelant, Nalmet 1689, reduced mercury concentrations to well below 200 ppt. Additionally, while the MerControl 7895 increased the amount of mercury capture from the flue gas – and therefore reporting to the FGD liquor – the use of chelant ensured that the mercury concentration in the clarifier effluent stream was maintained below 200 ppt.

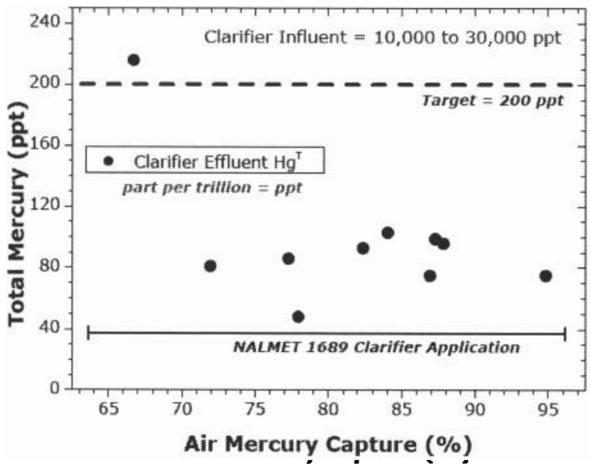

Figure 5. FGD waste water mercury concentration plotted as a function of percent mercury capture from air. As more mercury is captured from the air (by application of MerControl 7895) the application of Nalmet 1689 maintains mercury levels well below 200 ppt.

Figure 5 shows the measured total mercury concentration in the clarifier effluent as a function of increasing mercury capture from the air. Despite the increasing load of mercury being captured and delivered to the scrubber liquor, the chelant treatment was able to maintain the effluent concentration well below the allowable target concentration. As shown in Figure 6, the mercury content of the clarifier solids increases with increasing air mercury capture. One can conclude then that as the MerControl 7895 oxidizes the mercury, it shifts from the gas phase to the scrubber liquor. The chelant addition in turn transfers the added mercury load from the liquor to the clarifier solids. With the mercury partitioned to the clarifier solids, it is then easily removed by standard wastewater treatment equipment.

The application of this customized, low capital program enabled regulatory compliance for air *and* water mercury emissions, thereby shrinking the plant's environmental footprint.

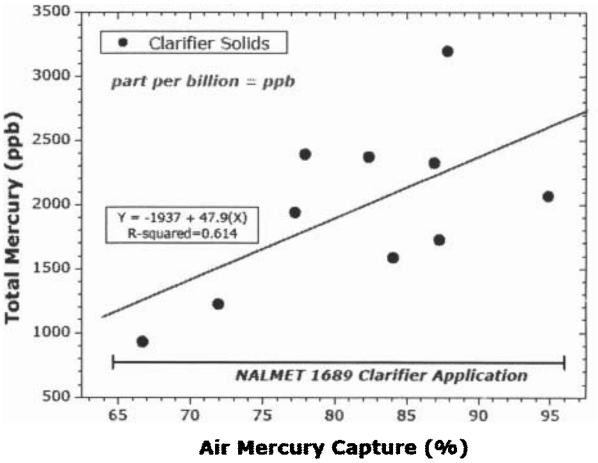

Figure 6. A plot of total mercury concentration of the FGD wastewater clarifier solids as a function of mercury capture from air. As capture of mercury from air increases, the concentration of mercury in the solids increases proportionately due to the application of Nalmet 1689.

The use of coal as a power source for Bayer plants is common with coal accounting for approximately 20% of the energy used in the production of alumina.[22] In many cases, the Bayer refinery operates their own coal-fired power plant as part of the overall refinery operations. Therefore, as noted above, such power plants can be a significant source of mercury emissions and in such cases, the control technologies described above, will clearly have a direct fit to the industry.

Conclusions

Atmospheric emissions from alumina refineries are increasingly a problem with mercury being a common issue across the industry. However, similar issues are being faced by a number of other industries and a range of potential solutions are being developed and used for air emission and wastewater control generally, and in particular for mercury capture and control.

Studies of various Bayer refineries have shown that both the amount of mercury emissions and the points in the process at which they are emitted vary quite drastically from refinery to refinery.[7] The complexity of the problem stems from the various sources of bauxite and the differences in operating conditions employed at particular refineries. As is the case with coal-fired power plants, the issue of mercury emissions is so highly plant specific that a detailed knowledge of the various process steps and chemistries as well as the ability to accurately measure mercury in various process streams will be essential to delivering a customized solution for each individual refinery. It is expected that the aforementioned mercury control technologies in use at coal-fired power plants can be adapted to meet the needs of the alumina industry. Whether this will involve the removal of mercury from digestion liquors or the oxidation and sorption of gas phase mercury from digestion vents and calciner stacks, or some combination thereof, will ultimately depend on the particular needs of the refinery in question.

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