

MERCURY EMISSIONS IN THE BAYER PROCESS – AN OVERVIEW

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Abstract

Bauxite contains trace amounts of mercury (0.02–1.5 mg/kg) but due to the large mass of bauxite processed in Bayer refining, mercury can accumulate in Bayer liquor, aluminium hydrate, and oxalate. The mercury emissions to air from Bayer refineries were speciated for elemental, ionic, and particulate mercury using a FMSS (flue gas mercury sorbent speciation) method. The mercury emissions to air from Bayer refineries are almost 100% elemental mercury from studies of emissions from Alcoa Bayer refineries. These emissions pose very little environmental risk to the local or regional environment because the residence time of elemental mercury in the atmosphere is 1–1.5 years. Elemental mercury emissions do contribute to the global atmospheric reservoir of mercury and reducing mercury emissions is important in reducing anthropogenic contributions to the global atmospheric mercury budget.

The study showed that mercury losses from Bayer refineries differed significantly from refinery to refinery. Some refineries had significant mercury emissions from calcination due to mercury in the aluminium hydrate while other refineries had a significantly higher portion of the mercury emissions from digestion vent gases. The data showed losses of mercury to air (emissions) from digestion vent gases for all the refineries studied. High concentrations of mercury on oxalate cake were found for some refineries. The proportion of input mercury reporting to the residue ranged from 12–60% for all Alcoa refineries.

1 Introduction

The amount of mercury released to the biosphere from human activity has increased since the beginning of the industrial age. Mercury is distributed in air, water, and soil in small amounts, and can be mobile within and between these media. Mercury has a ubiquitous distribution and is present throughout the environment in trace and ultra-trace quantities [Press, 1978]. The most commonly recognised form of mercury is metallic or elemental mercury. Additionally, ionic forms of mercury can exist in both inorganic and organic forms. Mercury, usually in inorganic form, is present in all classes of rocks including limestone, shales, sandstone, basalt, and others. It is found in igneous rocks of all classes and massive quantities were released into the early earth's atmosphere by volcanic activity. Normal soils typically contain 20–150 ppb mercury, but near known deposits of cinnabar the level can be much higher [WHO, 1976].

Mercury vapour can travel over great distances in the atmosphere, and is deposited worldwide into lakes and streams. Under anaerobic conditions, newly deposited and bioavailable mercury can undergo a biomediated transformation to monomethyl mercury (MMHg) or dimethyl mercury (DMHg). MMHg can bioaccumulate and bioamplify through the food chain especially in the aquatic food chain. Bioaccumulated MMHg in fish tissue can endanger populations of animals and humans that feed further up the food chain.

Human activities have resulted in the release of a wide variety of both inorganic and organic forms of mercury. Important sources of mercury to the biosphere are from the chloro-alkali industry, metal sulfide ore smelting, cement production, gold refining and especially fossil fuel combustion and incineration of sewage sludge and municipal garbage [Williams, 1994]. Natural gases found around the world contain trace amounts of mercury with reported contents from 0.005 up to 300 ppb depending upon the source [Yen, 1991]. The power utility industry, chloralkali industry, and the burning of fossil fuels (coal, petroleum, etc.) release elemental and ionic mercury into the atmosphere. Metallic and ionic mercury have also been released directly into

fresh and sea water by industry. Historically, both phenylmercury and methylmercury compounds have been released into fresh water and seawater – phenylmercury by the wood paper-pulp industry, particularly in Sweden, and methylmercury by a chemical manufacturer of acetaldehyde in Minamata, Japan.

Environmental concerns have brought about numerous regulations that have dramatically decreased both the use and production of mercury since the late 1980s. This trend is likely to continue into the future, as the world eliminates the demand for mercury to support prior industrial processes and products. The European Community has set a limit of 50 µg/m³ for mercury emission from municipal waste incinerators. Still there are no current regulations for mercury emissions from electric power utilities, although the United States Clean Air Act Amendments of 1990 have required the United States Environmental Protection Agency (US EPA) to perform a study of mercury emissions from several industrial sources to establish technically achievable and safe mercury emission levels. In the future the US EPA will establish significantly more stringent regulations for mercury emissions from coal power and other industries that emit mercury to the atmosphere.

Recent reporting for the Toxic Release Inventory (TRI) in the US and National Pollutant Inventory (NPI) in Australia by the aluminium manufacturing industry has shown that Bayer refineries emit mercury from the processing of bauxites that contain ultra trace amounts of mercury. The data presented in this paper will show that almost all of the mercury emitted from Bayer refineries is elemental mercury. These emissions pose very little environmental risk to the local or regional environment because the residence time of elemental mercury in the atmosphere is 1–1.5 years [Linqvist, 1985, Mason, 1994]. However, elemental mercury emissions do contribute to the global atmospheric reservoir of mercury and reducing mercury emissions is important in reducing anthropogenic contributions to the global atmospheric mercury budget. Alcoa World Alumina (Alcoa) is committed to a program to reduce mercury emissions to air from its Bayer refineries by 80% by the year 2008.

2 Air Sampling and Analysis Methods

Three complementary methods were used in the air emission sampling of process stacks and vents in Alcoa refineries. The choice of the method depended upon the information being sought for that emission source. The Sorbent Total Mercury (STM) method uses a single iodated, carbon sorbent trap and is very robust. The Fluegas Mercury Sorbent Speciation (FMSS) method added the selectivity of a mini-particulate filter and potassium chloride (KCl) coated quartz trap upstream of the iodated carbon trap to capture and quantify the particulate, gaseous oxidised and elemental mercury species, respectively. The third method, based upon the Lumex RA915+, Zeeman AAS detector, was selected to provide real time mercury concentration data with low detection limits and good selectivity for mercury. The Lumex detector relied upon a custom-built front-end dilution and water dropout module to handle the challenging gas matrix types and high mercury concentrations. Most vents were sampled in duplicate or better. Many of the emission sources were measured using two different methods, which provided independent confirmation of the mercury concentrations values.

The STM method is based on the quantitative adsorption of gaseous mercury to iodated carbon (IC) sorbent trap. A known volume (± 0.10 litre) of gas was pulled through the IC sorbent trap using standard sampling equipment including a quartz probe liner, heated probe, silica gel water trap, mass flow meter, and pump. The temperature of the IC sorbent trap was kept at $120 \pm 5^\circ\text{C}$ during sampling to avoid water condensation in the trap. The water in the vent gas condensed in the silica gel water trap behind the IC sorbent trap. The water is quantified by weight difference to provide a backup value for percent water and also to calculate a wet sample volume needed for select vents. The iodated carbon is leached of collected Hg in the lab using hot refluxing $\text{HNO}_3/\text{H}_2\text{SO}_4$, then further oxidised with 5% BrCl solution. Aliquots of the digest are analysed using cold vapour atomic fluorescence spectrometry (CVAFS) following the analytical procedures of EPA Method 1631. The STM method has been widely used for both ambient air and total Hg in flue gas matrices [Bloom, 1993, Bloom, 1995, Presbo, 1995]

The FMSS method relies on sequential selective capture to separate and quantify three mercury species, namely particulate Hg (PHg), gaseous oxidised Hg^{2+} , and gaseous elemental Hg^0 . A known volume (± 0.10 litre) of gas is pulled through the FMSS sorbent train using standard sampling equipment using a quartz probe liner, heated probe, silica water trap, mass flow meter and pump. The FMSS method was set up to sample semi-isokinetically to more accurately quantify the PHg using a buttonhook nozzle directed into the vent gas flow. The PHg was captured on a quartz fibre filter with the gas phase Hg^{2+} and Hg^0 passing through to be captured on potassium chloride (KCl) coated quartz sorbent trap, and finally the iodated carbon (IC) sorbent trap, respectively. The temperature of the FMSS sorbent train was kept at $120 \pm 5^\circ\text{C}$ during sampling to avoid water condensation in the trap. The water in the vent gas condensed in the silica gel water trap behind the FMSS sorbent train. The water was measured by weight difference to provide backup for the percentage water estimation, and also to calculate wet sample volume as needed for select emission sources. The sorbed Hg^0 on iodated carbon and the PHg on the quartz filter was leached of collected Hg in a clean lab using hot-refluxing $\text{HNO}_3/\text{H}_2\text{SO}_4$, then further oxidised by 5% BrCl solution. Aliquots of all three Hg species digests were analysed using cold vapour atomic fluorescence spectrometry (CVAFS) following the analytical methods of EPA Method 1631. The FMSS and precursor method has been widely used for measuring mercury species in flue gas matrices [Nott, 1995, Laudal, 1997, Grover, 1999]. The FMSS method has recently undergone rigorous validation experiments in coal flue gas against the ASTM promulgated Ontario-Hydro Method [DOE, 2001, EERC, 2001].

The development of a real time measurement capability to measure mercury in the challenging conditions in the stacks and vents was an integral part of the air emissions monitoring effort. The approach was to use a newly developed technology, the Lumex RA915+ instrument. Since, this instrument was untested in the harsh plant environments of a Bayer refinery; multiple sampling was needed to evaluate the

instrument for accuracy and precision. The Lumex RA-915+ mercury analyser is based upon cold vapour atomic absorption spectrometry at a wavelength of 253.7 nm characteristic of elemental mercury atoms. The Lumex achieves a low detection limit of 5 ng/m^3 by using a multi-path absorption cell with an effective pathlength of approximately 10 metres. Selectivity is achieved primarily by the Zeeman Effect using high frequency modulation of light polarisation (ZAAS-HFM). Briefly, the radiation source, a glow discharge mercury lamp, is placed in a permanent magnetic field, whereby the 253.7 nm mercury resonance line is split into three polarised components: pi, s+ and s-. The polarised light source is further manipulated by passing it through a polarisation modulator at 50 kHz so that each component of the signal can be separated in time. Narrow-band, high reflectivity mirrors in the absorption cell are used to help isolate only the 253.7 nm resonance light and suppression of all non-resonance and stray radiation achieves further selectivity. Only two components of the original light source, the circularly polarized s+ and s- are detected for quantification. When the polarized light is observed along the magnetic field lines, only the s-component's light is registered, one s-component being settled under the absorption line envelope and the other one being settled outside it. Thus in the absence of mercury vapour in the absorption cell, the intensity of the s+ and s- light will be equal. When elemental mercury atoms are present in the absorption cell, the greater the mercury concentration, the greater will be the difference in the s+ and s- light as detected by the photo-detector. Because the spectral shift of the s-components is significantly smaller than the width of any molecular absorption bands or scattering spectra, the background absorption caused by interfering components does not affect the analyser measurement of mercury concentration. Thus in this measurement technique, the analytical signal depends only on the mercury concentration and is independent of the presence of dust, aerosols, and other foreign contaminants in the analytical cell.

Over the course of the study, a standard protocol for the Lumex was employed at a selected set of stack and vent emission sources. However, the application of the Lumex dilution method is not routine and trouble free. Considerable operator skill is required to obtain meaningful data due to the complexities of vent and stack sampling in Bayer refineries.

The concentration of total mercury in the 20 selected air emission stacks and vents at Plant I (see Table 1) ranged from 0.009 to $31,881 \mu\text{g/m}^3$ – over six orders of magnitude. This range was not significantly different from the range in concentrations observed in the vents and stacks for Plant E in a similar type of study. The ranges in concentration make the analytical measurement of these stacks and vents very challenging. The vent/stack mercury concentration data are supported by quality assurance data, which suggest good precision in the measurements. The intercomparison of 13 of the 17 serial field duplicates for the air emissions measurements had a relative percent difference (RPD) less than 30% and 11 of the 17 were less than 20%. The 4 duplicate samples that had RPDs greater than 30% were not expected to be in good agreement because they were either close to the estimated detection limit or there was a trend observed in the mercury concentration. Considering the variability inherent in the process, challenging field conditions, non-simultaneous samples and only duplicates ($n = 2$), the precision of the data is excellent.

2.1 Process Solid and Liquid Analysis Methods

Solid and liquid process samples were taken in the Bayer refineries as part of the emissions and mass balance studies. Solid samples were thoroughly pulverized to aid complete dissolution. Digestions were carried out in ultra-clean 60 mL or 140 mL solid Teflon® digestion bombs. The bombs were pre-cleaned by filling with a mixture of 1.8% HNO_3 and 0.2% HF in deionized water, the caps screwed on tightly and the vessels heated overnight in a clean oven at 105°C . After cleaning, the vessels were thoroughly rinsed with deionised (DI) water and placed in a Class-100 clean air laminar flow bench to dry.

All solids were digested in Teflon® bombs using a mixture of HNO_3 – HF – HCl acids and the solutions were analysed using CVAFS [Bloom, in press]. An aliquot of the sample (0.5 grams) was weighed to the nearest milligram into a clean low-pressure Teflon® digestion

bomb (Saville, Minnetonka, MN, USA). To the sample were added 18 mL of HNO₃, 9 mL of HF and 3 mL of HCl. All acids used in this work were trace-metals grade, previously analysed and found to contain less than 10 pg/mL of Hg. The cap of the bomb was replaced, and tightened with manufacturer-supplied torque wrenches, and vigorously shaken to disperse the solids in the acid. This step is critical to avoid incomplete digestion caused by the formation of an insoluble coating on the surface of the solids. After all of the bombs were prepared, including method blanks, certified reference materials, duplicates and matrix spikes, the bombs were placed into a vented stainless steel oven heated to 125 ± 5°C. The samples were digested for 12–15 hours, with periodic shaking. The bombs were then cooled to room temperature and the contents diluted to 100 mL with DI water. The diluted sample was poured back into its original bomb for storage until subsequent analysis. Aliquots of the digest, ranging from 0.01 to 2.0 mL were analysed by dilution to 100 mL with DI water, reduction to Hg⁰ with SnCl₂, purge-and-trap on gold coated sand traps, thermal desorption into an argon gas carrier, and quantification by cold vapour atomic fluorescence spectrometry [Bloom 1988, Creclius, 1983].

3 Discussion

Mass balances based on mercury inputs and outputs were estimated at nine refineries worldwide. Measurement of the mercury concentration and mass flows of the major input and output streams for the Bayer refineries was the basis for preliminary mercury mass balance estimates. The graph in Figure 1 shows the concentration of mercury in bauxite for various sources used by Alcoa refineries. The data in Figure 1 demonstrate the considerable range (almost three orders of magnitude) of mercury concentrations between bauxite sources. Some bauxites like Bauxite 1 have mercury concentrations in the parts per million range while others (Bauxites 9 and 10) have very low mercury concentrations that range from 20–70 parts per billion.

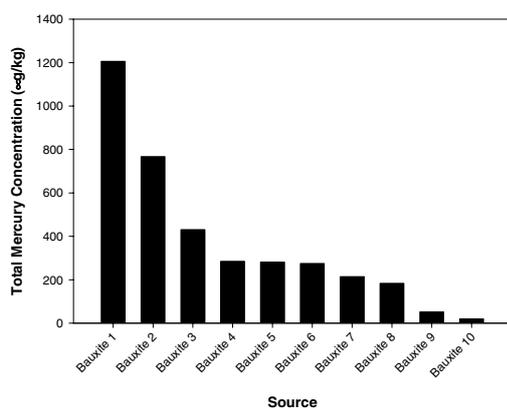


Figure 1: Concentration of Mercury in Various Bauxite Sources Worldwide

The mercury mass balance estimates for the various Bayer refineries reported in Table 1 were generated from composited samples of bauxite, samples representative of bauxite residue to lake (i.e. last washer underflow and sand), hydrate from the filters and alumina.

Annual composite samples were used for most of the data in Table 1. Table 1 shows the emission of mercury to air based upon mass balance estimates. The mass of mercury reporting as an air emission in kg per year is based upon the difference between the input and output mass of mercury in the particular refinery. The results of the mass balances were dominated by the mercury concentration and mass flow of both the bauxite input and bauxite residue. For some refineries a significant exit for mercury can occur in the oxalate or hydrate. Based upon the detailed sampling studies at two refineries, the yearly estimates for mercury emissions to air for some of the refineries in Table 1 are likely to be an overestimate. All mercury losses such as to oxalate or to the cooling ponds via condensate are not accounted for in the estimates in Table 1. In subsequent studies for Plant I in which air emission measurements were coupled with a very detailed process solid and liquid sampling program, a significant mercury mass loss was identified in oxalate cake, process condensate to lakes and residue. Although the initial studies in Table 1 provide a broad mercury balance for the refineries, a more detailed mass balance study is required to identify and quantify the specific emission sources at a refinery and improve the accuracy of the estimated air emission.

As described above, the data in Table 1 show that the amount of input mercury to a refinery is dependent upon the bauxite source (i.e. concentration and mass) and that the amount of mercury as a percentage of the input mercury that reports to the residue can be significantly different between refineries. For example, the percentage of mercury reporting to bauxite residue in Refinery H is significantly higher at 60% of the total input mercury mass than that of Refinery B, which is approximately 10–15% of the mercury input. The reason for this difference is not well understood.

Tests to show the relative extractability of mercury from bauxite were conducted to help explain the differences observed in mercury reporting in residue. A sequential extraction method was employed to investigate the nature of the mercury in various bauxites. The method chosen has been used successfully to differentiate the mercury binding capacity in various mine tailings and soils [Bloom, 1999]. The method can be used qualitatively to gain better insight into the mercury speciation of the sample. The graph in Figure 2 shows the results of a set of sequential extractions on bauxites from three different mines (sources). The data in the column-groups of Figure 2 labelled F1 to F5 are the percentages of the total mercury in the bauxite samples extracted at each sequential extraction step. The definitions of F1 to F5 are shown in Table 2. The species types extracted at each extraction step are also shown in Table 2. Inorganic Hg speciation was determined by sequential selective extractions of separate 0.4 g aliquots of the homogenized solids as indicated in the graph in Figure 2. The extraction was performed using a 100:1 liquid-to-solids ratio in 40 mL vials. Each extraction step was conducted for 18 ± 3 hr, with constant agitation at 18–22°C. At the end of each step, the samples were centrifuged and the supernatant liquid was filtered through a 0.2 µm filter. The residual solids were then re-suspended in the same extractant, re-centrifuged, and re-filtered. The two filtrates were combined in a 125 mL bottle, the mercury oxidized by the addition of BrCl and diluted to 125 mL prior to analysis for total Hg by EPA Method 1631. After the rinse step, the sample pellet in the centrifuge tube was resuspended in the next extractant, and the entire process was repeated.

Table 1: Comparison of Estimated Mercury Emissions for Alcoa Bayer Refineries Worldwide

Plant	Estimated Hg Losses (Air) (kg/yr)	Mercury Input (kg/yr)	% Reporting to Residue	Liquid Hg Collected (kg/yr)
Plant A	630	811	21	11
Plant B	311	353	12	0
Plant C	424	487	13	0
Plant D	22	27	19	0
Plant E	932	1261	25	15
Plant F	378	492	15	0
Plant G	351	790	43	0.3
Plant H	715	2830	60	100
Plant I	277	369	25	0

Table 2: Sequential Extraction Method

Step	Extractant	Description	Typical compounds
F1	DI water	water soluble	HgCl ₂ , HgSO ₄
F2	pH 2 HCl/HOAc	“stomach acid”	HgO
F3	1M KOH	organo complexed	Hg-humics, Hg ₂ Cl ₂
F4	12M HNO ₃	strong complexed	mineral lattice, Hg ₂ Cl ₂ , Hg ⁰
F5	aqua regia	cinnabar	HgS, m-HgS, HgSe, HgAu

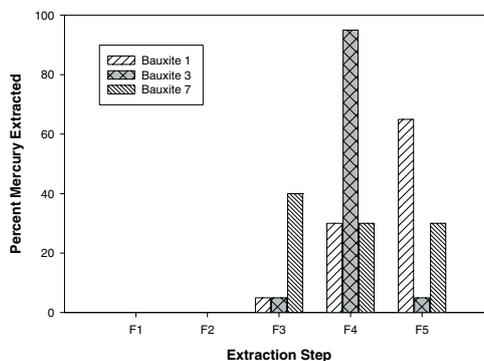


Figure 2: Percentage Mercury Extracted from Bauxite in Sequential Extractions

The graphed data in Figure 2 shows that mercury from Bauxite 7 is more easily extracted than the mercury from Bauxite 1, whereas Bauxite 3 lies somewhere in-between. The sequential extraction procedure demonstrates that mercury is bound quite differently in bauxites from various mines and may help partially explain the differences in the chemistry of mercury extraction observed in associated refineries. The data in Figure 2 also suggest that the mercury bound in Bauxite 1 is HgS or some other refractory mercury mineral that is not easily extracted in the Bayer liquor.

Selected solid and liquid process samples were taken during the survey of the nine refineries. Comparisons of the concentrations of mercury in the solid and liquid samples were made and the data are shown in Table 3. The data in the table are reported as µg/kg mercury.

Several important observations can be made from the data in Table 3. The concentration of mercury found in hydrate is low in all the refineries studied except for refineries E and G. These two refineries have significantly higher concentrations of mercury associated with the hydrate. The amount of mercury in liquor can also be significantly different across the refineries. For example, refinery H has high levels of mercury in the liquor, while refinery B and others have much lower concentrations of mercury in liquor. The amount of mercury reporting to the hydrate does not appear to be related to the concentration of mercury in the liquor to precipitation (LTP) based upon this small data set. More data are needed to draw a firmer conclusion. The data in this table demonstrate that the amount of mercury in oxalate can vary three orders of magnitude between the refineries.

Table 3: Comparison of Refinery Process Solid and Liquid Mercury Concentrations [Smith, 2002]

Sample	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F	Plant G	Plant H	Plant I
Bauxite	302	49	44	30	280	197	284	A 360 B 1153	47
Mud	111	9	12	11	250	90	347	1280	11
Sand	138	8	4	Na	Na	33	Na	670	7
Hydrate	5	8	13	1	200	7	84	6	7
Alumina	2	1	0	0	7	6	8	1	0
Condensate	20	12	1	10	6	1	1	4	2
Caustic	0	0.1	0.1	0	0.2	13	0	0	0
Lime	0.6	0.1	0.1	0.1	13	5.1	0.3	130	0.1
Lxp	Na	1	7	Na	14	Na	Na	329	34
Ltp	0.6	4	11	4	38 Reg 26 Iso	Na	8	372	34
Oxalate	18	9	2061	Na	4026 ¹	Na	Na	Na	2000– 3500

Liquids are in ug/L (ppb by volume) and solids are µg/kg (ppb by mass). ¹Oxalate cake contains fine carbon

The data in Table 3 have implications for the interpretation of mercury emissions from the refineries. Refineries which have high concentrations of mercury on hydrate as shown on the table and low concentrations of mercury in the alumina product will have mercury emission losses from their calciners. Mercury emission losses have been measured in the process gas stream using the Lumex analyser and iodated carbon traps from the calciner stacks for Plant E. These data have shown that for this plant, a large percentage of the input mass of mercury is lost from the calcination stack as mercury emissions to air. Refineries that have significant concentrations of mercury on their oxalate will have mercury losses to air if the oxalate is burned as a method for disposal. Air emissions measurements made from a kiln in Plant C, which burns oxalate-containing mercury, have shown measurable mercury emissions from these stacks.

The data in Table 3 are snap-shots in time and are taken from either composite or grab samples. Subsequent work has shown that the mercury concentration in process liquor and solids can vary significantly depending upon changes in bauxite source and changes in process conditions. For example, the mercury concentration in hydrate for Plant G has been shown to change an order of magnitude over a 6–8 month cycle. More time-series data will be required to better understand the process variability of many of these variables in both the long and short term.

Detailed mercury surveys were conducted at two refineries, I and E. Air emission samples, and solid and liquid samples were collected for each major unit process in the refinery. The air emission samples were taken as described in the sampling and analysis section of this report. The solid and liquid samples were analysed as described using an $\text{HNO}_3/\text{HF}/\text{HCl}$ digestion. All samples were analysed by Frontier Geosciences in Seattle, WA, USA. The data in Table 4 show the speciation of mercury in the major process gas streams in Bayer refineries using the FMSS method. These data clearly show that elemental mercury is the predominant form of mercury emitted to

air from Bayer refineries. This is in contrast to the power utilities and municipal waste incinerators, which emit mercury to air in elemental, ionic, and particulate forms.

The species of mercury emitted from an industrial source such as a Bayer refinery is important from an ecological risk perspective. Elemental mercury emitted from Bayer refineries does not pose an immediate environmental risk to the local ecosystem as does ionic and particulate mercury emissions. Ionic and particulate mercury emissions will generally deposit locally creating a local or regional environmental impact whereas elemental mercury with a residence time of 1.5 years is globally dispersed. Elemental mercury adds to the global mercury budget but does not present a local environmental or ecological risk.

The data in Table 5 show the estimated mass emissions of mercury from two Bayer refineries based upon an intensive program of sampling air emission sources and process solids and liquors over a week period. The data show a significant difference in the major mercury emissions source for each refinery. The data in Table 5 is the percentage mercury emission with respect to the total mercury input for the plant. Plant E emits most of the mercury into air from the calciner and digestion stacks. The process solid and liquid data in Table 3 show elevated levels of mercury on the alumina hydrate for this refinery and has much lower concentrations of mercury on hydrate for Plant I. Independent air emission measurements show much lower emissions for Plant I than Plant E from calcination, which is consistent with the concentration of mercury measured on hydrate. Evaporation and digestion are the major emission sources to air from Plant I. The data also show that oxalate cake in Plant I was between 2000–3,500 ppb. This, coupled with the significant daily mass of oxalate produced, resulted in the oxalate cake being a significant loss of mercury (~15% mercury mass input). The measurements of process gas emissions from the oxalate kiln shown in Table 4 show that the mercury emission is predominately Hg^0 as would be expected from these kinds of combustion processes.

Table 4: Results of Mercury Speciation in Bayer Process Streams using the FMSS Method

Sample	PHg $\mu\text{g}/\text{m}^3$	Hg^{2+} $\mu\text{g}/\text{m}^3$	Hg^0 $\mu\text{g}/\text{m}^3$	Total Hg $\mu\text{g}/\text{m}^3$	% Hg^0
Rod Mills	0.12	<MDL ¹	30.15	30.3	99.6
Slurry Storage	0.008	0.026	147	147	100
Non Condens.	0.063	0.603	5,287	5,288	100
Blow-Off	<MDL ¹	0.017	10.2	10.2	99.8
Vac Pump	2.52	0.244	31,878	31,881	100
Calciner Stack	0.09	<MDL ¹	2.91	3.00	96.9
Oxalate Kiln	0.30	0.598	477	478	99.8

¹ Method detection limit

Table 5: Data from Detailed Refinery Survey – Comparison of Two Refinery Mercury Emissions

Plant area	Plant I (%) ¹	Plant E (%) ¹
Digestion	30.2 ²	17 ²
Calcination	2	38
Mercury in Oxalate Cake	16	less than 1
Mercury in SGA or Hydrate Product	less than 1	5

¹Mercury mass as a percentage of total plant input. ²Includes digestion non-condensable, digestion vacuum vents, blow-offs, evaporation and slurry storage

4 Conclusions

Refinery mass balances for mercury can be estimated using careful air emissions and process sampling and analysis techniques. This paper has shown that with proper attention to detail in analysis and sampling, mercury emissions from a Bayer refinery can be estimated. Analytical techniques such as CVAFS and at-line measurements using AAS (Lumex) were found to be robust and provide the required sensitivity for Bayer refinery vent and stack measurements. The studies also showed that detailed mercury surveys offer more information about the fate and transport of mercury in the refinery than simple estimates using process solid inputs and outputs.

The concentration of mercury in bauxite varies significantly depending upon the source of the bauxite. Selective extractions of mercury from bauxite showed that the form of mercury is likely to be quite different between bauxite sources. This extractability difference is important for understanding the fate and transport of mercury under various digestion conditions.

The study presented in this paper compared the mercury emissions across nine Bayer refineries worldwide. This unique study allowed the comparison of plant emissions from refineries that have different sources of bauxite and different operating conditions. The comparison data for mercury emissions to air and mercury loss to bauxite residue show that refinery mercury outputs can differ significantly from plant to plant. Some refineries emit mercury to air primarily from calcination while other plants emissions are primarily from digestion. The high

mercury emissions from calcination originate from co-precipitated or adsorbed mercury on hydrate. The mechanism for mercury to co-precipitate with hydrate was outside the scope of this study.

One of the most important findings is that mercury emitted from Bayer refineries is predominately elemental mercury. This finding has important environmental implications in that elemental mercury emissions to air have a very small local environmental impact. Unlike Bayer refineries, power utilities burning coal emit mercury in three forms: elemental, ionic, and particulate. Power utility plants have a much higher impact on the local, regional, and global environment than do industries like Bayer alumina refining, which have fewer plants and emit predominately elemental mercury.

Acknowledgements

The authors would like to acknowledge the contribution of Carmelo Chiappalone from Environmental Consultancy Services and Phil Swartzendruber and Nic Bloom of Frontier Geosciences for their assistance in sampling and measurement of the mercury emissions presented in this report. Lastly, the authors would like to thank Michael Nunes and Winston Rennick, and the refinery laboratory teams for their valuable assistance and advice in sampling process liquors and solids in the refineries. The authors would like to thank Greg Peterson for his contributions to this paper.

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