

Case studies from the Cement sector

Case study on using alternative raw materials from Nigeria

To be completed

Case study from Pakistan

To be completed

Case study for sorbent injection

To be completed

Activated carbon filter - Lignite coke moving bed adsorber

Figure 7.1 shows the scheme of the cement works of Holcim in CH-Siggenthal equipped with a rotary cement kiln with a four-stage cyclone pre-heater. The clinker production capacity is 2300 t/d.

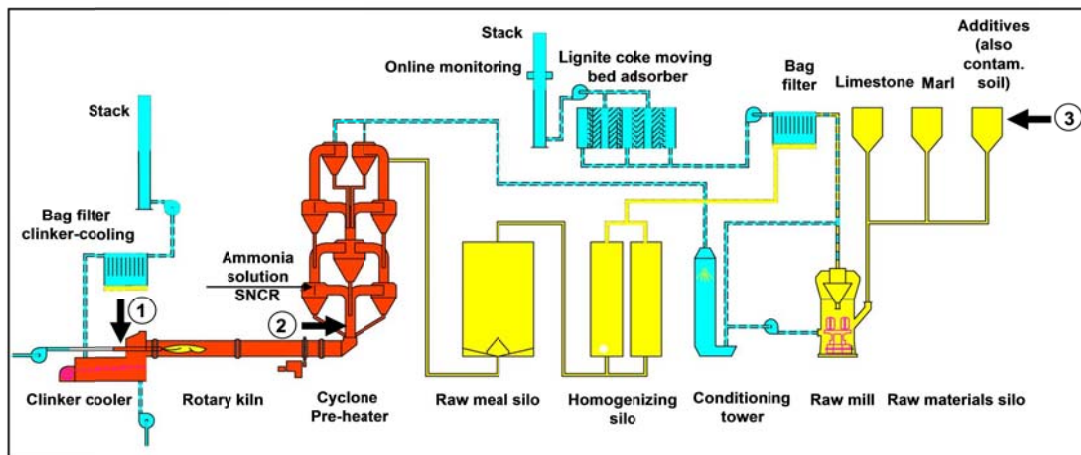


Figure 7.1: Scheme of the cement works of Holcim in CH-Siggenthal including the purification of the waste gas; the three input points for wastes and contaminated soils are indicated

Wastes and/or contaminated soils are fed into the system at three points (see the indications in Figure 7.1). At point 1, waste solvents, waste oil as well as meat and bone meal are fed; at point 2, dried anaerobically stabilised municipal sludge, tyres, PVC-free and ground plastic chips are fed; at point 3, contaminated soils and moulding sand are fed. Early in 1994, the plant was retrofitted with a lignite coke moving bed adsorber. For the application in cement works, the filter was developed as a prototype by the company Polysius AG. Although this plant is still successfully in operation, it remains the only one of its kind in the world in the cement sector.

In principle, the adsorber consists of several vertical filter beds packed with lignite coke. Each filter bed is subdivided into a thin bed (0.3 m) and a thick one (1.2 m). The waste gas from the bag filter is pressed through the lignite coke adsorber by the fan. The bed height is about 20 m.

In the first, thin bed, the waste gas is pre-cleaned while in the second, thick bed, the pollutants are further removed from the waste gas. The saturated lignite coke has to be replaced by fresh coke. This exchange takes place semi-continuously in small steps (every 3 h). Fresh coke is only charged to the thick beds through distribution troughs, moves down the filter bed (about 0.3 m/d). In the thin beds, the coke moves down to about 1.2 m/d. Therefore, it is called a moving bed adsorber. At the bottom of the thick filter beds, the lignite coke is withdrawn, and, by means of elevator conveyors, recycled back to the thin beds. Consequently, a counter current operation mode is achieved. In 2007, the former electrostatic precipitator was replaced by a well-designed bag filter to achieve low dust contents prior to the adsorber.

The laden coke is collected in a silo from where it is fed to the kiln at the burner's side (see position 1 in Figure 8.1). In the kiln, the organic pollutants are oxidised. The SO₂ is mainly incorporated as sulphate in the clinker. Most of the heavy metals are also incorporated in the clinker, except the volatiles ones, especially mercury and thallium which are not incorporated into the clinker but due to the adsorption to the lignite coke, the emission is low less than 5 µg/Nm³. As the lignite coke is recycled to the kiln, they accumulate in the system and have to be bled out from time to time. The concentration in the dust leaving the pre-heater is about 15- 25 ppm. When the raw mill operates in line with the kiln (about 80 per cent of the kiln operation time), this dust is mixed with the incoming raw material in the raw mill system. When the kiln is operating alone (raw mill down - about 20 per cent of kiln operating time), the filter dust can be discarded and high accumulation of mercury and thallium can be prevented. The shuttled dust is fed to the clinker during the final formulation of the cement (see paragraph 5.2.1).

Achieved environmental benefits

Mercury and thallium are adsorbed with an efficiency of more than 90 per cent.

Mercury and thallium are not fixed in the clinker and are present in the waste gas. They are removed in the bag filter via dust shuttling, and the lignite coke adsorber ensures that emitted concentrations are low (less than 5 µg/Nm³). More detailed measurement results are not available.

Cross-media effects

The electricity consumption of the main fan, which is placed prior to the lignite coke adsorber (see Figure 8.1), is the most important cross-media effect (about 900 kW). Related to the cement production in 2008 (953,000 t cement divided by 8424 H), it corresponds to 8.0 kWh/t cement. Compared to the overall electricity consumption for the cement production of 90-150 kWh/t cement, the percentage of this consumption is about 5.3 - 8.9 per cent

Operational data

The used lignite coke is produced on the basis of Rhenish lignite in the so-called hearth furnace process. For the adsorber in CH-Siggenthal, the size of the used grains is between 1.25 and 5 mm. The bulk density is 0.47 g/cm³ and the specific surface is about 300 m²/g (Specification of applied lignite coke, 2010). The consumption of lignite coke has been decreased from about 3,000 t/y to about 1,500 t/y (after the implementation of the bag filter – see above). So, today the specific consumption is about 2 kg lignite coke/t clinker. In order to avoid corrosion, the temperature prior to the adsorber must be kept at about 130 °C (temperature above the acid dew-point) and the walls of the adsorber have to be adequately coated. So, in the Siggenthal plant, there are no substantial corrosion problems. However, due to safety aspects, the

temperature in the waste gas prior to the adsorber should not exceed 150 °C because of the risk of hot-spots or even smouldering fires. For this purpose, a model-based delta-CO measuring system and a temperature distribution measuring system with an optical waveguide as the sensor have been developed and installed. Due to this system, the availability of the lignite coke moving bed adsorber is high (98-99.5 per cent).

Applicability

The described technique can be applied to new installations and can be retrofitted to existing installations. In case of the Siggenthal cement works, it was retrofitted to an installation that had been present on that site since 1912. The lignite coke moving bed adsorber has strong advantages when organic pollutants (except volatile C1-C4 hydrocarbons), volatile heavy metals (here especially mercury and thallium) and sulfur dioxide need to be efficiently removed at the same time. The applicability can be limited to plants with a substitution rate of conventional by waste-derived fuels of more than 60 per cent which contribute to the mercury emissions to more than 50 per cent.

Economics

In 1993/1994, the investment costs for the lignite coke moving bed adsorber were about CHF 46 million, DM 55 million and € 28 million respectively.. The Swiss capital city Zurich paid 30 per cent of the investment costs and can dispose of its anaerobically stabilised sewage sludge on the basis of a long-term contract. The investment in the moving bed adsorber enabled the operator to obtain the permit to feed a wide range of secondary fuels as well as of wastes, such as sewage sludge, waste solvent, waste oil, meat and bone meal, waste tyres, PVC-free, ground plastic chips, heavily contaminated soils and moulding sand, sludges containing oil and hazardous compounds from industrial waste water treatment, mother and washing liquors from chemical reactions, waste brake fluids, waste photo-finishing solutions, building wastes containing PCB, and non-chlorinated waste lubricants to the system. As the market prices for wastes were high at that time, the payback time period was calculated in the order of 6 years. Thus, the investment in the adsorber may be still attractive under the special circumstances in CH-Siggenthal.

The operation costs are mainly caused by:

- Consumption of lignite coke (about € 450,000/y, calculated with an annual consumption of lignite coke of 1,500 t and a price of € 300/t lignite coke),
- Electricity consumption for the fan (about € 500,000/y, calculated with a consumption of 900 kWh/h, an operation time of 351 days and 6.5 Cent/kWh,
- Labour costs for routine operation (about € 50,000/y, calculated with half a person-year),
- Costs for maintenance and retrofitting (about € 1,000,000/y).

In total, the operation costs (without depreciation) come to about € 2 million/y. Thus, the specific costs are about € 2/t cement produced. These additional costs are to be balanced with the above mentioned advantage to use secondary fuels and wastes as well as with higher emissions related to this input materials.

The only reference plant in the cement sector is the lignite coke moving bed adsorber at the cement works of Holcim in CH-Siggenthal.

Case studies in the waste incineration sector

Mercury Removal in a wet scrubber of a hazardous waste incineration plant in Sweden

At a hazardous waste incineration plant in Sakab, Sweden in the years 2004 and 2005 measurements of mercury concentrations were carried out.

The plant is equipped with a cyclon, a semi dry absorber with lime milk injection before a fabric filter with activated carbon injection and a MercOx and Adiox scrubber (see Figure 1). MercOx (Mercury Oxidation) is a wet scrubbing process which is based on hydrogen peroxide and an additive. SO_2 is adsorbed in the scrubber and oxidized to sulfuric acid. Hg^0 is oxidized to water soluble forms and absorbed in the scrubbing liquid. Hg can be precipitated producing small amounts of stabilized Hg-sludge. (Andersson and [Lindgren, 2010](#)).

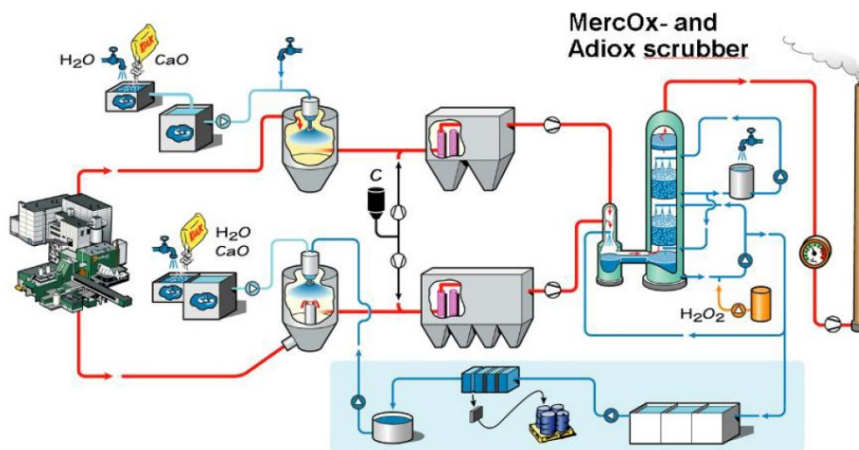


Figure 1 MercOx and Adiox Scrubber for simultaneous HCl, SO_2 , Hg and dioxin removal at the Sakab hazardous waste incinerator

Flue gases have been sampled in three campaigns between November 2004 and May 2005. During the first campaign a continuous emission monitor (CEM) was used. In the following two campaigns a wet absorption system with 200 ml impingers was used. The continuous instrument was not available at this time. In the April- and May-campaigns the mercury levels into the scrubber were raised by extra feeding of mercury waste to the kiln, i.e. from mercury containing batteries.

All impingers in the wet adsorption system were analyzed in triplicate with CV-ASS, and the detection limit of the instrument was $0.1 \mu\text{g}/\text{dm}^3$. (Löthgren et al. 2007)

Figure 22 shows the Hg concentrations in the MercOx scrubber inlet (after bag house filter with carbon injection) and at scrubber outlet taken by discontinuous measurements during sampling periods in April 2005 and May 2005. The outlet concentrations were stable between $1\text{-}10 \mu\text{g}/\text{m}^3$ (n.d.g.) of dry gas in all measurements, regardless of the inlet concentrations even when very high inlet concentrations in the range of $3,600 \mu\text{g}/\text{m}^3$ occur (note the exponential presentation). This

indicates that the outlet concentration is more a function of the concentration in the scrubber liquid than a function of the inlet concentration ([Andersson and Lindgren, 2010](#); Löthgren et al. 2007)

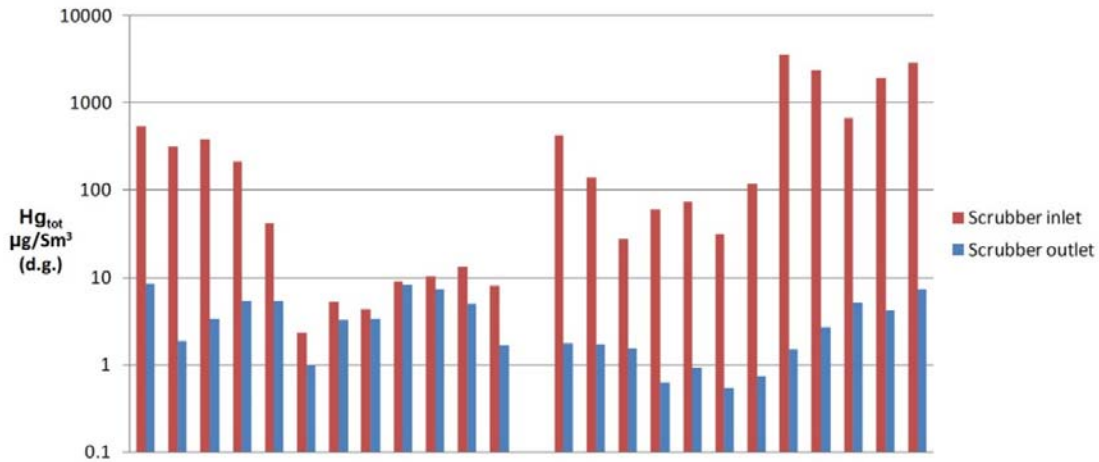


Figure 2 Hg concentrations in the MercOx scrubber inlet (after bag house filter with carbon injection) and at scrubber outlet

Mercury emissions from a sewage sludge incineration plant.

Plant Description

After a complete remediation and extension, the sewage sludge incineration plant in Frankfurt Sindlingen has operated since March 1997 with four incineration lines; from which a maximum of three are allowed to operate simultaneously (SEF 2013).

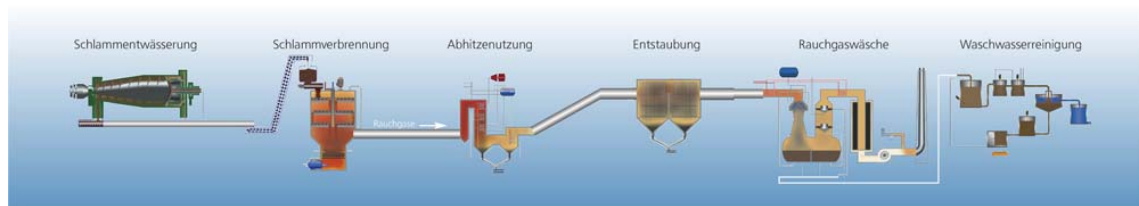


Figure 3 Sewage sludge incineration plant in Frankfurt Sindlingen, (SEF 2013).

The incineration of dewatered sewage sludge takes place in floor fluidized bed furnaces. The sludge moves down the system supported by stirring arms and across three drying floors to the incineration chamber. During this process the sludge is dried by a hot flue gas counter-flow stream and is subsequently incinerated at approx. 850°C. Air is pre-heated up to 600°C and introduced through a nozzle bottom into the incineration chamber. Here, it swirls through a sand bed, thereby creating a fluidized bed. The combustion heat ignites the sewage sludge particles in the fluidized bed which generates the energy necessary to maintain the nearly auto thermal combustion. To cater for disturbances and for start-up and shut-down processes, a light fuel oil based auxiliary firing is used.

Flue gas cleaning System

When the cooled flue gases reach 250°C they are conducted through a [ESP](#). The flue gases are cooled down to 40-50°C, when water vapour present is condensed. Any remaining dust, heavy metals - including mercury, and other pollutants are washed out in a three-stage scrubber. Additionally, an activated carbon filter removes remaining mercury. Before the gases leave the system via the stack they pass a measuring section. The emission limit values for the plant are 50 µg/m³ (half hourly) and 30 µg/m³ (daily) In 2013, the mercury emissions from the four lines were as follows:

line 1	7.3 µg/m ³
line 2	5.4 µg/m ³
line 3	2.8 µg/m ³
line 4	8.5 µg/m ³

Figure 4 4 shows the run of the mercury emissions of line 2 during the year 2013 (Schmid 2014) as a function of half hourly values measures with a continuous measurement device. In June, relatively high mercury emissions were observed. This was due to a malfunction of the fluidised bed. After correction of the problem, the mercury emissions were below 5 µg/m³

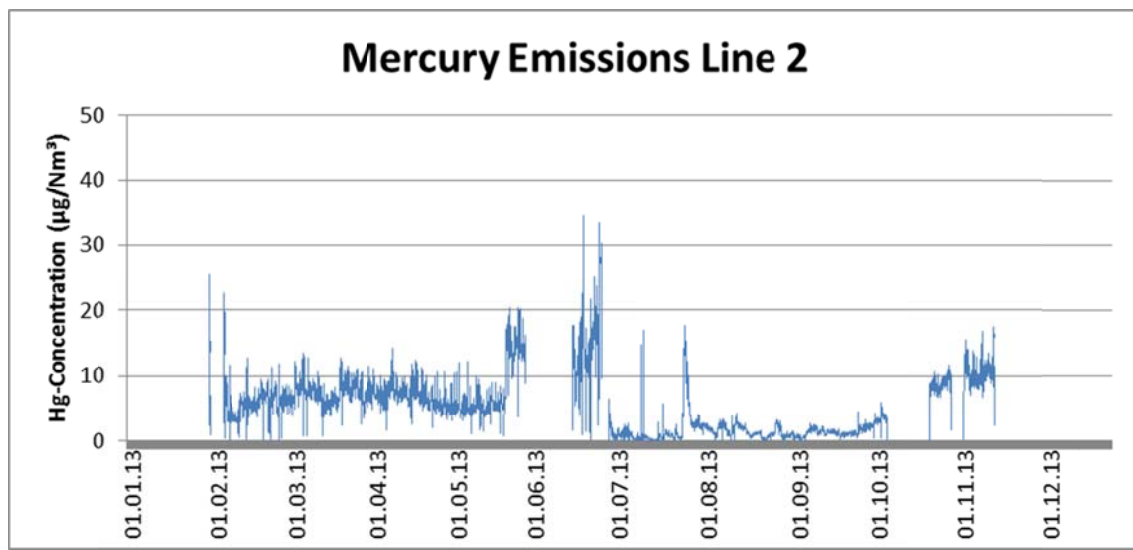


Figure 4 Mercury emission levels of the sewage sludge incineration plant in Frankfurt Sindlingen during the year 2013

Case studies in the sector on smelting and roasting processes used in the production of non-ferrous metals (lead, zinc, copper and industrial gold)

1. Case Study – Zinc/Lead Smelter and Refinery

This case study presents general information on mercury emissions controls at an integrated zinc-lead smelter and refinery in a developed country. The facility produces refined zinc, lead, silver, gold and other refined metals, as well as sulfur products including sulfuric acid. The facility also recovers mercury and mercury compounds (including mercury(I) chloride - calomel) as by-products.

Mercury enters the facility through various streams, primarily ore concentrates, with minor amounts from coal, coke and secondary feeds. The majority of the mercury in the zinc concentrates and other zinc feedstock is volatilized to the off gas during zinc roasting. Similarly, the majority of the mercury contained in the lead concentrates and other lead feedstock, including zinc plant residue and other reverts, is volatilized and departs to the off gas during the lead smelting process.

Initially, the process gas streams from both the zinc roaster and lead smelter are cleaned separately to remove particulate matter using dry electrostatic precipitators. The collected particulate matter is recycled back to the zinc or lead operations, as appropriate. The partially cleaned gas streams are quenched and then combined for final cleaning and treatment in the Mercury Removal Plant prior to being processed in the sulfuric acid plant.

The washing and cooling step utilises wet scrubbers to quench the process gas and further remove particulate matter. The quenched gas from the zinc and lead streams are combined and then passed through packed towers with cooling water to control the temperature of the gas. As a final gas cleaning step, the gas is passed through two sets of wet electrostatic precipitators to remove any remaining particulate and mist.

The cleaned gas is then passed through a Boliden-Norzink mercury removal tower prior to sulfuric acid production, where the gas is scrubbed with a solution of mercury(II) chloride (HgCl_2). The trace mercury in the gas reacts with the mercury(II) chloride to form mercury(I) chloride (Hg_2Cl_2 , calomel), which is insoluble and settles as a precipitate. To refresh the mercury removal tower scrubbing solution, a bleed stream containing calomel is removed and reacted with chlorine to reform mercury(II) chloride. The scrubbed gas is then processed in the acid plant for sulfuric acid production. The by-product calomel is stored or transferred off-site for recycling as appropriate.

Various internal residue and recycle streams are generated as a result of handling the mercury-containing gases and solids. These are re-introduced to the front end pyrometallurgical processes (zinc roasting and lead smelting) to maximize overall capture. In particular, the wash solution from the process gas quenching and cooling contains some of the volatilized mercury. The effluent from washing and cooling the gas stream is also weakly acidic. The wash solution is treated in an internal effluent treatment plant where metals are removed in a lime precipitation process. In addition, a small amount of mercury will deport to the zinc leaching circuit via dust collection and pressure leaching. This mercury is collected in zinc plant residues, which are dewatered and recycled to the lead smelter feed. As a result of smelting, mercury from these internal residues enters the hot process gas stream for eventual recovery, as already described.

To monitor its mercury emissions, the facility performs regular stack sampling, monthly at three stacks and quarterly on a fourth stack, aligning with regulatory requirements. Effluents are analyzed to confirm effluent treatment performance and to monitor effluent released to the environment. Product sulfuric acid is analyzed prior to shipment to confirm mercury content.

Overall, this facility achieves over 99.5% mercury capture based on inputs and recorded release in effluent and stacks. Mercury is recovered primarily as calomel but also as a minor amount of elemental mercury. The facility consistently produces sulfuric acid with mercury content well below 1.0 ppm.

2. Case Study on Mercury Controls for a Gold Ore Roasting Facility

Facility Name: Barrick Goldstrike Roaster

Facility Location: 26 miles Northeast of Carlin, NV

Process Description – General

The western United States, particularly the basin and range province that includes portions of California, Arizona, Nevada, Utah, and Idaho includes large areas where mercury occurs naturally. In 2000, Barrick Gold implemented an oxygen roasting process to treat carbonaceous sulfide ore from its Goldstrike property in Nevada. To meet the strict requirements on air emissions, the roaster gas cleaning system was designed to operate with high reliability and to achieve very high collection efficiencies for mercury, as well as particulate matter, SO₂, CO and NO_x. The Outotec BN Mercury Abatement Process is well established in base metal smelters and also was installed at the Goldstrike plant for reducing the mercury content of the roaster off-gas stream.

The Barrick Goldstrike Roaster processes approximately sixteen to eighteen thousand short tons of gold ore per day. The process includes crushing, grinding, roasting and leaching of the roasted ore. During the roasting process the ground ore is feed to two 2-stage oxygen roasters, operating at a temperature about 550-750 °C. During the roasting process the ore's contents of sulfur and carbon are oxidized, producing a calcine suitable for cyanide/CIL leaching to extract the gold. Mercury is volatilized during roasting and reports to the gas system. The roasting process produces a gas stream containing heavy particulate loading, strong SO₂, CO, NO_x and significant quantities of mercury. The following table shows the typical contaminant level found in the roaster off gas before treatment.

Typical levels of contaminants in roaster off-gas (dry basis)

Particulate (g/Nm ³)	500-720
Mercury (mg/Nm ³)	370-550
CO (g/Nm ³)	0.46 (peak level 17.2)
SO ₂ (g/Nm ³)	125-290
NO _x (g/Nm ³)	0.58-1.72

The gases produced from the roasting process are treated through several steps, some of which are co-pollutant controls, as well as specific unit processes that are applied to minimize mercury emissions to the greatest extent possible.

Gas Control Technologies Description

The process flow diagram is provided as reference to the function of each mercury emissions control process that is in place to treat the roaster off gas.

Unit Process Descriptions of Roaster Off-Gas Treatment

Cyclone Separation

The off gas from the roaster is first treated by cyclones to remove particulate matter (PM) which can have mercury coincident with the PM. Less than one percent of the total ore treated is carried to the cyclone overflow and thus continues farther into the gas stream treatment system as PM. The remainder of the ore, greater than 99%, is separated and thereby continues as the product stream.

Gas Quench

In the gas quench step, fresh water is sprayed into a large vertical pipe from the cyclone overflow. The primary purpose of the gas quench process is to cool the gases coming from the roaster; it also captures small amounts of PM including some oxidized mercury which is present in the gas. Mercury capture is measurable in the gas quench solution.

Venturi Gas Scrubbing

Further gas cleaning (both PM and oxidized mercury) is performed by a venturi style dust scrubber. The venturi scrubber functions through a pressure differential across a controlled opening (i.e., the throat). The gas and liquid become intimately mixed within the throat of the scrubber, thereby improving the extraction of the PM and other soluble or insoluble PM and oxidized mercury.

Gas Condenser

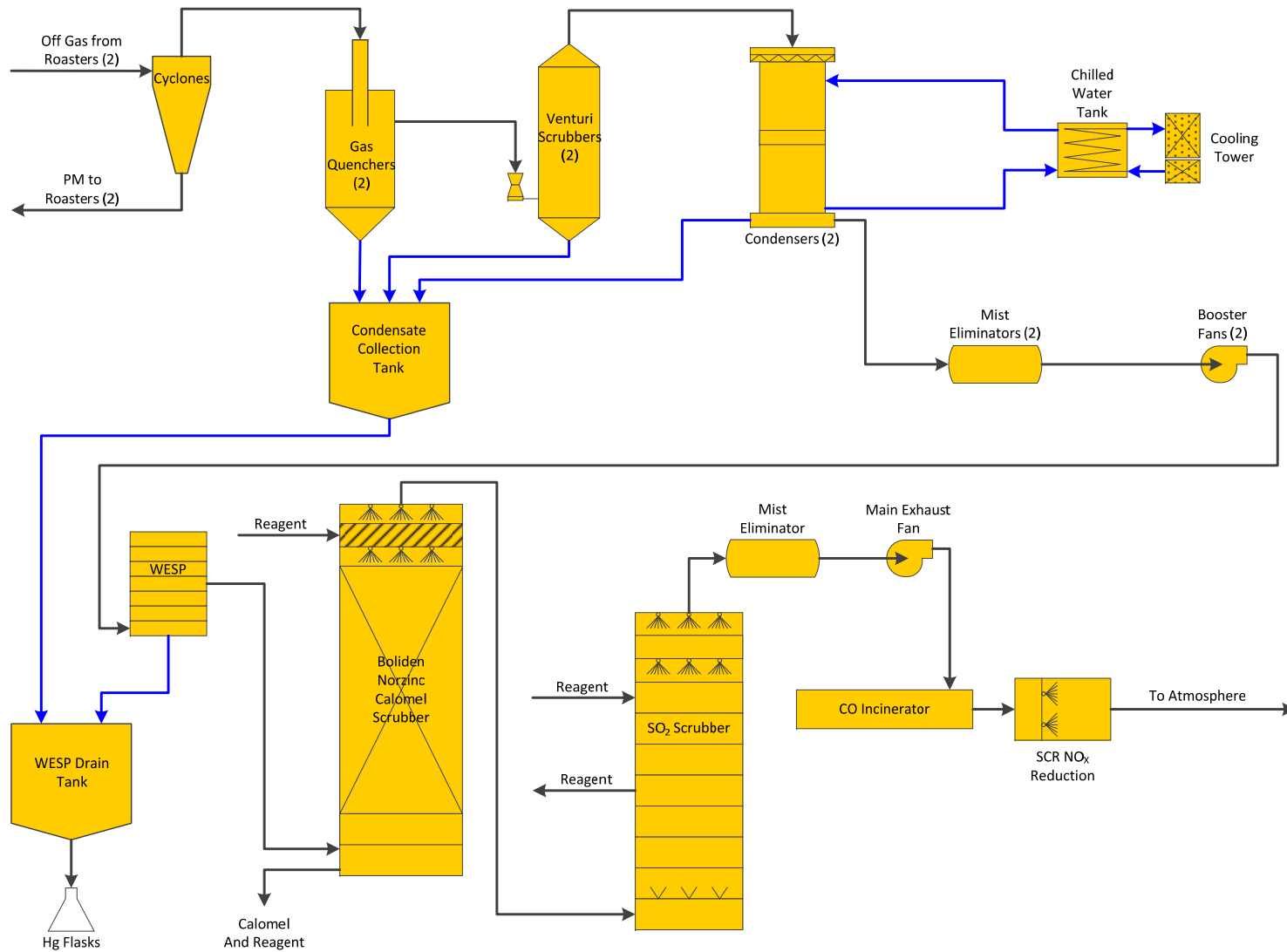
After the venturi scrubber, additional gas cooling and mercury separation is accomplished with a tube and shell indirect heat exchanger (shown in the diagram as a "condenser"); this cooling allows for a small amount of elemental mercury to be condensed and captured in the condensate collection tank.

Wet Electrostatic Precipitator (WESP)

The final removal of PM is accomplished in a wet electrostatic precipitator (WESP). The WESP provides co-benefits in that a significant quantity (up to 50%) of elemental mercury that is present is captured in the WESP.

Calomel Scrubber

Following the WESP, a calomel scrubber is used to treat the roaster off gas for mercury removal. The gas stream is contacted in a fixed bed scrubber arrangement with a solution of mercury (II) chloride (HgCl_2) which reacts with the elemental mercury in the gas to form a stable mercury(I) chloride (Hg_2Cl_2) compound known as calomel. The solid mercury(I) chloride, calomel (Hg_2Cl_2), is separated and a part is shipped for environmentally sound disposal. The remaining part is chlorinated with $\text{Cl}_2(\text{g})$ to regenerate HgCl_2 to be used again in the calomel scrubber.



Overall Operating Performance

The use of these various control technologies allows for changes in feed material characterization since removal efficiency does not rely on a single process step. The design intent and operation of this roaster and gas treatment facility has been successfully operated since its commissioning in 2000 with control efficiencies of greater than 99% as shown in the following table. The data shown below is based on actual stack testing for mercury emissions and the actual mercury produced as both elemental and calomel from the various control and capture points described above.

Roaster Mercury Emission Control Effectiveness

Year	Hg Emissions (kg/yr)	Hg Co-Product (kg/yr)	Control Efficiency (%)
2002	369	*	*
2003	75	*	*
2004	237	*	*
2005	49	*	*
2006	106	85,018	99.9
2007	203	50,829	99.6
2008	92	59,239	99.8
2009	78	54,545	99.9
2010	51	53,866	99.9
2011	196	53,455	99.6
2012	60	42,708	99.9
2013	112	50,672	99.8

* Data not available

3. Case study: mercury scrubbing during zinc smelting in ISF furnace

Facility Name: Hachinohe Smelting, ISP plant

Facility Location: 80 km East of Hirosaki, Japan

In this process, a mixed zinc–lead concentrate is sintered at a temperature of 1250°C in a sintering furnace. The mercury containing off-gas from the sintering furnace is directed to an air pollution control system to remove dust and mercury that consists of the following units:

- dry electrostatic precipitator (dry ESP),
- venturi scrubber (VS),
- first gas cooler (GC),
- first wet electrostatic precipitator (wet ESP)
- a second GC and
- a second wet ESP

Subsequently, off-gases enter the drying tower (DT). Downstream of the DT, the flue gases pass through a converting process and absorption tower (CAT), where Lurgi double conversion double absorption is used, and H₂SO₄ is produced.

Following the CAT, a wet scrubber (WS) employing caustic soda (NaOH) is used to remove the remaining SO₂ in the flue gases. The gas at the outlet of the WS is emitted via a stack. The H₂SO₄ is purified using cementation on aluminium.

Mass balance based on measurements (see table) show that the majority of mercury is removed in the control devices of the sintering furnace (90 – 95%) and can be found in sludges, containing > 1% of mercury. Crude sulfuric acid contains > 1 ppm and requires additional purification.

Mercury concentration in off-gases

Flue gas Samples	[µg/Nm ³]	
	Outlet of dry ESP	2600
Outlet of 2nd wet ESP	140	260
Outlet of converting process and absorption tower (CAT)	64	45
Outlet of wet scrubber (stack)	1.7	2.2

Mercury concentration in solids

Solid Samples	[ppm]	Standard Deviation [ppm]
Zinc ore	3.9	0.15
Fly ash	8.1	0.27
Sludge with high Hg	18000	3200
Aluminum residue	820	15
Sludge from total wastewater	17	-

Mercury concentration in liquids

Liquid Samples	[µg/L]	Standard Deviation [µg/L]
Waste water from WS	910	18
Waste water from VS	0.82	0.035
Crude sulfuric acid	1.1 ppm	1.3 ppm
Sulfuric acid product	0.13 ppm	0.14 ppm

This example confirms, that in the case of low content of mercury in raw material, standard procedure of gas cleaning (dry ESP, Venturi scrubber and wet ESP) is sufficient to limit stack gas mercury emission to achieve low emission levels.

Reference

Removal of mercury and sulfuric acid production in ISP zinc smelting, M. Takaoka, D. Hamaguchi, R. Shinmura, T. Sekiguchi, H. Tokuch, Japan, 2014.

4. Case study Zinc/lead/copper production at Boliden Rönnskär (Sweden)

Description

Boliden Rönnskär is the largest production site of the Boliden company. It was established in 1930. The main products are copper, lead, zinc clinker, gold and silver; by-products include sulfuric acid.¹ Copper and lead concentrates originate from Boliden's own mines and from external mines. For many years it has been one of the world's largest recyclers of electronic scrap.

Smelting takes place in different types of furnaces, depending on the raw material. In 2014, Boliden Rönnskär produced 217 kt copper cathodes, processing 844 kt copper concentrates and secondary materials.²

Technical description

Copper production

Boliden Rönnskär uses a Flash Furnace as well as a Fluidized Bed Roaster combined with an Electric Furnace for processing copper concentrates. Process gases from the bed roaster, smelting furnaces and converters are directed to the double contact/double absorption acid plants or a liquid SO₂ plant equipped with a Boliden Norzink technique, DOWA filter or selenium filters for mercury reduction.

The output of the Fluidized Bed Roaster enters into an Electric Smelting Furnace (also processing secondary material). The mattes of the Electric Smelting Furnace and the Flash Furnace enter a Converter Aisle producing blister copper.

Electronic scrap is fed to the TBRC Kaldo furnace (top-blown rotary converter) to produce crude copper containing precious metals. This "black copper" is fed to the converter.

Blister copper produced in the converter is deoxidised with ammonia in the anode furnace followed by anode casting and finally electro-refined.³

Lead production

Boliden Rönnskär uses a TBRC Kaldo furnace (top-blown rotary converter) for processing lead concentrates. Besides lead concentrates, the Kaldo furnace is also used for melting electronic waste to black copper. The furnace is housed in an enclosure to contain secondary emissions; ventilation gases are treated in a bag filter. Process gases from the Kaldo furnace are treated either in a liquid SO₂ plant (equipped with a selenium filter for mercury reduction) or a double contact/double absorption acid plants (equipped with a DOWA filter for mercury reduction).^{4 5}

¹ Boliden Rönnskär Website, accessed 4.3.2015
<http://www.boliden.com/Operations/Smelters/Ronnskar/>

² Boliden Rönnskär Website, accessed 4.3.2015
<http://www.boliden.com/Operations/Smelters/Ronnskar/>

³ Gas treatment at sulphuric acid plant, Rönnskär; presentation by M. Borell, Boliden, 2014

⁴ Gas treatment at sulphuric acid plant, Rönnskär; presentation by M. Borell, Boliden, 2014

⁵ EU NFM BREF, 2014 (p. 322)

Zinc production

Slag from the Electric Smelting Furnace enters a Fuming Furnace producing the input to the zinc clinker plant. No specific mercury reduction system is installed.⁶

Mercury control techniques

For mercury removal, Boliden Rönnskär uses dust cleaning techniques in combination with different specific mercury reduction techniques. For dust cleaning, electrostatic precipitators, bag filters and scrubbers are used; specific mercury reduction techniques applied are Boliden Norzink, DOWA Filter and Selenium Filter and injection of lime and activated carbon in combination with bag filters.

Environmental performance and operational data

Emission performance data is based on about 100 mercury measurements per year. Sampling time is between 1-14 days. Three methods are used:

- 1) Standard periodic sampling method (European Standard EN 13211)
- 2) Boliden periodic sampling method
- 3) Semtech 2000 on-line monitoring method

The Boliden method uses robust equipment, and the liquid is not as sensitive to cold weather conditions as when using EN 13211. It separates the sample into three fractions according to the mercury species and makes it possible to study the importance of different types of mercury:

- Filter: Mercury adsorbed on particulate matter
- H₂SO₄: Mercury ions (oxidized mercury as vapour)
- Iodized activated coal: elemental mercury

Semtech 2000 is an optical on-line measurement method (254 nm, UV). Boliden Rönnskär uses it only as an indicative measurement. It samples and measures elemental mercury. Ionic mercury (ion droplets) is not sampled (has to be converted into elemental mercury). The equipment does not sample mercury adsorbed on particulate matter.

Emissions from Flash Furnace (primary copper processing)

Process gases of the flash furnace (30 000 Nm³/h) are first cleaned from dust in an electrostatic precipitator (ESP) and a scrubber. Subsequently, off-gas passes to a Boliden Norzink mercury control before entering the double contact/double absorption acid plants. Mercury content of raw gas before the Boliden Norzink control varies from 42-1008 µg/Nm³ (periodic measurement). Accordingly, emission levels vary between 12-48 µg/Nm³, resulting in 71-95% mercury reduction.

Emissions from Fluidized Bed Roaster (primary copper processing)

Process gases of the fluid bed roaster (80 000 Nm³/h) are first cleaned from dust in an electrostatic precipitator (ESP) and a bag filter. Bag filter dust containing As and Hg is sent to storage in a closed system.

⁶ Gas treatment at sulphuric acid plant, Rönnskär; presentation by M. Borell, Boliden, 2014

In a mixing tower, off-gas from the fluid bed roaster, the electric smelting furnace and the converter aisle are combined. The emissions from the mixing tower are either directed to the double contact/double absorption acid plants, equipped with a DOWA filter for mercury reduction) or to the liquid SO₂ plant, equipped with a selenium filter for mercury control (performance levels are described below in the section on TBRC Kaldo furnace for primary lead).

Emissions from Electric Furnace and Converter (primary and secondary copper processing)

Process gas of the electric furnace is first cleaned in an electrostatic precipitator before being directed to a mixing tower. Process gas of the converter is first cleaned in an electrostatic precipitator. Subsequently it passes a quencher and a cooler before being directed to the mixing tower.

In the mixing tower, off-gas from the fluid bed roaster, the electric smelting furnace and the PS converter aisle are combined in a mixing tower. The emissions from the mixing tower are either directed to the double contact/double absorption acid plants, equipped with a DOWA filter for mercury reduction) or to the liquid SO₂ plant, equipped with a selenium filter for mercury control (performance levels are described below in the section on TBRC Kaldo furnace for primary lead).

Emissions from TBRC Kaldo furnace (primary lead smelting)

Ventilation gases of the Kaldo furnace enclosure (44 000 Nm³/h) are cleaned in a bag filter achieving dust emission levels in off-gas < 5 mg/Nm³ (continuous measurement).

Process gases of the Kaldo furnace are first cleaned from dust in a wet electrostatic precipitator (ESP) and passed to a liquid SO₂ plant, equipped with a selenium filter for mercury control. Mercury content of raw gas before the selenium filter (80 000 Nm³/h) varies from 42-1008 µg/Nm³ (periodic measurement). Accordingly, emission levels vary between 12-48 µg/Nm³, resulting in 71-95% mercury reduction.

Process gases from TBRC Kaldo furnace can alternatively be directed to a dust cleaning with a wet ESP and the double contact/double absorption acid plants equipped with a DOWA filter for mercury control. Mercury content of raw gas before the DOWA filter (170 000 Nm³/h) varies from 10,5-50 µg/Nm³. Accordingly, emission levels in off-gas vary between 1,2-1,4 µg/Nm³, resulting in 88-97% mercury reduction.

Emissions from TBRC Kaldo furnace (electronic scrap processing)

Ventilation gases of the Kaldo furnace enclosure (44 000 Nm³/h) are cleaned in a bag filter achieving dust emission levels in off-gas < 5 mg/Nm³ (continuous measurement).

Equivalent gas treatment equipment was installed in a new electronic scrap furnace (the E-scrap Kaldo plant built in 2012). Process gases pass a mercury control with activated carbon and lime injection followed by a bag filter. Oxidized mercury is adsorbed on the surface of the activated carbon and elemental mercury reacts with SO₂ and O₂ forming solid HgSO₄. Mercury content before entering the bag filter varies from 37,2-1206 µg/Nm³ (periodic measurement). Accordingly, emission levels vary between 2,7-32 µg/Nm³, resulting in 93-97% mercury reduction.

Summary of emissions from Boliden Rönnskär (copper and lead processing)

The following table presents performance data of each mercury control technique. For each technique, maxima and minima are provided for input and output of the control technique, as well as resulting efficiency.

Table: Overview on performance of mercury reduction techniques of Boliden Rönnskär/Sweden

Mercury control technique	Material input	Flow [Nm ³]	Load	Inlet [µg/Nm ³]	Outlet [µg/Nm ³]	Efficiency [%]
Boliden Norzink	Primary	30 000	Maximum	9879	30	99,7
			Minimum	51	13	74
DOWA Filter	Primary	170 000	Maximum	50	1,4	97
			Minimum	10,5	1,2	88
Selenium Filter	Primary	80 000	Maximum	1008	48	95
			Minimum	42	12	71
Activated carbon injection	Secondary	80 000	Maximum	1206	32	97
			Minimum	37,2	2,7	93

Source: Best available techniques (BAT) reference document for the non-ferrous metals industries European Commission, Joint Research Centre, Seville, 2014

Cross-media effects

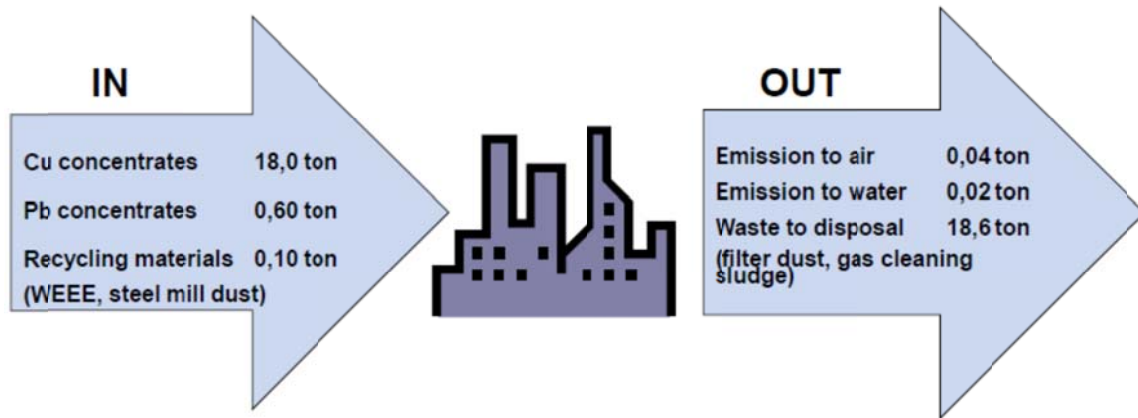
Dust cleaning before specific mercury controls leads to cross-media effects, as mercury from off gas is passed to filter dust and to scrubber waste water.

Filter dust containing mercury is sent to storage in a closed system.

Scrubber waste water is treated on-site. Resulting sulfide sludge containing mercury is returned as an input of the Fluidized Bed Roaster. The remaining waste water effluent is emitted to the environment with emission values of 130-200 ng/L.

The sulfuric acid produced after the Boliden Norzink and the DOWA filter has a mercury content of < 0,04 ppm. The mercury content of the liquid SO₂ produced after the selenium filter is 0.02 ppm.

The following picture presents mass balance data of mercury including emissions to air, water and contained in waste. Mercury in sulfuric acid is not considered.



Reference

Best available techniques (BAT) reference document for the non-ferrous metals industries
European Commission, Joint Research Centre, Seville, 2014.

5. Mercury Air Emission Sources and Controls - PT. Smelting - Gresik Smelter & Refinery

General

Location: Gresik, East Java, Indonesia

Ownership: PT. Freeport Indonesia (25%), Mitsubishi Materials Corp. (60.5%), Mitsubishi Corp. RtM (9.5%) and Jx Holdings (5%)

Commenced operation: May, 1999

Process: Mitsubishi Continuous Smelting & Converting Process

Output: 300,000 tonnes/year

The smelting process at Gresik involves:

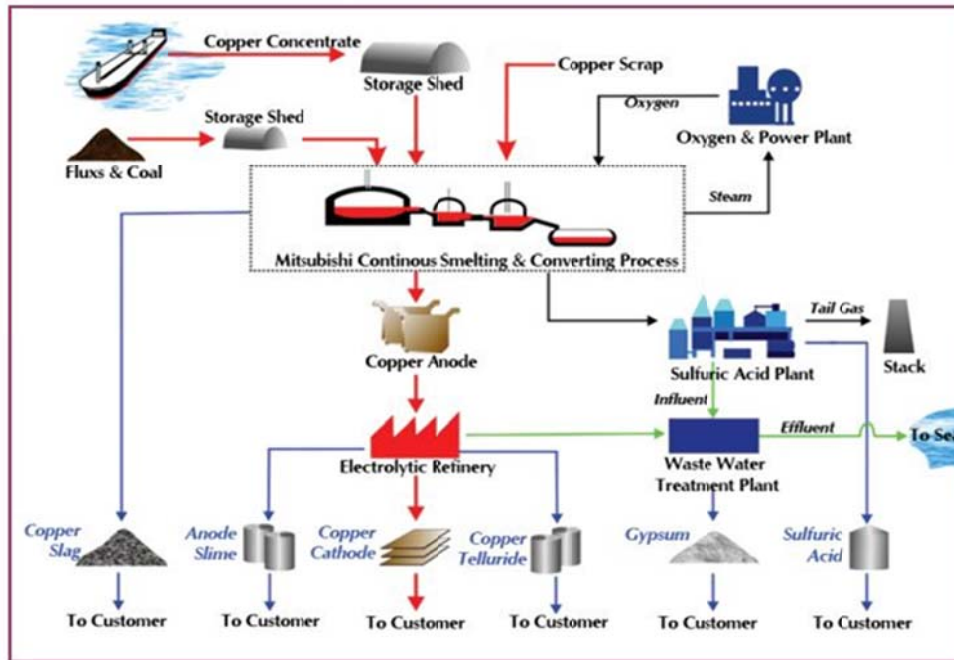
- drying ore concentrates;
- smelting of ore concentrates to produce matte;
- converting matte to produce blister copper; and
- fire refining the blister copper in an anode furnace.

A sulfuric acid production facility is also operated on-site, capturing sulfur dioxide (SO₂) and other gases from the smelting process, and producing a concentrated sulfuric acid that is sent to an adjacent fertilizer facility via pipeline. After fire refining, the 99.5 percent pure copper is cast into "anodes" and sent to an electrolytic refinery for further impurity removal. Finally, copper cathode with 99.99 percent pure copper is produced from electrolytic refining.

Figure 1 is a schematic showing general process flows. The operation has two regulated air emission stacks, one from the smelter and a second from the acid plant. The facility routinely monitors and reports on mercury concentrations in air emissions; all results to date have been below detection (non-detect).

Drying (not a potential Hg source)

Gresik smelter utilizes a rotary dryer to dry the concentrate. Temperatures in the dryer are not high enough to vaporize any mercury in the ore concentrate, and as such are not considered a potential emission source. Particulates from the dryer are controlled using both a cyclone and complex baghouse configurations, with captured particulates being fed into the smelting furnace.



Mitsubishi Process

In the Mitsubishi Process, feedstock materials are continuously fed to a series of enclosed furnaces. The furnaces are stationary, tightly sealed, and interconnected by enclosed launders. Small ventilation hoods placed above the furnace inlets and outlets capture all fugitive emissions.

1. Smelting (a potential Hg source)

The smelting produces a copper matte by melting the hot ore concentrates with siliceous flux in a furnace (S-Furnace). The mattes produced by domestic smelters range from 35 to 65 percent copper. Smelting furnace technologies operate at temperatures well above the boiling point of mercury with operating ranges as high as 1200°C.

2. Slag Separation (copper slag) at CL-furnace

Mixtures of matte and slag from smelting furnace are transferred through an enclosed launder to the electric furnace (CL-furnace) to be separated by differences in specific gravity. Matte is continuously siphoned out to a converting furnace and the slag, referred to as CL-slag (copper slag), is overflowed from the furnace for water granulation. Granulated CL-slag is one of the salable by-products from the copper smelter.

3. Converting (potential Hg source)

The final step in the production of molten "blister" copper is converting. Converting eliminates remaining iron and sulfur impurities, leaving 65 to 98.5 percent pure copper (blister copper). Converting involves molten matte, limestone flux and scrap copper being charged to a furnace (C-Furnace), where oxygen enriched air is blown from the top of the molten matte.

Blister copper is continuously siphoned out to the anode furnace via an enclosed launder. The molten converting slag formed in the converting furnace (C-furnace), is then water granulated, dried, and re-cycled to the S-furnace. Converting reactions are exothermic, therefore spent anode from the electrolytic refinery is utilized as a coolant to control the bath temperature. Off gas from the C-furnace is also delivered to the Sulfuric Acid Plant through a waste heat boiler and an electrostatic precipitator for cooling and de-dusting.

4. Anode Furnace (not a potential Hg source)

Blister copper contains approximately 1.5% sulfur. This characteristic influences the electro-refining process due to the copper anode degrading to low purity and density. This blister copper is purified in the Anode Furnace in two stages, oxidation and reduction. Copper scrap of high copper grade is also treated in the Anode Furnace, then melted together with blister copper from the C-furnace.

In the oxidation stage, oxygen-enriched air is injected to oxidize the remaining sulfur to SO₂ gas, and in the reduction stage, the excessive oxygen is reduced using natural gas or MDF.

The molten metal (around 99.4 % Cu) is cast as copper anode using a continuous casting machine and then delivered to the electro-refining process. The off gas from the anode furnace during the oxidation stage, is sent to the Acid Plant, while off gas from reduction is returned to the concentrate dryer, and finally discharged through the stack.

The gas stream to the sulfuric acid plant passes through a range of control devices, including at the Smelter:

- Waste Heat Boiler
- Electrostatic Precipitator (ESP)

and at the Acid Plant:

- Washing tower
- Venturi Scrubber
- Gas Cooler
- Wet Electrostatic precipitator or Mist Precipitator.

These control devices remove metal impurities to prevent destruction of the catalyst in the acid plant. Any mercury volatilizing in the smelting furnace is captured and removed either in these multistage control systems or in the sulfuric acid plant.

Following treatment, the smelter stack has an air discharge that is continuously monitored for SO₂, temperature and flow rate. Quarterly chemical analyses show no detectable mercury over the 13 years period of monitoring (DL = 0.008 mg/Nm³).

As the system is entirely enclosed, any mercury contained in the concentrate will be volatilized during the Mitsubishi Smelting process step, captured and directed toward the sulfuric acid plant.

Sulfuric Acid Plant (potential Hg source)

Data on sulfuric acid plant sludge show that the mercury is present in measurable concentrations. This sludge (containing mercury) is recycled back to the smelting and converter furnaces and vaporized again into the control system. This sets up an internal recycling loop for the mercury.

Acid plant off-gas passes through a scrubbing unit, and the final solution generated from gas absorbing process at the scrubbing unit is recycled to the acid production process in an absorption process, and finally discharged through the stack.

The stack is continuously monitored for SO₂, temperature and flow rate. Quarterly monitoring data for the last 13 years show no detectable mercury (DL = 0.008 mg/Nm³).