



**HUGO PETERSEN**  
Verfahrenstechnischer Anlagenbau

**MERCURY REMOVAL**  
**Environmental Expertise at its Glance**

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## The company Experience and in Detail

HUGO PETERSEN GmbH located in Wiesbaden, origins from the renowned company Hugo Petersen, founded in 1906, in Berlin. HUGO PETERSEN is part Chemieanlagenbau Chemnitz (CAC) group and as such can provide full for the development and implementation of small to large scale Initially using the expertise gained in the classical production of sulphuric acid generated in the refining of metallurgical ores, the company HUGO specialized in the field of manufacture of sulphuric acid, hydrochloric acid



Pic. 1:  
Hugo Petersen 1906

engineering  
of the  
support and security  
installations.

acid, from off-gases  
PETERSEN  
and gas cleaning.

### Efficiency First

Not only do the things right, but also, do the right things



Pic. 2: Patent 'Kammerregulator' 1905

The founder, Hugo Petersen was, from the beginning, ambitious to improve operations to reduce emissions, through his invention of the patented "Kammerregulator" for the classical lead-chamber process. The unit improved the control of the performance of the lead-chamber and hence the emission of noxious gases.

In 1923, he replaced the lead-chambers by irrigated towers, achieving a 6-fold increase in performance versus the original design.

Nowadays, sulphuric acid is produced by the well-known double contact process, which is based on the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  using a vanadium pentoxide catalyst, introduced by BAYER AG in 1964. Since then, the



Pic. 3: Tower Plant 1923

conversion efficiency has increased from 97.5% to 99.5%

HUGO PETERSEN supplies plants and equipment which ensure conversion rates of more than 99.92% and with its vast experience in gas cleaning it is possible to attain  $\text{SO}_2$ -free gases.

HUGO PETERSEN with its more than 110 years of experience in the design and operation of sulphuric acid plants and their equipment offers today a vast range of technology to the industry. The design, whilst incorporating HUGO PETERSEN's extensive experience, has been developed and optimised through a comprehensive research program, conducted using HUGO PETERSEN'S own pilot plant facilities.

The engineering company has evolved from HUGO PETERSEN - consulting engineers, to an operating entity with a worldwide network of representatives and subsidiary companies.

In the field of Manufacture of Sulphuric Acid, the focus is on planning, designing and supplying plants which use raw materials like elemental sulphur, metallurgical sulphides and the decomposition of spent acid. This also includes the efficient and intensive use of off-gases from metallurgical plants as well the effective energy recovery from sulphur burning plants.

HUGO PETERSEN is world-wide one of two companies that have the complete in-house-developed technology for metallurgical acid plants.

About 50 well trained process technologists and engineers contribute their knowledge and expertise in the fields of mechanical and electronic engineering, as well as material science, to their design work.

Since more than 25 years HUGO PETERSEN is doing site-surveys, plant-audits, operational and maintenance-consultancy.

### **Accurate Planning - the basis for our work**

HUGO PETERSEN has installed more than 400 turnkey plants and plant components for the manufacture of sulphuric acid, oleum and  $\text{SO}_2/\text{SO}_3$ .gaseous or liquefied

# Technology and Process Overview

## History, Toxicity and Environment

One of the most ancient known metals of human being and widely used from decoration over cosmetics and in medicine till its toxicity for the human body and the environment was discovered.

- Egyptians knew this metal from about 1500 BC. In tombs of that age Mercury was found. (1)
- Chinese used for life prolongation. (2) (3)
- The Maya civilization discovered the amalgam (Medieval Latin *amalgama*, "alloy of mercury") with other metals (500 BC). (4)
- The ancient Greeks used cinnabar (mercury sulphide) in salves.
- The ancient Egyptians and the Romans used it in cosmetics.

Alchemy was based on the idea that mercury is the First Matter from which all metals were formed. They believed that different metals could be produced by varying the quality and quantity of sulphur contained within the mercury. The purest of these was gold, and mercury was called for in attempts at the transmutation of base (or impure) metals into gold, which was the goal of many alchemists. (5)

The mines in Almadén (Spain), Monte Amiata (Italy), and Idrija (now Slovenia) dominated mercury production from the opening of the mine in Almadén 2500 years ago, until new deposits were found at the end of the 19th century. (6)

### Toxicity

Mercury and most of its compounds are extremely toxic and must be handled with care; in cases of spills involving mercury, specific cleaning procedures are used to avoid exposure and contain the spill. (7) Mercury can be absorbed through the skin and mucous membranes and mercury vapours can be inhaled, so containers of mercury are securely sealed to avoid spills and evaporation. Heating of mercury, or of compounds of mercury that may decompose when heated, should be carried out with adequate ventilation in order to minimize exposure to mercury vapour. The most toxic forms of mercury are its organic compounds, such as dimethylmercury and methylmercury. Mercury can cause both chronic and acute poisoning.

### Releases in the environment

Preindustrial deposition rates of mercury from the atmosphere may be about 4 ng / (1 L of ice deposit). Although that can be considered a natural level of exposure, regional or global sources have significant effects. Volcanic eruptions can increase the atmospheric source by 4–6 times. (8)

Natural sources, such as volcanoes emitting about half of atmospheric mercury emissions. The other half is considered to be released by the humans. The distribution of the human-generated half can be divided into the following estimated percentages: (9) (10)

- 65% from stationary combustion, of which fossil fuel-fired power plants (11)
- 11% from gold production. (12)
- 6.8% from non-ferrous metal production, typically smelters.
- 6.4% from cement production.
- 3.0% from waste disposal, including municipal and hazardous waste, crematoria, as well as sewage sludge incineration.
- 3.0% from caustic soda production.
- 1.4% from pig iron and steel production.
- 1.1% from mercury production, mainly for batteries.
- 2.0% from other sources.

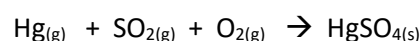
The above percentages are estimates of the global human-caused mercury emissions in the year 2000, excluding biomass burning, an important source in some regions.

A serious industrial disaster was the dumping of mercury compounds into Minamata Bay, Japan. It is estimated that over 3,000 people suffered various deformities, severe mercury poisoning symptoms or death from what became known as Minamata disease. (13) (14)

## Technology for Removal of Mercury out of Process Gases

Non-Ferrous metals and pyrite containing mercury will release the same into the off-gases as they are treated in pyrometallurgical processes. The volatilized mercury will be mostly present in elemental form.

Mercury will also react with the sulphur dioxide and oxygen in the gas to form mercury sulphate according to the reaction:



Mercury sulphate will be removed from the gas in the subsequent scrubbing and wet electrostatic precipitation stages.

The mercury that remains uncaptured appears as a contaminant in the product sulphuric acid, because it will be absorbed by strong acid in the downstream drying and absorption units.

The mercury contaminated acid cannot be used in any industry or products where there is the potential for the mercury to enter the food chain. Therefore, it is desirable to remove the mercury from the acid to produce a more saleable product.

In the presence of selenium in the ore it will also be liberated in the roasting/smelting process along with the mercury. The selenium will be in the amorphous state which will readily combine with mercury to form HgSe. Mercury in this form will be easily removed from the gas in the scrubbing and wet electrostatic precipitation stages. About this we discuss later.

Mercury the toxic and troublesome contaminant in many Metallurgical Processes has to be eliminated from gases as efficient as possible!

HUGO PETERSEN supplies to their clients several mercury removal processes, as there are:

- Calomel-Technology
- MERCUR<sup>EX</sup>-B-GON-Technology
- Thiosulphate-Technology
- Carbon-Technology.

All Processes have demonstrated its performance under industrial conditions. The right process application is down together with the client always envisioning for the advantage for client, product and environment.

### CALOMEL-Technology

In order to prevent the mercury vapour passing into the sulphuric acid plant, it is eliminated by the so-called "Calomel-Process":

This process is the most popular method for mercury removal due to its high efficiency of more than 99.8 % (Hg removal in the gaseous phases). A product sulphuric acid with less than 0.5 ppm mercury can be produced from a gas containing 150 ppm mercury.

#### Chemical Reactions

The calomel process is based on a **very rapid and complete reaction** that takes place when Hg vapour comes into contact with a scrubber solution, containing dissolved Hg<sup>++</sup> ions, under appropriate conditions.

Mercury molecules are oxidized by mercuric chloride HgCl<sub>2</sub> to form mercurous chloride Hg<sub>2</sub>Cl<sub>2</sub>, which is crystalized as calomel. Calomel has a low vapour pressure. See Figure 1

The main chemical reactions are the following:



The calomel process works best in a temperature range between 30°C and maximum of 40°C.

Above 40°C, the vapour pressure of mercury from the Mercuric Chloride becomes too high to obtain a good separation (compare next figure). The actual total vapour pressure also depends on other factors, particularly the  $\text{Cl}^-$  concentration. Therefore it is essential that the Hg-removal tower is placed downstream the cooling and halogen towers.

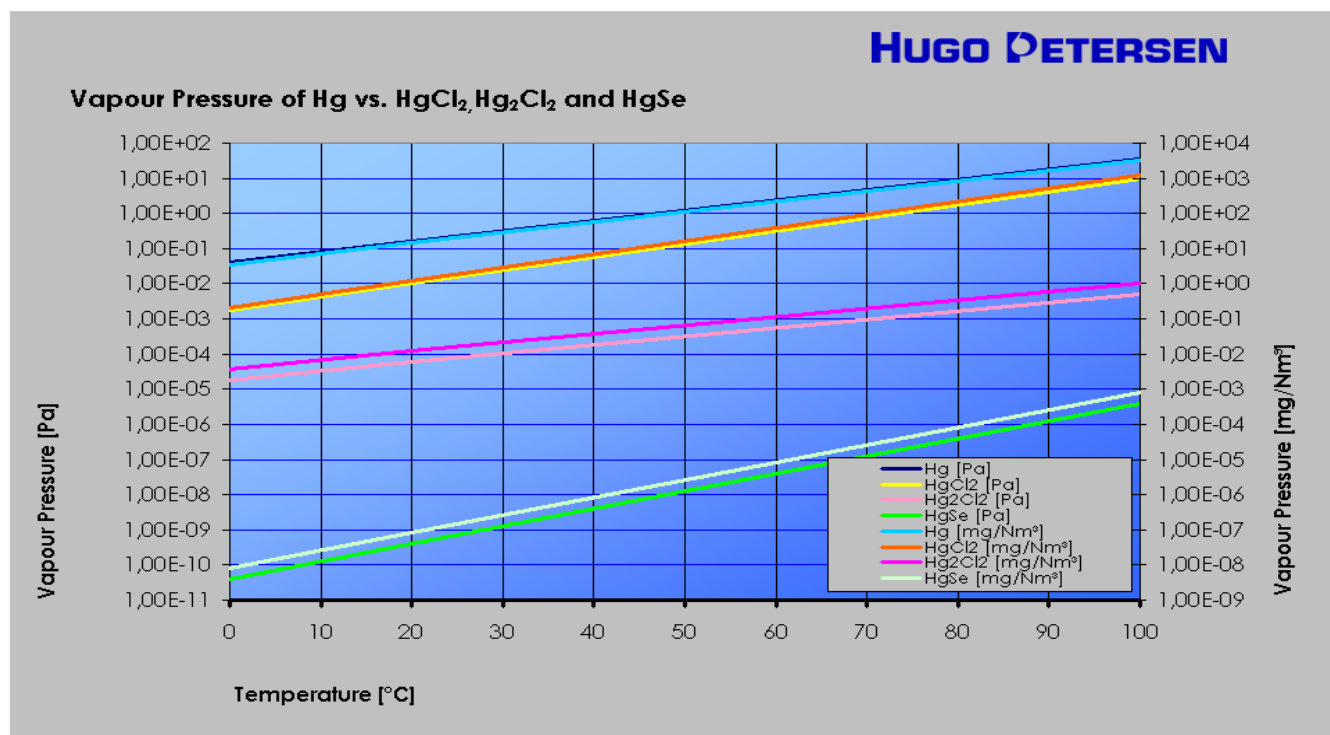


Figure 1: Vapour Pressure of Hg, HgSe, Hg<sub>2</sub>Cl<sub>2</sub>, and HgCl<sub>2</sub>

**Mercuric Chloride seems unique in the ability to oxidize metallic mercury vapours quickly and with minimum competing reactions.** However the presence of  $\text{Cl}^-$  ions is critical and serves to stabilize the  $\text{Hg}^{+2}$  from being reduced by the  $\text{SO}_2$  (or the equivalent species in solution). It seems that the various complexes of  $\text{Hg}^{+2}$  with Chloride in solution are remarkably effective in preventing its reduction by molecules other than  $\text{Hg}^0$ .

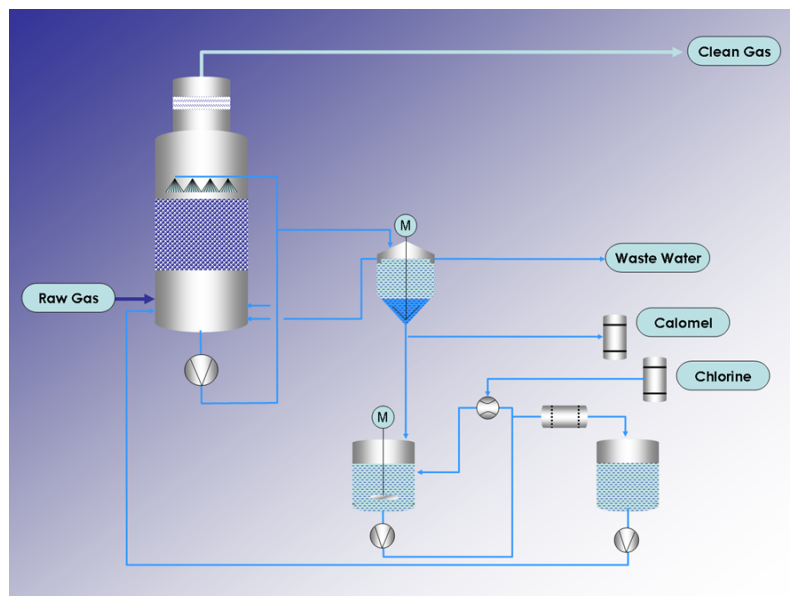
Taskinen et.al. (15) gives an indication of the complex nature of the Mercury speciation.

Lossin and Windhager (16) presented the work done at Norddeutsche Affinerie (now Aurubis) to produce acid with lower impurities. They verified temperature of the gas from the calomel scrubber as a factor controlling the concentration mercury in the treated gas.

### Description of Calomel Process

The mercury containing gas passes in a counter-current flow through a packed tower, where a solution of Hg-chloride in a complex form is circulating via redundant installed pumps.

In addition to the calomel-process, a vessel containing specially designed mist eliminator pad should always be installed at the outlet of the tower to prevent the carryover of scrubbing solution and to increase the removal even further in order to obtain the required quality of the product acid.



**Figure 2: CALOMEL Process**

During the reaction between the gas and the scrubber solution insoluble Hg Chloride (calomel) is precipitated. A part of the calomel containing solution is pumped to the Settler.

There the product (calomel) is isolated from the system by decantation as a heavy sludge. A portion of the calomel is then separated from the process.

The remaining calomel is re-oxidized in the chlorinator vessel with the oxidant chlorine ( $\text{Cl}_2$ ) dosed by an injection mixer and via circulation pumps to Mercuric Chloride ( $\text{HgCl}_2$ ).

A strong solution of Mercuric Chloride ( $\text{HgCl}_2$ ) is prepared in this manner and stored separately in the strong solution vessel via suction filter.

The solution is fed into the circulation system via

diaphragm dosing pumps at a rate that corresponds to the consumption according to the calomel process reaction.

A portion of the liquid of the settler is discharged to the reaction vessel for waste water separation.

### Factors not usually considered or publicized

Equation one is very simple and it fails to address fundamental issues on rates of mass transfer and rates of reaction. Germane facts include:

- The  $\text{HgCl}_2$  is (mostly) in solution with some as vapour, while the  $\text{Hg}^0$  is almost entirely in the gas phase, and the  $\text{Hg}_2\text{Cl}_2$  is a solid and can actually form nice crystals in the liquid phase.
- Mass transfer of  $\text{Hg}^0$  from the gas to the liquid should have large resistance to mass transfer resistance in both the gas phase and liquid phase.
- Mass transfer of  $\text{HgCl}_2$  from solution to the gas should also have large resistance to mass transfer in both the gas phase and liquid phase.
- If there is a gas phase reaction actually according to Equation 1 it would almost certainly result in sub-micron aerosol formation in the gas phase! Reactions between 2 gases to form a solid are well known and are the cause of many sub-micron aerosol problems. Many of these are so well known there seems no purpose in referencing them.
- $\text{HgCl}_2$  and  $\text{Hg}^0$  are known to be present in the gas, but no reference specific to Mercuric Chloride,  $\text{Hg}_2\text{Cl}_2$ , in the exhaust gas has been found.
- There will be small amounts of solids present in the gas as particulates. Solids may have passed the particulate gas cleaning equipment and the formation of small amounts of particulates containing mercury in the scrubber cannot be ruled out, so solids removal should be considered at the downstream side of the calomel contactor.
- There may be entrainment, which contains solids, in the gas. Entrainment is easily removed to any required level with good mist elimination; but adequate mist elimination is not always provided.

**The Calomel Process is an**

- Excellence Method for treatment of high Hg containing gases, but
- Limited in its performance for producing low Hg-containing product acids

**Therefore find an easy way to improve it!**

**Make it feasible to retrofit the solution!**

### **MERCUR<sup>EX</sup> B-GON<sup>TM</sup>-Technology**

So; what are the limitations of the conventional calomel process?

- Equilibrium vapour pressure of  $\text{HgCl}_2$  over the solution; a major factor
- Unreacted  $\text{Hg}^0$  vapour; also a major factor.
- Hg in particulate or aerosol form, coming into the primary scrubber with the gas.
- Aqueous fog formed anywhere in the system. Aqueous fog is very easily formed due to cooling of the gas. Such fog would inevitably contain  $\text{HgCl}_2$  and  $\text{HgCl}$ .
- The basic Calomel chemical reaction could occur in the gas phase and generate sub-micron aerosols and/or particulate nuclei remaining in the gas phase. Similar reactions are well known causes of smog. Such reaction would compete with those covered in 4 and would also serve as a precursor to the results in 4, above. The particulates resulting from this path, which would be sub-micron.

Intensive testing and long-term experience using the superior separation Technology of Florida USA showed excellent results.



KIMRE Inc.

This leads over to the improved CALOMEL-Process based on:

- A three transfer units of absorption, with or without reaction, and,
- Simultaneously and independently up to 3 transfer units of Enthalpy (water based transfer of heat and mass)
- Simultaneously and independently, collect 99+% of aqueous fogs and also,
- Simultaneously and independently, collect particulates to 1 micron or even lower.

The simplest design can be described as follow:

- The first stage using the strong regenerated  $\text{HgCl}_2$  provides for additional conversion of the  $\text{Hg}^0$  into the bulk solution, and in fogs. It also does fog and particulate removal and it provides all of the make-up of the  $\text{HgCl}_2$  for the main scrubber.
- The second Kimre-stage is irrigated with water (or even better a salt solution using required salt make up) collects the  $\text{HgCl}_2$  and provides the make-up water for the system. It can also easily be designed for more particulate removal.
- A final very efficient entrainment separator stage assures that none of the collected mercury contained in liquid is discharged with the gas. The exhausted gas that is saturated with water vapour, is very clean, and has very low mercury content.

Removal of essentially all the mercuric chloride is easily demonstrated and up to 95% removal of the total mercury is achieved.

The function of the Post Treatment of the Mercury Removal System is to remove:

- elemental mercury vapours,
- aerosols containing mercuric chloride and mercurous chloride,
- particulates, containing mercuric chloride and mercurous chloride, and
- vapours containing mercuric chloride;

from the off-gas stream to achieve consistent total mercury emissions of less than 0.015 mg/Nm<sup>3</sup>.

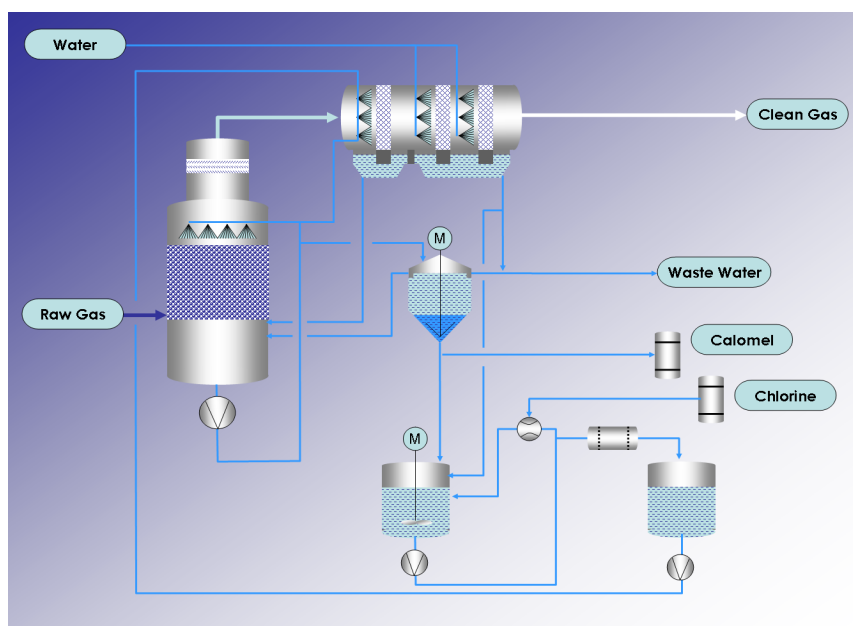


Figure 3: MERCUREX B-GON™ Mercury Removal Technology

A SXF™ scrubber will be placed at the outlet of the reactor tower and complement the current scrubbing system. The SXF™ will usually be comprised of two irrigated stages of KON-TANE® Scrubber and Tower Packing followed by one stage of B-GON® Mist Eliminator. The first KON-TANE® stage is irrigated with the regenerated solution to oxidize remaining Hg<sup>0</sup>, fog, and particulate, while the second KON-TANE® stage is irrigated with fresh make-up water to remove HgCl<sub>2</sub> vapour. A very small amount of make-up water is required by the overall system; only a very small amount is required for absorption of the HgCl<sub>2</sub> vapours. The

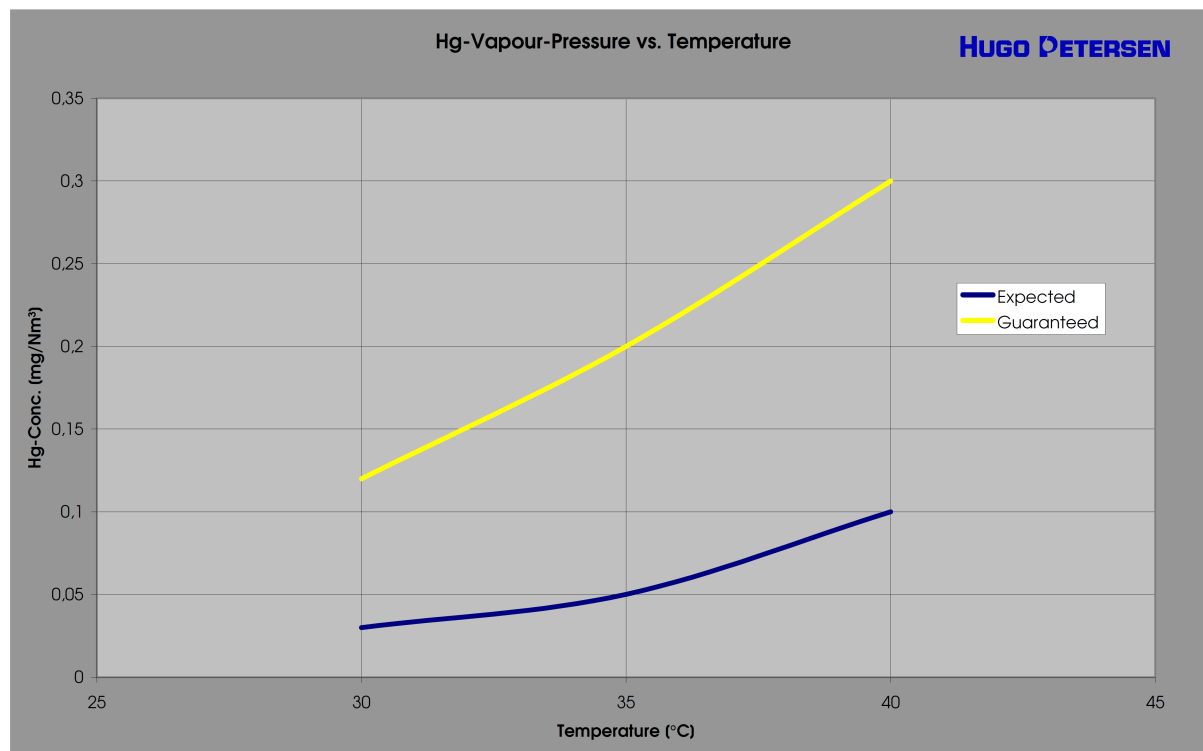
solutions from all stages are recycled to the current Calomel

process to balance the oxidation demand, and the make-up water demand. The B-GON® stage is a high-efficiency mist eliminator irrigated intermittently with make-up water provides removal of any entrainment.

The net result is a slight increase in pressure drop, and no material change in any other operation except for the reduced Mercury in the product acid

HUGO PETERSEN exclusively markets this Technology supported by KIMRE's expertise in the design of its superior B-GON®/KON-TANE® Technology.

- An improved process for the removal of Mercury from gases generated in smelting has been developed, Trademarked as **MERCUREX B-GON™**, and is now available for application..
- It is expected the process can be modified and combined with Kimre's AEROSEP® sub-micron removal technology for other applications; including power plant off gases, where it will remove mercury as well as Dioxins, and other heavy *metals*.

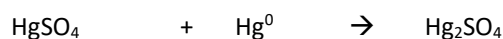


## Thiosulphate-Technology

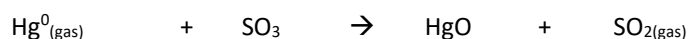
The advantage of this process alternative is the use of sulphur-containing chemicals and extremely low Hg values in the product acid of less than 0.5 mg/Nm<sup>3</sup>.

### Process Description

Mercury is removed by a two tower drying stage operating in series. The first drying tower operates at an acid concentration of 80% H<sub>2</sub>SO<sub>4</sub> and a temperature below 50°C and will not require a demisting. The second drying tower is a conventional tower operating at 96% H<sub>2</sub>SO<sub>4</sub>. Mercury reacts with the mercury dissolved in the acid to form mercurous sulphate. This 2-stage is used to allow a later treatment of the acids at a concentration of less the 75 to 85% H<sub>2</sub>SO<sub>4</sub>.



The mercurous sulphate is then oxidized to mercuric sulphate by the strong acid and oxygen in the gas.

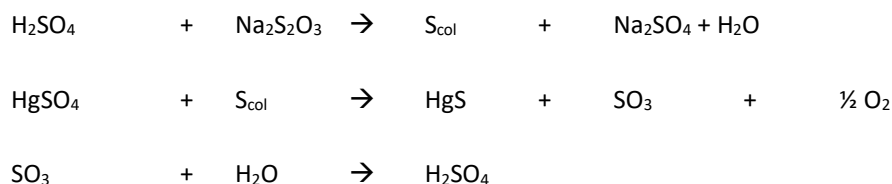


To maintain the acid concentration in the post-drying tower the concentration is kept by the addition of sulphuric acid out of the Intermediate-Absorption-Tower (IAT) or better with SO<sub>3</sub>-Gas. The Pre-drying Tower is strengthened by addition of sulphuric acid from the IAT, as well. The Post-drying Tower is operated at 97.5 to 99 % sulphuric acid.

The surplus acids out both drying towers are finally fed to a collecting tank to be mixed.

In the following liquid-treatment the acid is treated with sodium-thiosulphate to precipitate the mercury as mercuric sulphide. On this way first of all colloidal sulphur is needed.

Colloidal sulphur can be formed in the acid by the addition of sodium-thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). The reaction to form colloidal sulphur is as follows:



The sulphur will react with the mercury to form crystalline mercury sulphide ( $\text{HgS}$ ). Other metal contaminants in the acid will also react with the sulphur to form insoluble metal sulphides.

The method is restricted to acid concentrations less than 85%  $\text{H}_2\text{SO}_4$ . At higher acid concentrations the sulphur is oxidized to sulphur dioxide ( $\text{SO}_2$ ). As well, the product acid will also contain sodium sulphate which may be undesirable in the product acid. The proper dosage of sodium thiosulphate is also required otherwise a very fine mercury sulphide is produced which is difficult to filter. This method is capable of reducing the mercury levels from 15 ppm to 0.5 ppm after a holding time of 1 hour.

Hydrogen sulphide could also use as the source of sulphide for precipitation of mercury and other metals. This method is preferable, if the presence of sodium sulphate is undesirable in the final product.

## Carbon-Technology

Activated carbon/coke is used by HUGO PETERSEN since 1984 for various applications. The adsorption characteristic properties of this compounds are preferably used for the fixation and removal of traces of Hg, Dioxins/furans or any other heavy metal from process gases or off gases. For the adsorption of mercury, activated carbon can normally adsorb 10-12% of its own weight. The operating temperature of the carbon filter is limited to 50°C. The method is especially suitable for low mercury concentrations in the gas. A removal efficiency 90% is easily achievable.

This process has successfully been used in various applications and gases.

## Literature Citation

1. **Canada, Environment.** "Mercury and the environment — Basic facts". Canada : Federal Government of Canada, 2004. 8. / Archived from the original on 16 September 2011. Retrieved 27 March 200.
2. --. Qin Shihuang. s.l. : Ministry of Culture, People's Republic of China, 2003 / Archived from the original on 4 July 2008. Retrieved 27 March 2008.
3. **Wright, David Curtis.** The History of China. . s.l. : Greenwood Publishing Group. p. 49., 2001. ISBN 978-0-313-30940-3..
4. **W, Hesse R.** Jewellerymaking through history. s.l. : Greenwood Publishing Group. p. 120. , 2007. ISBN 978-0-313-33507-5..
5. **Stillman, J. M.** Story of Alchemy and Early Chemistry. s.l. : Kessinger Publishing. pp. 7–9., 2003. ISBN 978-0-7661-3230-6..
6. **Eisler, R.** Mercury hazards to living organisms. s.l. : CRC Press., 2006. ISBN 978-0-8493-9212-2.
7. **(EPA), Environmental Protection Agency.** Mercury: Spills, Disposal and Site Cleanup. s.l. : Environmental Protection Agency (EPA), Archived from the original on 13 May 2008. Retrieved 11 August 2007.
8. **(USGS), United States Geological Survey.** Glacial Ice Cores Reveal A Record of Natural and Anthropogenic Atmospheric Mercury Deposition for the Last 270 Years. s.l. : United States Geological Survey (USGS), Archived from the original on 4 July 2007. Retrieved 1 May 2007.
9. **Solnit, R.** Winged Mercury and the Golden Calf. s.l. : Orion Magazine, September–October 2006 / Archived from the original on 5 October 2007. Retrieved 3 December 2007.
10. **(EPA), United States Environmental Protection Agency.** What is EPA doing about mercury air emissions? s.l. : United States Environmental Protection Agency (EPA), Archived from the original on 8 February 2007. Retrieved 1 May 2007.
11. **G, Pacyna E, et al., et al.** Global anthropogenic mercury emission inventory for 2000. s.l. : Atmos Environ. 40 (22): 4048, 2006.
12. **Maprani, Antu C., et al., et al.** Determination of Mercury Evasion in a Contaminated Headwater Stream. s.l. : Environmental Science & Technology., 2005.
13. **Ministry of the Environment, Government of Japan.** Minamata Disease The History and Measures. Tokyo, Japan : Ministry of the Environment, Government of Japan, Archived from the original on 24 June 2009. Retrieved 7 July 2009.
14. **Normile, Dennis.** In Minamata, Mercury Still Divides. s.l. : Science. 341 (6153): 1446. Bibcode:2013Sci., (27 September 2013).
15. Increased Productivity of Zinc Roasters and SO<sub>2</sub>-Quality. **Taskinen, Metsaerinta, Saxen, Penttinen, Svens, and Kerstiens.** s.l. : The South African Institute of Mining and Metallurgy Lead and Zinc, 2008.
16. Improving the quality of Smelter acid,. **Windhager:, Lossin and.** 1999, s.l. : CRU, Sulphur, Vol. Sulphur 99, pp. 209-220.
17. ---. Mercury and the environment — Basic facts. s.l. : Environment Canada, Federal Government of Canada, 2004 / Archived from the original on 16 September 2011. Retrieved 27 March 2008.

## References

# Wet gas cleaning for metallurgical sources

## Turbulence Scrubber, Wet-Electro-Static-Precipitator



Pic. 4: Cleaning off gases by means of absorption and aerosol removal downstream of pyro-metallurgical processes in non-ferrous industries.



Pic. 6: Complex multistage wet scrubbing unit installed at a metallurgical plant.



Pic. 11: Cu-smelting based metallurgical DC-plant original 900 tpd and lately revamped to 1,500 tpd



# **HUGO PETERSEN**

Verfahrenstechnischer Anlagenbau

**HUGO PETERSEN GmbH**  
Rheingastr. 190-196, Geb. K330  
65203 Wiesbaden  
Deutschland

Tel.: +49-611-9627820 Fax: +49-611-962 9099  
E-Mail: [contact@hugo-petersen.de](mailto:contact@hugo-petersen.de) Web: [www.hugo-petersen.de](http://www.hugo-petersen.de)

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