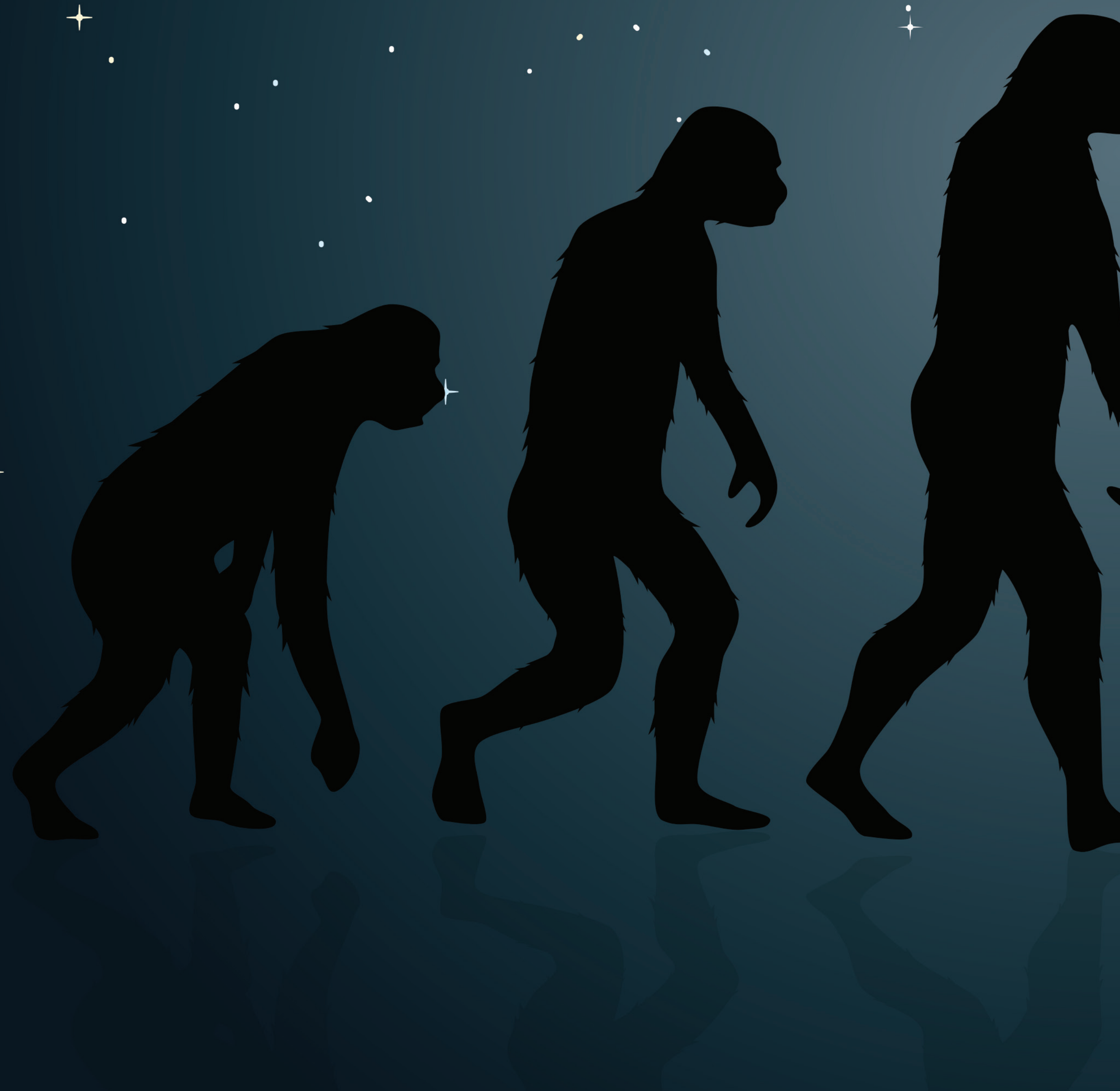
THE EVOLUTION OF THE CALOMEL PROCESS



Steve Fediw, Kimre Inc., USA, analyses how methods of mercury control have improved through trial and breakthrough, and which technologies are pushing the industry forwards.

Even well-run metallurgical sulfuric acid plants suffer from mercury contamination, and there is more to it than simply equipment corrosion. Mercury abatement is a matter of environmental regulatory compliance, and product integrity. Even trace amounts of mercury that end up in the product acid are hazardous, and it is the plant's responsibility to prevent this.

Over the past few decades, with increasingly stringent regulations and public scrutiny, the industry has been re-examining how to approach mercury removal. What used to be 'good enough' is not anymore. This article will take a close look at how methods to control mercury have improved through trial, breakthrough, and a keen

understanding of engineering realities. This article will analyse those challenges, examine successes and failures from the site, and showcase the kinds of technologies that are pushing the industry forward.

Understanding the problem of mercury contamination in metallurgical acid plants

Mercury is poisonous to the environment and removing it from metallurgical gas streams presents special challenges. In smelter-based sulfuric acid operations, mercury impurities can be present within the process in both vapour and particulate forms. Unless intercepted properly, this gets absorbed into the product acid, which can have detrimental effects on people's health, and make it difficult to comply with environmental regulatory requirements.

The traditional calomel process – relying on chevrons for mist elimination – used to be sufficient for sulfuric acid plants to meet regulatory requirements. However, increasing throughput specifications, more stringent emission limits, and greater process complexities have made meeting the target more challenging. For these reasons, new, innovative hybrid scrubber technologies and high-efficiency mesh-pad-style mist eliminators are becoming more common.

Technical spotlight: the chemistry behind the calomel process

The calomel process depicted in Figure 1 is a well-established process for removing mercury from the feed gas in sulfuric acid plants. The chemical pathway involves converting elemental mercury (Hg_2) into a solid, filterable form. The process is based on the oxidation of mercury vapour by mercuric chloride ($HgCl_2$) to form mercurous chloride ($HgCl_2$), also known as calomel.

Key reactions are as follows:

1) Hg^0 (gas) + $HgCl_2$ (solution) $\rightarrow$ Hg_2Cl_2 (solid)

2) Hg_2Cl_2 + Cl_2 $\rightarrow$ 2 $HgCl_2$ (regeneration step)

This reaction scheme allows for continuous cycling of the scrubbing solution. The solid calomel is separated from the circulating liquid in a settler or decanter, while chlorine gas is used to regenerate the oxidant. The efficiency of this process depends on several parameters, including the gas temperature, chlorine concentration, and liquid contact time.

One of the challenges in practical applications is managing the multi-phase nature of the system, as mercury in the gas stream may exist in the gas-phase as well as in aerosol and particulate-bound forms. Because of this, effective removal relies on both chemical reaction kinetics and physical separation techniques. This is where modern mist elimination and structured media scrubbers provide critical support since they capture droplets and aerosols that would otherwise escape the scrubbing tower.

Temperature control is also crucial. As temperature increases, the vapour pressure of mercury increases, reducing absorption efficiency (see Figure 2). Operating within the optimal range (typically 30 - 40°C) helps ensure that mercury remains in solution long enough for the conversion and precipitation reactions to occur.

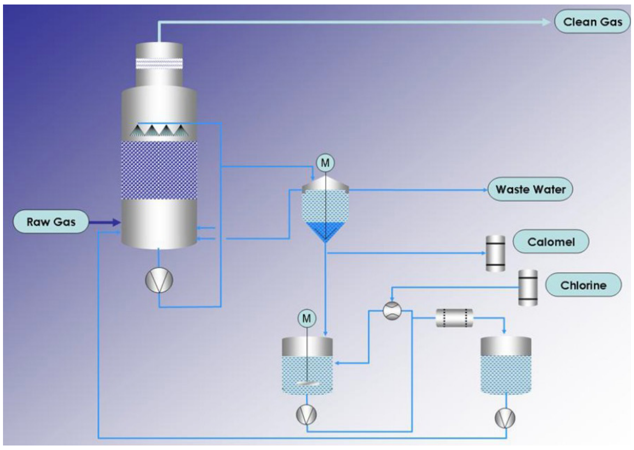


Figure 1. Calomel process.

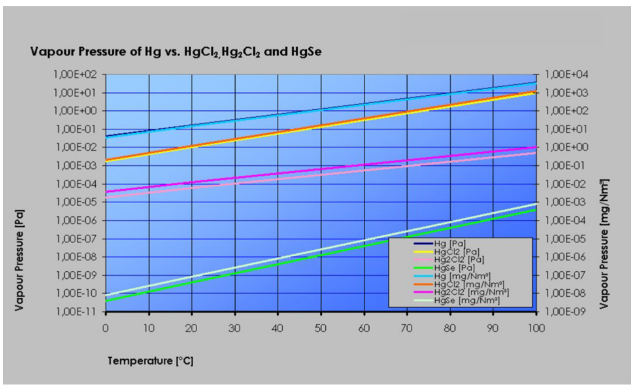


Figure 2. Vapour pressure of Hg, HgSe, Hg_2Cl_2, and $HgCl_2$.

Mercury removal: design best practices

A well-designed mercury control system begins with a thorough understanding of gas composition, flow characteristics, and phase interactions within the scrubber. Engineers must consider not only the chemical reaction kinetics of mercury-containing species, but also the physical behaviour of fine aerosols and liquid entrainment. This is why mist elimination should not be treated as just a final polishing step. It is a vital design element that can determine the overall success or failure of the system.

Key design considerations, such as mist eliminator placement, mesh pad composition, and irrigation strategy, must be carefully coordinated. It is important to never make the mist eliminator a better scrubber than the scrubber. Relying on the mist pad to compensate for weaknesses earlier in the process will ultimately result in reduced system performance, such as fouling and increased pressure drop.

Kimre's multi-stage B-GON® Mist Eliminators, with dedicated stages for scrubbing and entrainment removal, deliver consistent and reliable results. Proper pad sizing and placement to avoid bypass, spray nozzles specification and arrangement, and materials of construction (MOC) selection are all essential for long-term performance. Properly designed support structures and systems that allow for easy access and cleaning of the B-GON Media also help maintain system efficiency over time. To summarise, successful mercury control comes down to thoughtful engineering practices to design solutions that adapt to that sight's particular process.

Design considerations and material selection

An SXF™ Semi-Crossflow Scrubber is a system featuring Kimre technology whereby scrubbing liquid is sprayed from sets of pre-conditioning nozzles and flows horizontally through a series of mesh stages as the gas flows through it perpendicularly. A typical SXF configuration includes two or three irrigated stages using KON-TANE® Scrubber & Tower Packing or B-GON Mist Eliminator media which can be designed for high removal efficiency for particles down to 1 µm in size. The final stage is a high-efficiency mist eliminator that prevents mercury-containing droplets from re-entering the clean gas stream.

One of the defining features of such high-efficiency mercury scrubbing systems is the use of three-dimensional ladder-like B-GON Mist Eliminator media constructed of interlocking thermoplastic monofilament wires integrated within the SXF Semi-Cross Flow Scrubber System. Unlike conventional random knitted-mesh pads or vane-type mist eliminators, the fibres in this media are arranged to be perpendicular to gas flow ensuring maximum contact with mist droplets. This increased surface area drives highly efficient droplet coalescence, aerosol capture, and gas-liquid contact. This structured media design consisting of interlaced monofilaments arranged in a ladder-like geometry disrupts laminar flow and enhances droplet impaction. Different mesh styles with varying fibre diameters and void fractions allow for efficient removal of both large and small mist particles.

Material selection plays a critical role in performance and durability. For typical mercury service in sulfuric acid plants, polypropylene (PP) and high-temperature polypropylene (HTPP) are common due to their resistance to sulfuric acid mist and fouling. In more aggressive environments, media may be fabricated from PVDF or ETFE to withstand higher temperatures and other corrosive chemicals.

Additionally, void fraction and fibre spacing influence both pressure drop and liquid handling capacity. Pads with higher void space allow greater gas throughput while resisting fouling, though they must be paired with sufficient spray irrigation to prevent dry zones and the build-up of mercuric and mercurous chlorides. Ultimately, it is important to strike a balance between performance, complexity, and pressure drop.

Case history and plant benefits: redesigning the mercury scrubbing configuration

The final verification of any mercury removal technology is how it performs under real-world conditions. As an example, Kimre was contacted by a company in North America operating a zinc smelter struggling with excessively high mercury levels in their product acid, while operating a calomel-based scrubber. Kimre engineers re-evaluated the design of the system, keeping in mind the fundamental principles of mercury capture. It was determined that there were limitations to the process with its current vane-type set up that were making it unviable to achieve the extremely low mercury content required in the final acid. This is because particulates and fogs of mercury and mercury compounds were too fine to be effectively collected by the traditional chevron (vane) technologies.

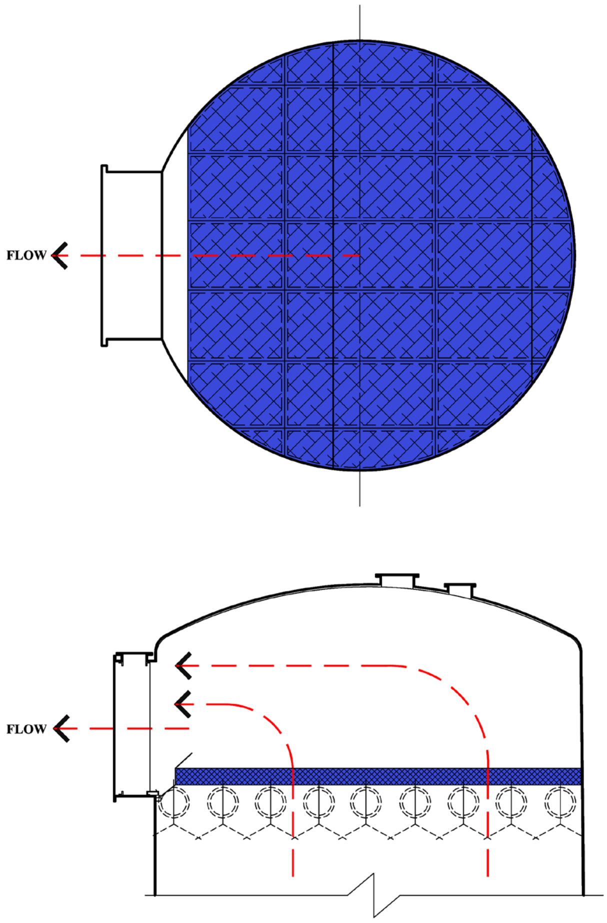


Figure 3. Single-stage Kimre™ technology installation.

For the initial solution, Kimre designed a single-stage B-GON Pad designed for maximum mist and particulate collection down to 1 - 2 µm in size (see Figure 3). Upon start-up, it was found that the B-GON Pad achieved significant reduction in the mercury content for the product acid, well below targeted values. However, the fine media employed could not remain clean due to build up of insoluble mercury compounds and other dusts. This then led to the installation of a 2-stage SXF™ Semi-Cross Flow scrubber design in which the first stage was comprised of the coarsest media used for maximum resistance to pluggage. Since it operated at a higher gas velocity due to the reduced cross-section, it also had excellent collection efficiency down to 5 - 8 µm. This was followed by a second stage B-GON Pad in a vertical orientation comprised of medium to finer media for collection of 3 - µm particulates and fogs. Further, the pads were supplied in V-bank type arrangement to increase the surface area to reduce velocity and pressure drop (see Figure 4). This SXF™ system used layered monofilament media, enabling particulate scrubbing and aerosol capture to occur simultaneously. After installing a two-stage B-GON Mist Eliminator pad system, the plant not only met but surpassed its targets. Mercury levels in the product acid dropped below 0.3 ppm, even when feed gas levels reached as high as 150 ppm. Since replacement of the tower was unnecessary as engineers were able to retrofit the existing scrubber, it was a cost-effective solution. This system continues to operate to this day with minor upgrades planned for the coming year.

Not only was this system able to achieve very low mercury levels in the final product acid, but there were other improvements as well. Operators reported reduced fouling, less maintenance, and longer pad life-cycles, due to the high liquid handling capacity compared to the initial single-stage mist eliminator installation. In this scenario, process teams were able to tailor the design to fit specific site requirements. The multi-stage configuration delivered consistent, positive results, despite facing entrained droplets, aerosols, and reactive fogs. Field data shows that these systems can consistently achieve emissions below 0.015 mg/Nm^3.

Environmental and regulatory impetus for mercury control

It is critical to remove mercury in sulfuric acid plants not only for operational efficiency and product quality, but also for health and environmental reasons. Mercury is a neurotoxin that can have long-lasting and sometimes irreversible effects on both human health and the environment. Exposure to mercury can impair neurological development and has also been linked to kidney damage, respiratory failure, and immune system disruption. Mercury can also accumulate in ecosystems, enter the food chain, and eventually impact wildlife and communities. If mercury becomes airborne in areas near smelting operations, it can contaminate the environment including local water bodies which could prompt public health warnings.

From a regulatory perspective, governments and international agencies are increasingly tightening control over mercury emissions. In the EU, waste incinerators and non-ferrous smelters are subject to strict limits under the Industrial Emissions Directive (IED). In the US, the Environmental Protection Agency classifies mercury as a hazardous air pollutant under the Clean Air Act. Globally, the Minamata Convention on Mercury, an agreement signed by more than 140 countries, aims to reduce mercury emissions and phase out its use in various industrial activities.

Ethical responsibilities aside, compliance with these regulations is mandatory for all metallurgical sulfuric acid plants. Therefore, implementing effective mercury control technologies is a good idea for any producer interested in avoiding serious legal litigations, hefty fines and irreversible reputational damage.

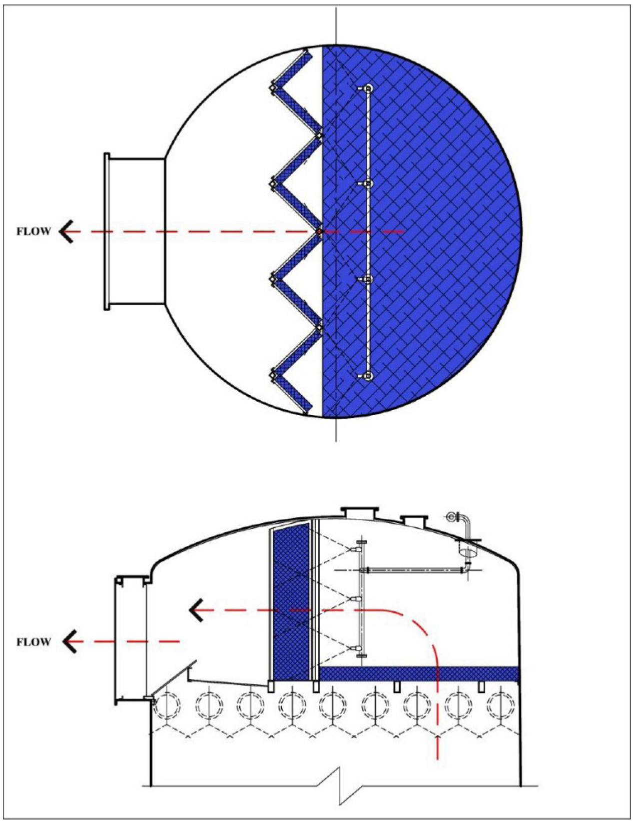


Figure 4. 2-Stage Mist Eliminator System.

Looking ahead: the future of mercury control technologies

As regulatory pressure intensifies and environmental responsibility becomes a higher priority across the industrial sector, the future of mercury control in metallurgical acid plants will rely on robust solutions that are adaptable and easy to maintain. Mercury removal solutions going forward are likely to centre around multi-functional systems that combine chemical absorption with physical separation, and in-line mercury monitoring tools that can detect performance issues early.

The main challenge moving forward will be striking the right balance between cost, complexity, and durability. Retrofitting older towers presents different engineering hurdles compared to building new installations from the ground up. Nonetheless, as global regulations become more stringent, plants will need to invest in stronger and more sophisticated mercury capture solutions.

Conclusion

Reducing mercury emissions is a critical operational and environmental challenge in metallurgical sulfuric acid plants that requires precise engineering and a thorough understanding of the production process. While the calomel process remains an effective mercury removal method, field experience has shown that performance can be significantly improved with enhancements like multi-stage, structured media scrubbers, optimised mist eliminator placement, and careful consideration of mist droplet behaviour.

The industry's path forward lies in effectively implementing droplet separation mechanics and established separation process design principles to customise the best solution. As metallurgical smelter plants continue to navigate a shifting regulatory environment, employing reliable mercury abatement strategies will be key to ensure compliance with environmental regulatory agencies. The solutions exist but they need to be applied in a technically sound and disciplined fashion. WF