CHAPTER 12.23

Mercury Abatement

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Mercury is a common element in ore bodies containing gold and silver. Alkaline cyanide solution will oxidize and leach mercury along with precious metal, resulting in pregnant solution containing all three metals. As with gold and silver, the mercury–cyanide complex is readily adsorbed by activated carbon, and mercury will be carried into any of the common carbon recovery schemes, including carbon-in-leach, carbon-in-pulp, and carbon-in-column.

The mercury–cyanide reduction potential (–0.33 V) is less negative than the potentials of silver (–0.45 V) and gold (–0.63 V) (Marsden and House 2006), and effectively all mercury in pregnant solution will be recovered along with the precious metal using zinc precipitation (Merrill–Crowe process) or electrowinning. Mercury leached with gold and silver will be present throughout the precious metal recovery operations, specifically the adsorption/elution circuits, and in the electrowinning solution, cathode sludge, zinc precipitate, and carbon regeneration kiln off-gas.

Mercury represents a significant health hazard for both acute and chronic exposure. The Mine Safety and Health Administration's current threshold limit value–time-weighted average (TLV-TWA; 8-hour shift) for airborne mercury is 0.05 mg/m^3 and the American Conference of Governmental Industrial Hygienists' TLV-TWA (8-hour shift) for skin contact with mercury is 0.025 mg/m^3 (MSHA 2015). In addition, mercury presents a persistent environmental hazard with industrial emissions heavily regulated by national and state governments. Mining operations must ensure effective process controls to minimize both employee exposure to mercury (including hygienic considerations and site monitoring) and control emissions to the environment.

Mercury regulation from the Nevada Division of Environmental Protection is widely viewed as a benchmark for the gold and silver mining industry. In reviewing mercury operating permits while working with gold and silver mining clients in Nevada during 2013–2015, the following was found: Mercury emissions (total mercury including airborne particulate and vapor) for process equipment, including retorts, electrowinning cells, smelting furnaces, and carbon regeneration kiln systems, are typically limited to 0.229–0.01145 mg/Nm^3, along with additional operating restrictions and requirements.

MERCURY AND PROCESS EQUIPMENT DESIGN

A review of the select physical properties in Table 1 shows that elemental mercury exists as a liquid with very low vapor pressure at ambient conditions. Condensed mercury will typically be recovered with water and is easily separated by decantation based on immiscibility and the large density difference.

Mercury has a low boiling point and high vapor pressure at elevated temperature compared to precious and base metals and can easily be separated by retorting (vacuum distillation). Retorts operate under reduced atmospheric pressure, typically 150–250 mm Hg (absolute) and temperatures up to 625°C. As an example, heating zinc precipitate or cathode sludge to a temperature of 400°C results in rapid vaporization of mercury (vapor pressure of 1,574 mm Hg) in a retort oven operating at a pressure of 200 mm Hg (absolute).

Heat input for retort oven design, along with operating cycle time, are largely dictated by water content of the zinc precipitate or cathode sludge. The latent heat of vaporization for water is 2,260 J/g compared to 296 J/g for mercury. The difference in latent heat is also a factor in condenser design, where again, the equipment sizing is largely driven by water loading.

Removal of mercury from gas streams in high-temperature systems (retorts and carbon regeneration kiln off-gas) is generally a two-step process. First, the water and mercury vapor

Table 1 Select physical properties of mercury

Vapor pressure, mm Hg/400°C	1,574
Vapor pressure, mm Hg/38°C	0.0052
Melting point, °C	–38.9
Boiling point, °C	356.6
Heat of vaporization, J/g	296
Specific gravity	13.6
Solubility in water	Trace

Source: Weast 1968

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are condensed and removed from the process gas, typically in a shell-and-tube-style heat exchanger. The process gas is then passed through a vessel containing sulfur-impregnated carbon (SIC) to adsorb more than 99% of the remaining gas phase mercury. A design strategy is to take advantage of the low mercury vapor pressure by reducing process gas temperature prior to the SIC bed. As shown in Table 1, mercury vapor pressure drops from 1,574 to 0.0052 mm Hg by reducing the process temperature from 400° to 38°C. Reducing process gas temperature to condense as much mercury as possible results in reduced mercury load to the SIC carbon bed (decreasing the operating cost for SIC replacement and maintenance time).

RETORTS AND MERCURY ABATEMENT SYSTEMS

Design and operating details are provided for a typical mercury retort-abatement system used in the gold and silver mining industry to remove mercury from air streams exhausted from carbon regeneration kilns, electrowinning cells, and smelting furnaces.

Retorts

A process flow diagram for a typical retort is shown in Figure 1. The system consists of a retort oven (electric, gas, or diesel fired), condensers, mercury/water trap, mist eliminator, HEPA/coalescing filters, adsorption vessel with SIC, and vacuum pump. Cathode sludge or zinc precipitate is discharged from a filter press into pans (larger retorts use trays and are loaded with a forklift) and loaded into the retort oven. Retorts are operated from a centralized control panel with interlocks and alarms. The vacuum pump is started, and the system is brought to an operating pressure of 150–250 mm Hg (absolute). A minimum system pressure must be maintained (this is often a mercury operating permit requirement) and is interlocked with the oven heating system and an alarm.

The retort oven undergoes a series of ramp and soak temperature increases, operating between 200° and 600°C. Water is evaporated at a lower temperature, followed by mercury vaporization at high temperature and finally cooldown. Retort operating cycles typically run from 18 to 24 hours. Water and mercury vapor leaving the oven pass through a series of two to three water-cooled condensers in series. Cooling water is circulated through the shell side of the condenser, while process gas makes a single pass through the tubes. A refrigerated chiller is typically supplied with the retort system and provides cooling water at 7°C. Condensed water and mercury are collected in a vessel (trap) that is equipped with a decant drain for water and lower discharge for mercury. Provision is made to collect drained mercury in a 1-t (metric ton) container or 34.5-kg flask.

The cooled process gas then passes through a demister vessel and duplex coalescing HEPA filter (one operating and one standby) before entering the adsorption vessel with SIC. The demisting vessel and HEPA filters are key elements to prevent fine aerosols and submicrometer-sized particulate from entering and fouling or passing through the SIC bed. HEPA filter media is specified to resist moisture and provide a collection efficiency of 99.97% at 0.3 µm. The SIC bed is designed to provide a mercury removal efficiency of 99.99% and service life of up to five years before replacement. A final HEPA filter is provided on the discharge of the SIC adsorption vessel to prevent submicrometer carbon fines from discharging from the system to atmosphere.

A liquid ring vacuum pump is used on the retort system with seal water provided from the chiller supply sump. Figure 2 provides an isometric view of a current retort design showing the equipment layout.

Retort systems are designed for regular maintenance and include integral spray systems to wash out particulate that accumulates in the condenser tubes and demister media. The sprays are turned on at the end of the retort cycle to flush out solids that are collected in the mercury/water trap. This system has been developed based on feedback from silver mining operators (Merrill–Crowe process) that experience problems with high solids carryover from the retort oven to the condensers.

Smelting Furnace Systems

Retorts are very effective at removing mercury from cathode sludge and zinc precipitate, typically achieving higher than 99% efficiency. However, residual mercury will be present in the retorted solids that are smelted into doré in the refinery furnace. Dust and fumes from the furnace, doré molds, and slag pots must be contained and captured to prevent exposure to refinery operators and release to the atmosphere.

Figure 3 provides a process flow diagram of a typical furnace system. Fume collection systems must be sized and designed based on furnace type. Gas- and diesel-fired furnaces require much higher extraction rates to accommodate flue gas along with fume and dust compared to electric induction furnaces. In addition, fuel-fired furnaces generate exhaust gas at higher temperatures than equivalent induction furnaces.

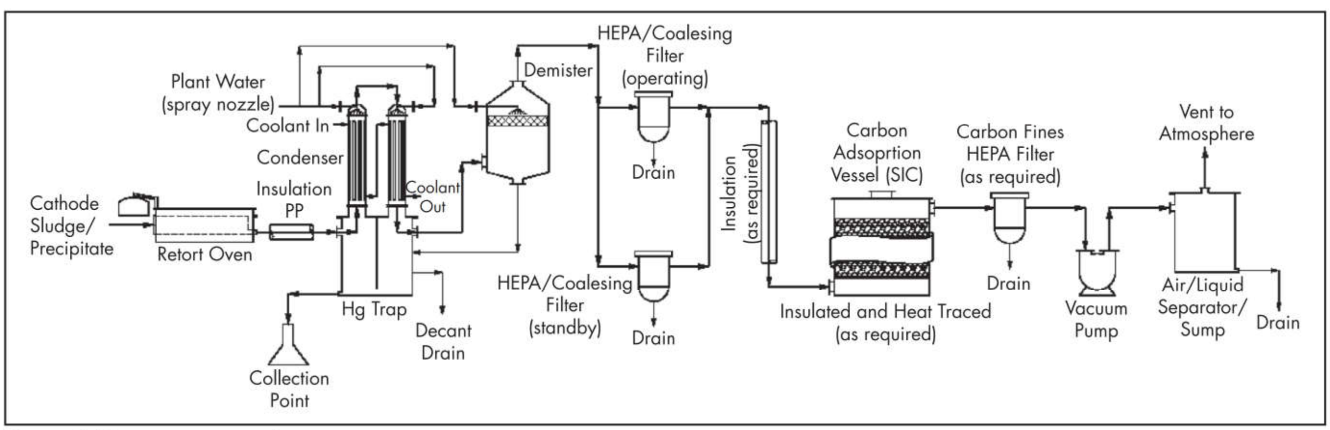


Figure 1 Retort mercury abatement system process

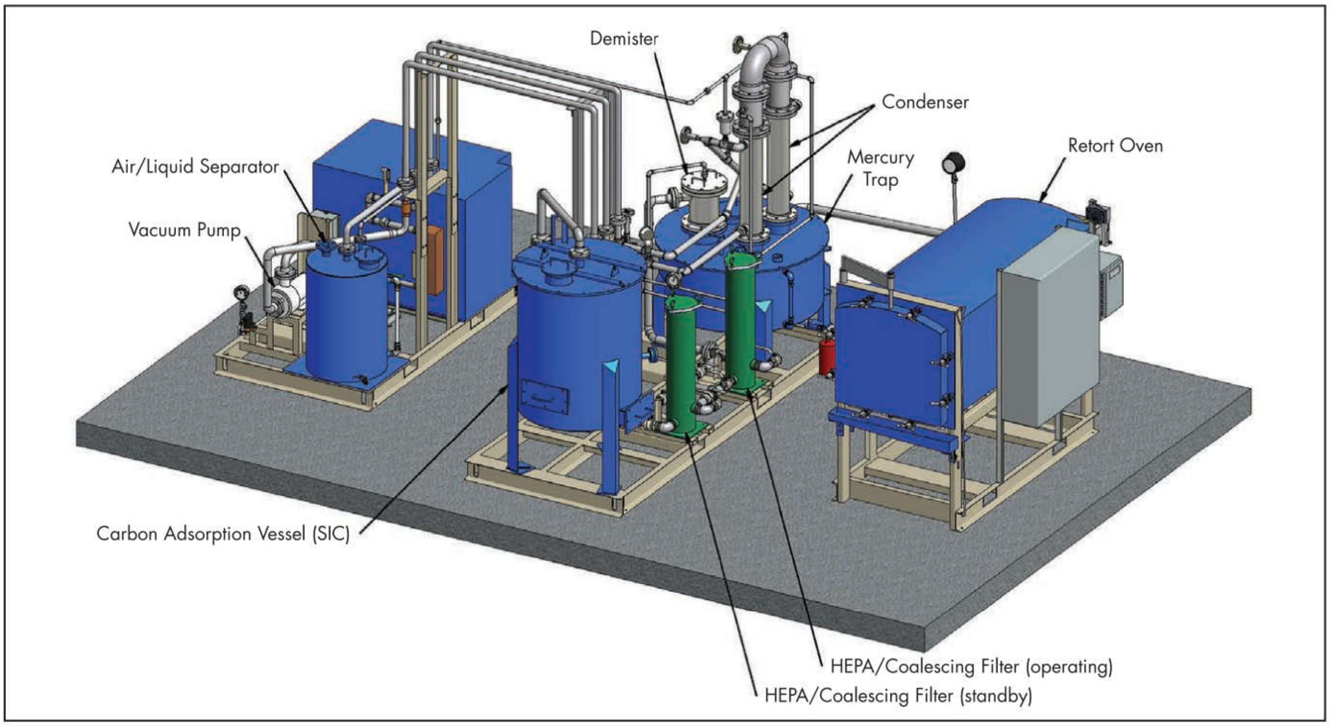


Figure 2 Retort system equipment

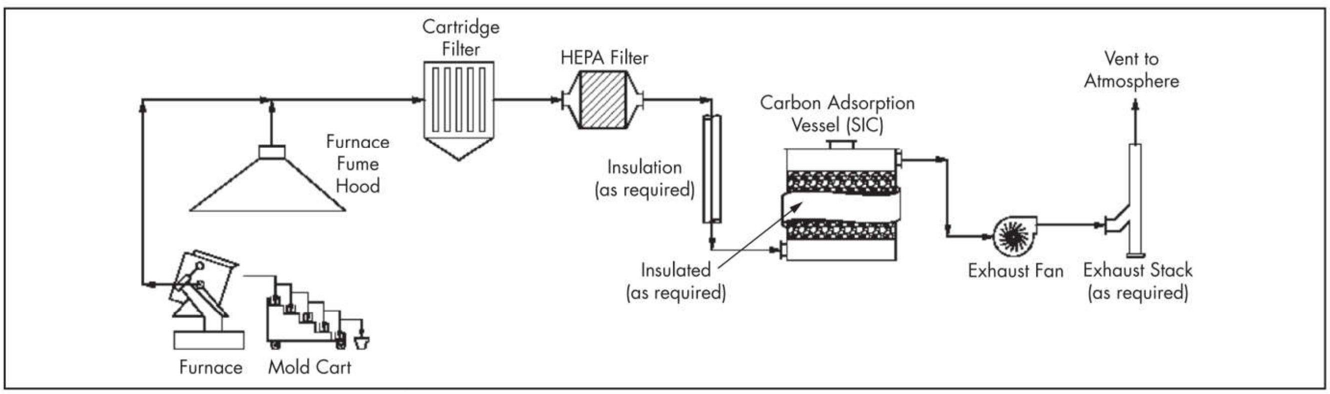


Figure 3 Furnace extraction mercury abatement system process

Primary pollution control for the furnace is a cartridge-style dust collector. Filter media can be specified for moderate- or high-temperature operation at 82° or 138°C, respectively. Following the dust collector is a HEPA filter specified for collection of particulate down to 0.3 µm at an efficiency of 99.97%. An SIC adsorption vessel provides removal of mercury vapor from the furnace off-gas.

An isometric view of a furnace system is shown in Figure 4; depending on the on-site climate, the pollution control equipment will be located inside a refinery building or outdoors. Typically, the exhaust fan for the system will be located outdoors or at a distance from the furnace to reduce noise exposure for operations staff in the refinery.

Electrowinning Cell and Process Solution Tank Ventilation Systems

Ventilation systems for electrowinning cells and process solution tanks must be designed to accommodate saturated gas and condensate. Pregnant solution from an elution circuit will typically enter electrowinning cells and pregnant/barren/return solution tanks at a temperature between 66° and 90°C. Ventilation for electrowinning cells and process solution tanks is critical for removal of gases, including hydrogen and oxygen that are evolved during electrowinning, ammonia that is formed from thermal decomposition of cyanide during elution, and mercury vapor from both pregnant and barren solution that is circulating in an elution/electrowinning circuit. In addition, steam from unventilated electrowinning cells and process solution tanks will create a hot and humid work environment in the refinery.

A process flow diagram for an electrowinning cell ventilation system is shown in Figure 5. Process gas from electrowinning cells and process solution tanks is typically saturated or supersaturated with water vapor and ranges in temperature from 38° to 60°C. The process gas passes through a mist eliminator vessel designed to remove condensate and aerosol

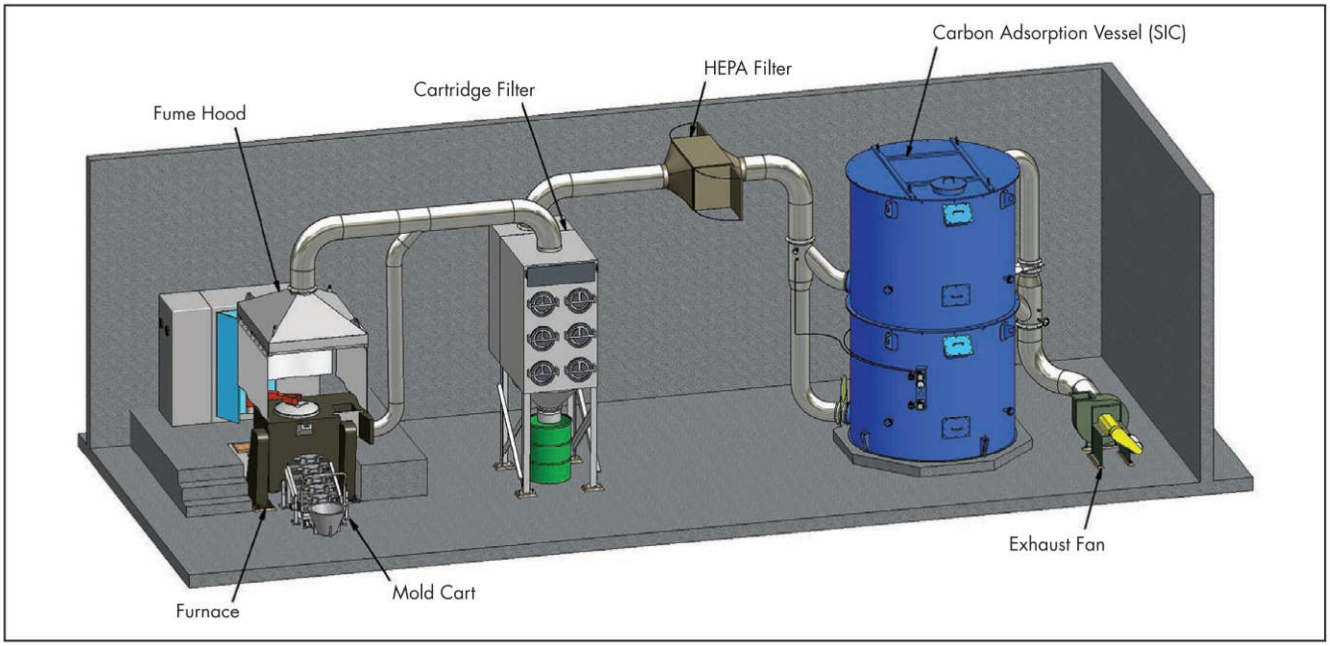


Figure 4 Furnace system equipment

down to 3 μm (98% removal efficiency). The demister vessel is designed with an upper decant drain with a U-bend to discharge collected condensate. A lower drain for condensed mercury is designed for discharge into a 34.5-kg flask and includes a sight glass to monitor accumulation of mercury. A spray nozzle is provided above the mist eliminator media to wash out any accumulated solids buildup.

Process gas exiting the mist eliminator will be saturated at the operating temperature and can condense in the downstream SIC adsorption vessel. An electric duct heater (or fuel-fired unit) is installed immediately after the mist eliminator to heat the process gas and maintain a relative humidity less than 80% through the SIC bed. The temperature of the SIC bed must be maintained at or above the temperature of the process gas, leaving the mist eliminator to prevent condensation and moisture buildup in the SIC. Insulation is typically specified for ductwork leaving the duct heater and for the SIC adsorption vessel, particularly for outdoor installations. An isometric view of a typical electrowinning cell ventilation system is shown in Figure 6.

Carbon Regeneration Kiln Systems

Mercury abatement systems for carbon regeneration kilns are similar to the design for electrowinning cells with the added requirement of addressing particulate. Figure 7 provides a process flow diagram for a kiln system. Kiln off-gas is passed through a coarse particulate filter to remove entrained carbon fines. The filter design is similar to the mist eliminator in the electrowinning cell system as kilns can operate over a range of temperatures and process gas can vary from 80° to 315°C. At lower temperatures, condensate can be present and must be removed with a decant drain and potential for condensed mercury in the lower drain. Construction is all 304 stainless steel to provide corrosion resistance and performance at elevated temperatures. A differential pressure gauge indicates solids buildup, and a spray wash is provided above the filter media to flush out accumulated carbon fines (discharge is typically routed to the plant carbon quench or carbon fines/clarifier tank).

Following the coarse particulate filter, process gas is passed through a water-cooled condenser (shell-and-tube-style heat exchanger). Plant water, if available at a temperature less than 27°C, can be used to cool the process gas; otherwise, a refrigerated chiller is supplied to provide cooling water at 7°C. Condensed water and mercury are collected in and drained from the mist eliminator vessel. The mist eliminator is similar in design to the electrowinning cell system described earlier in the "Electrowinning Cell and Process Solution Tank Ventilation Systems" section.

Following the mist eliminator, process gas is heated through an electric duct heater to prevent condensation in the SIC bed. Installation of a HEPA filter is an option before the SIC bed for kiln systems that generate higher quantities of carbon fines. The HEPA filter is similar in design to the unit described in the "Smelting Furnace Systems" section for furnace systems. The SIC adsorption vessel follows the HEPA filter for removal of final vapor-phase mercury. As with the electrowinning cell ventilation system, the kiln SIC bed must be maintained at a temperature equal to or greater than the gas temperature leaving the demister vessel to prevent condensation and buildup of moisture in the carbon. Insulation on ductwork and the adsorption vessel is a requirement to maintain temperature, particularly on outdoor installations. An isometric view of a typical carbon kiln ventilation system is shown in Figure 8.

SULFUR-IMPREGNATED CARBON AND ADSORPTION VESSEL DESIGN

A key element for all mercury abatement systems is the SIC adsorption bed. After separation of the condensed mercury upstream, the SIC bed is the final pollution control device to remove mercury vapor from process gas before release to the atmosphere. Unimpregnated activated carbon does not adsorb much mercury because its adsorption mechanism is based on

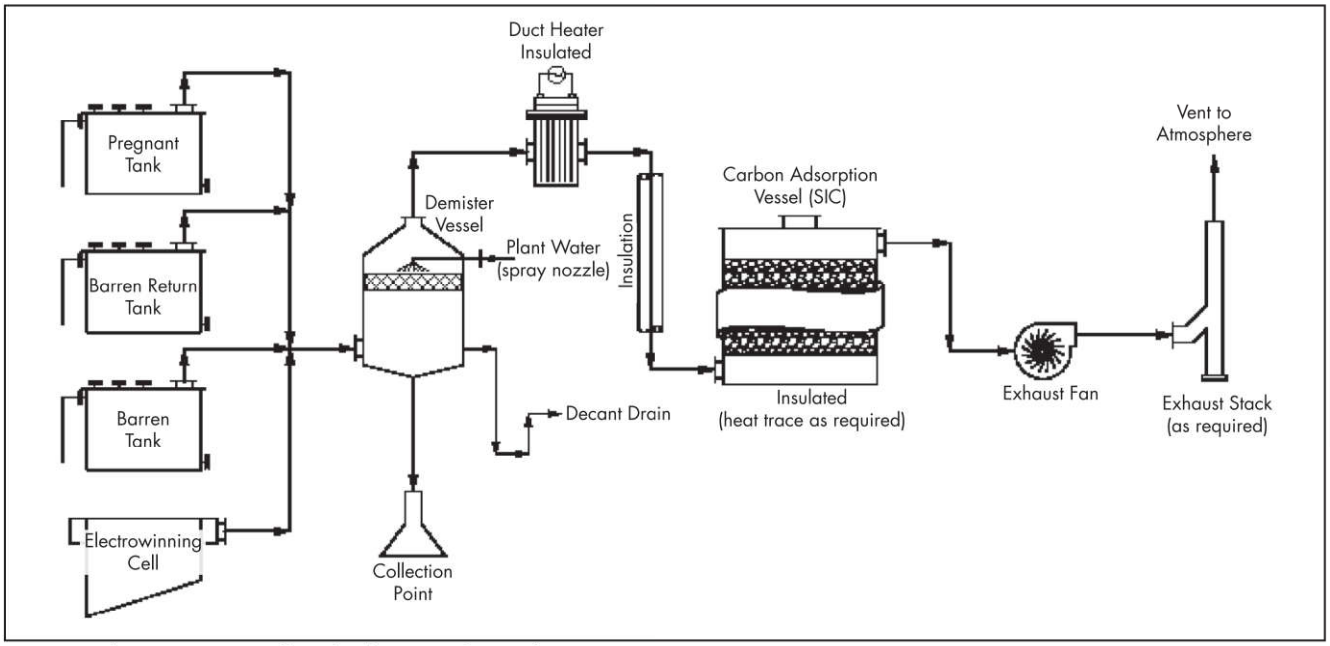


Figure 5 Electrowinning cell and solution tank ventilation process

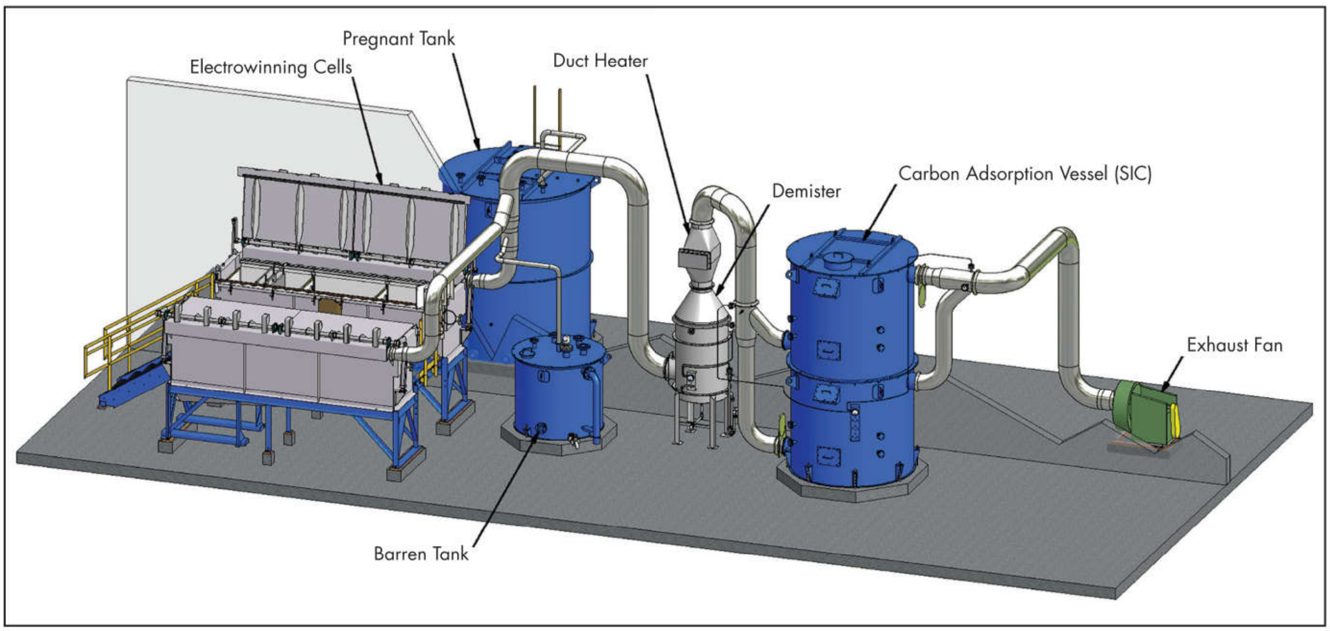


Figure 6 Electrowinning cell and solution tank ventilation equipment

physisorption and depends on intermolecular forces (van der Waals forces) that are relatively weak. SIC is preferred for scrubbing mercury from process gas for two reasons: SIC causes mercury to be strongly adsorbed, and SIC has a high mercury adsorption capacity, which is caused by chemisorption (valence forces) (Perry et al. 1984). Mercury reacts with the elemental sulfur in the carbon, forming mercury sulfide, which is a stable solid that will not revolatilize at operating temperature.

Many variables are important for SIC bed design, specifically process gas temperature, pressure, mercury concentration, flow rate, and moisture concentration (relative humidity). Bed diameter and depth must be sized to provide sufficient residence time for efficient mercury removal, reasonable pressure drop, and service life before replacement. Test data from the SIC manufacturer is key for bed design.

The plotted data in Figure 9 provide a comparison of mercury removal efficiency for varying residence times at an inlet concentration of 32 mg Hg/m^3 in air and velocity of 0.015 m/s. This is a high mercury concentration as air is saturated with mercury at this temperature. Yet mercury removal efficiencies remain at the 99.99% or higher levels for more than a year of operation at a residence time of ~10 seconds.

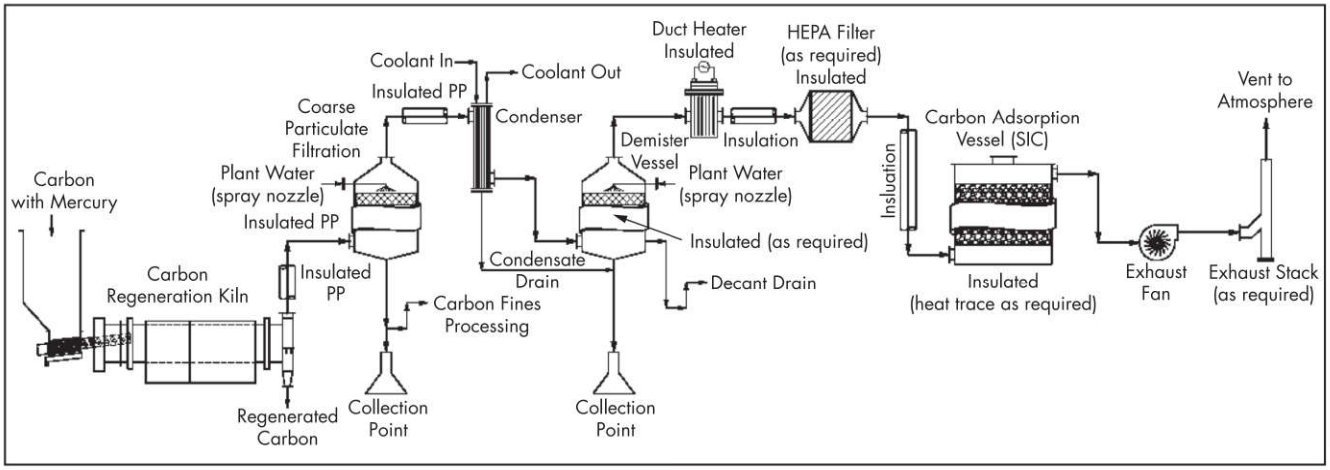


Figure 7 Carbon regeneration kiln process

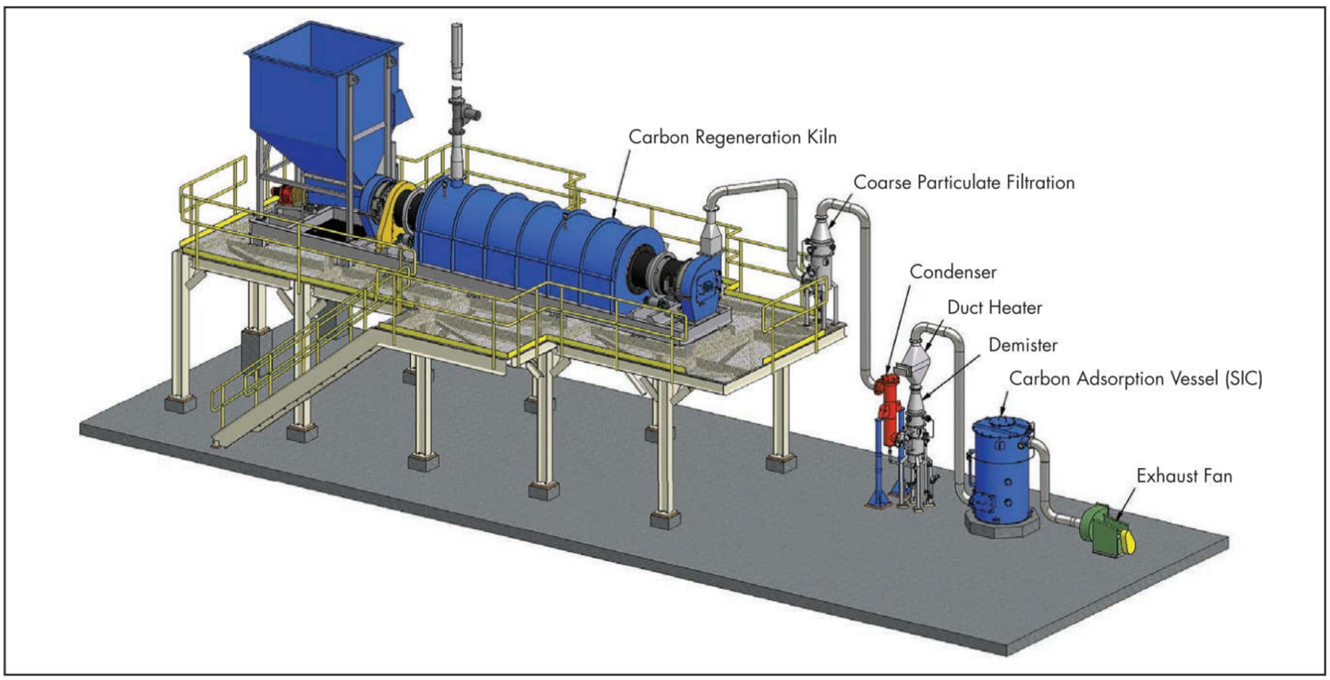


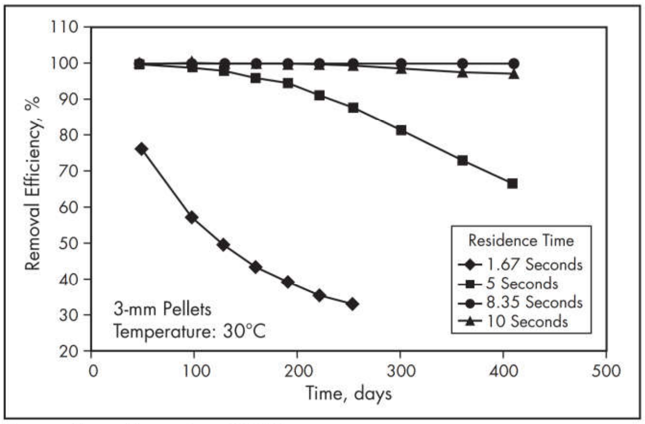
Figure 8 Carbon regeneration kiln equipment

The data were created using Mersorb 3-mm diameter mercury adsorbent pellets. Selective Adsorption Associates Inc. (SAAI) is the exclusive worldwide distributor of Mersorb, which is manufactured by Nucon. Cost-effective and long-wearing SIC adsorption systems have been designed by FLSmidth–Summit Valley Technologies (SV) working in close conjunction with SAAI, and FLSmidth-SV specifies Mersorb HT mercury adsorbent pellets for high-temperature applications.

Most SIC systems operate at temperatures less than 66°C; however, fuel-fired melting furnaces generate combined fume and flue gas that will enter the SIC bed at temperatures up to 135°C. The elemental sulfur impregnant will volatilize from ordinary SIC at elevated temperatures. Another consideration is that all activated carbons can pose a fire risk caused by rapid oxidation when exposed to hot gas and O_2 under certain conditions. Key contributors to rapid oxidation of activated carbons and proven preventive measures are reported in the literature (SAAI 2012).

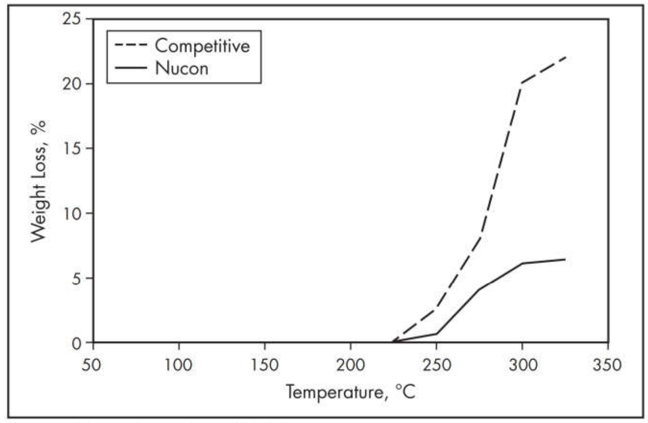
Figure 10 is a plot showing weight loss of the elemental sulfur impregnant in Mersorb HT mercury adsorbent pellets versus increasing temperature. The impregnant loss remains negligible to 250°C and less than 7% at 300°C. The ignition temperature of Mersorb 3-mm mercury adsorbent pellets is approximately 450°C under the conditions of ASTM test method D3466-06.

SIC adsorption vessel design must include provision for the collection of carbon samples and bed maintenance. The maximum mercury adsorption capacity of SIC is reported as 20-g Hg/100-g adsorbent (16.7 wt % Hg based on weight of used adsorbent) (Nucon 2012). Beds are typically sampled at multiple points and depths to confirm loading. Quarterly testing is often a requirement of the site mercury operating permit. In this author's experience (working with gold and silver



Source: Nucon International 2012

Figure 9 High-inlet-mercury concentration removal efficiency from air



Source: Nucon International 2012

Figure 10 Elemental sulfur impregnant weight loss

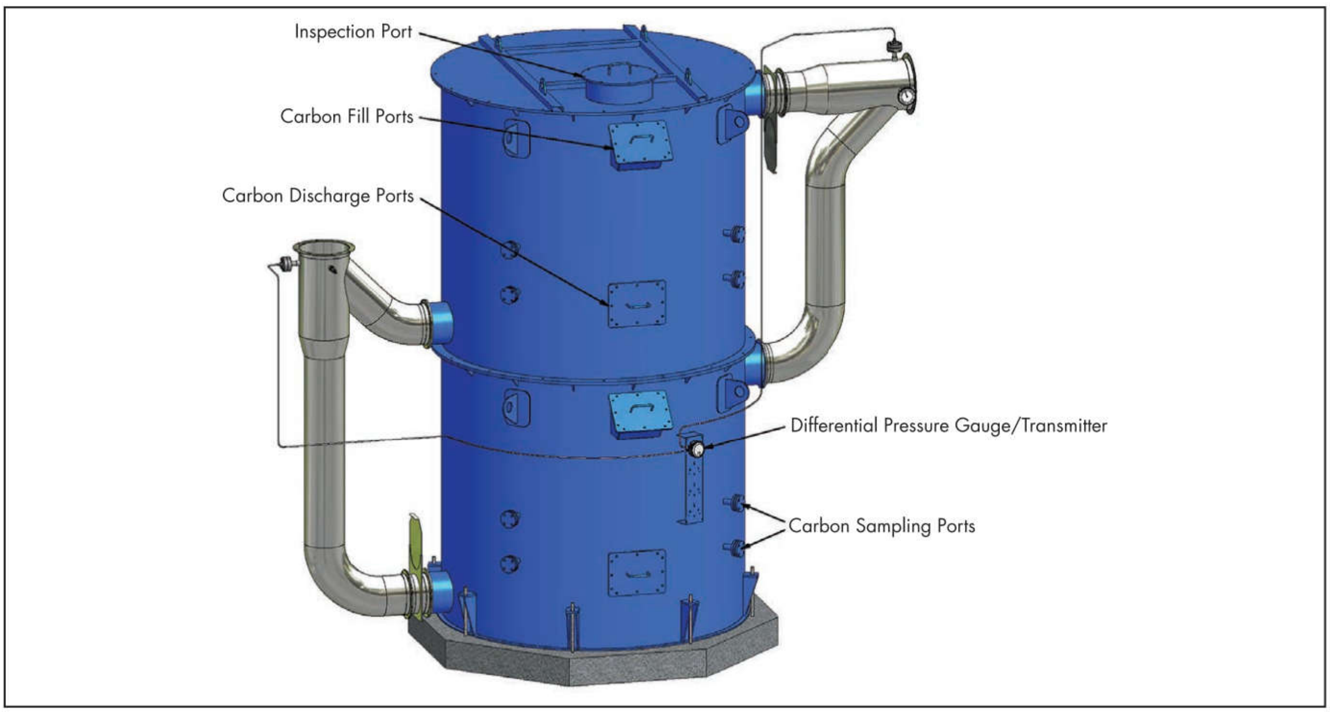


Figure 11 SIC adsorption vessel (parallel bed)

mining clients in Nevada from 2013 to 2015), once 50% of its maximum mercury capacity loading has been confirmed, sampling frequency is increased to monthly, and the carbon bed must be replaced within 30 days of reaching 90% of its maximum mercury capacity loading.

Figure 11 shows a schematic of a typical FLSmidth-SV SIC adsorption vessel. The vessel consists of two SIC beds operating in parallel with the flow split evenly between the upper and lower beds. This is a compact design for higher-process gas flow applications and keeps bed pressure drop below 100-mm H_2O with a reasonable bed diameter. Differential pressure gauges and transmitters are supplied to monitor pressure drop across the SIC beds. Baseline pressures are noted at start-up and are monitored over time to indicate potential problems with moisture or particulate buildup in the beds.

The adsorption vessel is designed with carbon-sampling ports at multiple locations and bed depths and includes an auger tool for convenient collection of samples. Each bed (vessel) is supplied with a lower carbon discharge port to remove spent SIC (typically discharged into a used bulk bag) and an upper fill port. The top inspection port can be used for collection of samples and for filling the vessel. The fill ports accommodate replacement of SIC supplied in bulk bags using a forklift.

MATERIAL HANDLING AND REFINERY HYGIENE CONSIDERATIONS

Refinery design requires consideration of ergonomics and equipment layout for material handling and good hygiene and housekeeping practices. Silver mining operations (Merrill–Crowe process) can generate large volumes of zinc precipitate

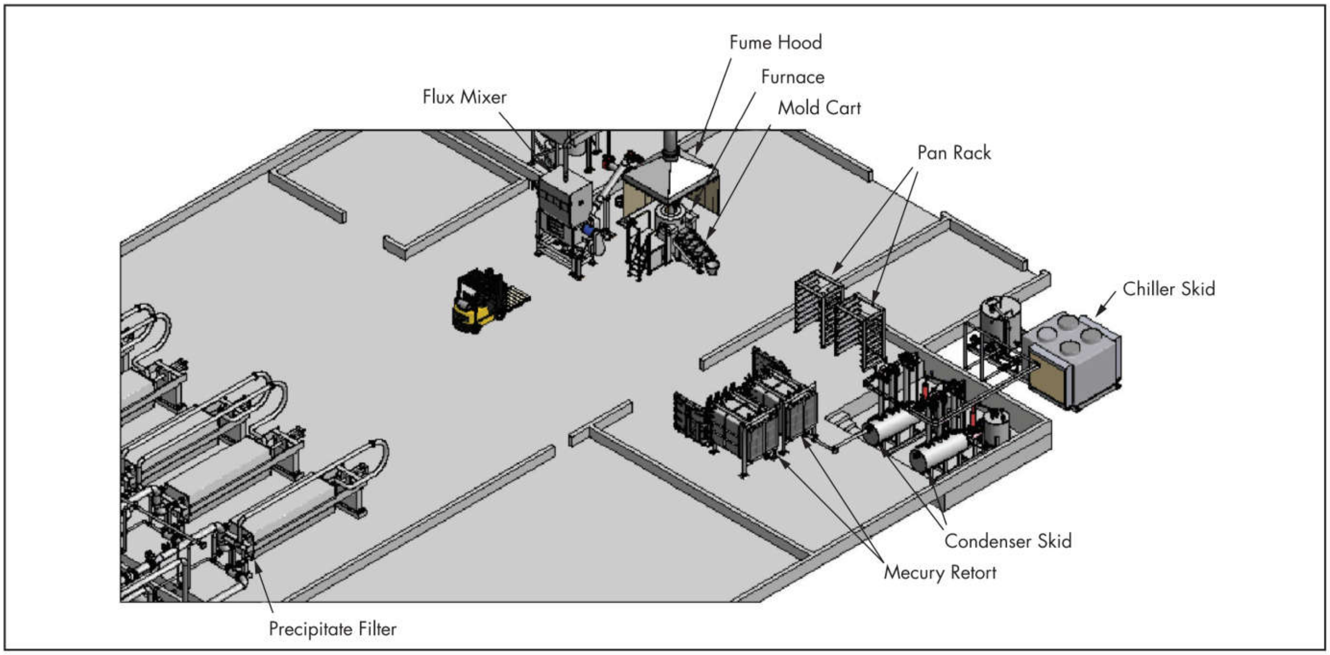


Figure 12 Merrill–Crowe process, silver mine refinery equipment

with mercury concentrations exceeding 20% by weight. Employee exposure to material containing mercury can be significantly reduced with implementation of mechanical handling equipment. Figure 12 shows the equipment layout of a recently commissioned silver mine refinery.

Zinc precipitate is discharged into steel trays below the filter presses. Once filled, the trays are taken by forklift and loaded into the retort ovens. Tray racks are provided for cooling the retorted precipitate and for staging the material prior to smelting. Trays of retorted precipitate are loaded by forklift into the tray-tipper at the top of the flux mixer. The tray-tipper and flux mixer are fully automated and operate under extraction to prevent release of dust. Along with the retorted precipitate, flux is added by tray to the mixer, and the material is fully blended for smelting. The precipitate/flux mix is metered and fed to the furnace using an auger conveyor. Operator contact with material containing mercury is minimized in a refinery with mechanized equipment and safety is improved by significantly reducing repetitive motions such as shoveling or scooping.

The refinery has been configured to provide separation and isolation of the retort room from the zinc precipitate filters and smelting area. For ventilation, the retort room is designed with slightly negative pressure compared to other areas of the refinery to contain any fugitive mercury emissions. The refinery areas are designed with floor sumps to collect and contain process solution and solid materials that may contain mercury or precious metal. Floors and walls are specified to have smooth surfaces with coatings and/or paint to allow frequent wash down with water. The refinery is designed with a locker room for operators to change into work clothing that is contained and laundered separately from regular clothing. Shower and wash facilities adjoin the locker room area to promote operator hygiene.

CONCLUSION

Modern mining technology and techniques enable economic recovery of precious metal from lower-grade ore bodies that often contain deleterious elements such as mercury. Gold and silver recovery processes and equipment must be designed and planned holistically with respect to operator safety, emissions to atmosphere, and efficiency. Environmental regulation will continue to increase and become more stringent, with the expectation that mining owners and operators will employ the best technology currently available. Mining owners will require the support and close collaboration with proactive partners to design processes and equipment for their specific operations.

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