A Review of Sulfide Smelting Process Gas Handling Systems

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1.0 SMELTER PROCESS GAS CHARACTERISTICS

Off-gas handling systems for sulfide smelting processes are a major source of downtime and scheduled maintenance activities. Most smelters are faced with similar operational and maintenance problems, although the degree varies depending on the smelting process and the type of gas cooling and cleaning system utilized. Typical problems include:

- Plugging of uptakes and flues due to the carryover of dust from the primary smelting vessel
- Corrosion of off-gas handling equipment due to the high acid dew point of the high strength SO_2 gas produced in modern non-ferrous processes
- The gas must be cooled in a manner that maintains the SO_2 strength required for sulfuric acid production
- Mechanical problems with dust collection equipment
- Carry-over of dust to sulfuric acid production facilities

1.1 Sulfide Smelting Process Gas Characteristics

SO_3 Formation and Acid Dew Point

Thermodynamics of SO_2 conversion to SO_3 has been reviewed in a number of technical papers. A brief review is presented here. The SO_2 laden smelter process off-gases are partially converted to SO_3 as the gases are cooled. SO_3 forms dilute sulfuric acid upon reaction with water. The degree of SO_3 formation in the furnace off-gas handling system depends on a number of factors:

- Off-gas temperature
- Off-gas oxygen content (and off-gas system infiltration)
- Off-gas residence time
- Dust content and characteristics

The conversion rate of SO_2 to SO_3 is small at elevated temperatures. As the gas is cooled below 760°C (1400°F), however, rapid conversion of SO_2 to SO_3 can take place in the presence of suitable catalysts such as oxidized steel and flue dust. Once the gas is cooled below 371°C (700°F) further SO_3 formation is limited. In addition SO_3 formation requires long residence times in this favorable temperature range. SO_3 generation can, therefore, be effectively minimized by:

- Rapid quenching of the off-gas to below 371°C (700°F)
- Minimization of air infiltration in the off-gas handling system
- Minimization of furnace dust generation
- Proper design of ducting to achieve optimal gas velocities

The dew point of sulfide smelting off-gases depends primarily on the SO_3 content. Water vapor content can play an important role in acid generation at low SO_3 concentrations. It is, therefore, interesting to note that the gas dew point temperature is not affected by spraying water to cool the gas. This point is illustrated in Figure 1.1 that shows the relationship between the gas dew point temperature and the SO_3 content for various water vapor levels.

Dust Sulfation

The dust carried over from the smelting vessels is mainly in the sulfide form with some components in metallic and oxide form. The major constituents are copper and iron based sulfides and oxides, along with a wide range of volatile impurities. This flue dust is highly reactive and can oxidize and sulfate in the presence of oxygen and SO_2. Typical oxidation and sulfation reactions include:

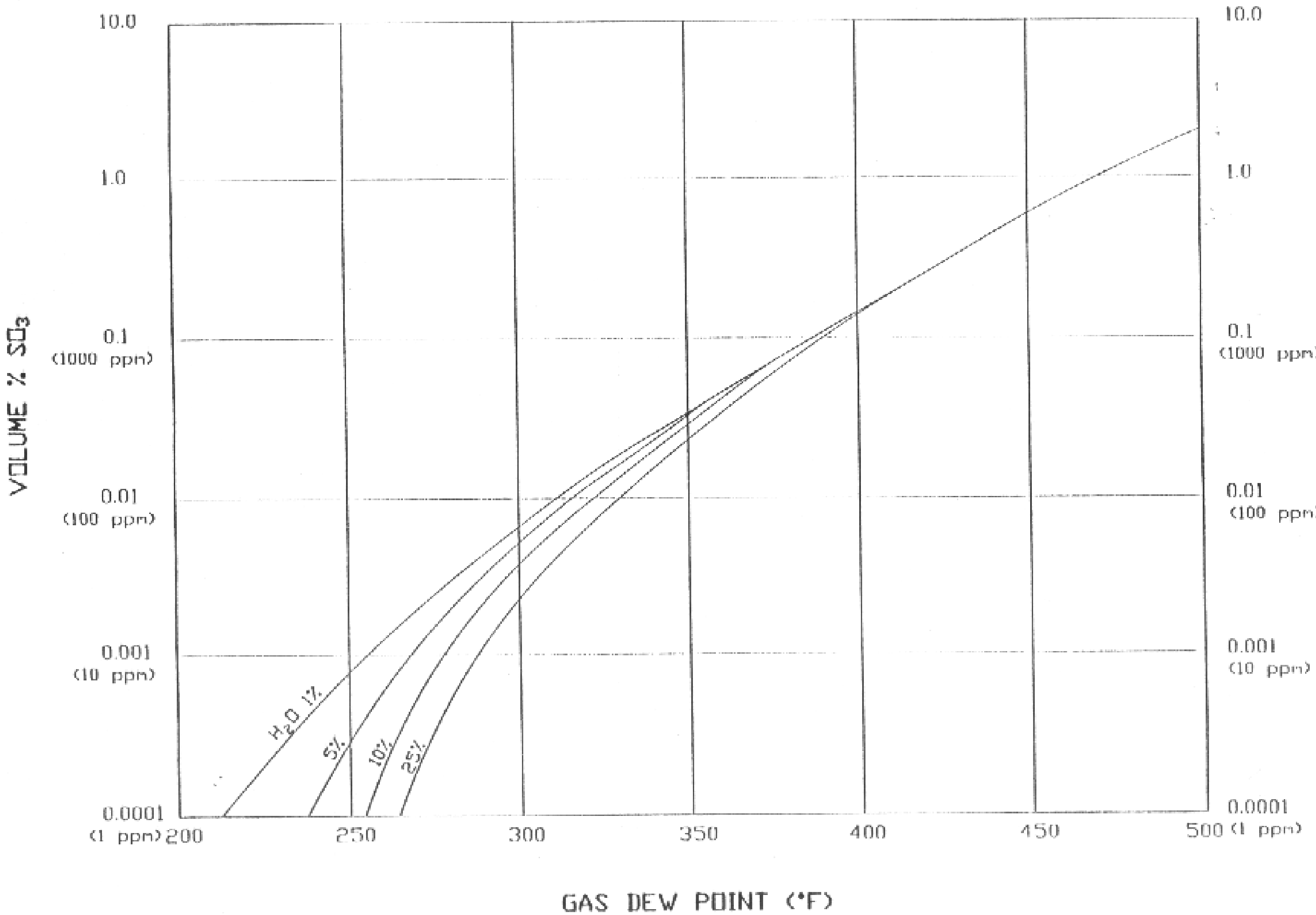
- Oxidation: $Cu_2S + 2O_2 = 2CuO + SO_2$
  $FeS + 3/2\ O_2 = FeO + SO_2$
  $CuFeS_2 + 3O_2 = CuFeO_2 + 2SO_2$

- Sulfation: $CuO + SO_2 + ½O_2 = CuSO_4$
  $2FeO + 3SO_2 + 2O_2 = Fe_2(SO_4)_3$

These reactions are very important (and desirable) in sulfide smelting off-gas handling systems due to the nature of the sulfide dusts. Unreacted sulfide dust can cause extensive operational and mechanical problems due to its sticky and highly reactive nature. Convection tube banks in waste heat boilers are highly susceptible to fouling and plugging if the dust composition is primarily sulfide. Many smelters intentionally after-burn their furnace dust through the addition of air or oxygen, either in the furnace or near the entrance to the gas cleaning equipment. From a design standpoint, therefore, the following points must be considered:

- Thermodynamically, sulfate formation can be expected under similar conditions leading to SO_3 formation (high concentration of SO_2 and oxygen, reduced temperatures and long residence times)
- Sulfation occurs in the temperature range 427°C to 871°C (800°F to 1,600°F)
- Sulfation reactions are strongly exothermic and could cause localized fires/overheating in downstream gas cleaning units (ESP's) if they are not completed in the furnace or gas cooling device

FIGURE 1.1 SO_3 Content and Dew Point of Converter Gas



2.0 PROCESS GAS COOLING SYSTEM DESIGN CONSIDERATIONS

There are a number of gas cooling methods to condition the process off-gas. The selection of each method affects the overall gas volume and capital cost of the system.

2.1 Gas Cooling Alternatives

Many of the operating problems in sulfide smelting operations occur upstream of, or in the cooling device because of the sticky nature of the molten fume and dust. The following are available for gas cooling and conditioning prior to cleaning.

- **Radiation Cooling** – Radiation coolers reduce the temperature of the off-gas using radiant tubes exposed to ambient air. The radiation cooler consists of a number of parallel radiant U-tubes with a hopper at the end of the radiant tubes to collect dust. This arrangement and design is based on the relationship between the flue surface area, off-gas flow conditions, and ambient air conditions. This type of system has been reported to operate successfully at Chilean smelters in their Peirce Smith converter gas handling systems.

  The control of gas temperature in radiation coolers is more difficult than other cooling methods. Some designs use butterfly dampers in some of the radiant tubes to control the surface area available for heat transfer and thereby the temperature of the outlet gas. Another design uses radiant tubes to cool the process gas to a temperature higher that the desired outlet temperature. The hopper assembly in this design contains a single water spray nozzle at the radiant tube exit for final temperature control.

  Radiation coolers work well in hot/dry climates where the ambient conditions are relatively constant. Cold or wet climates present less attractive operating conditions for radiation coolers. Rain on the outside of the coolers will rapidly cool the steel because of evaporation. This results in duct surface temperatures below the dew point of the process gas, which leads to condensation and corrosive conditions inside of the coolers. Facilities in cold or wet climates have to replace the radiant tubes about every 18 months.

- **Waste Heat Boiler** – Heat is removed from the gas and transferred to circulating steam by radiation and convection. Boilers are common in copper smelter gas handling systems. A common problem is dust build-up, particularly in the convection section.

- **Evaporative Cooling** – This method reduces gas temperature down to 300-400°C by vaporizing atomized water and is often used to increase moisture content ahead of an ESP. Dust build-up could be a problem in evaporative cooling if the water sprays contact any surface before it is completely evaporated.

- **Direct Quench** – The direct quench cools the gas to the saturation temperature by the introduction of a large amount of water. This is only feasible where wet scrubbing is utilized.

- **Air-to-Gas Heat Exchanger** – An air-to-gas heat exchanger system can often be used to cool process gas where gas volume and heat content is a concern. This option still requires some water-cooled ductwork or dilution air to reduce the temperature of the off-gas within a range suitable for flow in common carbon steel ducting prior to the heat exchanger.

Overall, air-to-gas heat exchangers require regular down time due to fouling of the tube bundles. This type of cooler is not recommended for dust laden smelter gas service. Also, due to the cyclical nature of some furnace operations, the heat exchanger would be exposed to excessive thermal cycling. This could cause cracks, deteriorate the integrity of the equipment, and be a source of air infiltration into the gas handling system.

- **Water-Cooled Ductwork** – This option uses water-cooled ducts close coupled with the furnace off-gas opening to cool the off-gas. Water-cooled ducting effectively reduces the off-gas temperature to below 500°C. Dilution air can then be used to further reduce off-gas temperature if necessary.

  This option reduces the total gas volume reporting to the gas cleaning section, thereby reducing the size of the cleaning equipment. However, this option has a very high capital cost associated with the installation and operation of the water-cooled duct systems.

- **Dilution with Air** – In this method, ambient air is drawn into the off-gas duct near each furnace as required to bring the mixed gas temperature down to the limiting temperature. This is the simplest and least expensive cooling method. This results in an increase in gas volume and reduction of SO_2 strength. However, the overall capital cost is higher when considering the larger gas cleaning system required to handle the additional dilution air. The operating cost would also be higher because the fans would require more power to handle the larger gas volumes. This is not feasible for sulfuric acid production.

2.2 Review of Smelting Processes Gas Handling Systems

The recent copper smelter installations and modernizations include applications of the following technologies: Outokumpu Flash Smelting Process; Inco Flash Smelting Process; Mitsubishi Process; Noranda Process; El Teniente Process; Isasmelt Process; and the Contop Process.

- **Outokumpu Flash Smelting** – This process utilizes a horizontal waste heat boiler for cooling the off-gas and an ESP for particulate removal. Since the Outokumpu process utilizes oxygen-enriched air a large volume of off-gas containing considerable heat content exits the furnace. Recovery of this available heat is an important economic factor for this process.

- **Inco Flash Smelting** – This process is based on using bulk oxygen for smelting which results in a very low process off-gas volume with little sensible heat content. A proven gas cooling/cleaning technology applied to this process is a close-coupled saturation tower for gas conditioning followed by a wet scrubbing based gas cleaning system.

- **Mitsubishi Continuous Smelting Process** – The process gas is cooled in a waste heat boiler and cleaned in an ESP similar to the Outokumpu process.

- **Noranda Process** – The Noranda process uses oxygen enriched air to bath smelt concentrate in a cylindrical vessel. Since the vessel rotates there is considerable air infiltration at the hood that partially cools the process gas. An evaporative spray cooler achieves final off-gas cooling.

- **El Teniente Process** – This technology is very similar to the Noranda process from a gas handling perspective. Recent installations utilize a dry bottom spray cooler followed by an ESP to treat the process gas.

- **Contop Cyclone Process** – The cyclone smelting process practiced at the ASARCO El Paso smelter is equipped with a vertical waste heat boiler and uses an ESP for particulate removal.

- **Isasmelt Process** – The unit at Mount Isa utilizes a FLUXFLOW circulating fluid bed waste heat boiler followed by an ESP. The Isasmelt reactor utilized by Phelps Dodge in Globe, Arizona utilizes a vertical waste heat boiler followed by an ESP.

3.0 PROCESS GAS CLEANING SYSTEM DESIGN CONSIDERATIONS

3.1 Gas Cleaning Alternatives

The available methods of cleaning smelter gas are reviewed below:

Electrostatic Precipitator

In an electrostatic precipitator (ESP), a high voltage (40-60kV) electric field is established between discharge and collecting electrodes of opposite polarity. Ionization of the gas leads to collection of the dust on the collecting electrodes. The ESP performance is a sensitive function of dust resistivity and is influenced by the moisture content of the gas. An ESP can operate at high temperatures up to 370°C, and is an effective device for removal of fine particles.

ESP's are widely used in sulfide smelting operations as primary gas cleaning equipment. One of the benefits of operating in this temperature range is fractionation of the dust. Many species present in concentrate are in the vapor phase at ESP operating temperatures (As, Se, F, Cl). The ESP allows these components to pass while collecting the components of value (Cu, Ni). This enables a recycle of the desired components and a bleed of the undesirable volatiles.

Wet Electrostatic Precipitator

Wet ESPs are generally used for saturated wet gases. They are used to remove fine (submicron) particles from the gas stream and are often placed downstream of wet scrubbing systems. A typical application for a wet ESP is downstream of a wet scrubber in an acid plant gas cleaning system.

Wet Scrubber

Scrubbers have the ability to handle high temperature and moisture-laden gases. Some dusts present explosion or fire hazards when dry; wet collectors eliminate, or at least reduce, the hazard. However, the use of water may introduce corrosive conditions within the scrubber.

Scrubbers are widely used as an effective gas cleaning device for fine particles. However, the soot produced during the reduction phase of some anode furnace operations is very difficult to collect with a scrubber. Soot particles are difficult to wet and therefore difficult to collect in a scrubber and could lead to visible stack emissions.

The biggest disadvantages of scrubbers are inability to segregate dust, high energy consumption due to high pressure drops and the need to handle a liquid effluent; scrubbers essentially turn an air pollution problem into a water pollution problem.

Baghouse

Baghouses are used in some sulfide smelters to remove dust and fume particles from some low temperature process gas streams by direct filtration through porous media. Some anode furnace off-gas cleaning systems include baghouses. Baghouses are generally operated below a temperature of 200°C although higher temperatures are possible when using high cost bag materials such as Teflon® and fiberglass.

Baghouses that use porous metal or ceramic materials for filtration and are capable of operating at much higher temperatures are under development. However, these are still experimental and cannot be considered for a commercial process.

Baghouses offers a relatively low pressure drop relative to the pressure drop of wet scrubbers. When considering a baghouse, the moisture and SO_3 content of the off-gas must be considered. High SO_3 moisture content can cause problems in a baghouse when the off-gas approaches its dew point.

Cyclone

The cyclone collector is commonly used for the removal of coarse dust (>25 micron) from gas streams and as a pre-cleaner for more efficient dry or wet dust collectors. Cyclones are not effective for removal of fine dust particles, and have never been used effectively as a final source of gas cleaning in a copper smelting off-gas system. The presence of fine dusts and fume in the off-gas will result in unacceptably low dust removal efficiency. Cyclones have been used in some smelters and severe dust build-up problems were experienced in the flue system.

Summary

The major concerns with handling sulfide smelter off-gas are the high temperature, high strength SO_2, and high loading of molten dust and fume. The gas must be conditioned in a manner that maintains the SO_2 strength required for sulfuric acid production. The feasible gas cooling technologies for conditioning the process gases are: waste heat boilers; saturation towers; radiation coolers; and evaporative spray coolers. Various copper smelting gas-handling systems were reviewed and key design criteria were discussed.

The major design objectives that should be considered when designing smelter gas handling systems include:

- Rapid process gas cooling to stabilize the dust, minimize equipment size, prevent excessive thermal cycling and potential air infiltration,
- Utilize short interconnecting flues to minimize build-up,

- Gas cooling systems should ensure minimum weak acid formation and required effluent handling system,
- Dust sulfation must be completed prior to the gas cleaning system,
- Dust segregation to recycle the valuable components to the smelting vessel and to bleed the impurities from the process circuit, and
- Minimize gas handling equipment to reduce maintenance requirements.