# PROCESS OFF-GAS COOLING DESIGN CONSIDERATIONS FOR NON-FERROUS METALLURGICAL PROCESSES

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### Abstract

This paper reviews various process off-gas cooling options available for sulfide smelting processes. Advantages and disadvantages of each system are discussed along with the selection criteria for a reliable and cost effective system. Various systems are presented to demonstrate typical process parameters for smelter off-gas handling systems and to outline operating difficulties associated with each system.

### Introduction

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:

- Pluggage 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<sub>2</sub> gas produced in modern non-ferrous processes
- The gas must be cooled in a manner that maintains the SO<sub>2</sub> strength required for sulfuric acid production
- Mechanical problems with dust collection equipment
- Carryover of dust to sulfuric acid production facilities

# SO<sub>3</sub> Formation

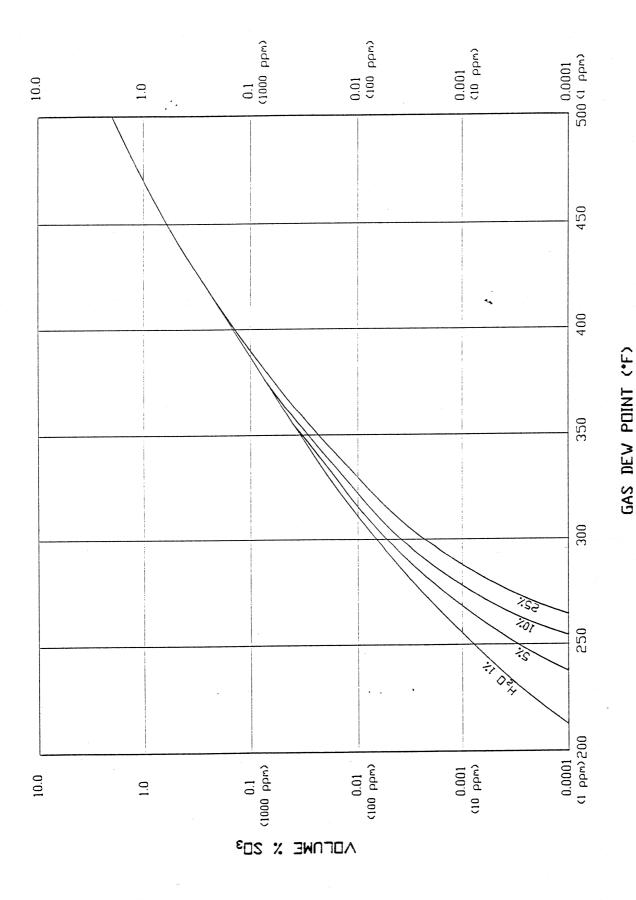
The thermodynamics of SO<sub>2</sub> conversion to SO<sub>3</sub> has been reviewed in number of technical papers (1). For brevity, only a brief review is presented here. The SO<sub>2</sub> laden smelter process off-gases are partially converted to SO<sub>3</sub> as the gases are cooled. SO<sub>3</sub> forms dilute sulfuric acid upon reaction with water. The degree of SO<sub>3</sub> 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 air infiltration)
- Off-gas residence time
- Dust content and characteristics.

The conversion rate of SO<sub>2</sub> to SO<sub>3</sub> is small at elevated temperatures. As the gas is cooled below 760°C (1400°F) however, rapid conversion of SO<sub>2</sub> to SO<sub>3</sub> can take place in the presence of suitable catalysts such as oxidized steel and flue dust. Once the gas is cooled below 370°C (700°F), further SO<sub>3</sub> formation is limited. In addition, SO<sub>3</sub> formation requires long residence times in this favorable temperature range. SO<sub>3</sub> generation can, therefor, be effectively minimized by:

- Rapid quenching of the off-gas to below 370°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 the sulfide smelting off-gases depends primarily on the SO<sub>3</sub> content. Water vapor content can play an important role in acid generation at low SO<sub>3</sub> concentrations. It is, therefore, interesting to note that the gas dew point temperature is not effected by spraying water to cool the gas. This point is illustrated in Figure 1, which shows the relationship between the gas dew point temperature and the SO<sub>3</sub> content for various water vapor levels.



SD3 Content and Dew Point of Converter Gas (Extracted from Reference 1) FIGURE 1.

### Sulfation of Dust

The dust carried 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<sub>2</sub>. Typical oxidation and sulfation reactions include:

### Oxidation:

$$Cu_2S + 2O_2 = 2CuO + SO_2$$
  
 $FeS + 3/2O_2 = FeO + SO_2$   
 $CuFeS_2 + 3O_2 = CuFeO_2 + 2SO_2$ 

### Sulfation:

$$CuO + SO_2 + 1/2O_2 = CuSO_4$$
  
 $2FeO + 3SO_2 + 2O_2 = Fe2(SO_4)_3$ 

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 SO3 formation ( high concentration of SO<sub>2</sub> and oxygen, reduced temperatures and long residence time)
- Sulfation occurs in temperature range 430°C to 870°C (800°F to 1600°F)
- Sulfation reactions are extremely exothermic and could cause localized fires/overheating in downstream gas cleaning units (ESPs), if they are not completed in the furnace or gas cooling device.

### Review of Smelting Processes Gas Handling Systems

The recent copper smelter installations and modernization's application 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. Table 1 provides a representative list of the type of gas handling systems associated with these smelting processes. The information in Table 1 suggests:

- 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 economical 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 closed-coupled saturation tower for gas conditioning followed by a wet scrubbing-based gas cleaning system.

Table 1: REVIEW OF SMELTING PROCESS GAS HANDLING SYSTEMS

Gas	Cleaning	ESP	ESP	ESP	ESP	ESP	Scrubber	Scrubber	ESP	ESP	ESP	ESP
Gas Cooling		Horiz. Boiler	Saturation Tower	Saturation Tower	Horiz. Boiler	Spray Cooler	Spray Cooler	Vertical Boiler				
Dust	Loading Gr/SCF	30	ı	75	100	35	100	80	30	5	5	10
	% SO2	25	44.8	22	25-50	13.5	08	70-80	25	15	15	12
Fce Off Gas	Temp (°F)	2400	1	2370	2500	1830	2200	2300	2200	1500	1500	2050
Fc	Volume (SCFM)	50000	23500	53000	12500	31000	10000	12000	20000	74000*	76400*	44700
% O2 in	Blast	50-70	70-90	35	26-52	35	96	95	40-45	35-40	28-30	50
te	(t/day)	3800	3000	2200	1600	1360	2280	3200	1600	0091	1600	2000
Smelting	Process	Outokumpu	Outokumpu	Outokumpu	Outokumpu	Outokumpu	Inco Flash	Inco Flash	Mitsubishi	Noranda	Teniente	Isasmelt
Facility		BHP Copper	Kennecott	P.D. Hidalgo	Harjavalta	Tamano	P.D. Chino	Inco (Cu/Ni)	KCML	Noranda, Horne	Caletones Smelter	Cyprus Miami

Note: \* Included air filtration at the reactor hood.

- <u>Mitsubishi Continuous Smelting Process</u> The process gas is cooled through a waste heat boiler and cleaned in an ESP similar to the Outokumpu system.
- Noranda Process The Noranda process uses oxygen-enriched air to bath smelt concentrate in a cylindrical vessel. Since the vessel rotates, a very cose seal between the vessel and the gas duct cannot be maintained and there is considerable air infiltration at the hood that partially cools the process gas. Final cooling is achieved by an evaporative spray cooler.
- <u>El Teniente Process</u> This technology is very similar to the Noranda process from a gas handling perspective. Recent installations use a dry bottom spray cooler followed by ESP to treat the process gas.
- <u>CONTOP Cyclone Process</u> The cyclone smelting process operating at the ASARCO El Paso smelter is equipped with a vertical waste heat boiler and uses an ESP for particulate removal.
- <u>Isasmelt Process</u> The unit at Mount Isa utilizes a FLUXFLOW circulating fluid bed waste heat boiler followed by an ESP. The Isasmelt reactor operated by Cyprus-Miami Mining Corporation utilizes a vertical waste heat boiler followed by an ESP (2).

The process parameters listed in Table 1 have been gathered from literature (3-8).

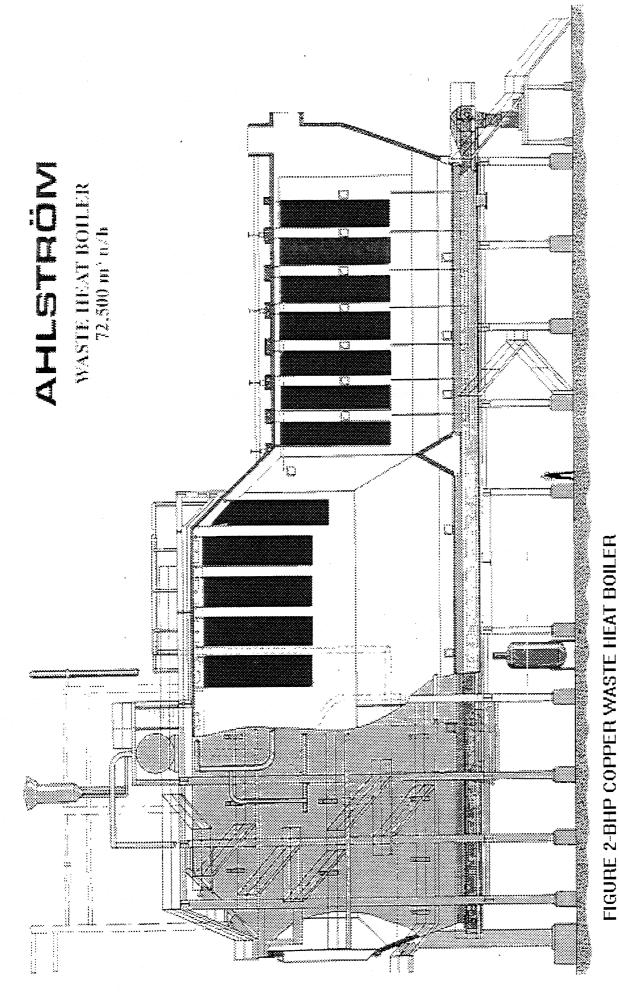
### **Discussion of Various Gas Handling Systems**

Operating examples of three different off-gas cleaning technologies are reviewed here to highlight operating problems and design considerations. The smelting processes are:

- Outokumpu Flash Smelting (WHB & ESP) at BHP Copper Metals
- INCO Flash Smelting Process (Saturation Tower & Scrubbing)
- Noranda/El Teniente rocess (Spray Chamber & ESP)

## Outokumpu Flash Smelting Process (WHB & ESP)

BHP Copper Metals – BHP Copper Metals operates a 4000 short ton per day (stpd) Outokumpu flash furnace at San Manuel, AZ which was commissioned in 1988 and is still on its first campaign. Hot 1315°C (2400°F) off-gas from the furnace is cooled in a single horizontal Ahlstrom waste heat boiler (See Figure 2). Cooled off-gas from the boiler is ducted to two Flakt designed ESP's arranged in parallel. Cleaned off-gas is ten directed to one of two double-contact Monsanto-designed sulfuric acid plants for the removal of SO2. The WHB is of typical Ahlstrom (now Foster Wheeler) design. The WHB consists of two sections: a large radiation section to allow solidification of molten droplets carried over from the furnace, and a convection section where the cooled gas, typically less than 620°C (1150°F), is forced to contact tube bundles arranged in the path of the off-gas. The radiation section utilizes 5 screen tube pendants and the convection section has eight tube banks. 90 Ahlstrom spring hammers (63 in the radiation, 27 in the convection) remove dust from the tube surfaces. Dust from the WHB is directed to a roll crusher for lump reduction and then to a pneumatic conveying system for transport to the flue dust bin. All dust, amounting to 3-3.5% of the total furnace charge, is recycled to the Outokumpu flash furnace. A number of problems were encountered with the WHB during the first 3 years of operation. These problems included:



- Rapid buildup of unsmelted accretions in the uptake/WHB interface
- Fouling of the tube surfaces with unsmelted/partially smelted concentrate
- Pluggage of the ducts between the WHB & ESP
- Tube leaks

The majority of these problems have been effectively dealt with. The Flash Smelting Furnace (FSF) dust generation has been significantly reduced through redesign of the concentrate burner (4). In addition, sulfating/oxidizing air was added to the waste heat boiler inlet to effectively sulfate the FSF dust. These modifications have virtually eliminated the bulk of the problems associated with dust carryover. The WHB experienced 26 tube leaks during the first 3 years of operation. A review of the leaks revealed that the majority of them were at or near rappers. The rappping frequency was gradually reduced to 20% of the original frequency without any loss of WHB efficiency. The second major cause of tube leaks was related to poor welding practices. These types of leaks occurred early on during the first 3 years of the campaign (due to their nature) and have ceased to be an issue. Tube leaks have now been effectively reduced to a low level. The single largest cause of WHB tube leaks today is due to uneven expansion between the radiation and convection sections. This problem will be dealt with through the installation of an expansion joint during the overhaul of the FSF, currently schedule for 1999.

The ESP's have also experienced a number of problems. The most serious of these include:

- Wire failures (resulting in shorted fields)
- Broken internal rappers
- Localized corrosion of hoppers/doors
- Scheduled downtime to repair internal rapper components

These features should eliminate the majority of the problems associated with the Flakt units.

### Inco Flash Smelting Process (Saturation Tower & Wet Scrubbing)

In the recent years all INCO Flash Smelting Furnaces have modified (or in the process of modification as at ASARCO Hayden Smelter) their off gas handling systems by replacing the conventional settling chamber with a close-coupled saturation tower to rapidly quench the process gas exiting the furnace. The final gas cleaning is accomplished through wet scrubbers, gas coolers and wet ESPs before treating the process gas in the sulfuric acid plant.

The gas cleaning system at the INCO Copper Cliff Smelter was discussed in reference (4) in detail addressing the benefits, operating problems and subsequent modifications to the saturation tower system.

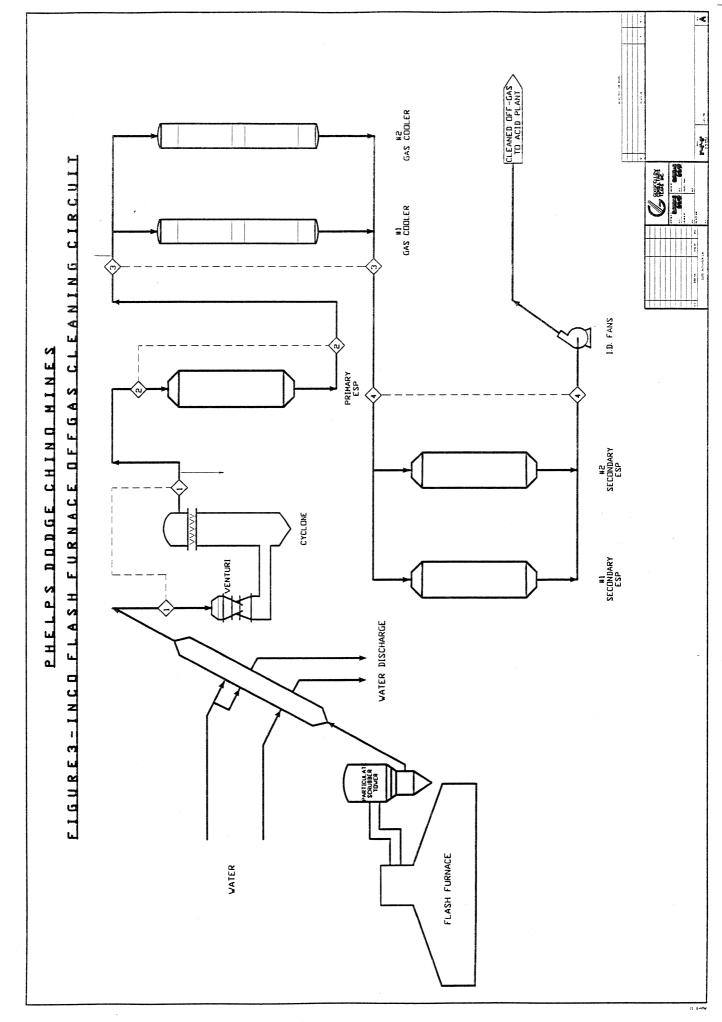
The gas cooling and cleaning system for the INCO Flash Furnace at the Phelps Dodge Chino Mines smelter is presented in Figure 3. The system includes a short interconnecting flue connecting the furnace uptake to the saturation tower followed by a scrubber duct for further conditioning of the off-gas prior to the venturi scrubber. The scrubber duct acts as a retention vessel which further cleans and cools the process gas and also allows for the volatile components in the dust ( such as arsenic and selenium ) to agglomerate and form solid particles prior to entering the venturi throat. These components are in the vapor phase leaving the furnace; once the gas is quenched, they require about 3 to 5 seconds retention time to form stable solid particles in order to be effectively removed in the venturi scrubber. The final gas cleaning is accomplished through the primary wet ESP, gas coolers and secondary wet ESPs.

The function of the saturation tower is to rapidly quench the process gas from about 1205-1260°C (2200 - 2300°F) to about 79-82°C (175 - 180°F). This is accomplished by relying on high liquid-to-gas ratio in the order of 2 to 2.7 L/m³ (15 to 20 USgal/1000 acf). The required residence time to achieve the saturation level is in the range of 1.5 to 2.5 seconds. A typical pressure drop through the saturation tower is in the range of 3 to 5 in. w.g. with dust removal efficiencies of about 70 to 90%. A typical off-gas dust loading at the inlet to the saturation tower represents about 3 to 5 % of the furnace dry solid charge. The above figures represent a typical range of the operating parameters for the saturation towers.

The major advantages of the saturation tower based gas handling system are itemized below:

- The process gas is quickly quenched and partially cleaned. This would eliminate handling hot gas and extremely sticky dust, which lead to build-up problems that are the major cause of furnace downtime.
- Since most of the gas handling system will be operating at relatively cool temperatures, system leaks caused by thermal cycling is minimized which results in a reduction in air infiltration and better furnace draft control. Low operating temperatures provide a better inplant environment and reduce SO<sub>2</sub> and dust fugitive emissions.
- The formation of SO<sub>3</sub> is minimized compared to a dry based gas handling system since the process gas rapidly reaches the saturation temperature. This should reduce the weak acid formation. Also, problems associated with sulfation of dust (i.e. overheating/fires in hot ESP's) in dry gas handling systems are eliminated.
- The saturation tower is capable of providing relatively high dust removal efficiencies at low pressure drops. Also, since the gas is saturated and the coarse particles are removed, it should enhance the performance of the wet scrubbing system.
- It is reported that the saturation tower based gas handling system, with proper material of construction, has high campaign life due to lower operating temperatures and minimum build-up problems

Some of the typical problems and key design considerations associated with the saturation tower based gas handling systems include:



- Build-up due to the hot-cold interface at the inlet of the saturation tower and the interconnecting flue. The systems are equipped with soot blowers that provide on-line cleaning, and, if required, off-line cleaning is provided using pneumatic chipper or shotgun through the access doors.
- Build-up due to formation of accretion on dry areas in the tower. A properly designed spray pattern and nozzle selection should ensure a proper flushing of the sidewalls and roof.
- Spray nozzles and lines pluggage due to precipitation of copper/lead salts and recirculating of
  the fines needs to be addressed through proper spray nozzle passage area and line
  size/velocity selection.
- Coarse solid separation to prevent the large chunks from entering the recycle tanks and the underflow pumps should be provided by utilizing proper screening systems in the tower and underflow lines.
- Proper venting of the weak acid recirculating tanks should be considered to prevent adverse in-plant environmental conditions since the dissolved SO<sub>2</sub> in the solution has a tendency to be liberated due to the high vapor pressure values.

One concern with the wet system is the impurity distribution. This is due to the fact that a wet scrubber will collect volatile components, unlike the hot ESP. Some of the other major disadvantages with the wet system include:

- After burning of elemental sulfur is required in the furnace uptake to prevent sulfur accumulation in the gas handling system.
- The saturation towers need to incorporate acid-resistant refractory lined to protect the shell from weak acid.
- Heat is not removed from the process, as it is used to evaporate the spray water. The heat associated with evaporation must be removed in a gas cooler when the spray water condenses before treating the gas in the acid plant.
- Wet scrubber based gas handling systems operate at much higher pressure drops compared to the hot ESP operations. These systems also consume water, require effluent handling systems, and suffer from potential corrosion problems in the weak acid pipe lines.

### Noranda/Teniente Process (Spray Chamber & ESP)

Both Noranda and El Teniente processes utilize an evaporative cooling chamber to condition the furnace gas prior to the hot ESP. Since the reactors rotate there is about 100% air infiltration at the water-cooled hood that partially cools the off-gas. The process gas exits the reactors at about 1260°C (2300°F) and is cooled by infiltration air to around 650°C (1200°F). A typical gas retention time in the water-cooled hood is about 0.5 seconds. A dry bottom evaporative cooler is used to cool the process gas from about 650°C (1200°F) to 320°C (600°F). Some of the key design parameters for an evaporative cooler are listed below:

Inlet Gas Temperature 650°C (1200°F) Outlet Gas Temperature 320°C (600°F)

Gas Velocity 1.5 - 3 m/s (5 - 10 ft/sec)

Gas Residence Time 6 -8 seconds

Dust Recovery 20 % of inlet dust loading

Compressed Air Requirements 0.06 Nm<sup>3</sup>/l H<sub>2</sub>O ( 8.5 SCF/Gal H<sub>2</sub>O)

Droplet Size Diameters 30 - 50 microns (with maximum droplet @300

microns)

The major positive aspects of an evaporative cooler and ESP configuration are the dust segregation and the capability of bleeding higher percentage of impurity levels from the system. The spray cooler and the ESP will collect primarily Cu, Fe and S based components and the volatiles will report to the acid plant scrubber sludge where they could be bled from the system. Partial cooling of the process gas at the reactor hood by infiltration air assists in formation of simple mineral compounds to be collected at the spray cooler/ESP and volatile oxides which pass through the gas cleaning system and will report to the acid plant. The dust carried over from the furnace is quenched at the exit of the water-cooled hood and it should be completely sulfated when it exits the spray cooler ( spray cooler typically provides 6-8 second residence time which should be sufficient for complete sulfation of dust). This would ensure favorable operating conditions at the ESP due to the stable nature of the dust and low resistivity caused by increased off-gas moisture contents.

Some important design criteria regarding the spray coolers are summarized below:

- Complete evaporation of the water in the chamber must occur to prevent build-up and
  corrosion problems in the flues and downstream equipment. Water droplets should not
  impinge on the spray cooler walls. Also, the collected dust in the hoppers should not be
  exposed to water to form sticky particles and cake that create difficulties for the conveying
  systems.
- Water flow rate per spray nozzle should be as large as possible to minimize the number of spray nozzles. The droplet size diameter, however, should be consistent with the above specifications.
- Spray chamber/nozzles should be located as close as possible to the reactor hoods to minimize the length of the interconnecting flue and to rapidly cool the process gas. Every effort should be made for the spray pattern to provide a proper liquid-to-gas contact and to maintain a uniform gas flow distribution through the spray chamber.
- Spray water flow rates need to be adjusted based on the gas temperature set point; the water droplet size should be decreased as water flow rates decrease. This can be accomplished by operating at constant compressed air flow rates for various water flows.
- The spray coolers would need to be well insulated to minimize build-up problems and corrosion caused by acid condensation.

Spray coolers are an effective method to cool and condition the gas ahead of ESPs, This method, however, transfers an extra heat load on the scrubber cooling circuit because of the increased offgas moisture content.

The spray cooler alternative for non-rotary smelting vessels such as INCO or Outokumpu flash smelting furnaces, where sufficient air is not available to after burn the sulfur or ensure complete dust sulfation is not an attractive option as either air or pure oxygen will need to be added to the system to oxidize/sulfate the dusts. This will require additional equipment and it will increase the overall system heat load.

### **Summary and Conclusions**

The major concerns with handling sulfide smelter off-gas is 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 gas include:

- Waste heat boilers
- Saturation towers
- Evaporative spray coolers

Various copper smelting gas handling systems were reviewed and key design criteria were discussed. Table 2 gives a comparison summary of the alternatives discussed, including advantages, disadvantages and the key design considerations. The major design objectives that should be maintained when designing smelter gas handling systems include:

- Rapid process 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 system 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.
- Minimize gas handling equipment to reduce maintenance requirements.

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# Table 2: COMPARISON OF GAS COOLING ALTERNATIVES

Alternatives	Waste Heat Boiler and ESP	Wet System	Spray Chamber and ESP
Gas Cooling	Waste Heat Boiler	Saturation Tower	Spray Chamber
Gas Cleaning	ESP	Wet Scrubber	ESP
Advantages	Steam Generation	Minimum air infiltration	Dust Segregation
	• Boiler is a good	<ul> <li>Handling cold gas</li> </ul>	<ul> <li>Minimum equipment and</li> </ul>
	sulfation chamber	<ul> <li>High campaign life</li> </ul>	capital cost
	<ul> <li>Reduces heat load and</li> </ul>	Good in plant	• Low operating cost/
	gas volume	environment	energy requirements
	<ul> <li>Dust Segregation</li> </ul>	Reasonable	<ul> <li>Easy to implement in</li> </ul>
	• Low pressure drop	Implementation	retrofit
Disadvantages	<ul> <li>Potential tube leaks</li> </ul>	Minimum dust	<ul> <li>No heat removal</li> </ul>
	<ul> <li>Moderate air infiltration</li> </ul>	segregation	<ul> <li>High air infiltration</li> </ul>
	<ul> <li>Layout difficulties</li> </ul>	<ul> <li>High energy</li> </ul>	<ul> <li>High maintenance</li> </ul>
	• Difficult in retrofit	Acid pipeline	Poor in-plant
	• Need air at WHB inlet	Corrosion	environment
	for Sulfation	<ul> <li>No heat removal</li> </ul>	• Need for air/O2 in uptake
	<ul> <li>High maintenance due to</li> </ul>	• Water usage/	for non-rotary process
	build-up at convection	Effluent Handling	vessels
	section	• Fan noise	
Design	<ul> <li>Fouling of tubes</li> </ul>	<ul> <li>Need after burning of</li> </ul>	Spray pattern/Droplet
Considerations	<ul> <li>Pluggage of inter-</li> </ul>	S/H2S	Evaporation
	connecting flues	<ul> <li>Hot/Cold Interface</li> </ul>	• Controls
	Rapid build-up at WHB	build-up	<ul> <li>Potential of sticky</li> </ul>
	interface	<ul> <li>Acid resistant refractory</li> </ul>	dust handling
	<ul> <li>Rapping systems</li> </ul>	Coarse solid separation	
	Expansion between	<ul> <li>Venting of weak acid tanks</li> </ul>	
	radiation and convection		
	section		

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