CLEAN AND EFFICIENT ROASTING SOLUTIONS WITH OUTOTEC'S CUTTING-EDGE TECHNOLOGY

*A. Charitos, J. Hammerschmidt, K. Hasselwander, K. Knabel

Outotec GmbH
Ludwig-Erhard Strasse 21
61440 Oberursel, Germany
(*Corresponding author: alexandros.charitos@outotec.com)

ABSTRACT

A significant area of Outotec’s business involves fluidized bed roasting. With several decades of experience, more than 300 reference plants and strong R&D capabilities, the company provides several industries with optimum processing solutions. Applications include oxidation and sulfation of sulfides found in copper, pyrite and zinc concentrates. Gold production and de-arsenifying roasting are also within this scope. This paper describes the latest furnace developments and includes novel trends. Moreover, hot and wet gas cleaning systems are examined focusing on unit operations related to the removal of components such as dust, SO₂ for sulfuric acid production, fumes, halides, Hg, hydrocarbons, nitrous oxides and metals.
INTRODUCTION

Generally, when defining roasting processes, it can be stated that the respective primary pyrometallurgical reaction is exothermic, of gas-solid nature and relates to a value solid product. These processes are a key focus within Outotec’s scope and include: (i) dead roasting (ii) sulfating roasting (iii) partial de-arsenifying roasting and (iv) two-stage, de-arsenifying roasting.

Dead roasting involves the oxidation of a given sulfide, thus allowing for a subsequent leaching process, and has been applied to producing ZnO. Dead roasting of pyrite has also been extensively utilized with a primary goal of producing sulfuric acid. In contrast, sulfating roasting involves converting a sulfide to its sulfate, enabling a selective sulfation of components, such as Cu or Co, and their separation from ferrous components during leaching (produced sulfates are soluble). Partial roasting involves partially oxidizing the metal sulfide to its oxide with the simultaneous production of gaseous As₂O₅ which is handled during gas cleaning. The solid product, containing hardly any As, is rich in S and can be fed to a respective smelter (e.g. in the case of Cu). Alternatively, if the production of oxide is required, a dead roasting step is added after the partial roasting step, with the overall process considered as two-stage roasting.

Typical applications are gold roasters that have arseno-pyrites as feed material. The bulk of related applications employ the bubbling fluidized bed (BFB) reactor which makes use of its excellent gas-solid mixing characteristics allowing close process condition control. Due to its characteristics the BFB reactor replaces the multiple hearth furnace (MHF), with only a few exceptions such as Mo and Vn applications. However, in instances where even tighter control over process temperature and atmosphere are needed, the circulating fluidized bed (CFB) reactor is a better suited choice since it exhibits uniformity in terms of the noted attributes throughout its volume. Moreover, a CFB application is sometimes preferable since it significantly reduces the reactor footprint in contrast to the BFB, and allows higher throughputs to be attained. A CFB application for gold roasting applications is a typical example of how these benefits have been utilized. However, the benefits gained using a CFB may also be applied to all other roasting process variants including the dead roasting of ZnS. Taking into consideration that a CFB reactor can handle finer concentrates than a BFB, it can be viewed as a key solution for more efficient roasting. Finally, the roaster arrangement will also be briefly discussed including the concentrate feed, product cooling/grinding, heat recovery, granulation of fine concentrates as well as hot de-dusting, though the latter aspect is handled as part of this paper’s gas cleaning section.

Moreover, one of the direct results of the roasting reaction occurring in the BFB or CFB furnace is that sulfur contained in the ore is released in the gas phase as sulfur dioxide, which is an acidic gas and can be harmful to humans, vegetation and property if released into the atmosphere. Thus, in most regions of the world, SO₂ must be eliminated before the off-gas is released. In general, SO₂ is processed into sulfuric acid in a contact acid plant. Unfortunately, in the pyrometallurgical process, not only is SO₂ released, but also many other gaseous and non-gaseous substances as well. In addition, a lot of dust and fumes leave the furnaces along with the hot SO₂ gas. Depending on the ores, the substances released can have very different properties in terms of their build-up formation, stickiness and occasionally even their ignitability. Depending on the roasting process and the type of ore processed, the dust fumes may contain a high concentration of halides, As and, in some cases, selenides. To allow the continuous production of sulfuric acid, which fulfills certain contamination requirements, the gas must be thoroughly cleaned. All inorganic matter which can contaminate the acid or have an impact on the plant’s operation by decreasing the on-stream time, must be removed from the gas. This requires a careful design of both the hot gas system and the wet gas cleaning system.

Next follows an analysis of hot gas systems, including gas cooling and hot de-dusting, as well as wet gas cleaning systems including gas cooling/water vapor systems, wet electrostatic precipitators, mercury and halide removal systems and finally SO₂ removal.
ROASTING FURNACE TECHNOLOGY

The characteristics of the two primary reactors, the BFB and CFB as shown in Figure 1, utilized for roasting applications are discussed followed by a look at the four roasting processes carried out in these reactors, namely dead, sulfating, partial and two-stage roasting in terms of their respective theories and issues. Finally, plant arrangements, periphery units, latest references and future trends are reviewed.

Figure 1 – Fluidized bed reactors which are extensively used for roasting applications

BFB or CFB Reactor?

The reactor characteristics mentioned by Hammerschmidt et al. (2005), are summarized later in this section. BFB reactors are characterized by their rather low operating velocities, which are in the range of an order of magnitude lower than those of a CFB. A distinct border exists separating the bed of solids with a region, known as the ‘freeboard’, which has a very low solid concentration. The reactor bed exhibits good solid mixing characteristics, which can be attributed to the solid flow patterns initiated by the up-flow of bubbles growing in size within the bed. An amount of solids exits the reactor through the freeboard exit (see Figure 1), while the rest exits the bed through an overflow (above the particle bed) or underflow (below the particle bed) arrangement. The portion of solids exiting through the freeboard outlet is significant; it can account for up to 60 percent of the total product outlet flow. This value is justified based on the significant amount of fines present in a typical concentrate particle size distribution (PSD).

The elutriation mentioned also explains why the temperature gradients of up to 50 °C occurring between the distributor and a BFB roaster’s exit, which, in some cases, such as in gold roasters, are considered undesirable. Lowering the bed velocity to reduce elutriation leads to the also undesired effect of lowering capacity unless oxygen enriched air is used instead of pure air. BFB elutriation can be handled with de-dusting solutions thus recovering the corresponding product. BFB roasters have reached significant size (138 m², 13 3 m diameter). Thus, the introduction of secondary gases is limited; however, BFB reactors can cause particles to reside in the bed for up to of up to several hours. Applications include dead roasting of ZnS and pyrite/pyrrhotite for producing sulphuric acid, the sulphating roasting of Cu Co concentrates, partial roasting of As-containing Cu concentrates and the two-stage roasting of gold-bearing minerals.

CFB reactors may operate in the turbulent or fast fluidized bed regime, see regime map (Bü and Grace, 1995), depending on their operating velocities. The latter value varies widely; from 2 m/s to 11 m/s. The exact border of the two regimes is case dependent; however, it can be said that a typical range for the turbulent fluidized bed is 2 – 5 m/s. In both cases, there is no distinct surface in the reactor bed and the solids concentration decreases exponentially with the height. In the case of the fast fluidized bed, the solid
concentration decay within the CFB is more gradual, while in the fast fluidized bed, it is more abrupt (Kunii and Levenspiel, 1991). This explains the higher solids entrainment of the latter compared to the former.

A recycle cyclone is necessary to aid in the recycling of solid flow back to the furnace after passing through a scal pot, as shown in Figure 1. The differences associated with solids entrainment explain why heat recovery from the solid recycle arrangement (within the scal pot or external cooler) is possible when operating in the fast fluidized bed regime. CFB operation within the two types of regimes also differs in terms of the solid flow pattern between the furnaces, i.e. the operation in the turbulent regime allows more particle horizontal mixing, which is limited in the fast fluidized regime, primarily occurring within the reactor’s lower zone. Additionally, the typical core/annulus flow pattern, where particles travel upwards within a reactor’s center and downwards around the walls, is present when a CFB operates in the “fast fluidized” bed regime (Kunii and Levenspiel, 1991). To date, operation in the turbulent regime has been applied to gold-ore roasting and pre-reduction of iron ore, while operation in the fast fluidized bed regime has been applied to coal combustion and alumina calcination (Hammerschmidt et al., 2005).

Types of Roasting Processes and Arrangements

The primary reaction occurring during dead roasting is described using the ZnS example in Equation 1 and involves the full oxidation of the respective sulfide. Secondary reactions involve the oxidation of Fe and Cu sulfides, while Pb sulfides and CaCO$_3$ are transformed to their sulfates. Moreover, ferrite formation also takes place (ZnO-Fe$_2$O$_3$), which is decomposed to respective components during leaching. The resulting reaction during the roasting of pyrite/pyrrhotite is described later in this section and has been used as a major route to produce sulfuric acid. This route still remains economically feasible depending on the price of elemental sulfur and the availability of pyrite/pyrrhotite (Runkel et al., 2009). With gold roasting, sulfur oxidation is required since gold is often encapsulated within pyrite, while simultaneous carbon oxidation is necessary since the presence of carbon can reduce gold recovery during leaching (Hammerschmidt et al., 2005). Reactor temperatures depend on the ore - 550- (slightly above) 700 °C for gold roasters and above 850 °C for zinc and pyrite roasters for sulfuric acid production. Roaster temperature and conditions in the latter cases are limited-defined based on impurities, such as Cu, Pb, SiO$_2$, concentrations and their combinations. Outotec has a wide reference base for both BFB and CFB plants related to dead roasting. Respective arrangements are shown in Figures 2 and 3.

\[
\begin{align*}
\text{ZnS} + 3/2 \text{O}_2 & \rightarrow \text{ZnO} + \text{SO}_2 \\
2 \text{FeS}_2 + 11/2 \text{O}_2 & \rightarrow \text{Fe}_2\text{O}_3 + 4 \text{SO}_2 \\
3 \text{FeS}_2 + 8 \text{O}_2 & \rightarrow \text{Fe}_3\text{O}_4 + 6 \text{SO}_2 \\
\text{FeS}_2 + 3 \text{O}_2 & \rightarrow \text{FeSO}_4 + \text{SO}_2
\end{align*}
\]

The company’s installed capacity between 1990 and 2010 was 4,570 metric tons per day (mtpd), 2,960 mtpd and 10,610 mtpd for zinc, pyrite and gold roasters respectively. The latest zinc references include the Hindustan Zinc facilities, i.e. number IV/V with a capacity of 900 mtpd (India: 2009/2011) and the 970 mtpd Cajamarqulla plant (Peru: 2007). These units are BFB’s with an area of 123 m$^2$. In addition, when it comes to pyrite roasting, the two 1130 mtpd plants of Tongling (China: 2004/2009) must be mentioned since they exhibit the largest BFB cross-sectional area to date: 138 m$^2$. The latest dead roasting plant for gold production was built in Syama (Mali: 2010) and has a capacity of 590 mtpd and utilizes a CFB furnace.

However, the CFB gold roaster plant with the greatest capacity is the Newmont Gold plant (USA: 1994) utilizing two units and treating 7,680 mtpd of refractory ore. These gold roasters treat concentrates which have As concentrations below 1 wt%. If this value is exceeded, the two-stage roasting process is
applied. As can be seen in Figures 2 and 3, BFB and CFB arrangements are essentially similar with the main difference being the definition of the reactor type. The CFB arrangement’s furnace footprint may be reduced up to an order of magnitude. In the case of dead roasting, the concentrates are primarily fed to the furnace in dry feed modus, i.e. with use of a table feeder and slinger belts. On the other hand, screw feeding can be selected to avoid gas leakage in the CFB roaster case.

![Figure 2 - Typical schematic of a BFB dead roasting arrangement](image1)

![Figure 3 - Arrangement of a CFB roaster (structure height exceeds 25 m)](image2)
The heat produced in the roaster is recovered through heating surfaces located (i) within the furnace itself, (ii) within the waste heat boiler (WHB) and (iii) within the product (also known as ‘calcine’) cooler. Heat recovery of 20 – 70 mtpa of steam has been realized, which may be utilized for producing electricity (5 – 15 MW). Heat recovery within the furnace is realized with cooling coils, whereas in the CFB, it can also be realized using membrane walls. The WHB is a horizontal-pass boiler, consisting of membrane walls and bundles which accommodate an evaporator and super-heater surfaces. Since the waste heat boiler handles roasting gases which have very high dust content, a mechanical rapping device must be available. The calcine cooler is preferably a fluidized bed, though drum coolers have also been used.

The de-dusting functions of the cyclones, WHB and hot electrostatic precipitator (ESP) are explained separately in the hot gas treatment section of this paper. In any case, the collected dust is part of the product and is directed to the leaching plant. Finally, though not shown in Figures 2 and 3, Outotec can offer granulation solutions customized for a specific concentrate or mixture. This is particularly important when considering that concentrates worldwide are getting finer, and extremely fine particles, i.e. of the Geldart C category, are difficult to handle in FB systems since they are cohesive, lead to bed channeling and are separated with less efficiency in the cyclones.

Proceeding to the sulphating roasting process, the main reactions are noted here: Me denotes Cu, Co, Fe, Ni and also Ca and Mg. These reactions occur in three steps. In the first step, the metal sulfides are oxidized to their oxides as shown in Equation 5. The second step involves the oxidation of SO$_2$ to SO$_3$, which is aided by the presence of Cu and Fe acting as catalysts, and is shown in Equation 6. Finally, the MeO reacts with SO$_3$ to form sulphates or basic sulfates, as presented in Equations 7a and 7b.

$$Me_2S_y + (x/2+y)O_2 \rightarrow xMeO + ySO_2$$  \hspace{1cm} (5)

$$SO_3 + 1/2O_2 \rightarrow SO_3$$ \hspace{1cm} (6)

$$MeO + SO_3 \rightarrow MeSO_4$$ \hspace{1cm} (7a)

$$2MeO + SO_3 \rightarrow MeO\cdot MeSO_4$$ \hspace{1cm} (7b)

Sulfating roasting is carried out using a BFB arrangement; however, differences exist as shown in Figure 2. Since the process is achieved at a lower temperature than dead roasting, i.e. 650 °C to 700 °C and the off-gas dust is sticky, a WHB is not utilized. Moreover, wet slurry feed is preferable (using lances) since water is utilized to keep the reactor temperature within acceptable levels. Usually, the treated concentrates are rich in chalcopyrite and contain a portion of chalcocite leading to Cu, Co and S concentrations around 20 wt%, 3 wt% and 25 wt%, respectively. In such cases, an auto-thermal process realization is easily achieved.

However, in cases where the chalcocite concentrates are more significant, i.e. leading to concentration of Cu, Co and S of 38 wt%, 3 wt% and 15 wt% respectively, additional measures are needed for this purpose (Günther and Hammerschmidt, 2011). These may include; (i) higher slurry solid content (up to 70 vol.%), (ii) solid feeding instead of slurry feeding (as by dead roasting), (iii) pre-heating of roaster air (up to 400 °C) and (iv) utilization of oxygen-cushioned air. The most effective solution involves pre-heating the roaster air using fluidized bed cooler, as is commonly performed, e.g. in alumina calcination applications. Moreover, the low SO$_2$ in the resulting gas (1 – 2 vol%) does not allow for the production of sulfuric acid and is removed through a scrubber solution. Finally, the calcine’s copper components will be subjected to stringent leaching conditions (in contrast to standard concentrates with approx. 25 wt % of S), i.e. higher acidity. Longer retention times and higher temperature due to their expected lower solubility. The latest Outotec reference for sulfiting roasting is the Kitwe 500 mtpd roasting plant (Zambia: 2005).

By utilizing a partial roasting process, arsenic and antimony-containing concentrates can be partially roasted to produce a calcine low in both arsenic and antimony. The process, also known as
‘magnetite giving roasting’, is operated to partially oxidize the concentrate and ensure an efficient removal of arsenic and antimony as volatilized elemental, oxide- and sulfide compounds. Controlling the oxygen potential to magnetite formation during roasting is essential since the massive formation of hematite must be avoided as otherwise it will reduce the arsenic removal efficiency. When hematite is formed, the arsenic present will react to form stable iron-arsenates and will thus end up in the product. Partial roasting is very common for copper concentrates containing As. Unoxidized gaseous As compounds (As$_4$ and AS$_2$S$_3$) and sulfur compounds (S$^0$ and H$_2$S) are oxidized within the post-combustion chamber at 700 – 800 °C. Details from three plants (Lepanto finished operation in 1997) are in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Start</th>
<th>Capacity tpd</th>
<th>Cu wt.-%</th>
<th>S wt.-%</th>
<th>As wt.-%</th>
<th>Calcine As wt.-%</th>
<th>Calcine S wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boliden</td>
<td>1980</td>
<td>1080</td>
<td>26-30</td>
<td>25-30</td>
<td>&lt; 2.5</td>
<td>0.2</td>
<td>16-20</td>
</tr>
<tr>
<td>Lepanto</td>
<td>1983</td>
<td>180</td>
<td>31</td>
<td>34</td>
<td>10-12</td>
<td>0.3</td>
<td>22</td>
</tr>
<tr>
<td>Codelco MMH</td>
<td>2013</td>
<td>1700</td>
<td>36</td>
<td>34</td>
<td>5</td>
<td>0.3</td>
<td>22</td>
</tr>
</tbody>
</table>

Figure 4 – Partial roasting for As-containing Cu concentrates

The calcines produced are still rich in S and have a concentration of approx. 20 wt% and can be fed to a Cu smelter. In cases where residual sulphur from the calcine needs to be oxidized, it is termed a two-stage roasting process. For these instances, the flowsheet in Figure 5 is supplemented with a second BFB roasting stage connected in series (in terms of solid flow), which operates under oxidizing atmospheres. This addition is typical for gold-bearing minerals containing As mainly in the form of arseno-pyrites (FeAsS) (Hammerschmidt et al., 2011). Hence, in the first roasting stage, operating under reducing or neutral atmospheres, the As is removed from the solid phase, while the formation of hematite is avoided and the gas-cleaning train remains practically the same as in Figure 5. The removal of As in this stage is important since As compounds consume cyanide and this disturbs the cyanide leaching process. Oxidation of residual S, occurring in the second stage, is also necessary as has been previously explained. The operation of the second stage in oxidizing atmosphere which may lead also to hematite formation is not problematic since As has already been removed in the first stage. The latest respective Outotec reference is the 200 mtpd Tongguan smelting facility (China: 2008) and is based on BFB technology.
GAS CLEANING AND SULFURIC ACID QUALITY

The generic gas train utilized in cleaning gas from metallurgical applications, which allows companies to produce sulfuric acid and helps them adhere to contamination limitations, is indicated in Figure 5. All inorganic matter which can contaminate the acid, or which can have an impact on a plant’s operation by decreasing the on-stream time, must be removed from the gas. This requires a careful design of both the hot gas system and the wet gas cleaning system. The design data for gas treatment systems are usually within the ranges provided in the Figure 5 block diagram. Depending on the roasting process and the type of ore that is processed, the dust and fume may contain high concentrations of halides, arsenic, and in some cases, tellurides. Table 2 provides concentrations limits for respective sulfuric acid contaminants. To ensure that these allowable low levels of dust and fumes reach the sulfuric acid plant, it is necessary to carefully design a wet gas cleaning system. These systems are generally designed to include several stages. Table 3 shows the type of equipment and its related impact on gas cleaning.

Figure 5 – Block diagram of a roasting gas treatment train (Hasselwander and Hintze, 2005)

Table 2 – Quality requirements for sulfuric acid

<table>
<thead>
<tr>
<th>Attribute/Component</th>
<th>Value</th>
<th>Attribute/Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Water clear</td>
<td>NH₄⁺</td>
<td>&lt; 1 ppm</td>
</tr>
<tr>
<td>Colour</td>
<td>40 Hazen</td>
<td>NO₃⁻</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt; 0.5 ppm</td>
<td>As</td>
<td>&lt; 0.2 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt; 25 ppm</td>
<td>Cu</td>
<td>&lt; 0.2 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 1 ppm</td>
<td>Cd</td>
<td>&lt; 0.02 ppm</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 1.5 ppm</td>
<td>Pb</td>
<td>&lt; 0.3 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt; 0.3 ppm</td>
<td>Zn</td>
<td>&lt; 0.1 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>&lt; 30 ppm</td>
<td>Sb</td>
<td>&lt; 0.02 ppm</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt; 2 ppm</td>
<td>Bi</td>
<td>&lt; 0.02 ppm</td>
</tr>
<tr>
<td>F⁻</td>
<td>&lt; 5 ppm</td>
<td>Se</td>
<td>&lt; 0.1 ppm</td>
</tr>
</tbody>
</table>
Table 3 – Wet gas cleaning unit operations and gas cleaning

<table>
<thead>
<tr>
<th>Unit operation</th>
<th>Dust (Si, Cu, Zn, Fe, Pb)</th>
<th>Fumes (As, Cd, Se, Sb, Bi)</th>
<th>Acid (H₂SO₄, mist)</th>
<th>H₂O</th>
<th>Halides (Cl, F)</th>
<th>Hg</th>
<th>CₓHᵧ</th>
<th>NOₓ</th>
<th>Me (Fe, Cr, Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WH Boiler</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclone</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot ESP</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quench tower</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scrubber</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas cool tower</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet ESP</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halid tower</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg removal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decolorisation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Denox</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Construction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hot Gas Treatment Systems – Gas Cooling / Hot De-Dusting

Since de-dusting systems normally cannot be operated at the temperatures the SO₂ gas has when it leaves the metallurgical process, the gas must be cooled. For hot gas cooling, a number of technical options can be considered. Wherever technically and commercially feasible, a waste heat boiler should be applied. The boiler must be designed so that it guarantees a reliable operation with acidic gases and frequently sticky dust. But some applications do not justify boiler usage due to low heat recovery and technical problems with boiler operation. In these instances, horizontal spray chambers or vertical evaporative coolers are used. A de-dusting system generally follows the hot gas cooling. Simple de-dusting systems such as settling chambers and cyclones only use mass-based forces such as gravity and centrifugal forces for separating dust and gas.

Optimizing cyclone operation may lead to significant improvements of process efficiency, as has been shown e.g. from alumina calcination applications (Missalla et al., 2011). If de-dusting needs to be more efficient, bag-house filters and electrostatic precipitators are applied. As a general rule, it can be said that bag-house filters are efficient solutions for temperatures lower than 200 °C and a non-sticky dust. When dew point-related problems can be expected at temperatures of 200 °C and more, the use of hot gas electrostatic precipitators is recommended. However, an alternative to hot gas coolers and hot gas de-dusting may be a very proficient wet gas cleaning system which consists of high efficient scrubbers installed downstream of a quencher. The scrubber and the connecting scrubbing circuit must be designed to minimize the problems associated with a high dust load such as dust build-up, or pipe and nozzle clogging.

Wet Gas Cleaning Systems

Whether designed with or without hot gas treatment system, a wet gas cleaning system for a metallurgical sulphuric acid plant consists of a series of unit operations. If no hot gas treatment system is planned, the required de-dusting process must be achieved in the scrubbers and the overall wet gas cleaning system must be designed for high solid loads. Individual unit operations are described in Figure 6.
Figure 6 – A typical Outotec wet gas cleaning system flowsheet (Hasselwander and Hintze, 2005)

1. Quench Cooler: This operation unit is always installed. Depending on the requirements, the quencher can also be designed for scrubbing or dust elimination. The gas is fully saturated with water at the quencher outlet.

2. Scrubber: A scrubber is designed for removing dust from the gas flow. The liquid injected into the scrubber captures the dust particles. Scrubbing efficiency depends on the energy input into the system. Depending on the dust removal efficiency required, the gas flow characteristics and the dust type, scrubbers may have different designs.

3. Gas Cooler, Water Vapor Condenser: In this stage, the amount of water vapor in the gas is reduced to the maximum amount allowed for the sulphuric acid plant. The amount of water vapor allowed depends on the SO$_2$ content of the gas. When gas is cooled, water vapor is condensed.

4. Two-stage Wet Electrostatic Precipitators (wet ESPs): Fine dust particles and aerosols are removed from the gas in wet ESPs.

5. Other stages: Elements (gaseous metallic mercury) or compounds (halides) which cannot be sufficiently removed from the gas by applying the unit operations are treated in additional stages.

The quencher has a temperature- and acid-resistant brick lining. If the downstream installations are sensitive when exceeding 80 °C, the quencher needs to be equipped with two fully independent liquid circuits. Each circuit has its own pump, pipes and nozzles. In addition, an emergency spray system that will start up in case of temperature excess and power failure is also recommended. Scrubber and quencher design as well as selection depend on process requirements including gas flow rate, dust load, presence of condensable matter in the gas efficiency required, dust type and particle size distribution as well as the amount of solids and dissolved matter in the scrubbing liquid. The most critical area in a quencher is the transition zone from hot and dry to wet and acidic. Both areas require different types of mortar and bricks. To ensure that there is a clearly defined transition zone, a venturi-type quencher is used (known as the “Conturi”) equipped with a ring zone, allowing for a clearly defined wet/dry transition zone. For high dust loads, Outotec has a scrubber with an adjustable throat and a wet cyclone for droplet elimination.
Gas Cooling / Water Vapour Condensing Systems

To produce concentrated acid, water vapor is condensed. Direct gas cooling in gas/liquid heat exchangers made of acid-resistant materials such as plastic and lead reduces the gas temperature close to the cooling water value. The most popular gas cooler/condenser model is the packed gas cooling tower, where liquid cooled in plate heat exchangers is circulated over a packing of filling bodies. This “indirect” gas cooler/condenser can be designed to minimize build-up in the packing and cooling liquid circuit.

![Image of gas cooling systems](image)

Figure 7 – Empty tower scrubber (left), internals (middle) and erection (right) of wet ESP (Hasselwander and Hintze, 2005)

Mercury Removal Systems

If a significant amount of gaseous mercury is in the gas, the Boliden Norzink Process (calomel process) is preferred. The process is described in Figure 8. The main principle of the calomel process is that gaseous metallic mercury present in the SO₂ gas reacts with mercury chloride dissolved in a reaction liquid and forms a solid mercury chloride compound, calomel, as shown in Equation 8.

\[ \text{Hg} \text{ (gaseous)} + \text{HgCl}_2 \text{ (dissolved, complex form)} \rightarrow \text{Hg}_2\text{Cl}_2 \text{ (Calomel, precipitates as solids)} \]  

(8)

![Image of mercury removal process](image)

Figure 8 – Mercury removal process flow diagram (Hasselwander and Hintze, 2005)
Calomel is removed from the reaction liquid circuit by liquid/solid separation in a settling tank and stored in a tank arranged beneath the settler. Prior to discharging the excess liquid, the dissolved mercury chloride is also precipitated by adding zinc dust. Depending on the temperature for operating the process, a content of 0.3 – 0.5 ppm mercury in the sulfuric acid can even be achieved. An additional gas cleaning stage ensures the production of sulfuric acid with less than 0.1 ppm of mercury in the acid.

**Halide Removal Systems**

The majority of halides have already been removed in the scrubber and in the packed gas cooling tower by absorption in the circulated liquid. If high liquid temperatures and high concentrations of absorbed matter occur, there may be significant amounts of gaseous halides which can reach the acid plant. This may lead to damage to the cascade filters due to fluoride attack. To reduce the concentration of dissolved fluorides, sodium-silicate can be added to the liquid circulated in the packed gas cooling tower.

**SO₂ Removal**

The final gas processing stage is usually a contact sulfuric acid plant. 'Contact' defines the type of catalyst which is made up of various layers containing solid catalyst in the form of rings or star rings. Modern sulfuric acid plants can be designed for SO₂ recovery rates exceeding 99.9% and consequently SO₂ emissions of less than 100 ppm. Applying highly efficient cascade filters also ensures an aerosol emission (sulfuric acid mist) of less than 10 ppm. Since the sulfuric acid process is exothermic and releases significant amounts of excess energy, processes for its recovery have been developed. The excess energy can be made available in the form of hot water steam of different pressures. Outotec’s HEROS© process utilizes the heat released during the absorption of SO₂ in concentrated acid for the production of steam with a pressure up to 10 bar. The HEROS© process can also be easily installed in existing plants. The SO₂ recovery of existing sulfuric acid plants can be improved by optimizing the catalytic conversion process, which involves selecting the optimum catalyst designed for high SO₂ contents or low bed temperatures. Higher SO₂ recovery rates may require the installation of a tail-gas treatment system, utilizing chemicals for SO₂ removal. Examples involve the use of hydrogen peroxide, lime, caustic soda, zinc oxide and ammonia. Reaction products include sulfuric acid, gypsum, sodium sulfate, zinc sulfate/sulfide and ammonium sulfate. All process decisions are based on operational and investment costs.

**CONCLUSIONS AND OUTLOOK**

Major roasting applications include (i) dead, (ii) sulphating, (iii) partial de-arsenifying and (iv) two-stage de-arsenifying roasting. These technologies handle pyrite/pyrrhotite, gold-bearing minerals, copper minerals and minerals containing high concentrations of arsenic. Corresponding BFB and CFB systems for these processes enable a potential heat recovery of up to 20 – 70 mtpy (5 - 15 MW). Solutions are based on Outotec’s vast experience (over 300 reference plants) and testing at its Frankfurt R & D center utilizing a 50 mm and 700 mm FB reactor. Two trends can be underlined: the more extensive use of the CFB reactor for roasting processes (due to temperature/environment uniformity, increased throughput as well as the improved handling of very fine particles in comparison to the BFB) and the potential granulation of too fine concentrate feed.

Gases produced within the roaster contain SO₂ dust (Si, Cu, Zn, Fe, Pb), fumes (As, Cd, Se, Sb, Bi), acid mist, vapor, Hg, halides (Cl, F), hydrocarbons, NOₓ and metals (e.g. Fe, Cr, Ni). SO₂ recovery rates exceed 99.9% leading to SO₂ emissions below 100 ppm and acid mist below 10 ppm. To achieve sulfuric acid production, which withholds all respective component concentration constraints, a series of unit operations may be applied within the gas cleaning train. Hence, these impurities are handled by hot de-dusting/ gas cooling systems (cyclones, waste heat boiler, hot electrostatic precipitators) and by wet gas cooling vapor condensing systems (quench coolers, scrubbers, gas coolers/water vapor condensers, two-stage wet electrostatic precipitators). Halide removal may require special consideration in some cases,
while Hg emissions are reduced so that the respective concentrations in the sulphuric acid are only 0.3 – 0.5 ppm or even below 0.1 ppm if required.

Based on the analyzed continuous development of furnace technology to conduct any roasting process variant, and on the ability to handle all emission components, it can be concluded that the current roasting processes can keep up with demanding emission limits and offer efficiency through process integration.

REFERENCES


