INCREASED PRODUCTIVITY OF ZINC ROASTERS AND SO\textsubscript{2} - QUALITY

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Abstract

Advanced optimizing control of the fluidised bed zinc roaster has been in use for an extended period at Boliden Kokkola and the implications are seen as extended bed stability, increased throughput and far better on-line availability. The roaster furnace control system developed is based on a dynamic and predictive furnace model, with parameters determined experimentally at the site. The controller maximises the concentrate feed and keeps the furnace operational parameters inside limits given by raw material mix and equipment constraints.

The products of a zinc roaster, calcine, sulphur dioxide and the side products, such as mercury, meet gradually more stringent requirements, in particular as to their assays and total recoveries in the process chain. The end users of sulphuric acid in northern Europe, among others in the pulp and paper industry, require mercury levels much less than the conventional 0.2-0.4 ppm Hg. Therefore, secondary de-mercurising circuits have been used over the last five years for further cleaning the SO\textsubscript{2} stream allowing production acid grades with less than 0.08 ppm Hg.
1 Introduction

Boliden Kokkola Oy is a custom smelter and it uses 10-15 different concentrates each year and a number of other raw materials as components of the feed mixture. The today’s zinc production uses two main technologies at the site. The roasting-leaching-electrowinning route has been in use since late 1960s and the more recent atmospheric direct leaching [1] as the first treatment step to the sulphidic concentrates, has been in use since 1998 and comprising today about 40% of total zinc production. Two parallel technologies give clear advantages and increased flexibility in the use and selection of raw materials. The produced sulphur dioxide gas is led from the roaster to sulphuric acid plant by Kemira Oy.

**Figure 1.** A schematic flow sheet of the combined zinc roaster-acid plant in Kokkola, by Boliden Kokkola Oy and Kemira Oy, respectively. Over the recent years, an extensive development program has been carried out for increasing the treatment throughput of the two 72 m² fluidized bed (FB) lines. The
production equipment is basically the same as in 1969 when the smelter was started up [2], Figure 1, but now significant improvements have been gained in the on-line availability and production rate.

The development program included laboratory-scale and industrial-scale test runs on the roasting kinetics and the mechanisms of selected sulphidic zinc concentrates, the factors behind the bed instability phenomena, as well as introduction of a new advanced control system to the two FB roaster lines. Improvements were also made in the roaster gas handling, where the emphasis has been in reducing the mercury traces in the product acid to a new level. This has been accomplished by the primary scrubbing stages at the roaster were optimized and a secondary scrubbing step was added to meet the strict requirements of pulp and paper industry.

2 Roaster gas handling

2.1 The gas train

The roaster gas train post the FB furnace consists of a waste heat boiler, cyclones and two ESPs before the de-mercurising steps. The gas duct from the roaster to the acid plant is long, about 1.0 km, separating thus the first scrubbing stage within the roaster area and the second scrubbing stage at the acid plant, see Figure 1.

2.2 De-mercurising steps

The gas train consists of two separate de-mercurising steps, and allows thus production of high-purity sulphuric acid from all zinc concentrates, sulphidic and oxidic, independently of their mercury content. The first step is carried out in the immediate vicinity of the roaster, and the second step is an additional and new feature of the washing section of the sulphuric acid plant, see Figure 1.

The first de-mercurising step is composed of two physical stages. In the first stage the de-dusted roaster off-gas post ESP is cooled by direct water quenching to below 200 °C and then in the second stage it is scrubbed with a carefully controlled sulphuric acid solution containing chloride and selenium [3] at about 60 °C. The mercury scrubbing chemistry is based on the reactions:

\[
\begin{align*}
\text{Hg}^0(g) + \text{Hg}^{2+}(aq) &= 2\text{Hg}^{+}(aq) \quad (1) \\
\text{SeO}_2^{2-}(aq) + \text{SO}_2(g) &= \text{Se}^0 + \text{SO}_4^{2-}(aq) \quad (1') \\
\text{Hg}^0(aq) + \text{Se}^0 &= \text{HgSe} \quad (1'') \\
2\text{HgSe} + \text{Hg}^+(aq) + 2\text{Cl}^-(aq) &= \text{Hg}_3\text{Se}_2\text{Cl}_2 \quad (1'''')
\end{align*}
\]

In a strongly complexed aqueous medium, containing a spectrum of chloride-complexes of mercury, as shown in Figure 2, the de-mercurising reactions must thus be capable to remove both elementary and oxidized forms of mercury from the gas. In spite of the fact that the stable form of mercury in the roaster off-gas is an oxidized substance,
elementary mercury is typically determined in such circumstances and it forms a significant fraction of total mercury [4].

A comprehensive thermodynamic model was built for the scrubber liquid using the Pitzer model [5], including the complexation of mercury with chloride ions in a strong sulphuric acid matrix. Description of the acid matrix was taken from a study where water-sulphuric acid has been modelled to high concentrations and temperatures [6]. The gas phase was assumed to be ideal. The thermodynamic data for the double salt, equation (1’’’), are not available and thus its saturation limit in the various operational points could not be optimized.

A typical acid strength of 33-36% H$_2$SO$_4$ is used in the counter-current scrubbing at the roaster. The other operating parameters of the step have been optimized by extensive thermodynamic modeling of the gas-liquid –system and by observations at the site on the mercury content of the off-gas and its speciation between metallic mercury vapour and nonmetallic gaseous compounds. The formed mercury-selenium double salt is separated from the scrubber liquid by filtering. The first scrubbing stage is also used for controlling halogen carry over to the acid making, as the vapor pressured of HCl(g) and HF(g) are very sensitive to the acid strength and the prevailing outlet temperature of the scrubber.

![Figure 2. Speciation of aqueous mercury in the scrubber liquid, at the cooling stage in the first gas purification step at Kokkola zinc roaster, calculated by the thermodynamic model; the thermodynamic data were taken from [6,9].](image)

The second de-mercurising step is carried out using carefully controlled chemistry and proper ‘side-reactions’ in the washing section of the acid plant [7]. Instead of pure water, slightly acidified aqueous solution containing chlorides and selenium is used. The chemistry is basically the same as shown in equations (1), but the actual process conditions are different, in particular the scrubber temperatures.
This solution chemistry has been successfully used at Kokkola since 2001, and the purity of product acid is typically 0.05 ppm Hg (mg/kg H$_2$SO$_4$), which is much lower than obtained with the calomel process [8]. In addition to the actual mercury concentration of each feed mixture, the selenium-to-mercury –ratio is currently actively controlled at Kokkola, and displayed in the daily roasting reports and instructions.

3 Development work for the operational window of the roaster

In order to improve the stability of the roasting process and to increase the on-line availability and thus the throughput of the roaster, an extensive series of development projects was carried out in 1998-2006. It included several limited tests series on the industrial scale in the roaster area [10-11], dealing with the dynamics of the FB furnace as well as with the behaviour of various feed mixtures in the roaster line. Various raw materials were also studied on the laboratory scale [12], in order to get detailed information about the accretion formation in the roaster vessel and the industrial roasting kinetics. The overall procedure used is depicted below as the flow chart [13].

3.1 De-mercurising steps

The FB roasters at Kokkola use bed overflow only for the calcine outlet from the furnace, in addition to WHB and cyclone products. Thus the physical properties of the furnace calcine produced must meet the requirements of smooth material flow from the overflow gates and no oversize agglomerates are allowed.

All laboratory scale investigation on the FB roasting of zinc concentrates were carried out using a small batch-wise operating fluidized bed furnace with an internal diameter of 40 mm and a typical batch size of 100 g. As the feed mixture in the roaster is agglomerated by itself or assisted by water additions to conveyer belts or storage bins, most high-impurity concentrates were additionally roasted as agglomerates in a horizontal tube furnace [11]. The reason for it was to find out the details of the roasting mechanisms and origin for the growth of agglomerates during FB roasting.
The results obtained gave a lot new information about the behaviour of several impurities in the oxidizing sphalerite concentrate, as to the bed non-stability phenomena and furnace build-up formation [2,10-11]. The micrometer-scale phenomena observed within the primary ZnS grains and on their oxidising surfaces at roasting temperatures indicate, for example, that some common components of the zinc concentrates cannot be the origin of bed non-stability, as typically iron dissolved in the sphalerite lattice, Figure 3, which also indicates a specific type of sulphide mineralogy in the concentrate where iron sulphides are of pyrrhotite type instead of pyrites. The detailed process mineralogical structure analyses of partially roasted sulphides indicated the prevailing oxidation mechanisms that involve copper and lead, if present at high concentrations,
migrating in the system. Due to their low melting point compounds they are prone to forming sinters and thus agglomerating the calcine, Figure 4.

3.2 Impurity control in the feed mixture – heat generation and oxygen requirement

As various impurities in the concentrates behave in a different manner in the FB roasting process, their active control is necessary [13]. That typically involves controlled and limited concentrations for some key elements, as well as for their sum concentrations and restricted operational temperatures, based on the feed mixture assay.

Therefore, a number of components in the feed mixture have their specific upper (maximum) limits allowed, as generally used in this industry [14], but also the mineralogical features of some elements in the concentrates are taken into account when selecting the feed mixture assay. This typically refers to the distribution of such elements and their presence in stable, high-melting compounds and less stable phases, melting around the roasting temperature.

![Figure 5](image)

**Figure 5.** The heat value and oxygen requirement of selected sulphide concentrate raw materials used in zinc production at Kokkola, organized according to their energy content [16].

An important and general feature of the FB roaster is its essentially fixed cooling capacity, which is not a function of the production rate. As the volumetric process air flow rate is essentially determined by the desired oxygen coefficient of the FB (true oxygen feed rate to stochiometric oxygen need of the fed mixture) the cooling effect of the process gas can not be used for controlling the furnace temperature. For this
requirement, secondary air introduced above the FB can be used if high bed temperatures are allowed, but the off-gas should be cooled and possibly after-burned to lower the residual sulphidic sulphur level of the boiler calcine [15]. This feature is, however, dependent on the bed calcine outlet, whether it is realized as bed underflow or overflow. The former design ends up with a higher sulphide sulphur in the calcine, due to the mixing properties of the fluidized bed.

For stabilising the feed mixture preparation routines, the generation of heat in the roasting (the oxidation enthalpy of the minerals in the feed mixture to the typical substances in the calcine) and the amount of oxygen needed (Nm$^3$/dmt) in the roasting is estimated at Kokkola for all the concentrates and other raw materials used, see Figure 5. The roasting heat generation and oxygen consumption values are determined from the chemical assay and a mineralogical characterization done from time to time for each raw material.

4 Furnace control development

Controlling the FB roasting optimally is demanding, since many of the process variables interact. Thus there is a need for multivariable control strategies, and development of such requires good knowledge of the dynamic dependencies between input and output variables. In 2003-2004, a model for the furnace dynamics was developed [17-18] based on data from plant experiments at Boliden Kokkola. Based on the dynamic model, a multivariable control application was developed and implemented in 2005. The controller maximises production within the limits given by process metallurgy and the equipment.

4.1 Measurements and control variables

Furnace bed temperatures are measured in various locations at the bottom and at the wall of the lower part of the furnace. The bed temperature has to be kept within certain ranges to maintain proper conditions for roasting. The temperature at the upper part of the furnace, which is measured at the boiler inlet, is also important. The concentrate feed is the primary manipulated variable. Also two water feeds are adjusted: water is added to the concentrate feed on the load conveyor, but can also be fed directly into the furnace. Air, which is both the fluidising medium and the source for oxygen, is normally kept at a fixed value. There is a possibility to feed technical oxygen to the furnace, although this is option currently not used.

The oxygen coefficient, i.e. the ratio between the actual oxygen feed and the amount of oxygen needed stoichiometrically to combust the feed mixture, should be kept within ranges given by the concentrate properties. Current plant practice is to control an estimate of the oxygen coefficient, based on the oxygen demand of the rated concentrate mixture. There is a measurement of the oxygen content in the boiler off-gas, which gives information of the realised oxygen coefficient. However, this measurement is somewhat uncertain due to air leakages into the furnace and the boiler.
4.2 Dynamics

A large number of step-change experiments were carried out to identify the dynamic behaviour of the FB furnaces. The experiments comprised of changes in six manipulated variables, see Table 1. During the experiment periods, the existing automatic controllers for furnace temperature and boiler inlet temperature were switched off to obtain data from the open loop system. The sampling time was chosen to ten minutes, since the data collection system at the roaster plant did not store values more frequently.

The observed effects are qualitatively shown in Table 1. The dependencies are highly interconnected. For instance, not only the concentrate feed but also the feeds of water and air affect the furnace temperature. An example of the effect of changes in load conveyor water feed is shown in Figure 6. The load conveyor water has a rather complex effect on the furnace bed temperature, the long-term effect is positive, but there also is an inverse response during the first hour.

Table 1. Dependencies between manipulated and observed variables in the fluidised bed furnace.

<table>
<thead>
<tr>
<th>Step-change increase in</th>
<th>Bed temperatures</th>
<th>Boiler inlet temperature</th>
<th>Offgas oxygen content</th>
<th>Windbox pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate feed</td>
<td>increase</td>
<td>increases</td>
<td>decreases</td>
<td>-</td>
</tr>
<tr>
<td>Air feed</td>
<td>decrease</td>
<td>increases</td>
<td>increases</td>
<td>increases</td>
</tr>
<tr>
<td>Oxygen feed</td>
<td>diverge</td>
<td>-</td>
<td>increases</td>
<td>increases</td>
</tr>
<tr>
<td>Overflow grate area pressure</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>decreases</td>
</tr>
<tr>
<td>Load conveyor water feed</td>
<td>temporary decrease, then increase</td>
<td>decreases</td>
<td>temporary increases</td>
<td>-</td>
</tr>
<tr>
<td>Furnace water feed</td>
<td>decrease</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Quantitative modelling of the dynamic effects shown in Table 1 was made using ARMAX type time series models. It was known that this linear model structure could not describe the furnace behaviour in all situations, e.g. when the oxygen coefficient is shifted to values below one. However, the primary goal was to develop a model for normal operation conditions, where a linear description was assumed to be adequate. As a first step in the identification, partial models (sub-models) were identified for the single input-output pairs. The aim was to find models as simple as possible describing the dependencies between input and output observed in the experiments. Zero order and different first order models were used. Finally, the partial models were combined into one model for each output, which also included disturbance models.
In addition to the step-change experiments, tracer tests were carried out to clarify the residence time of the solid material in the bed and in the gas line. In the tests, TiO$_2$ material with a density and a particle size distribution close to that of calcine was used as tracer. The tracer was fed in impulses (batches) to the feed mixture at the slinger belt feeder. The results indicate that the mean residence time of the solid particles in the bed is approximately 20 hours, as can be seen in Figure 7. For the gas line, however, very short residence times were observed. The peak concentration in the cyclone (post boiler) was obtained around one minute after the impulse in the furnace feed.

**Figure 6.** The effect of step changes in load conveyor water feed on temperatures in the furnace bed.

**Figure 7.** Tracer content in the bed overflow in two experiments: the tracer was fed as an impulse at time 0 h. A first order model with a time constant of 20 h is shown for comparison.

The results are quite similar to the results by Dimitrov’s [19] in a small FB furnace. Also Themelis [20] has reported results of retention time tests, using a radioactive tracer. He showed experimentally that various particle size fractions have different retention times.
5 Control system

A control system was developed to enable real-time production maximisation within the limits given by process metallurgy and equipment. The input and output signals of the control application are shown in Figure 8. The optimising control system maintains a concentrate feed as high as possible so that all variables are within given limits. Water additions (to the concentrate on the load conveyor and/or directly to the furnace) are used if they enable a higher concentrate feed.

As described in previous chapter, the interactions in the fluidised bed furnace are cross-coupled. Thus, a MIMO (multiple input – multiple output) control structure was used, since separate single-input, single-output controllers would not operate optimally. The control system includes a state estimator based on the dynamic ARMAX models identified in the step-change experiments, an optimisation routine based on the SIMPLEX algorithm, and a controller based on state prediction. The algorithms were developed in MATLAB®, which is also the environment used for control system implementation. OPC is used for the communication between the control system on a PC and the Honeywell TP® Alcont automation system of the roaster. The operator interface, where the limits are specified, is in Alcont.
Figure 9. Data from the model-based control of a FB furnace. See text for explanation of periods 1 and 2.

The calculation interval of the control system is 5 minutes, and the main steps in a calculation round are:
1. Pre-treatment and validity check of process data
2. Updating the state of the dynamic model
3. Searching optimal set of manipulated variables
4. Control actions based on 30 minutes prediction.

Figure 9 shows history trends from 20 days operation of a furnace, and the actions of the control system. In period 1, the upper limit for bed temperature limits the production, and the feed of furnace water is at maximum limit. In period 2, the lower limit for oxygen coefficient limits the production.

6 Conclusions

The complex nature of material flows and the increased requirements as to their quality and on-line availability, in particular in a large industrial network of several independent companies, are a major challenge for the metallurgical process industry. Therefore, an intensive R&D programme has been accomplished at Boliden Kokkola zinc smelter for securing the quality issues in the zinc production, including also its by products such as sulphuric acid.

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