The roasting of PGM-ore concentrates in a circulating fluidized bed

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Outotec Metals

Lurgi Metallurgie GmbH became part of Outotec in 2002. The company is now known as Outotec GmbH. It has been developing and applying different systems of fluidized-bed reactor to a variety of industrial processes for almost fifty years. The versatility of its fluidized-bed technology has been demonstrated in the treatment of a variety of minerals, including solid fuels, and in ferrous and non-ferrous metallurgical processes. Process applications include roasting, calcining, combustion, and the charring of coals. Outotec also supplies equipment for off-gas treatment and acid plants.

One possible application for this fluidized-bed technology is as a part of Mintek’s ConRoast process, where PGM-ore concentrates are dead-roasted prior to smelting in a DC arc furnace. Unlike the conventional matte-smelting process that collects PGMs (platinum group metals) in a base-metal sulfide (matte), the ConRoast process does not require sulphur for this purpose; instead it produces an iron alloy for collecting the PGMs. This process offers the possibility of dramatically decreasing emissions of sulphur dioxide from PGM smelters.

Introduction

PGM producers predict an increase in PGM-containing, but chromium-rich and sulphur-containing concentrate – a trend that has been followed since the 1990s. These concentrates are metallurgically difficult to treat by the technology in use today. There is a process, however, that addresses the challenge and can overcome the difficulties by a combination of fluid-bed roaster and electric arc furnace. This process is called ConRoast and was designed some years ago for this specific purpose by Mintek in South Africa.

The goal of dead roasting a PGM-ore concentrate is a decrease in the sulphur content to an acceptable maximum of about 0.5% by mass. Outotec conceived a design for producing a PGM calcine with a low concentration of sulphur. Besides reducing the sulphur content, the design also includes the treatment of the produced off-gas, a development facilitated by the historical connection of the fluid-bed department with the gas-cleaning and acid-plant department at Outotec. Central to the calcination step is a circulating fluidized bed (CFB). It is important that the off-gas produced in the CFB fulfill the pre-conditions of an auto-thermally running acid plant.

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Theoretical background to fluid bed technology

The conventional, or stationary, fluidized bed system (also known as a bubbling fluidized bed) is characterized by a lower fluidizing velocity, a high particle density within the bed, and a clearly defined interface between bed and freeboard. The use of a cyclone for the separation of particles in the reactor off-gas depends on the application and is not always required. Conventional fluidized beds and their supporting systems have been widely used in the roasting of sulfide ores and concentrates with the subsequent production of sulphuric acid and utility steam.

Typically in circulating fluid bed (CFB) systems, the calcine produced in the reactor is carried over with the gas into the recycling cyclone and returns to the CFB reactor (see Figure 1), thus forming the so-called circulating fluid bed system. Unfortunately, the efficiency of cyclones decreases with increasing temperature, and, in the temperature range of 900 to 1 100°C used in CFB calciners, it is impossible to avoid the carry-over of some material. Thus, some of the concentrate is carried over together with the off-gas into the next process step. But most of the solids are separated from the off-gas and are recycled through the seal pot into the main reactor (see Figure 1).

The development of such CFB systems started in the 1960s, when the bauxite industry needed an efficient, compact calcination stage. Consideration was given to an alternative design, a bubbling fluidized bed, but the fine particles of feed would require that low gas velocities be employed to maintain a well-defined fluidized bed. Also, as large volumes of gas were to be handled (at the high temperatures required for the reactions and heat transfer to take place), this would have meant the construction of large, difficult-to-control, fluidized-bed reactors. The basis
conventional FB systems can be summarized as follows: major advantages of CFB systems in comparison with appropriate fluid-bed technology. The typical features and feed material, and retention time, affect the choice of an process. Some examples of these various applications are:

- The calcination of alumina hydroxide
- The calcination of gold ore
- The combustion of coal and lignite (in power plants)
- The calcination of cement raw meal
- The combustion of wood and other materials
- The oxidation of other sulfide concentrates

Several parameters, such as throughput, properties of the feed material, and retention time, affect the choice of an appropriate fluid-bed technology. The typical features and major advantages of CFB systems in comparison with conventional FB systems can be summarized as follows:

- Operation at high slip velocities, which allows for high specific throughputs and small unit sizes, which lowers capital costs
- Improved control and uniform temperatures throughout the reactor system – this ensures uniform dead-roasting of the material
- Constant gas conditions and composition in the reactor system and its uniformity
- The residence time of solids can be adjusted over a wider range, with the potential to improve the extent of roasting. This also includes the possibility of running with part load and load changes according to the concentrate composition.
- Suitability for exothermic and endothermic processes
- Acceptance of feed material with variations in chemical composition and particle-size distribution. The main limitations, however, are placed on the operation of the CFB by subsequent process steps, those of gas cleaning and the sulphuric acid plant.

- Suitability for operating with highly oxygen-enriched roasting air
- Suitability for injecting fuels such as coal directly into the reactor
- A reduction in energy losses

The process advantages of a CFB system increase at higher feed rates, as bed mixing (homogeneity) in conventional FB roaster units decreases with increasing roaster cross section, whereas CFB systems operate with comparably smaller reactors - approximately one tenth (to perhaps one fifth) of the cross section of a conventional FB. These features result in a high roasting efficiency, and along with the other advantages, mark CFB technology as a preferable alternative to conventional FB technology for processes with high concentrate throughputs.

**Fluid bed technology R&D and scale-up**

Outotec’s pursuit of new fluidized bed applications for customer needs is supported by experimental work in the company’s in-house R&D Centre in Frankfurt. Key elements in any test programme include the development of neural networks, in situ monitoring systems, and modern mathematical methods, including computational fluid dynamics (CFD) modelling. Outotec has developed theoretical models of fluidized-bed systems and acquired knowledge in scaling up these processes. A unique set of pilot plants, suitable for the processing of feeds from batches of 100 g to a continuous 1 000 kg/h, is available for developing new, and improving existing, technologies for clients. These pilot plants are designed to be flexible: they can run under different temperatures, pressures, gas compositions, and fluidizing conditions, and they can be configured either as single- or multi-stage units. However, the data gained in laboratory-scale fluidized-bed systems provide insufficient design and performance criteria of industrial plants without the experience of operating facilities.

Outotec’s largest CFB test unit at the R&D Centre in Frankfurt is a 700 mm diameter CFB demonstration plant. This CFB is equipped with a recycle cyclone, an integrated heat generator, a char separator, a magnetic separator, a gas-cleaning system, and other indispensable ancillary equipment. The R&D Centre also houses smaller CFBs of 300 mm and 200 mm diameter.

In the design of new CFB plants, the process parameters developed for the new plant - such as particle size, fluidizing gas, and gas velocity - are compared with data from existing CFB operating plants. The comparison is done in dimensionless units. The so-called Reh diagram illustrates the different phase behaviour of gas-solid interactions based on dimensionless units (see Figure 2). The yellow region at the bottom right of the diagram represents the fixed-bed operating domain. The blue region indicates the domain of the bubbling fluidized bed, where gravity and drag forces on the particles are in balance. The grey section represents the pneumatic transport domain. The orange triangular region represents the area of the circulating fluidized bed. However, as the diagram is calculated for ideal spherical, homogeneous particles, it provides only an approximation of the extents of the domains of fluidization for systems in industry. Nevertheless, coupled with experience from industrial
plants, the CFB operating range can be extended into area ‘a’ of the diagram. This knowledge gained from operational experience is applied to the design of new plants and processes.

In the course of over fifty years of experience in the engineering and supply of fluidized bed reactor plants, Outotec has developed scale-up criteria for plant design, starting from pilot-plant test work at its R&D Centre. It has, consequently, been able to demonstrate the technology on a smaller, less-expensive scale than would otherwise be required. Table I shows examples of the scale-up figures of former Outotec projects.

The following CFB conceptual designs were developed for the roasting of PGM-ore concentrates, based on the above-mentioned know-how.

### Roasting designs for PGM concentrates

The major objective of the roasting process is the decrease of sulphur in the PGM-ore concentrate to an acceptable level, in order to produce a calcine suitable for subsequent smelting in a DC arc furnace. The basis for our calculation is a concentrate containing approximately 7% sulphur. The simplified chemical composition of this concentrate is shown in Table II.

In test work with this material, a roasting temperature of ~1 000°C was found to be appropriate for lowering the sulphur concentration in the calcine. The sulphur occurs as sulphides, of which pyrite (FeS₂), pyrrhotite (Fe₇S₈), and chalcopyrite (CuFeS₂) are just three significant ones. The following simplified equations show some of the expected reactions in the CFB reactor.

\[
\begin{align*}
2\text{FeS}_2 &+ \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4 \text{SO}_2 \quad [1] \\
3\text{FeS}_2 &+ 8\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3 + 6\text{SO}_2 \quad [2] \\
\text{Fe}_7\text{S}_8 &+ \frac{3}{2}\text{O}_2 \rightarrow \frac{7}{2}\text{Fe}_2\text{O}_3 + 8\text{SO}_2 \quad [3] \\
\text{Fe}_7\text{S}_8 &+ \frac{5}{2}\text{O}_2 \rightarrow \frac{7}{3}\text{Fe}_3\text{O}_4 + 8\text{SO}_2 \quad [4] \\
\text{CuFeS}_2 &+ 3\text{O}_2 \rightarrow \text{CuO} + \text{FeO} + 2\text{SO}_2 \quad [5]
\end{align*}
\]

Equations [1] to [5] describe the dead-roasting of major sulfides present in the concentrate. The reactions are all exothermic and generate a considerable amount of thermal energy during the roasting process in the CFB system. Nevertheless, because sulfides make up only a small fraction of the concentrate (7% in this case), the energy generated is not sufficient to run the CFB in autothermal mode at 1 000°C, as pyrite roasters are operated. Therefore, coal or natural gas is added to the reactor to maintain a high roasting temperature. Both sources of energy are suitable, but coal was used in this study, as it is readily available in South Africa.

As mentioned above, some of the solids pass through the cyclone, together with the off-gas, into the next process step.

After decomposing the sulphur from the pyrite etc., the back-formation of MeSO₄ has to be avoided. The influencing factors for the back-formation of the metal oxides with SO₂ gas to MeSO₄ are:

- Metal oxide with high affinity to form metal sulfates
- Temperature
- Excess Oxygen
- High Retention time

In the case of the present concentrate, the oxides CaO and MgO are the most critical compounds, which can form metal sulfates. Figure 3 shows the influence of temperature on the formation of MgSO₄ and CaSO₄ for the given calcine composition, which should be produced in the CFB and would be carried over into the ‘colder’ steps after the CFB. Beside MgSO₄ and CaSO₄, FeSO₄ and NiSO₄ are

### Table I

<table>
<thead>
<tr>
<th>Process</th>
<th>Year</th>
<th>From pilot plant size (D = 1000 mm; 24 t/d)</th>
<th>To industrial plant size (D = 5 000 mm; 500 t/d)</th>
<th>Scale-up factor</th>
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<tr>
<td>Alumina calcination</td>
<td>1970</td>
<td></td>
<td></td>
<td>1 : 20</td>
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<tr>
<td>Coal combustion</td>
<td>1982</td>
<td>D = 460 mm; 20 kg/h</td>
<td>D = 5 000 mm; 500 t/d</td>
<td>1 : 1000</td>
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<tr>
<td>Gold ore roasting</td>
<td>1990</td>
<td>D = 200 mm; 22 kg/h</td>
<td>D = 3 800 mm; 2 000 t/d</td>
<td>1 : 4000</td>
</tr>
<tr>
<td>Circored</td>
<td>1999</td>
<td>D = 200 mm; 18 kg/h</td>
<td>D = 5 000 mm; 1 500 t/d</td>
<td>1 : 3500</td>
</tr>
</tbody>
</table>

### Table II

<table>
<thead>
<tr>
<th>Chemical composition of the starting PGM-ore concentrate</th>
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<tbody>
<tr>
<td>Element</td>
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<tr>
<td>---------</td>
</tr>
<tr>
<td>Fe</td>
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<tr>
<td>Ni</td>
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<tr>
<td>Cu</td>
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<td>Al</td>
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<tr>
<td>Si</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>Other</td>
</tr>
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</table>
also shown. These latter compounds have only a very low concentration compared to the compounds mentioned before. Any increase in the CaO concentration would raise the sulfate concentration in the calcine due to the high affinity to form CaSO₄.

The formation of the MeSO₄ decreases with increasing temperature as shown in Figures 3 and 4. Both diagrams show the influence of the temperature on the formation of MeSO₄. The difference between the two diagrams is the assumed oxygen concentration in the off-gas stream. This factor also has a strong influence. Any decrease of oxygen concentration in the off-gas stream would suppress the formation of MeSO₄. On the other hand, it is necessary to ensure that all CO gas has been burnt completely in the roaster off-gas before entering the off-gas treatment stage. According to Outotec’s experiences from other projects, the oxygen concentration should be in the range of 2–3 %. Otherwise, an additional CO-afterburning stage has to be installed to avoid any CO gas at the exit.

The calculations of the metal sulfate (MeSO₄) formation can only indicate qualitative tendencies. They are based on the thermodynamic equilibrium of the system and don’t consider the influence of the chemical kinetics of all the reactions. The thermodynamic equilibrium implies an infinite retention time, which is one known pre-condition for a high sulfation of the above-mentioned compounds CaO and MgO, etc. Therefore the following diagram, Figure 5, can only show the absolute maximum of the

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**Figure 3.** The effect of temperature and excess of oxygen on the formation of MeSO₄

**Figure 4.** The effect of temperature and deficit of oxygen on the formation of MeSO₄
sulphur concentration in the calcine for a certain temperature and concentrate composition. The real values will give better results for the S concentration than Figure 5 is indicating, even for the blue line with a high oxygen concentration of 3% by volume in the off-gas.

**Energy efficiency**

These days, one of the most-discussed topics in the world is energy recovery and saving in all areas of human life, including technology. Outotec is well known for considering this aspect very eagerly in their technologies. Saving energy was a strong consideration in the conceptual design of the roaster. By recovering the energy from the hot discharged off-gas or calcine, less coal need be introduced into the roaster. The energy of the discharged calcine can be used in the form of hot charging the calcine into the electric arc furnace (EAF). This hot charging into the EAF reduces the coal and energy consumption in the EAF and increases, furthermore, the throughput of the furnace. For the internal energy recycling in the CFB plant, only the energy in the off-gas can be used. Two designs give substance to the recovery of this energy. In the first design, energy is transferred to the fluidizing air; in the second design, the energy in the off-gas is used to dry the wet feed before it is fed into the CFB. Both designs are described in the following section.

The first PGM-CFB concept recycles the energy to the fluidization air in the recuperator (air pre-heater). As in the second concept, the process starts with the CFB plant including the cyclone and continuous with the recuperator. The off-gas is cooled down in the recuperator while the fluidization air is heated up. Figure 6 shows the schematic arrangement of the process steps and flow streams.

The second PGM-CFB concept is shown in Figure 7. This concept differs from the first one in the use of a venturi dryer combined with a second cyclone instead of a recuperator. The feed material is charged into the venturi dryer, and this concentrate is dried by the counter-current flow of off-gas from the CFB plant. The dried concentrate is carried over together with the off-gas into the second

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**Figure 5.** Sulphur concentration of the calcine product depending on the reactor temperature

**Figure 6.** Block diagram of the first concept. Air heated by a recuperator
cyclone, where most of the concentrate is separated from the off-gas. The concentrate passes into the CFB, while the off-gas flows to the evaporation cooler. In both concepts, the evaporation cooler assures a constant temperature in front of the hot electrostatic precipitator (ESP) (the first step of the gas cleaning). In the hot ESP, the solid particles from the off-gas are precipitated and mostly recycled to the CFB. Figure 7 shows the main process steps and the flows of the concept.

In both concepts, the consumption of coal in the CFB is less than in a plant without any energy recovery. The reduced consumption of coal decreases the off-gas volume and increases the concentration of SO$_2$ in the off-gas stream. This higher SO$_2$ concentration in the off-gas enables and supports the operation of the sulphuric acid plant in autothermal mode. The SO$_2$ concentration in front of the acid plant should be in the range of 3.5 to 5% by volume. These low SO$_2$ concentrations are acceptable only because the design of acid plants by Outotec provides sufficient thermal insulation, optimizes the recovery of high-grade energy, and minimizes losses through radiation.

Depending on whether or not a flash dryer is used in front of the CFB, the moisture content of the feed material can vary between approximately 2 and 16%. The amount of moisture in the concentrate has the biggest impact on the gas volume flow. By feeding less moisture into the reactor, the coal consumption and off-gas volume can be decreased. Furthermore, the amount of ash (from the coal) is reduced.

An alternative means of reducing the volume of the off-gas stream is by the use of technical oxygen in the CFB. The use of technical oxygen reduces the flow of nitrogen into the CFB, which consequently increases the concentration of SO$_2$ in the off-gas. The lowest volume of off-gas, and highest concentration of SO$_2$, can be reached with 2% moisture in the feed and the use of technical oxygen.

Concentrates from UG2 and Merensky ores typically have a sulphur content of 3 to 7% by mass. All calculations gave a minimum range of sulphur concentration of 2.5 to 4.5% by mass in the feed concentrate to fulfil the required SO$_2$ concentration in front of the sulphuric acid plant. These values show that a PGM concentrate with the lowest-expected sulphur content (3% by mass) can be treated in a plant that draws on the concepts presented here.

Conclusions

Our investigation has produced two process concepts for dead-roasting PGM-ore concentrates. The processes are efficient and flexible to operate; they meet the requirement of reducing sufficiently the moisture and sulphur contents in the concentrates. After roasting the concentrate at 1000°C in a CFB, the hot calcine is sent to an electric arc furnace. The two concepts have a number of process steps (such as the CFB) in common. The main difference is the inclusion of a recuperator in one of the designs, and a venturi dryer followed by a second cyclone in the other design. These conceptual designs will lower the sulphur concentration in the calcine; they will also meet several other conditions. The principal features of the first design are:

- The recovery of energy from the off-gas in a recuperator
- The direct recovery of energy in the recuperator and the reduction of coal consumption in the CFB
- The reduction in volume of the off-gas and, therefore, a decrease in the size of equipment
- An increase in the concentration of SO$_2$ in the off-gas and a fulfilling of the expected SO$_2$ concentration at the inlet to the acid plant
- The treatment of PGM-ore concentrates with lower sulphur concentrations
- Great flexibility in the concentrate composition
- The principal features of the second design are:
  - The recovery of energy from the off-gas in a venturi dryer
  - A reduction in coal consumption needed otherwise to dry a wet concentrate in a flash dryer and/or a CFB
  - A saving of the additional equipment cost for a recuperator and/or flash dryer
  - A reduction in volume of the off-gas and an increase in the concentration of SO$_2$ in the off-gas
  - The treatment of PGM-ore concentrates with lower sulphur concentrations
  - Great flexibility in the concentrate composition

The principal features of the second design are:

- In addition of using pure air for the fluidization, one can replace some part of the fluidization air with technical oxygen. This option has the following advantages:
  - A reduction of the volume of the off-gas stream
  - An increase in the concentration of SO$_2$ in the off-gas
  - A slight reduction in the consumption of coal in the CFB
  - Greater flexibility for treating concentrates low in sulphur

Outotec has developed and introduced features in the acid plant designed to promote plant quality and availability for sulphuric acid plants. A principal feature of the plant is its autothermal operation with SO$_2$ contents of only 3 to 3.5%. The acid plant will run without any additional heating. In treating PGM-ore concentrates containing only 2.5 to 4.5% by mass, the designs will still exceed the minimum SO$_2$ concentration in the off-gas required by the acid plant. This range covers the sulphur concentrations expected in PGM-ore concentrates, for which the minimum is approximately 3%.
References


3. Anon., Fluidization Technology, Prospectus, Outotec


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Jörg Hammerschmidt studied mechanical engineering/process engineering at the RWTH Technical University of Aachen. From 1998 too 2002, he worked as a scientific assistant at IME Process Metallurgy and Metal Recycling, RWTH Aachen. In 2003 he defended his Ph.D. thesis titled γ-TiAl with Aluminothermic Reduction and Electro Slag Remelting. In January 2003 he started his professional career at Outotec GmbH (former Lurgi Metallurgie) as Process Engineer for non-ferrous technologies. He participated in different projects in the engineering- as well as commissioning-phase for Roaster and hydrometallurgical zinc plants. In 2006 he was appointed as project manager for the new zinc plant at Hindustan Zinc Ltd./India.