PROCESS APPLICATION NOTE 1006

Online analysis of zinc, sulfuric acid, and iron during zinc refining

Global zinc production relies heavily on zinc blende processing. Over 95% of the world's zinc is produced from this mineral source. Before metallic zinc can be recovered through hydrometallurgical or pyrometallurgical methods, the sulfur present in the concentrate must be eliminated. This is done by heating zinc sulfide (ZnS) at high temperatures, turning it into the more active zinc oxide (ZnO).

The sulfur dioxide obtained during this process is then converted into sulfuric acid. However, the iron sulfide in the ore causes issues, as it changes into zinc ferrite ($ZnO{\cdot}Fe_2O_3$) when reacting with zinc oxide. To ensure high-quality zinc production, the dissolved solution undergoes purification stages prior to electrolysis.

This Process Application Note details the online analysis of key parameters like zinc, sulfuric acid, and iron content. The 2060 TI Process Analyzer from Metrohm Process Analytics offers precise and efficient measurements, cutting down on time, labor, and human errors.

Metrohm
Process Analytics

INTRODUCTION

More than 95% of the world's zinc comes from zinc blende (ZnS) [1]. Before obtaining metallic zinc, which can be done using hydrometallurgical or pyrometallurgical techniques, the sulfur in the concentrate must be removed.

This is accomplished by roasting or sintering at high temperatures (>900 °C), causing zinc sulfide (ZnS) to change into the more reactive zinc oxide (ZnO) (Equation 1). The acquired sulfur dioxide is converted into sulfuric acid within a nearby plant connected to the smelter.

$$2\,ZnS + O_2 \rightarrow 2ZnO + SO_2$$

Equation 1.

If there is any iron sulfide in the ore, it will be transformed into iron(III) oxide (Fe_2O_3), which then reacts with zinc oxide (ZnO) to produce zinc ferrite ($ZnO{\cdot}Fe_2O_3$). This zinc compound is challenging to recover, making ores with low iron content more desirable.

In the leaching step (hot acid leach) shown in Figure 1, zinc oxide is isolated from the other calcines formed in the roasting process. The isolation is done by using sulfuric acid (spent electrolyte) to create zinc sulfate ($ZnSO_4$) and water (Equation 2).

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

Equation 2.

Zinc dissolves and iron precipitates, while other metals like lead and silver remain undissolved. However, the resulting solution also contains impurities, like trace metals, which must be removed to produce high-purity zinc.

First- and second-stage purification prior to electrolysis is carried out by zinc dust precipitation or cementation. The resulting purified neutral zinc sulfate solution is then subjected to electrolysis in the cell room to create zinc metal.

In the complex process of zinc refining, efficient and accurate analysis of key parameters such as zinc, sulfuric acid, and iron is crucial to maintaining optimal process conditions and ensuring high-quality zinc production. Traditional laboratory analysis methods have long been used to determine these parameters, but they are often time-consuming, labor-intensive, and prone to human error. This is where online analysis systems come into play, revolutionizing the way these critical measurements are made in the zinc refining industry.

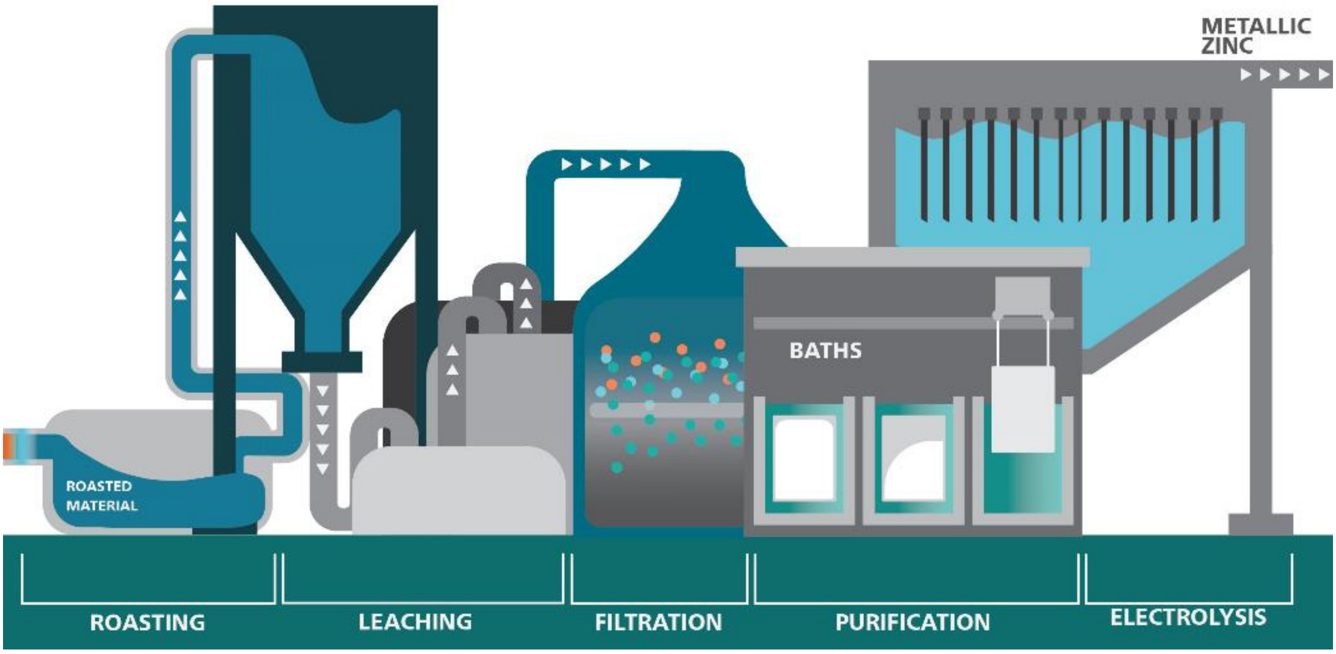

Figure 1. An illustrated diagram showing the major steps in the zinc refining process.

In several stages of the zinc refining process, online process analyzers are used to determine the acid, zinc, and ferric concentrations for completion rate monitoring. Metrohm Process Analytics offers a multi-parameter process analyzer solution for the simultaneous analysis of such analytes over a wide concentration range: the 2060 TI Process Analyzer (Figure 2). Other combinations of measurements (e.g., pH), as well as measurement points taken from multiple streams, can be realized with this process analyzer.

Figure 2. 2060 TI Process Analyzer with preconditioning panel in a zinc refining plant.

APPLICATION

The acid concentration is measured by a straightforward acid/base titration while the zinc concentration is analyzed by a complexometric titration. The ferric iron is analyzed by redox titration. Another common impurity, cobalt, can be measured with photometry, and other trace metals can be measured by voltammetry (Table 1).

Besides the chemical analysis, sample preconditioning is a crucial factor for the success of online analysis. Figure 2 shows a 2060 TI Process Analyzer with a customized preconditioning panel able to handle this type of slurry sample. Due to the acidic environment and high sample temperature, all parts are made (or coated) with perfluoroalkoxy (PFA) or polytetrafluoroethylene (PTFE).

TYPICAL RANGE

Table 1. Parameters to monitor in the zinc refining process. Different measurement techniques are suggested based on the concentration range.

Parameter	Concentration range	Technique
Zn^{2+}	0–2 mg/L	Photometry
Zn^{2+}	10–90 g/L	Titration
H_2SO_4	50–200 mg/L	Titration
Cobalt	0.01–1.5 mg/L	Photometry
Trace metals	<0.05 mg/L	Voltammetry

REMARKS

It is necessary to also measure impurities like nickel, cobalt, copper, cadmium, antimony, and germanium for product quality control, process efficiency, environmental compliance, health, and safety reasons. Additionally, measurement of these impurities is crucial for troubleshooting process issues and potentially recovering valuable resources.

These impurities can be monitored with a dedicated voltammetric process analyzer in the purification filtrates and reactor trains (Figure 1). This process analyzer can also be applied to monitor trace metals in the effluent of the zinc plant for environmental purposes.

CONCLUSION

In conclusion, zinc production from zinc blende involves removing sulfur, recovering zinc oxide, and purifying the solution. Online analysis systems like the 2060 TI Process Analyzer play a vital role in monitoring various parameters and ensuring high-quality zinc production. They also help measure impurities for quality control and process optimization. These tools have revolutionized the zinc refining industry, improving efficiency and environmental compliance.

REFERENCE

[1] Production - Zinc.Org India. http://zinc.org.in/why_zinc/production/

RELATED APPLICATION NOTES

- AN-PAN-1019 Online and atline analysis of acids and iron in pickling baths
- AN-PAN-1034 Analysis of Bayer aluminate liquors using thermometric titration

BENEFITS FOR ONLINE PROCESS ANALYSIS

- **Guarantee compliance** with governmental regulations
- **Safer working environment** for employees (e.g., no exposure of the operator to dangerous environments)
- **Enhanced control of chemical dosing** (H_2SO_4) of the zinc refining process
- Monitor multiple parameters for **more savings per measurement point** and results

Analytes:	**Acids – inorganic; Boron, silicon, germanium, arsenic, selenium, antimony, tellurium; Sulfur – sulfate; Transition metals – copper, zinc, cadmium, lead, thallium; Transition metals – iron, chromium; Transition metals –nickel, cobalt**
Matrix:	**Ores, minerals; Metals in solution**
Method:	**Process Analysis; Titration**
Industry:	**Environmental; Metals & mining**