

APPLICATION REVIEW SELECTIVE PRECIPITATION IN METAL REFINING

In hydrometallurgy metals are extracted from there ores, concentrates, recycled or residual materials using aqueous chemistry. Different processes are used such as leaching, solvent extraction, ion exchange, electrolysis, selective precipitation, or electro winning. Since the feedstock has variations in metal content and ratio of the different elements involved, these processes need constant adjustment and control. Process control is widely done by taking small samples over the day and subsequent analysis in the lab. This approach has several drawbacks; it can take hours to get results, you only get a few data points per day, and sample handling can compromise your results. This is not ideal for process control purposes and has relative high running costs due to extra man-hours and chemical consumption involved.

REAL-TIME MEASUREMENT

Having an on-line analysis solution gives you continuous feedback in real-time, and is less prone to errors due to sample handling. The most suitable on-line technology is high resolution EDXRF analysis as used by the C-QUAND analyzer.

The C-QUAND uses a flow cell which is continuously flushed with fresh sample and has an internal reference for gain and normalization. This analyzer requires little sample preparation, uses no buffers or reagents, can measure at process temperatures (up to 80°C), and can identify multiple elements giving you thorough inside in your process. The C-QUAND is a very robust technique and works completely automated with very little maintenance compared to other techniques. The analyzer software can control automated stream switching, up to four streams, can control automated validation or calibration and flushing cycles. There is no need for extensive DSC programming or an external PLC.

C-QUAND XRF ANALYZER

ANALYSER BENEFITS

- On-line analyzer
- Highly sensitive silicon drift detector (SDD)
- Continuous non-destructive analysis
- Close to zero maintenance; only cleaning of the flow cell window
- Flow cell can be easily removed
- Analyzer data available via 4 - 20 mA, MODBUS TCP/IP or MODBUS RS485
- Analysis up to 15 elements possible with a single analyzer
- Linear results from ppm to percentage levels
- Automatic drift correction



SELECTIVE PRECIPITATION PROCESS

In this paper, we will review the C-QUAND EDXRF analyzer in the control of a selective precipitation process as found in zinc or nickel refining which takes place in big open tanks at low pH and elevated temperatures. In these process impurities, such as copper, cobalt, or cadmium are removed from a concentrated zinc or nickel sulfate solution.

In this case, we will look at the step where copper is removed from a nickel sulfate (NiSO_4) solution (pH 1-1.5, $\sim 80^\circ\text{C}$) by the following reaction:
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$

The dissolved copper ions take up electrons and will precipitated as small particles which can then be filtered from the zinc sulfate solution. As an electron-donor metallic nickel powder is added;
 $\text{Ni}(\text{s}) \rightarrow \text{Ni}(\text{aq}) + 2\text{e}^-$

Nickel powder is continuously being dosed by an auger until most of the copper is precipitated. Continuous measurement of the copper concentration in solution is vital as adding too much nickel powder will lead to hydrogen formation and an explosive atmosphere. In that case all the copper has reacted and the following reaction will take place due to the low pH:
 $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

So, for this process there is a need for a reliable continuous, fast on-line measurement that can quantify small amounts of copper in a nickel sulfate matrix. The nickel concentration will be hundreds of grams per liter and the copper

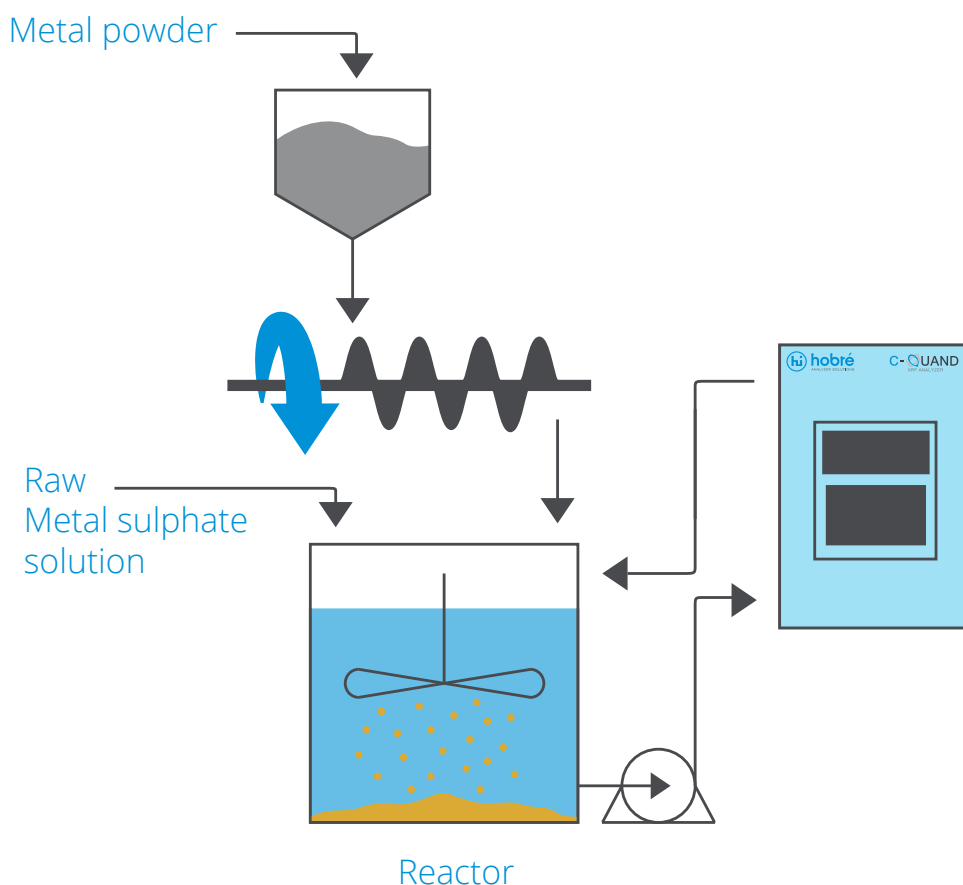
concentration will be grams per liter at the start of the process. Other elements in solution include iron, cobalt, zinc, calcium, or manganese for instance. At the end of the process the copper concentration will be tens of milligrams per liter and the ratio between nickel and copper is a factor 3000. High resolution EDXRF can distinguish the fluorescence peaks of Cu and Ni even though the $K\alpha$ energy values are very similar.

During the reaction particles are formed and they need to be removed in the sample handling system to prevent clogging or false positive reads from the EDXRF instrument. Filtering should be very fine to make sure that only the copper in solution is being measured as this is the analyte of interest. The sample handling system and analyzer should not only be capable of handling fine solids, but should also handle the acidic conditions and high temperature of this process.

Hobré instruments has developed a proprietary sampling system specially designed to handle these challenges. The sample window and other sample wetted parts are suitable to be used in combination with extreme pH, and high temperatures, and the sampling system can handle high particle loads. Sample switching, gain adjustment, normalization, calibration or validation, and flushing can all be controlled by the analyzer software.

Combined with the powerful C-QUAND high resolution EDXRF analyzer this is the perfect solution for process control in metal refining.

SELECTIVE PRECIPITATION



ANALYTICAL	
Measurement principle	Energy dispersive X-ray fluorescence
Element range	Si to U (Z=14 to 92)
Measurement range	From 0.5 ppm to % levels (application specific)
Simultaneous elements	up to 15 elements
Filter wheel	6 filters
Accuracy	Appropriate to application
Calibration	Less than 5 samples

CENTRAL PROCESSING AND CONTROLLING UNIT	
Industrial PC	Linux operating system, custom touch keyboard with 8" TFT color display
Analog outputs	2 or 4 x 4-20mA active
Communications	MODBUS via RS485 or TCP/IP
Ambient temperature	5 – 40°C

MEASUREMENT HEAD	
X-ray detector	Silicon drift detector, resolution 135eV (equals 2.3% at 5.89keV)
HV power supply	0 - 50kV
Source	15 W X-ray tube, Ag anode
Stability	Automatic drift and back scatter peak correction, temperature and ambient pressure correction
Sample window	Kapton® or Upilex®

UTILITY REQUIREMENTS	
Power supply	110-230 VAC 50/60 Hz
Power consumption	100 VA (150 VA with heated sample cell)
Instrument air	< 4 L/min for Exp. version and required for standard pneumatic valve (electrical actuated valve optional)

GENERAL	
Size	HxWxD = 1000 x 400 x 360 mm
Valve control	Automatic stream switching, automatic cell flushing, automatic validation Liquid Sample Recovery Control done by analyser (optional)
Inputs	Flow and level alarms (optionally) read by analyser
Diagnostics	High level of diagnostics
Remote supervision/control	External control of analyser possible
Hazardous Area Classification	Exp. (pending)

SAMPLE PROPERTIES (TYPICALLY)	
Temperature	50 – 80°C
Pressure	Atmospheric tank
Particle load	< 150 g/l
Particle size	1 – 150 micron
Medium	Sulphuric acid solution
pH	1 – 2.5
Elements of interest	Fe, Co, Ni, Cu, Zn

SAMPLE CONDITIONING SYSTEM	
Air driven fast-loop pump	10 l/min
Sample flow rate to analyzer	50 - 500 ml/min
Particle filtering	< 2 micron (typically)
Flushing connection	On fast-loop and analyzer flow (optionally automated)
Sample cell temperature	< 80°C
Sample cell pressure	Atmospheric drain
Viscosity	Less than 100 cSt at cell temperature (heated sample cell available)
Wetted materials	Stainless Steel / PVDF/ PTFE / Polyimide
Size	H x W x D = 900 x 900 x 400 mm