HYDROMET 2014
Boliden Odda

Background

The flow sheet for the Zinc production at Boliden Odda is illustrated in Appendix 1. The production consists of several steps from roasting, leaching, purification, electro winning to casting. After 2004 zinc concentrates are added not only to the roaster, but also to the direct leaching. The most cost efficient way of increasing the total production and productivity of a Zn smelter is to increase the feed of raw materials through direct leaching. However it will harm the leaching and purification process if the amount of Zn from the direct leaching process is higher than the amount of oxidic Zn from calcine, ZnO, and secondary zinc sources. In order to utilize more secondary zinc resources halogenides have to be removed. If this project leads to improved technology for removal of halogenides BOLIDEN Odda will have a greater variety of raw materials to choose among. This will open the door for another capacity increase.

Cathode wear is one of the major costs in the cell house for Zn electro winning. Both F^- and Cl^- reduce the lifetime of the cathodes by pitting corrosion and general corrosion. If the amount of halogenides is reduced, an increase of cathode lifetime by 4 months should be possible, reducing the cost of cathodes on a yearly base by 5 million NOK. In general high levels of fluoride and chloride also contribute to corrosion of process equipment in the leaching and the cell house which will reduce the lifetime of process equipment. In addition high chloride levels in the cell house can result in Cl_2 (g) formation which has a negative impact on the working environment.

In addition to halogenides the raw materials contain elements of high value and elements that can be toxic and harmful to the process and the environment if released. Today metals such as Cd and Cu are recovered in the process, but yearly several tonnes of high value metals such as Ag and Pb are deposited into mountain caverns together with the main by-products jarosite and elemental sulfur. Some zinc plants have already installed technology that recovers e.g. Ag and Pb, but the investment to install these technologies are high.

Priority list work packages

All of the four work packages have elements of relevance for Boliden Odda, but for this project a priority list is given below

- **WP1**- Removal and handling of halogenides in minute concentrations from aqueous solutions.
- **WP4**: Removal and handling of toxic and other unwanted elements from aqueous solutions, e.g. As, Ni, Mn, Mg, Zn, Cd.
- **WP3**: Recovery of metals in low concentration from fluids at high flow-rate. E.g. purification of effluents from mine tailings.
- **WP2**: Recovery of high value metals in low concentrations, e.g. Pd, Pt, Ag, Au, Cu, In from aqueous solutions.

In the following mainly work package 1 will be discussed.

Aim WP1

Ensure that halogenides, in particular Cl and F, are efficiently removed before entering the electro winning. With todays operation practice the maximum level of F^- and Cl^- accepted in the purified zinc solution is 35 mg/l and 270 mg/l respectively. This limits the amount of halogenides that can be present in the concentrates and zinc oxides added to the process.

Design basis

As illustrated in Appendix 1 the leaching consist of many process step from neutral leaching, jarosite precipitation, hot acid leach, direct leaching and purification. The different steps have their own set of operating conditions and technical limitations. All reactions take place in a sulphate environment with varying acid strength and temperature. Figure 1 illustrate a part of the leaching, the neutral leaching. Here zinc calcine from the roasting is mixed together with the solution from the jarosite part, JFF11 and spent acid from the cell house. Zinc oxide in the calcine and clinker, a secondary zinc oxide, is added in NLT1 and NLT2. This neutralizes the flow from JFF11 and spend acid from the cell house. Two of the main reactions in the neutral leaching can be written as

$ZnO + H_2SO_4 = ZnSO_4 + H_2O$

$Fe_2(SO_4)_3 + 3\ ZnO + 3\ H_2O = Fe(OH)_3 + 3\ ZnSO_4$

During the natural leaching the pH increase from ~1.6 in neutral leaching tank1, NLT1 to ~ 4.5 in NLT5. Sampling data from the leaching has illustrated that the concentration of chloride is relatively stable throughout the neutral leaching, while F^- is reduced from ~150 mg/l in NLT1 to ~20-30 mg/l in NLT3. The process solution contain amongst others iron and aluminium, and a possible explanation for the reduction of fluoride is precipitation F^- together with iron hydroxides or as AlF_3. This precipitation mechanism is a topic of interest.

Dissolved F^- in the solution that flows through the neutral leaching continue into the purification area so an alternative to remove F^- would be to precipitate it during the neutral leeching or to add an additional purification step prior to the cell house.

It is seen that that fluoride that precipitates during the neutral leaching dissolves when entering the jarosite and hot acid leaching, but it is assumed that some fluoride will bleed out together with jarosite into the mountain caverns. A sampling campaign with focus on fluoride is at the planning stage and is likely to take place late 2014 or early 2015.

In table 1 some process values are listed.

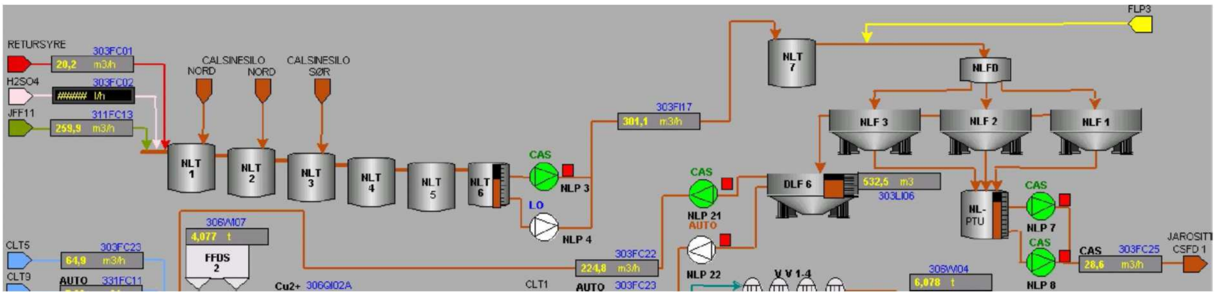


Figure 1: Flow sheet neutral leaching

Table 1: Example of chemical environment. Not all elements in the process solution are included.

Area	Zn^{2+} [g/l]	Fe^{2+} [g/l]	Fe^{3+}	F^- [mg/l]	H_2SO_4 [g/l]	pH	Flow, m^3/h
JFF11- Jarosite thickener 11	~115	4-6 g/l	1-2 g/l	~156	10-12 g/l		250
NLT1-Neutral leaching tank 1				~150		~1.6	
NLT2- Neutral leaching tank 2				~30		~3.9	280
NLT3- Neutral leaching tank 3				~30		~4.1	280
NLT5- Neutral leaching tank 5		<6 mg/l		~30		~4.45	280
DLFD6-Thickner 6	~150			~30			225
Purified solution into electro winning	~150			~30			260

During the neutral leaching process other elements are precipitated in order to prevent them from entering the electro winning. E.g Fe^{3+} and Al^{3+} precipitates as hydroxides in the neutral leaching when the pH increases. A too high pH can lead to precipitation of copper hydroxide which is not desirable because copper is recycled and also used as a component in the chlorine removal (see text below). When the chemical experiments are to be design it is important that changes does not influence the purification of other elements.

Chloride removal at Boliden Odda

In combination with the installation of the direct leaching, Boliden Odda also installed a technology for chloride removal. The technology is patented by Outotec, Method for the removal of chloride from zinc sulphate solution, patent number EP2504459 A1. Boliden Odda has a licence to use this process. The step was installed due to the amounts of chloride added in the direct leaching. A part of the process flow from the neutral leaching, DLF6 , goes into the chloride removal part see Figure 2. Purified solution with a Cl^- concentration of ~150 mg/l is then returned and mixed in DLF 6 with solution from the neutral leaching. The process acts as a chloride bleed.

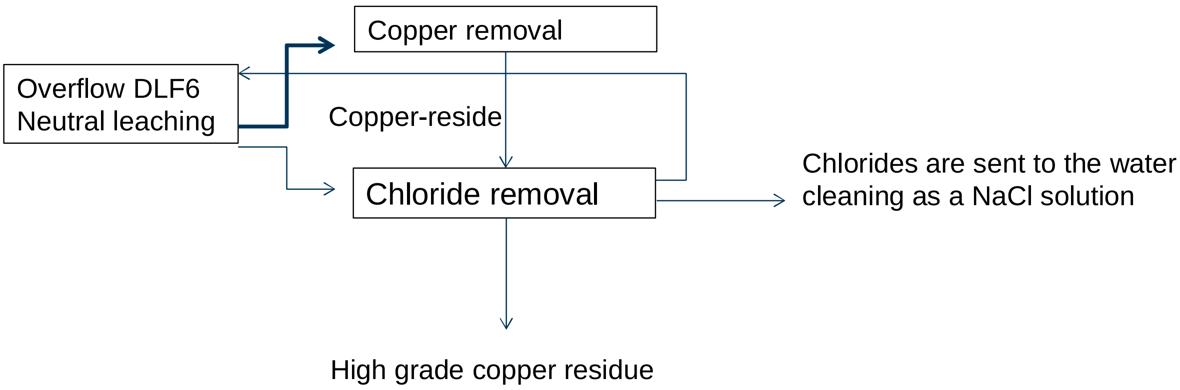


Figure 2: Simplified flow sheet for the chloride removal.

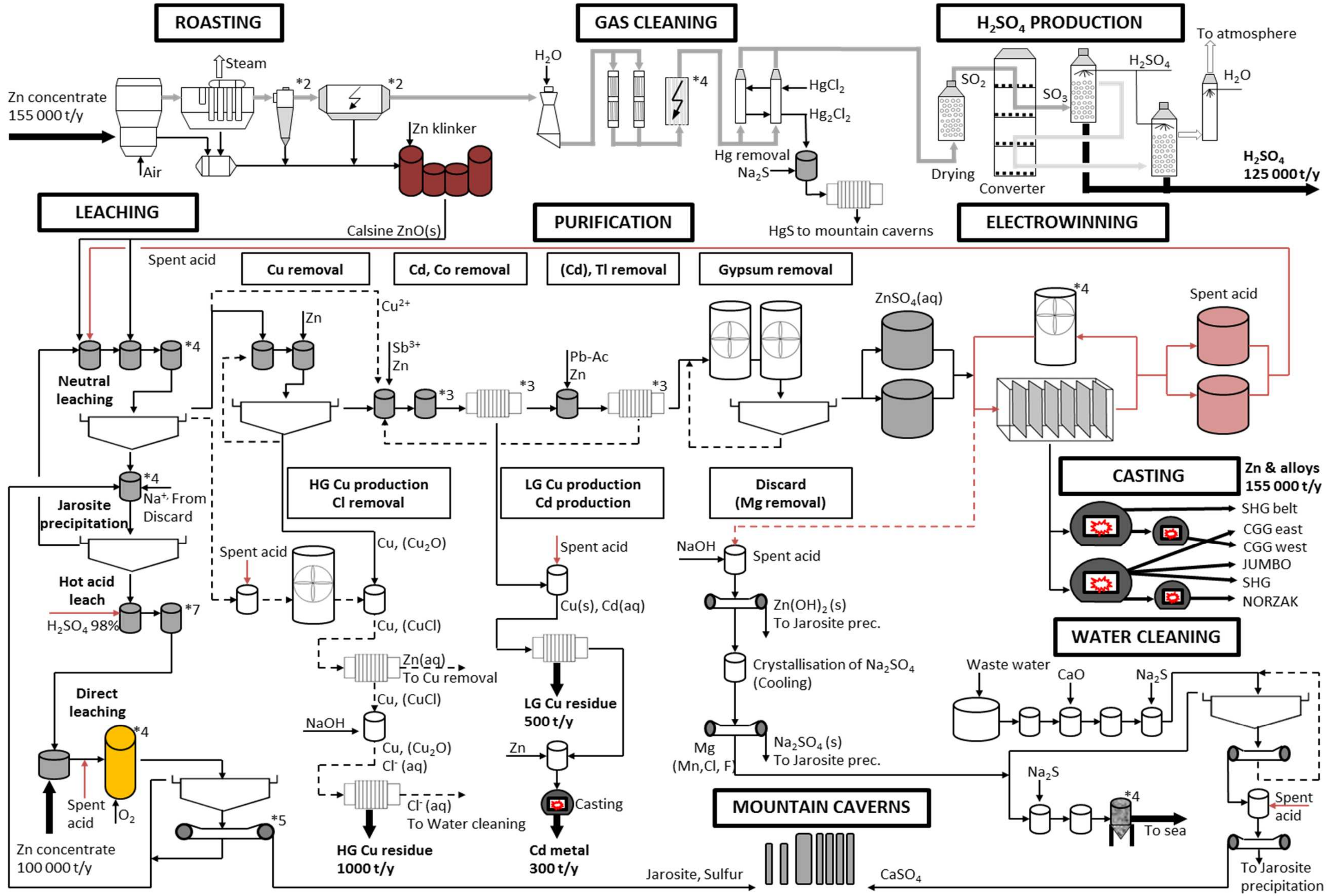
It would be of interest to optimize this process or to look at alternative methods for chloride removal that would reduce the chloride level additionally. There might be some restrictions here since the technology is patented.

Ongoing projects

Boliden has a cooperation with the University of Luleå that focuses on removal of halogenides from zinc oxides such as Waelz oxide, mainly by different washing methods. Here there can be possibilities for cooperation between this project and HYDROMET.

Analytical method in industry

The laboratory at Boliden Odda has 10 fulltime employees handling the samples delivered from the production. At the laboratory XRF and ICP analysis, optical emission spectroscopy and atomic absorption are amongst the method used. Fluoride and chloride are determined by potentiometric method using an automatic titration device. Appendix 2 lists some of the instruments available.



Appendix 1: Flow sheet Boliden Odda

Appendix 2: Overview of some instruments available at Boliden Odda

No.	Instrument	Producer	Type	comment
1.1	Atomic absorption	Perkin Elmer (USA)	AA300 PinAAcle 900F AA200 3stk	
2.1	ICP	Thermo Scientific	IRIS Intrepid ICAP 6300	
3.1	Hg-analyzer	Perkin Elmer	FIMS400	
4.1	XRF-	Thermo Scientific	Advant`x	
	XRF-	Outokumpu	X-Met 820	in L & P. : Cd
5.1 5.3	Emission-spectrometer (optical emission)	Thermo Scientific	ARL 4460 SMS 1000 ARL 4460	in Foundry : Pb, Cd, Fe, Sn, Cu, Al, Cr, Mg, Mn, Ni, Si, Tl, Ce, La Laboratory, Zn and Cd samples
5.2		Baird (USA)	FSQ	for Cd- metal: Cu, Pb, Zn, Tl Stand by for Zn-metal
6.1 6.2	Spectrophotometer	Hitachi (Japan) Spectro/unicam	U-1100 Genesys 20	 in L & P.: Co, Fe
7.1	Titrator	Mettler	DL 40 RC	not in daily use
7.2		Metrohm (Switzerland)	pH 632 Impulsomat 614 Dosimat 655	not in daily use