ZINC PLANT EXPANSION BY OUTOTEC DIRECT LEACHING PROCESS

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ABSTRACT

Outotec's direct leaching process is an atmospheric leaching process for sulphidic zinc concentrates. The direct leaching process, based on special leaching reactors developed by Outokumpu and leaching know-how, is the most economical way to produce electrolytic zinc. The newest industrial-scale application of Outotec's direct leaching process will be started up in 2008 in China at Zhuzhou smelter. The process is integrated to the existing production plant, replacing part of the old production facilities by modern technology and increasing the production capacity significantly. The process equipment supplied by Outotec includes also tailor-made reactors designed on the basis of the work and experience of Outotec Research Centre.

INTRODUCTION

In April 2007 Outokumpu Technology's name was changed to Outotec. The choice of name Outotec represents the company's evolution from a technology division within Outokumpu, through expansion and several acquisitions, to an independent listed company with its own brand values and identity. Outokumpu Technology was famous for its innovative and environmentally sound proprietary technologies, many of which had become industry benchmarks. Outotec is the name that has a strong link to the company's past and the expertise the customers have learned to trust.

Outotec developed atmospheric direct leaching technology of zinc concentrates in the middle of 1990s [1,2]. This technology has been practiced in industrial scale since 1998 in Kokkola, Finland [3] and since 2004 in Odda, Norway [4]. Originally the technology was developed for Outokumpu's internal use only, but due to the rearrangement of the company's business goals Outotec atmospheric direct leaching technology is now a commercially available product, which offers a way to produce zinc without generating sulphur dioxide that is formed in the conventional roasting-leaching-electrowinning route.

A new full-scale application of Outotec's direct leaching process will be started in 2008 in China. Zhuzhou Smelter Group, the leading Chinese zinc producer, selected Outotec's direct leaching process to increase zinc production capacity by 100 000 t/y. The direct leaching process is integrated to the existing production plant, replacing part of the old production facilities by modern technology. As some neutral leach residue is also leached together with zinc concentrates in the direct leaching process, the capacity of the leaching department will be increased with about 130 000 t/y zinc. Besides high zinc extraction the plant expansion and modernization offers also indium recovery, iron precipitation as goethite and solution purification processes. The process equipment includes tailor-made reactors designed on the basis of the work and experience of Outotec research centre.

INTEGRATION OF OUTOTEC DIRECT LEACHING TO ZHUZHOU ZINC SMELTER

Zinc production in Zhuzhou started in 1968 with 100 000 t/y Zn roasting-leaching-electrowinning process. In early 1990s, annual zinc production capacity was increased to 150 000 t and the installation of a second RLE-plant in 1996 resulted in 250 000 t/y capacity in 1997. The leaching stage consists of neutral and weak acid leaching steps of calcine. The leach residue, which contains zinc mainly as zinc ferrites and also a significant amount of indium, is treated in Waelz kilns. The Waelz oxide is treated in multi-hearth furnaces in order to remove halogens before oxide leaching. The soluble zinc is returned to neutral leaching step and indium is recovered by solvent extraction and electrolysis. Now Outotec atmospheric direct leaching process is integrated to the existing production plant replacing part of the old production facilities. Integration of direct leaching process will result in a nominal zinc cathode production capacity of 350 000 t/y in 2008. Outotec's delivery consists of counter-current atmospheric direct leaching, indium precipitation, iron precipitation processes as well as arsenic based solution purification process, main equipment supplies, process control and automation supply, supervision of installation and commissioning.

The production capacity increase of the existing zinc plant by utilizing Outotec's atmospheric direct leaching process of zinc concentrates offers several advantages that are described by Lahtinen et al. [5]. A significant example of versatility of Outotec direct leaching technology is including the treatment of neutral leach residue in the same leaching process together with zinc concentrates. Lahtinen et al. [5] compared also the atmospheric process to pressurized direct leaching and summarized the environmental benefits that the direct leaching process can give. Environmental issues played an important role, when Outotec's direct leaching technology was chosen to Zhuzhou. Modern technology enables to reduce SO_2 emissions by processing leach residue by atmospheric direct leaching technology. Lead can be recovered from the leach residue by separating the elemental sulphur and remained sulphide minerals from the Pb-rich fraction. The separation of lead residue and elemental sulphur can be done by Outotec's flotation process. In addition, Outotec's direct leaching technology is very flexible regarding the requirements of iron precipitation processes, because ferric-ferrous iron concentrations can be accurately controlled in the two stage leaching process.

Zhuzhou Smelter Group selected goethite precipitation processes for iron removal, because Zhuzhou zinc smelter is surrounded by settled area and there is no possibility for waste storage pond construction. When precipitating iron as goethite the amount of iron residue decreases compared to jarosite. In addition, the goethite precipitate can be further treated in a pyrometallurgical process, like some zinc producers are already doing, enabling the recycling of the material. Besides iron precipitation, Outotec developed a process to precipitate indium selectively from the leaching process solution. Indium cake is leached and recovered by existing solvent extraction and electrolysis facilities [9].

Outotec solution purification technology can be based either on arsenic technology or antimony technology. Outotec's arsenic based solution purification process, comprising copper, chloride, cobalt/nickel and cadmium removal steps, was chosen for Zhuzhou, because of significantly low zinc dust consumption. In addition, the process has proven to be very reliable and safe process at Kokkola zinc plant. In the direct leaching process chloride in the raw material ends up to the process solution. Outotec's chloride removal process is used to control chloride content in the process solution in order to avoid corrosion problems in the process equipment. The chloride removal process is in use also at Boliden's Kokkola and Odda zinc smelters.

In order to expand the use of Atmospheric Direct Leaching Process in China, Outotec Oyj has also signed a Collaboration Agreement with Zhuzhou Smelter Group Co. Ltd.

A schematic drawing of Outotec's counter-current direct leaching of zinc concentrates [6], indium recovery and iron precipitation processes together with the connections to the existing production facilities is presented in Figure 1. Solution from the existing neutral leaching is fed to the new solution purification area delivered by Outotec.

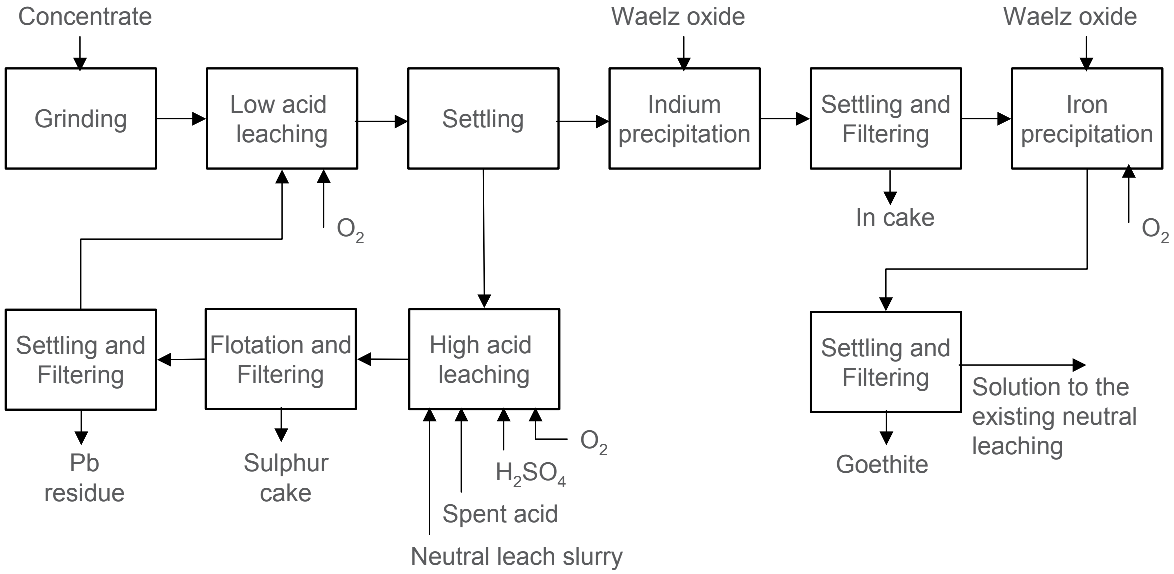
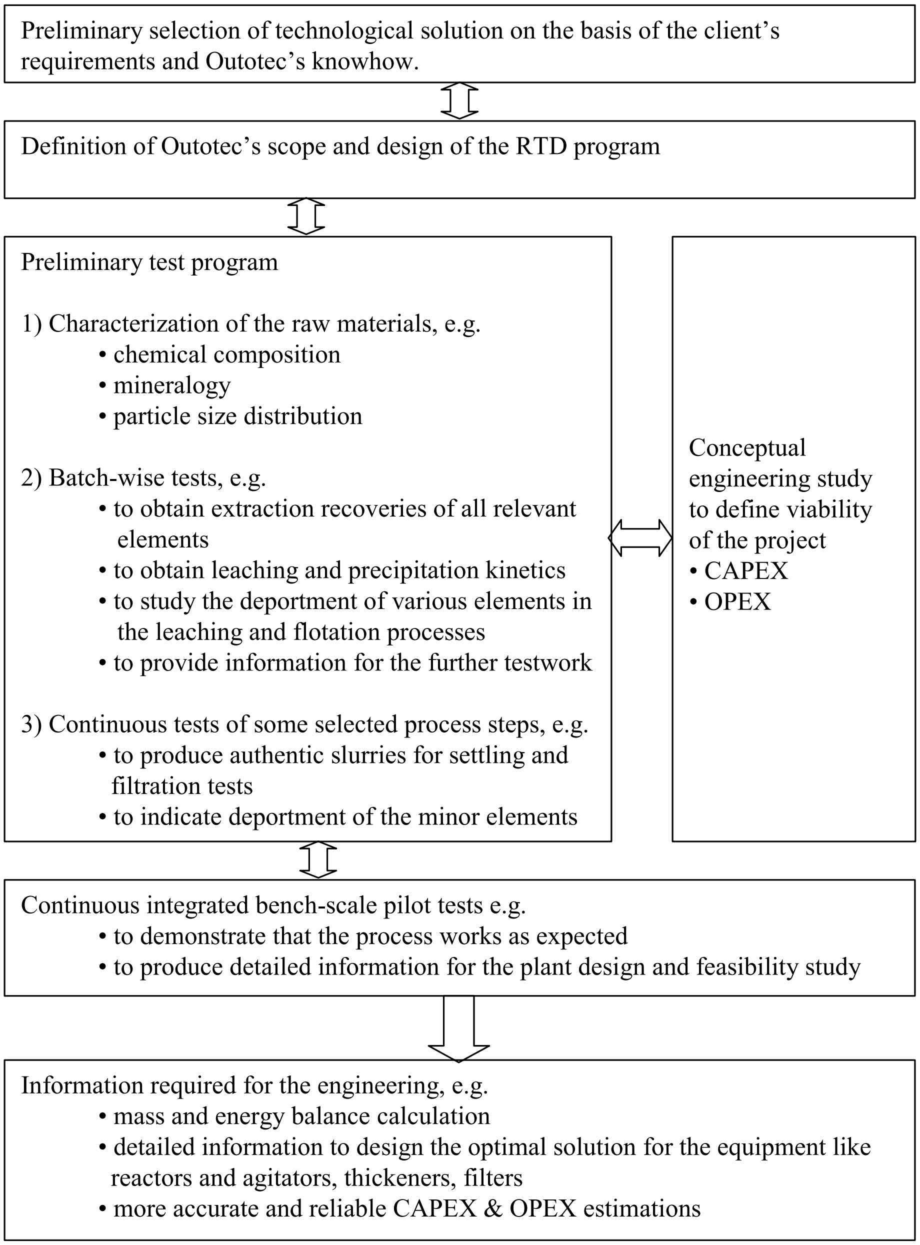


Figure 1 - A block diagram of the process implemented for the capacity increase including direct leaching, indium recovery and iron precipitation steps

RESEARCH AND TECHNOLOGY DEVELOPMENT IN OUTOTEC

Besides the innovative and environmentally sound proprietary technologies, extensive research and development resources are Outotec’s key strengths. Outotec have two in-house research centres, located in Pori, Finland and in Frankfurt, Germany. Extensive RTD facilities enable to develop new technological solutions as well as to apply the existing technologies to new customer industries.

The expansion in Zhuzhou is mainly based on existing and proven technology, which has been tailored to meet the client’s requirements. Outotec’s approach to process development in this project is described in Figure 2. The approach is cost effective and provides reliable and detailed information needed in process and plant design as well as in economical evaluation.



Preliminary selection of technological solution on the basis of the client’s requirements and Outotec’s knowhow.

Definition of Outotec’s scope and design of the RTD program

Preliminary test program

1) Characterization of the raw materials, e.g.
  - chemical composition
  - mineralogy
  - particle size distribution

2) Batch-wise tests, e.g.
  - to obtain extraction recoveries of all relevant elements
  - to obtain leaching and precipitation kinetics
  - to study the deportment of various elements in the leaching and flotation processes
  - to provide information for the further testwork

3) Continuous tests of some selected process steps, e.g.
  - to produce authentic slurries for settling and filtration tests
  - to indicate deportment of the minor elements

Conceptual engineering study to define viability of the project
- CAPEX
- OPEX

Continuous integrated bench-scale pilot tests e.g.
  - to demonstrate that the process works as expected
  - to produce detailed information for the plant design and feasibility study

Information required for the engineering, e.g.
  - mass and energy balance calculation
  - detailed information to design the optimal solution for the equipment like reactors and agitators, thickeners, filters
  - more accurate and reliable CAPEX & OPEX estimations

Figure 2 - Outotec’s RTD strategy in the technology package projects of zinc production

EXPERIMENTAL

Atmospheric Direct Leaching of Zinc Concentrates and Neutral Leach Residues

Several different sulphidic zinc concentrate mixtures and leach residues of the existing neutral and weak acid leaching steps provided by Zhuzhou zinc smelter were tested by batch wise tests in the early stage of the test program. Later two concentrate mixtures and leach residues were selected for the more detailed study. Waelz oxide was used as a neutralization agent in precipitation steps. Main components and particle sizes of the tested samples are shown in Table 1.

Table 1 - Composition of the raw materials tested

		Concentrate Mixture 1	Concentrate Mixture 2	Leach Residue 1	Leach Residue 2	Waelz Oxide
Cu	%	1.0	0.63	1.1	0.85	0.07
Fe	%	10.6	10.7	15.5	22.4	0.59
S	%	32.7	32.6	7.7	4.5	2.2
Zn	%	45.4	45.9	28.4	21.8	63.8
In	g/t	190	125	164	315	840
Particle size after basic pretreatment:						
D50%	µm	46	53	35	33	
D90%	µm	148	184	86	157	

The tested concentrates had relatively high iron and indium contents and low zinc concentration, but otherwise rather typical composition. Zinc occurred in leach residues mainly as zinc ferrites and zinc sulphates. Small amounts of zinc oxides, zinc silicates and zinc sulphides were also present in the leach residues.

It is important to notice the relatively high particle size of the concentrates shown in the Table 1. Based on Outotec's standard batch leaching tests the concentrate mixture 1 was leached well even without grinding, whereas the concentrate mixture 2 needed to be ground in order to reach good leaching results in reasonable retention time. This example shows that in addition to the characterization of chemical composition and particle size distribution of the raw material, it is important to study carefully also the mineralogy of the material in order to understand the behavior of the raw material in the leaching process.

Leaching of zinc concentrates is based on the oxidation of zinc sulphide in an acidic environment. Several parallel and consecutive reactions take place simultaneously and also physical phenomena play an important role in the leaching system. However, the direct leaching of sulphide minerals can be written with the following simplified reaction equations. The reduction of ferric iron is accomplished by metal sulphides, which are leached:

$$MeS_{(S)} + Fe_2(SO_4)_3 \rightarrow MeSO_4 + 2\ FeSO_4 + S^0 \qquad (1)$$

where Me = Zn, Fe, Cu, Co, Ni, Cd, Pb etc. Formed ferrous iron is oxidized by molecular oxygen back to the ferric form:

$$2\ FeSO_4 + H_2SO_4 + 0.5\ O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (2)$$

The reaction rate is catalyzed by copper. The overall reaction can be written as the following simplified equation:

$$MeS_{(S)} + H_2SO_4 + 0.5\ O_2 \rightarrow MeSO_4 + H_2O + S^0 \qquad (3)$$

Zinc in the leach residues of neutral and weak acid leaching steps is mainly as zinc ferrites but also small amount of unreacted zinc sulphide is present. Leaching of zinc ferrites can be described with the following simplified equation:

$$ZnO\cdot Fe_2O_3 + 4\ H_2SO_4 \rightarrow ZnSO_4 + Fe_2(SO_4)_3 + 4\ H_2O \qquad (4)$$

Leaching of ferrites requires temperature close to 100 °C and acid concentration of above 30 g/L H_2SO_4.

The leaching tests with zinc concentrates and leach residues of neutral and weak acid leaching steps were performed in a 10-litre reactor with intensive mixing and oxygen feed at a temperature of 95 ºC. Samples were withdrawn with discrete time intervals in order to follow the progress of the leaching. Besides the leaching recoveries of zinc and indium, also the leaching rate of both elements was obtained. Elemental sulphur was separated from the leach residue in order to produce Pb-rich fraction that is suitable for the existing lead smelter. The deportment of elements into sulphur concentrate and Pb-rich fraction was evaluated.

Iron Precipitation

Batch wise iron precipitation experiments were carried out in 10 - 20 litres laboratory scale stirred tank reactor at 75 - 90 °C temperature. Reactor was equipped with temperature and pH-control units, Redox-measurement, baffles and a reflux condenser. Several Outotec impellers, e.g. OKTOP GLS and OKTOP VFF were tested and compared to standard turbine impeller. Oxygen was fed under the impeller. Both synthetic solution and solution retrieved from direct leaching and indium precipitation were used in the test and Waelz oxide was used as neutralising reagent. The effect of the most important parameters on the iron precipitation rate and the quality of the goethite precipitate was determined.

The most relevant reactions occurring in the goethite precipitation process are described below. Ferrous iron is oxidized to ferric iron, which is precipitated as goethite:

$$2\ FeSO_4 + 3H_2O + 0.5\ O_2 \rightarrow 2FeO(OH) + 2H_2SO_4 \qquad (5)$$

Neutralization of the formed sulphuric acid is made by zinc oxide:

$$2\ H_2SO_4 + 2\ ZnO \rightarrow 2\ ZnSO_4 + 2\ H_2O \qquad (6)$$

The reaction system can be written as an overall reaction:

$$FeSO_4 + ZnO + 0.5\ H_2O + 0.25\ O_2 \rightarrow FeO(OH) + ZnSO_4 \qquad (7)$$

The effect of mixing efficiency on iron precipitation rate is shown in Figure 3. In this Figure 3 “cFe,0” is the iron concentration in the solution in the beginning and “cFe” is the iron concentration in the solution during the precipitation test.

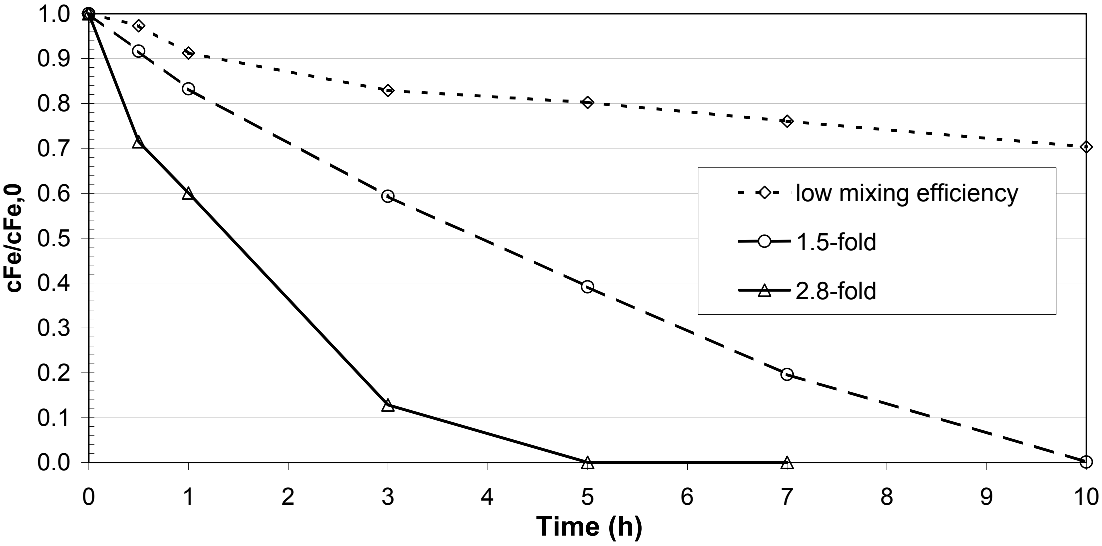


Figure 3 - The effect of mixing efficiency on iron precipitation rate

Continuous Bench-Scale Pilot Tests

Based on the result of the batch tests, a continuous bench-scale pilot test run consisting of counter-current leaching of zinc concentrate and leach residue mixtures in two steps (HAL & LAL), indium recovery from the leach solution and iron removal as goethite was carried out. A schematic drawing of the pilot set-up in illustrated in Fig 4.

Leaching Section

The tested leaching circuit consisted of a high acid leaching step (HAL) and a low acid leaching step (LAL). By using a counter-current leaching process, a high acidity required for leaching the ferrites of the leach residue (4) could be obtained simultaneously with a product solution of low acidity. Also, the counter-current process enabled a low ferric (Fe^{3+}) concentration of the product solution, which was favorable to precipitate iron as goethite.

Both LAL and HAL consisted of successive stirred tank reactors of 10-litre size. The reactors were thermostated to 95°C and gaseous oxygen was fed into the bottom of the reactors. At the end of both lines, a thickener was used for solid-liquid separation. The concentrate was fed to LAL, and the leach residue, together with unleached material from LAL, was fed to HAL. Sulphuric acid was fed to HAL in the form of spent acid, having 176 g/L H_2SO_4 and 56 g/L Zn. The product solution from LAL, having around 10 g/L H_2SO_4, was fed to indium recovery.

The solution coming from low acid leaching step consist only minor amount of ferric iron as shown in Figure 5. Only this ferric iron precipitates in the indium precipitation step and this enables an excellent possibility to precipitate the most of the iron as goethite.

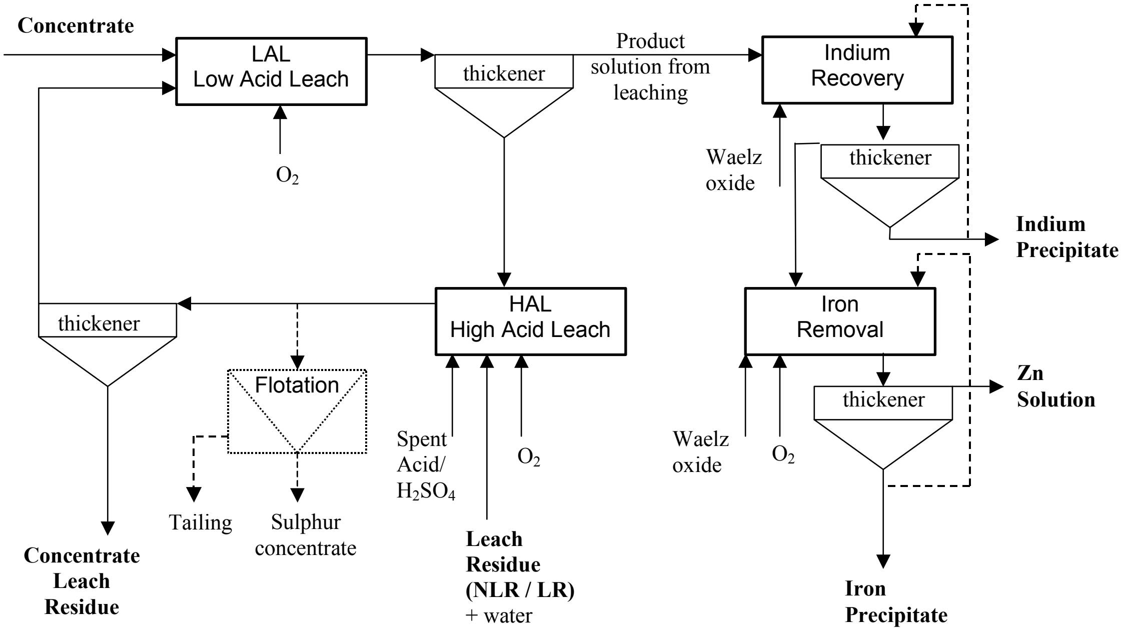


Figure 4 - Schematic drawing of the continuous pilot set-up

Flotation of Leach Residue

The flotation tests with slurry from last HAL reactor were performed batch-wise. In the flotation step, a concentrate (overflow fraction) containing the elemental sulphur and remaining sulphides is separated from the tailings (underflow) fraction containing e.g. lead sulphate, gypsum and silica. The tests were carried out in two stages, a rougher stage and a cleaner stage, using 4 and 1.4 litre test cells with mixing and air feed.

Settling and Filtration Tests

The settling and filtration properties of the slurries from all piloted stages were evaluated in batch tests during the pilot campaign. In such a test, a 250 mL sample was taken from the reactor; the settling rate was observed at controlled temperature, and the filtration time of the settled phase was measured.

The performance of the main process steps was verified. Some results of the leaching test run are shown in Figure 5. A very high zinc recovery of about 96 – 97 % was achieved and maintained almost during the whole test run. In addition, there was enough copper in the solution for catalyzing the iron oxidation. Finally, the ferric iron level in the product solution was controlled to a very low level giving good solution composition for the next process steps.

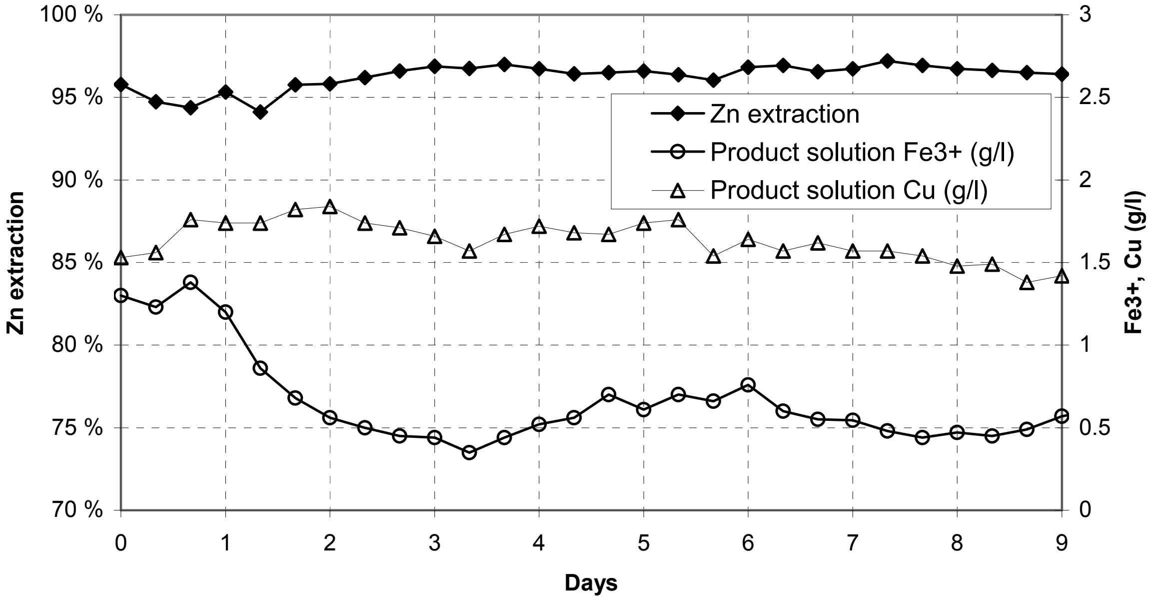


Figure 5 - Zn extraction (leaching recovery) as well as Cu and Fe^{3+} concentrations of product solution

Iron Removal

After indium recovery, iron was precipitated in two successive stirred reactors of 5-litre size, kept at 75 °C temperature. Oxygen gas was fed to the bottom of the reactors. pH was kept between 3 and 4 by Waelz oxide feed. The slurry was fed to a thickener, and the goethite precipitate was obtained from the thickener underflow. Part of the thickener underflow was circulated to the reactors for seeding purpose. High iron concentration in goethite precipitate can be achieved by controlling carefully pH at the end of the precipitation step.

The results of the continuous iron precipitation tests were good, resulting in low iron content in the solution with typical iron concentration of the product solution of 0.5 – 1.0 g/L. In addition, the characteristics of the formed precipitate were excellent as shown in Figure 6 and Table 2.

Table 2 - Average composition of the goethite precipitate

Element	Weight-%
Fe	38-40
Zn	4-6
Cu	1
Pb	7
S	5

Based on the test results it was possible to design the goethite precipitation reactors to precipitate relatively high concentration of iron in very reasonable retention time. The optimised reactor design giving shorter retention time decreases the number of the reactors needed and, thus minimised the investment cost of the process.

The concentration of iron after goethite precipitation can easily control to a suitable level according to the needs of neutral leaching step and avoid so too big iron load in neutral leaching step. In the case of jarosite precipitation iron concentration is at least 5 g/L after iron removal.

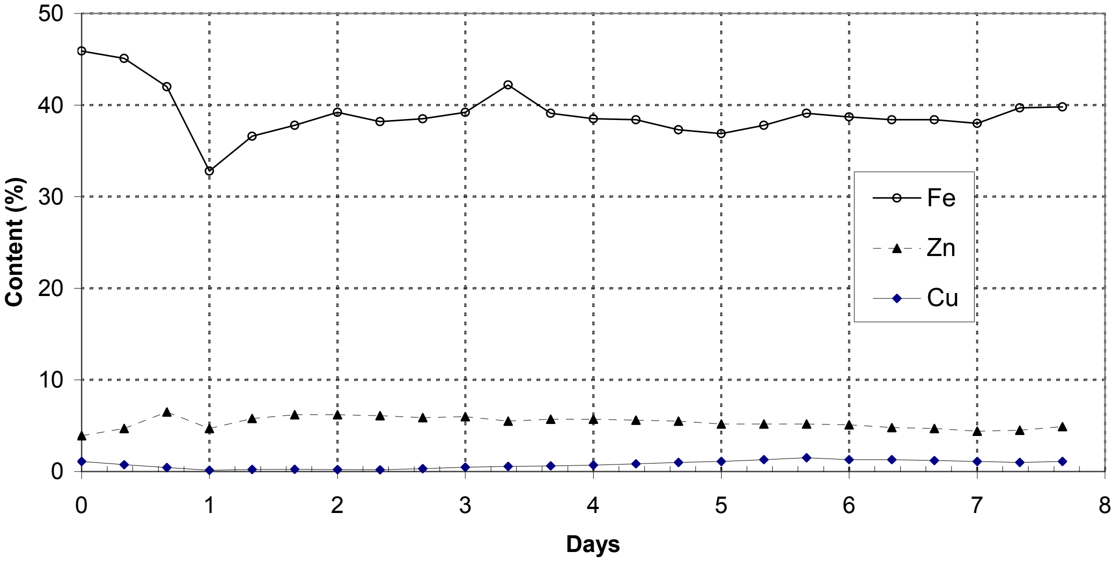


Figure 6 - Fe, Zn and Cu contents in the goethite precipitate

In addition to a verification of the process concept, the test runs produced essential data for process and equipment design. Based on the results, mass and energy balance calculations of the process were made with HSC Sim software [7]. This HSC model was a highly important tool in the next phases of the project, i.e. in the Basic Engineering of the process.

OUTOTEC'S ENGINEERING SERVICES

When enough test work has been carried out and the process concept has been proven feasible and economically viable, the next step is normally design and engineering of the plant. Outotec offers tailor-made engineering packages to fit the needs of the customer. Typically the package is called as Basic Engineering and it may include process engineering, plant engineering, mechanical engineering, electrical engineering, HVAC (Heating, ventilation, air-conditioning) engineering as well as engineering for process control and automation.

The most central part of the equipment, e.g. the leaching reactors [8], must be designed and constructed utilizing all the process know-how that has been gathered during the years of development work. These units are considered as Outotec proprietary equipment, for which Outotec is in charge of the entire design and construction, i.e. will carry out in addition to basic engineering also detailed engineering for its proprietary equipment.

For Zhuzhou, basic engineering was made for both the direct leaching plant, including indium and iron precipitation, and for the solution purification plant. The first step of the basic engineering phase was the process design, where the results from the tests and the preliminary calculations were applied to decide on the detailed flowsheet of the plant and make the mass and energy balances for this. The next steps were the plant design, equipment design, electrical design and automation design. The entire basic engineering phase was carried out during the first half of 2007. In parallel with the basic engineering, the proprietary equipment was designed in detail and purchased.

ENVIRONMENTAL ASPECTS

Environmental impact of processing methods is of major concern today. One key issue for selecting Outotec's direct leaching processes is that the production of sulfur dioxide and other harmful gaseous compounds is almost totally avoided, especially in comparison to the conventional pyrometallurgical methods. On the other hand, elemental sulphur, which requires special storage area, is formed. Small amounts of compounds like Se, Cd, As, Hg and Pb, hinder further usage of the sulfur residue without purification. Lead rich fraction of leach residue is utilized in the existing lead smelter.

The amount of iron precipitate is dependent on the iron content in the concentrate and also on the iron removal methods. Iron precipitation as goethite was chosen for Zhuzhou in order to minimize the amount of iron precipitate and also to enable further processing of precipitate to stabilize the residue and on the other hand to recover the residual zinc.

CONCLUSION

Outotec, former Outokumpu Technology, has developed a new Atmospheric Direct Leaching Process for zinc concentrates, which eliminates the conventional roasting phase in zinc processing. The process is already used in Boliden's Kokkola zinc plant in Finland and Odda zinc plant in Norway. Now the leading Chinese zinc producer, Zhuzhou smelter group, selected this process for its expansion because it is an environmentally sound way to produce zinc, it includes recycling of process residues, and it represents the latest technology. In addition, a wider selection of zinc concentrates can be used as raw materials in the existing and new processes, which improves the use of resources.

In addition to extensive research and development program to create a tailor-made solution to Zhuzhou Smelter Outotec's delivery includes the engineering of a zinc plant with new Atmospheric Direct Leaching Process, iron precipitation and solution purification processes, main equipment supplies as well as supervision of installation and commissioning. The expansion will increase the plant capacity by 100 000 t/y zinc and the plant is estimated to be operational by September 2008.

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