DISSOLUTION OF SIX SULFIDE CONCENTRATES IN THE HYDROCOPPER® ENVIRONMENT

¹M Lundström, ²J Liipo, ²J Karonen, ³J Aromaa
¹Outotec Oyj, Base Metals, Finland
²Outotec Research Oy, Finland
³Helsinki University of Technology, Finland

Abstract

Outotec is a worldwide technology leader in minerals and metals processing providing innovative and environmentally sound solutions for a wide variety of customers in the field of bio-hydrometallurgy, sulfate and chloride –based leaching of base metals. All Outotec processes are tailored to meet customer's needs, so that all valuable metals can be recovered.

HydroCopper® technology, developed and registered by Outotec Oyj, is one efficient process, leaching variable sulfide minerals using cupric chloride solution. The leaching process is operated in several stages, at atmospheric pressure in a stirred tank reactor, near the boiling point of water and the pH is kept between 1.5-2.5. In this study, six different concentrate samples were leached for two hours under conditions similar to those used in the first leaching stage of HydroCopper® process. To determine the leaching behaviour of sulfide minerals, the chemical and mineralogical composition of the concentrates were studied in detail. The leaching behaviour of the tested sulfides was strongly dependent on the pH. It was shown that chalcopyrite, bornite, covellite as well as sphalerite dissolved well in the first, non-oxidative leaching stage. Pyrite, hematite and magnetite did not dissolve in the studied environment. This is advantageous for leaching solution purification and decreases the investment costs.

1) Introduction

There are several refractory high- and low-grade ores containing valuable metals, such as copper, zinc, cobalt, nickel, gold, silver, cadmium, indium etc. around the world. Most of these ores can be produced economically into metals using hydrometallurgical technologies. Outotec is a worldwide technology leader in minerals and metals processing providing innovative and environmentally sound solutions for wide variety of customers in the field of sulfate and chloride –based leaching and bio-hydrometallurgy. Own state-of-art research center with extensive experience on leaching of different ores and concentrates allows off-the-shelf processes and tailored process modifications to fit customers' raw materials.

A leaching plant can be built for a specific concentrate or it can work as a custom refinery treating raw materials from various sources. The process features are ready to meet the variations in the feed material. This gives room for optimization for the whole

M Lundström, J Liipo, J Karonen, J Aromaa

metallurgical process chain from mine to metal. Outotec has tailored processes, such as Cobre Las Cruces in Spain, for the customer. At Cobre Las Cruces, pyrite-covellite ore is leached in sulfate solution using proven hydrometallurgical unit processes, leaching – SX – EW, producing 72 000 t/a of copper. The tailored process allows the best recovery for the customer.

Outotec's HydroCopper® process is one of the several leaching processes by Outotec Oyj and technically applicable for concentrates with remarkable gold and silver concentrations. In HydroCopper® gold and silver can be leached directly in chloride solutions, and no separate gold leaching stage is needed. Depending on the chemistry and mineralogy of the concentrates as well as geographical position, HydroCopper® can came up as an attractive process to economically produce copper and gold even from low-grade ores.

2) HydroCopper®

Outotec HydroCopper® process has been designed to produce a copper product directly from concentrate. The HydroCopper® process treats sulfidic concentrates with various mineralogy and copper grades and produces high quality copper as copper wire rod, bars or billets. The process has a large tolerance for varying copper and impurity grades. Generally, several sulfide minerals readily dissolve into concentrated cupric chloride solutions near the boiling point of the solution (Lundström et al. 2007). This makes it economically beneficial to produce copper and precious metals, such as gold and silver, using chloride solutions (Haavanlammi et al 2007a). In HydroCopper® process, Cu^{2+} is used as an oxidant in concentrated chloride solution. Chalcopyrite can be oxidized in a chloride solution with the help of Cu^{2+} ions according to the reaction (1):

$$CuFeS_2(s) + 3Cu^{2+}(aq) \rightarrow 4Cu^+(aq) + Fe^{2+}(aq) + 2S^0(s) \qquad (1)$$
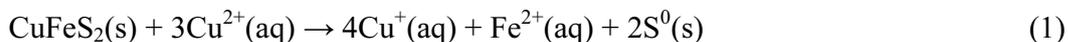
The other base metal sulfides present in the concentrate (Zn, Pb, Ni, Ag) are dissolved into the solution e.g. by the reaction (2).

$$ZnS(s) + 2Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + 2Cu^+(aq) + S^0(s) \qquad (2)$$
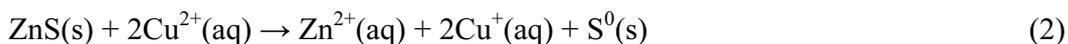
In the first leaching stage of HydroCopper® there is no oxygen feed, but the main purpose is to reduce cupric ion concentration in the solution with reactions such as (1-2).

The leaching is completed using oxygen purging in the second leaching stage. In the final leaching stage oxygen purging increases the redox potential enabling the gold leaching as chloro-complexes. Gold is leached at potentials >600 mV vs. Ag/AgCl and recovered from the solution by precipitating it on activated carbon or copper concentrate (Hyvärinen et al. 2004, Haavanlammi et al., 2007b, Sinisalo et al. 2008). The operational expenses in the HydroCopper® process consist of electricity (ca. 50%) and chemicals, personnel, maintenance and other consumables (ca. 50%). However, this distribution is greatly dependent on the location, price of electricity and type of raw material.

Sulfide minerals are complex in nature and it is quite difficult to determine precisely their exact dissolution behavior. This study focuses on studying six different concentrate

samples, their mineralogy and the dissolution behavior in concentrated cupric chloride solution. The concentrate samples used were different in mineralogy. They originated from Gibraltar Mines - Canada, Erdenet - Mongolia, Vale Salobo - Brasil, Boliden Tara - Ireland and Inmet Pyhäsalmi - Finland. The chalcopyrite-bornite rich and covellite and sphalerite –bearing copper concentrate was used as a reference.

3) Materials and Procedures

Four copper concentrates, one zinc concentrate and one pyrite concentrate were selected for test work to determine the leaching behavior of main sulfide and accessory minerals commonly forming the sulfidic copper concentrates, The used copper concentrates were selected based on their chemical and mineral composition to represent different chalcopyrite- secondary copper sulfide ratios with different amounts of pyrite. The main object of including also zinc and sulfur (pyrite) concentrates was to test the leaching behavior of sphalerite and pyrite, common accessory minerals and impurities in copper concentrates.

The mineralogical characterization of concentrates, based on detailed optical (Zeiss Axioplan2) and scanning electron optical microscopy, mineral analyzes by electron probe micro analyzer and chemical assays of concentrates, was carried out at the laboratories of Outotec Research Oy.

The chemical composition of minerals was analyzed by Cameca SX50 micro probe and by JEOL 7000F filed emission scanning electron microscope equipped with both EDS (energy dispersive spectrometry) and WDS (wave length dispersive spectrometry) analyzers fabricated by Oxford Instruments. The minerals were analyzed under routine conditions using 20kV acceleration voltage and 20 nA probe current. Used standards were both pure metals and minerals.

The main element content of concentrate was analyzed after total leaching by ICP (inductively coupled plasma) and combustions analyzes. The copper contents were analyzed also by using sequential phase analyzes, based on Young (1974) and Penttinen et al. (1977), and further developed at Outotec Research Oy. The copper phase assay consist of sequential copper analyzes after water-, acid-, bromine- methanol and nitric acid leaching. Based on this method, the copper sulfates, copper oxides and silicates, secondary copper sulfides, like covellite and bornite and primary chalcopyrite can be chemically distinguished. The mineral composition of concentrate was calculated based on chemical composition of main minerals and concentrate assay by HSC Geo –software.

3.1) Concentrate mineralogy

The copper grade of four copper concentrates ranges between 21.1% Cu to 39.5% Cu with varying iron and zinc contents. The Gibraltar concentrate is typical chalcopyrite-

pyrite concentrate with accessory covellite, copper oxides and sphalerite and chalcopyrite is the main carrier (96.5%) of copper. The reference concentrate and concentrate from Erdenet are typical concentrates from porphyric copper deposits and most of copper is

carried by secondary copper sulfides, like covellite and bornite, Chalcopyrite carries about 32% of the total copper contents. Additional carriers of copper in Erdenet concentrate are enargite and tennantite. The Salobo copper concentrate comes from hydrothermal iron oxide-copper-gold deposit, and most of concentrates copper is carried by bornite with accessory copper oxides and chalcopyrite.

The Tara zinc concentrate is typical from sedimentary-hosted zinc deposit and consists mainly of low iron sphalerite and pyrite with gangue carbonates. Pyhäsalmi pyrite concentrate consists almost completely of pyrite with traces of chalcopyrite and sphalerite.

Table 1. Chemical and mineral composition of used concentrates

No:			1	2	3	4	5	6
Concentrate			Gibraltar	Reference	Erdenet	Salobo	Tara	Pyhäsalmi
Cu	P1	%	0.69	<0.01	0.06	0.03		
	P2	%	0.24	1.23	2.04	1.23		
	P3	%	0.67	24.60	12.21	20.80		
	P4	%	24.90	13.50	7.00	0.25		
	Sum	%	26.50	39.33	21.31	22.31		
Cu	TOT	%	26.50	39.50	21.08	23.50	0.06	0.02
Fe	TOT	%	28.30	17.20	23.84	25.60	2.40	45.10
Zn	TOT	%	0.06	5.90	0.31	0.004	53.20	0.02
S	Leco	%	32.90	28.70	32.30	7.40	32.00	56.60
Mineral composition								
Chalcopyrite		%	72.0	40.1	20.5	0.7	0.1	0.1
Bornite		%		29.5	2.2	32.9		
Covellite		%	1.0	8.9	15.7			
Cu-oxides		%	0.4	3.4	5.9	2.2		
Sphalerite		%	0.1	9.3	0.4		80.5	0.0
Tennantite		%		3.6	0.1			
Enargite		%			1.0			
Pyrite		%	13.4		36.1		9.0	99.9
Iron oxides		%				22.5		
Others		%	13.1	5.2	18.1	41.7	10.4	0.0

Distribution of copper							
Chalcopyrite	%	96.5	32.7	32.0	1.1	100	100
Bornite	%		45.4	5.7	93.4		
Covellite	%	2.6	14.3	50.7			
Cu-oxides	%	0.9	3.0	9.4	5.5		
Enargite	%			1.9			
Tennantite	%		4.6	0.2			
Distribution of iron							
Chalcopyrite	%	77.8	76.6	27.6	1.1	0.1	0.04
Bornite	%		20.6	1.7	18.4		
Sphalerite	%		2.9			12.0	0.01
Enargite	%			0.1			
Pyrite	%	22.2		70.6		87.0	99.9
Iron oxides	%				80.5		

TOT= total dissoulution, P1= H2O-, P2= acid soluble, P3= Bromine- methanol dissolution P4= nitric acid dissolution

3.2) Leaching experiments

The concentrate samples were dried in an oven at 110 °C for 2 hours prior to leaching. 10 g of concentrate (100% -105 μm) was leached into 150 ml of solution. The solution had [NaCl] = 280 g/L (4.8M), [Cu^{2+}] = 19.5 g/L, T = 95 °C and pH was adjusted to 2 in the beginning of the experiment.

A standard three-electrode electrochemical cell with a thermostated water jacket was employed. The cell was stirred with a magnetic stirrer for 500 rpm; no purging of gases was done. The working electrode was glassy carbon (GC), counter electrode a platinum sheet and the reference electrode Ag/AgCl (REF201, Radiometer Analytical, France). The reference electrode was placed in a sintered glass tube containing a gel of agar powder, potassium chloride and distilled water and positioned in an external beaker and connected to the cell via a liquid bridge and a Luggin capillary. Working electrode and counter electrode was positioned in the cell. In order to record the solution potential as a function of time, also redox potential was measured with using platinum redox electrode. The measurements were carried out using electrochemical workstation PAR 273 Potentiostat/Galvanostat controlled by EG&G PAR´s Model 352 Corrosion Analysis Software 1.00.

Prior to concentrate leaching, the solution was treated electrochemically in order to increase the amount of cuprous copper. This was done by polarizing an inert working electrode (GC) for 2 hours at 380 mV vs. Ag/AgCl. Simultaneously the redox potential of the solution was recorded against Ag/AgCl reference electrode. Redox potential of the solution was originally ca. 700 mV vs. Ag/AgCl, which agrees well with the earlier data,

M Lundström, J Liipo, J Karonen, J Aromaa

Lundström et al. (2009). During the 2 hours potentiostatic pretreatment, the redox potential in the solution decreased ca. 50 mV. This simulates the first leaching stage in HydroCoppe$^{r®}$ process, in which solution contains both cupric and cuprous ions.

After 2 hours of potentiostatic treatment 2g of concentrate was added to the cell. The leaching time for concentrate was 2 hours. Redox potential and current on the working electrode were recorded as a function of time (not presented). After concentrate leaching, the solution was filtered and analyzed for S, Fe, Cu and Zn concentrations by ICP at Outotec Research, Pori. Filtered leach residue was analyzed by X-ray diffraction (XRD), but the amount of residue was too small for phase analysis.

4) Leaching behavior

The solution used in the leaching experiments was treated potentiostatically for 2 hours, after which the concentrate was added to the solution. After leaching the solution was analyzed for S, Fe, Cu and Zn (Table 2). Solution had originally total copper concentration of 19.5 g/L. It can be seen that the copper concentration increased by 0.9 to 2.5 g/L with copper rich concentrates (1 - 4). With zinc concentrate (5) the increase in Zn concentration was 4.6 g/L. Pyrite concentrate (6) did not dissolve remarkably.

Table 2. Solution compositions after 2 hours of leaching in cupric chloride solution.

Concentrate	S(mg/L)	Fe(mg/L)	Cu(g/L)	Zn(mg/L)
1. Gibraltar	187	1980	20.2	4.2
2. Reference	285	2030	21.9	82
3. Erdenet	62	840	20.4	15.3
4. Salobo	21	62	22	2.2
5. Tara	456	71	N/A	4550
6.Pyhäsalmi	88	94	N/A	8

4.1)   Dissolution of copper sulfides

Figure 1 presents the amount of copper in concentrate and the distribution of phases in which copper was present. During leaching, the precipitation of CuS decreased the amount of soluble Cu in the solution (concentrates 1 - 3). This precipitation was strongly dependent on the solution pH. In the experiments using concentrates 1 – 3 the pH value after dissolution was <2 and remarkable CuS precipitation occurred. With concentrate 4, pH was >2 after the leaching experiment and no precipitation was observed.

Pyrite did not dissolve in the studied environment as discussed later in chapter 3.2. For that reason the amount of dissolved iron from Gibraltar chalcopyrite-pyrite concentrate (Table 2) shows well the dissolution of chalcopyrite during the 2 hours of leaching. Totally 50% of concentrate total iron was dissolved, showing that 64% of chalcopyrite could be dissolved from the Gibraltar concentrate.

In the Reference concentrate 77% of iron was carried by in chalcopyrite and 22% by bornite (Table 1). Ca. 85% of iron was dissolved into the solution (Figure 2), which shows that almost all chalcopyrite and bornite could be leached. 50% of the dissolved copper precipitated as CuS (Figure 2).

In Erdenet concentrate chalcopyrite carried 28% of concentrates total iron and the rest by pyrite. 25% of iron was leached, which shows that nearly all the chalcopyrite present (89%) was dissolved. It is likely that covellite was leached more efficiently but precipitated as CuS.

Bornite carried almost all the copper in Salobo concentrate (Figure 1). Figure 2 shows that over 85% of copper was leached. This shows that bornite was eager to leach in cupric chloride solution and that over 85% of bornite could be leached in 2 hours.
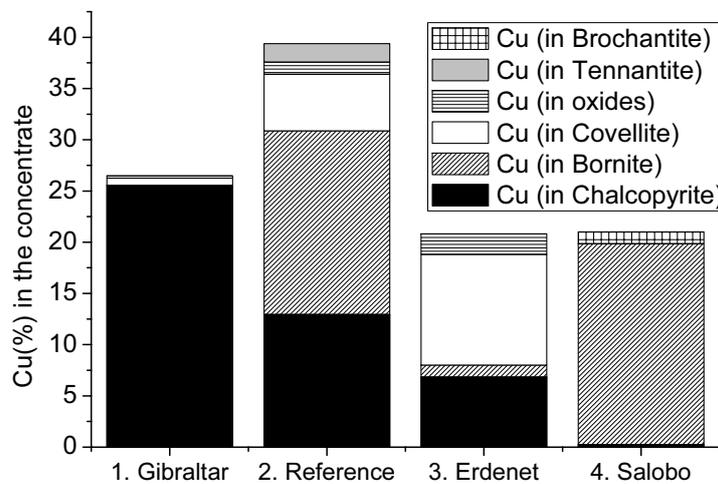

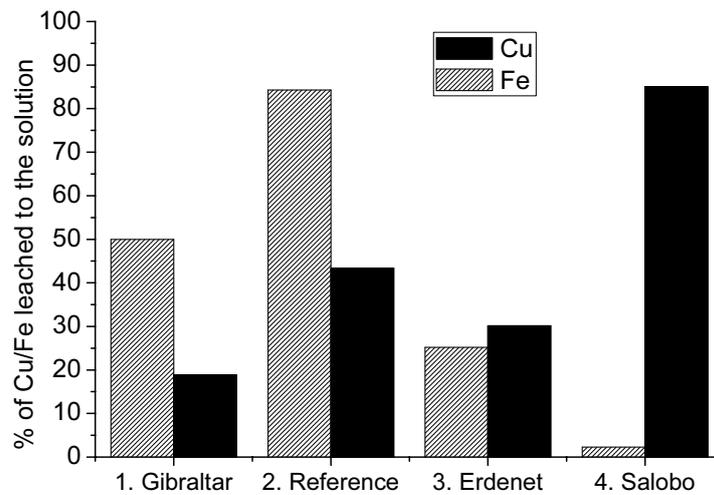Figure 1. Distribution of copper in concentrate

Figure 2. The amount of Cu and Fe leached in to the solution from copper sulfide concentrates.

All the copper concentrates studied dissolved well in the HydroCopper® environment. Almost all copper sulfides in concentrates 1, 3 and 4 could be leached and 64% of chalcopyrite in Gibraltar concentrate. Bornite, covellite and chalcopyrite dissolved well in the studied environment, secondary copper sulfides like bornite and covellite dissolving faster than chalcopyrite.

4.2)   Pyrite, magnetite and hematite dissolution

The leaching experiments showed that in HydroCopper® environment pyrite did not dissolve. Pyrite concentrate from Pyhäsalmi was very pure (99.8% pyrite) having 45% of

iron (Figure 3). However, only 1.5% of iron from Pyrite concentrate was dissolved into the solution. This corresponds to 94 mg/L in the solution (Figure 4).

Also hematite and magnetite were shown to be resistant for leaching in cupric chloride solution. Salobo concentrate had ca. 20% iron, which was mostly included in magnetite and hematite (Figure 3). After 2 hours of leaching there was 62-mg/L iron in the solution (Figure 4) indicating that only 2.3% of iron from the Salobo concentrate dissolved. It is most likely that the dissolved iron originated from bornite and digenite. This shows that neither magnetite nor hematite dissolve in the HydroCopper® environment.
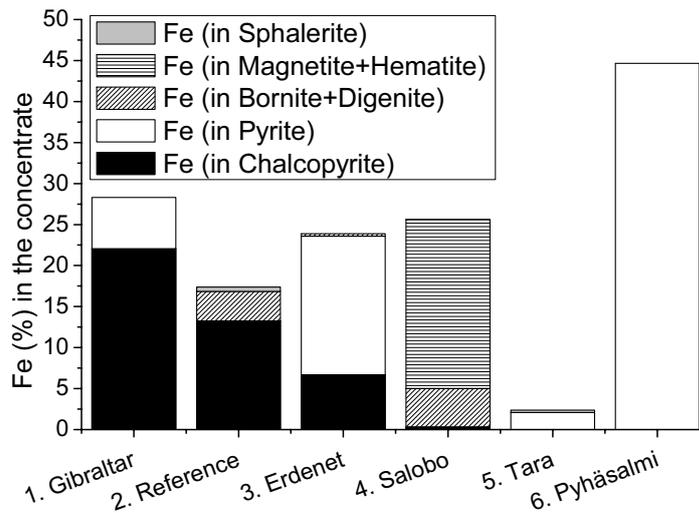
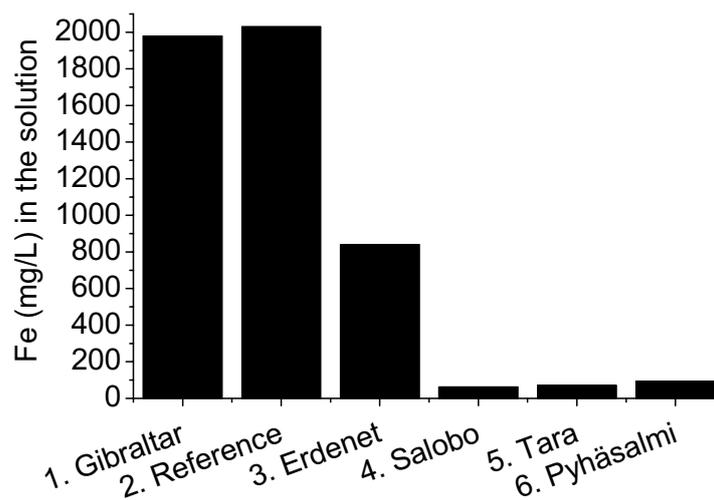Figure 3. Distribution of the iron in the concentrate.

Figure 4. Fe concentration (mg/L) in the solution after 2 hours of leaching

4.3)   Sphalerite dissolution

Tara concentrate had 80% of sphalerite (Table 1). After dissolution the zinc concentration in the solution was 4550 mg/L indicating that 61% of zinc was leached in 2 hours i.e. sphalerite was partially leached in the HydroCopper® environment.

5) Conclusions

The leaching experiments in this study demonstrated the first leaching stage of HydroCopper® process. It was shown that the most common copper minerals such as chalcopyrite, bornite and covellite dissolved well in the first, non-oxidative leaching stage. Almost all copper sulfides (>85%) in concentrates 1, 3 and 4 could be leached and 64% of chalcopyrite in Gibraltar concentrate. This suggests that major part of the copper sulfides can be leached already in the first leaching stage of HydroCopper®. The leaching process can be tailored so that >99% of copper in concentrate will be leached in two or three leaching stages.

Pyrite, hematite and magnetite were shown not to dissolve in the studied environment. This is advantageous for solution purification and decreases the investment costs. Iron can be remained in the solid phase, which allows also the use of lower grade concentrates.

When smelter concentrate cannot be cost efficiently produced, HydroCopper® will come to picture as a cost competitive, feasible process for all kinds of copper concentrates and a wide range of other valuable metals, or impurities.

Acknowledgments

References

Haavanlammi, L., Nurmisalo, M. and Hietala, K. (2007a): Hydrocopper® - moving up in the copper production chain, 2007 China International Copper Conference, Kunming China, October 25-27, 2007.

Haavanlammi, L., Hietala, K., Karonen, J. (2007b): HydroCopper® for treating variable copper concentrates. Riveros, P.A., Dixon, D.G., Dreisinger, D., Collins, M.D., The John E. Dutrizac International symposium on copper hydrometallurgy, August 25-30, 2007, Toronto, Canada, pp:369-377.

Hyvärinen, O., Hämäläinen, M. Lamberg, P. and Liipo, J. (2004): Recovering gold from copper concentrate via the HydroCopper® process, JOM 56 (8), pp. 57-59.

Lundströn, M. Aromaa, J. Forsén, O. and Haavanlammi, L. (2007): Concentrated cupric chloride solutions: Possibilities offered in copper production, Acta Metallurgica Slovaca, 13 (3) pp. 447- 459.

Lundström, M., Aromaa, J., Forsén, O.: Redox potential characreristics of cupric chloride solutions. Hydrometallurgy, 95 (2-4), pp. 285-289.

Penttinen, U., Palosaari, V., and Siura, T. (1977): Selective dissolution and determination of sulfides in nickel ores by the bromine- methanol method. Bulletin of Geological Society of Finland 49 (2): 79-84.

Sinisalo, P., Tiihonen, M., Hietala, K. Gold recovery from chalcopyrite concentrates in the HydroCopper® process. ALTA 2008 Conference, June 19-20, 2008, Perth, Australia, pp: 1-8.

Young, R.S. (1974): Chemical phase analysis, Charles Griffin & Co.,Ltd. 138p.

The Author

Mari Annukka Lundström, *Process Metallurgist*, Outotec Oyj

Mari Lundström is a Process Metallurgist at Outotec Oyj, Base Metals Division. Her job includes process design, commissioning new processes, sales support and process development. Mari Lundström is about to finish her Doctoral Thesis "Chalcopyrite Dissolution in Cupric Chloride Solutions" in September 2009 in the Laboratory of Corrosion and Materials Chemistry, Helsinki University of Technology (TKK). The study is closely related to the Outotec HydroCopper® process. Her Master´s Thesis "Leaching of Chalcopyrite in Cupric Chloride Media" was awarded at the Helsinki University of Technology (2004), prize for Master's Thesis of the year. She has also carried out research in the field of copper precipitation, nickel leaching, black schist ore bioleaching and nickel cementation. She has published 5 papers in peer reviewed journals, 4 other articles and 13 conference articles. She has also been a reviewer for 6 international journals.