Integrated treatment (electrolytic recovery and cascade line) of highly contaminated wastewaters

Dr.-Ing. Srećko Stopić , Prof. Dr.-Ing. Bernd Friedrich

IME Process Metallurgy and Metal Recycling, RWTH University Aachen, Germany

Abstract

This study addresses environmental pollution problems associated with effluents produced by complex sulphide ore mining and metallurgical activities in Copper Mining and Smelting Complex Bor (RTB-BOR), Serbia. In order to develop an innovative, cost effective and environmentally acceptable technology, continuous precipitation system for selective neutralization and chemical precipitation was built as cascade line reactor. However, since the minimum solubility for the different metals usually found in the polluted water occurs at different pH values and the hydroxide precipitates are amphoteric in nature, maximum removal efficiency of mixed metals cannot be achieved at a single precipitation pH level. For this reason, acid mine water has to be treated in multiple stages.

The results concerning an electrolytic recovery of copper from wastewaters formed after mixing of the streams from Copper Refining, Precious Metals Plant and Electrolyte Regeneration will be shown. An electrolytic recovery represents pre-treatment of wastewater for the subsequent treatment in a cascade line in order to remove copper and other metals (Se, Ni, Fe, Mn) from wastewaters.

It is envisaged that the application of the proposed technologies at an industrial scale will improve working conditions at mining/metallurgical sites and therefore the quality of life and the ecology at the affected regions.

1 Fundamentals

The uncontrolled discharge of wastewater from industry seriously affects the quality of natural running waters. It presents a high risk for the population and can cause great ecological damage which can be economically evaluated. The Balkan Peninsula is rich in polymetallic complex sulphide ore deposits; it is used for the production of base and precious metals. Exploitation of these ore deposits is one of the most dynamic sectors in the Western Balkan region. The sulphide ores are the most important copper bearing ores that are commercially available [1, 2].

The exploitation of these deposits can promote the development of this region which, during the last decade, has suffered from poverty, wars and political instability. The exploitation of sulphide ores, along with the metal extraction that follows cause severe environmental pollution problems in the area, related to contamination of soi1 (floating tailings) and rivers (waste water from Electrolysis Plant).

These wastewaters are characterized by low pH due to the high content of residual sulphuric acid and heavy metals, such as Cu, Cd, Hg, Bi, Sb, Ni, Sn, etc. The majority of these wastewaters are released untreated into the natural water streams and through the network of the existing rivers, contaminants end up to the River Danube. This research will try to reduce the content of copper and other metals in the waste water.

This research will try to remove copper from the waste water using electrolysis method as a continuously electrochemical pre-treatment. The application of rotating cylinder electrodes (RCEs) to electrodeposition has progressed significantly over the last decade [3]. The device of this experiment will be an electrolysis cell with rotating cathode discs. The second step is the precipitation in cascade line reactor using sodium hydroxide [4, 5]. Precipitation is currently the most widespread technology as regards neutralization and metal removal, industrially speaking. Hydroxide precipitation of soluble heavy metals can be reached by adding alkali-precipitating agents, where ions are converted to relatively insoluble metal-hydroxide precipitates, with caustic soda NaOH and lime $Ca(OH)_2$ as the most usual hydroxide-agents available [6]. A major disadvantage of this technology relies on the fact of adding impurities like sodium, in order to decrease hydrogen ion concentration, polluting effluents and impeding its reutilization in industrial process cycles [7].

The main important aim is to investigate the optimal parameter during an electrolytic treatment and cascade line neutralization of highly contaminated real waste water in order to obtained the concentration of copper below 0.1 mg/l. In order to decrease the consumption of NaOH during a cascade line treatment an electrolytic treatment is previous performed. This combination of processes might be very important for the obtaining one cost effective process in order to clean the highly contaminated wastewater. In comparison to the traditional electrolytic treatment (T=60°C) this cleaning of wastewater was performed at room temperature.

2. Experimental

2.1. Real waste water from Copper Smelter, Bor, Serbia

Content of real waste water amounts (g/l): 8.33 Cu, 0.66 Ni, 0.63 As, 0.26 Se, 0.09 Fe, 0.08 Sb, 0.07 Te, 0.04 Al, 0.03 Zn, 0.03 Bi, 0.02 Si, 0.07 Cl^-, 0.003 Pb, 0.001 Mn, 0.0001 Cd, 117.04 H_2SO_4. The synthetic metal-bearing wastewater had a chemical composition taken from the wastewaters formed after mixing of the streams from Copper Refining, Precious Metals Plant and Electrolyte Regeneration at RTB Bor with a flow rate of 5.33 m^3/day.

2.2. Procedure

2.2.1. Electrolytic treatment with rotating discs

Experimental part was performed using an electrolytic cell as main component of the equipment shown in Fig. 1 [8]. The cathodes (two rotating discs) with diameter of 30 cm were made by stainless steel. Anodes were made from titanium coated with platinum. The real wastewater and

sulphuric acid were used for the investigation. Using two pumps the initial solution was transported from the canister into the first cell and later to the second cell. The laser sensor was used for the control of solution level in the electrolytic cell. The copper was deposited at the rotating discs. After an electrolytic removal of copper in the first cell the wastewater was transported to the second cell for the following recovery process and later moved to the canister. The experiments were performed at a room temperature. The other experimental conditions were: current density 50-240 A/m^2, flow rate of solution 0.5; 1.0 and 2.0 L/h, current intensity I= 4.4, 7.5 and 9.9 A, voltage U= 2.3-2.7 V, time t = 11- 20 h; rotating speed two rotations per minute. The content of wastewater was determined using the Induced Coupled Plasma ICP analysis. The waste water was filled into the source tank, and than was pumped into the first cell. The first pump is in charge of flow rate parameter of the process. In the first cell, the high amount of copper should be removed. The other important parameter of this process is the current density. The current flows into the cathode through the axis of the rotating discs. The current density is measured inside the cell continuously. The wastewater was pumped into the second cell after reaching a certain level. The solution level in the first cell was monitored by a pair of laser beam, which have operated the second pump to prevent over flooded. The second extraction step in the second cell was aimed to get the rest of copper substance after the first extraction. The process is finish after the solution arrives in the final tank. The duration of the whole process depends on the flow rate of the waste water into the cell and the volume of waste water in the source tank. The experiments divided into two series, using synthetic solution and real wastewater. In difference to the traditional electrolytic recovery of copper this treatment was performed at room temperature in order to spare energy for the heating.

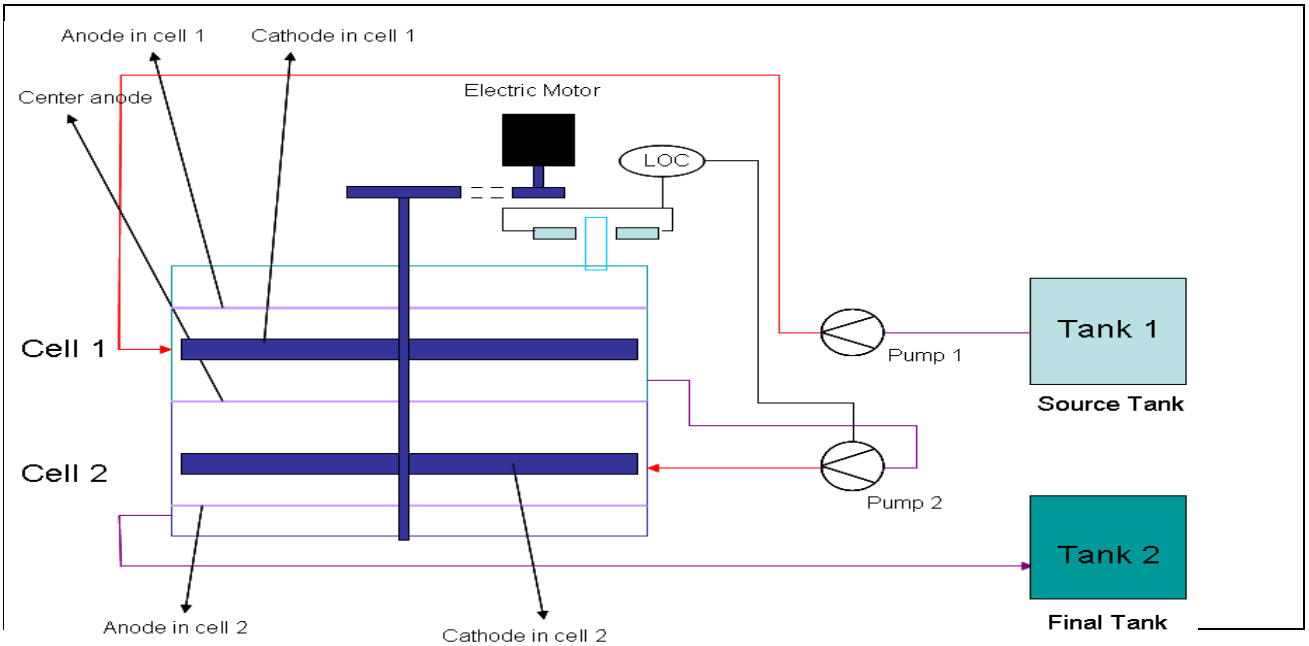

Figure 1: An equipment for electrolytic recovery at the IME, Aachen (an electrolytic cell with two rotating discs, two pump, two canisters, laser sensor, exhaust system, rectifier)

2.2.2. Cascade line treatment

All experiments were conducted in a continuously operating cascade line with 3 stirring 10 l glass reactors. A view of the equipment is given in Fig. 2. The main components of the systems are:

- system for adjustment and continuous feed of wastewater, (10 l vessel for feed adjustment; valve for regulation; flow meter)
- systems for injection of the neutralization agent,
- systems for pH measurements and control,
- collection of process gases,
- three indirect wall heated glass reactors, identical in layout and volume of 10l with 3 mixers and one thermostat)
- 200 l storage tanks for wastewater and purified solution.

Measurement and control of pH was conducted using pH transmitters (2100e, Mettler-Toledo, Germany) with glass electrodes InPro 4250 SG (ISM) (Mettler-Toledo, Germany). Based on the specific pH set-point, which was defined for each reactor, the analyzer transmits signals to recorder or control systems that activate (or deactivate) pumps for dosage of neutralization agent automatically. As neutralization agent 4M and 1M solutions of NaOH were used, which were injected from individual tanks into the three reactors using three solenoid diaphragm dosing pumps (BT4a 1005 ProMinent with self-dosing head and maximum capacity 4.5 l/h).

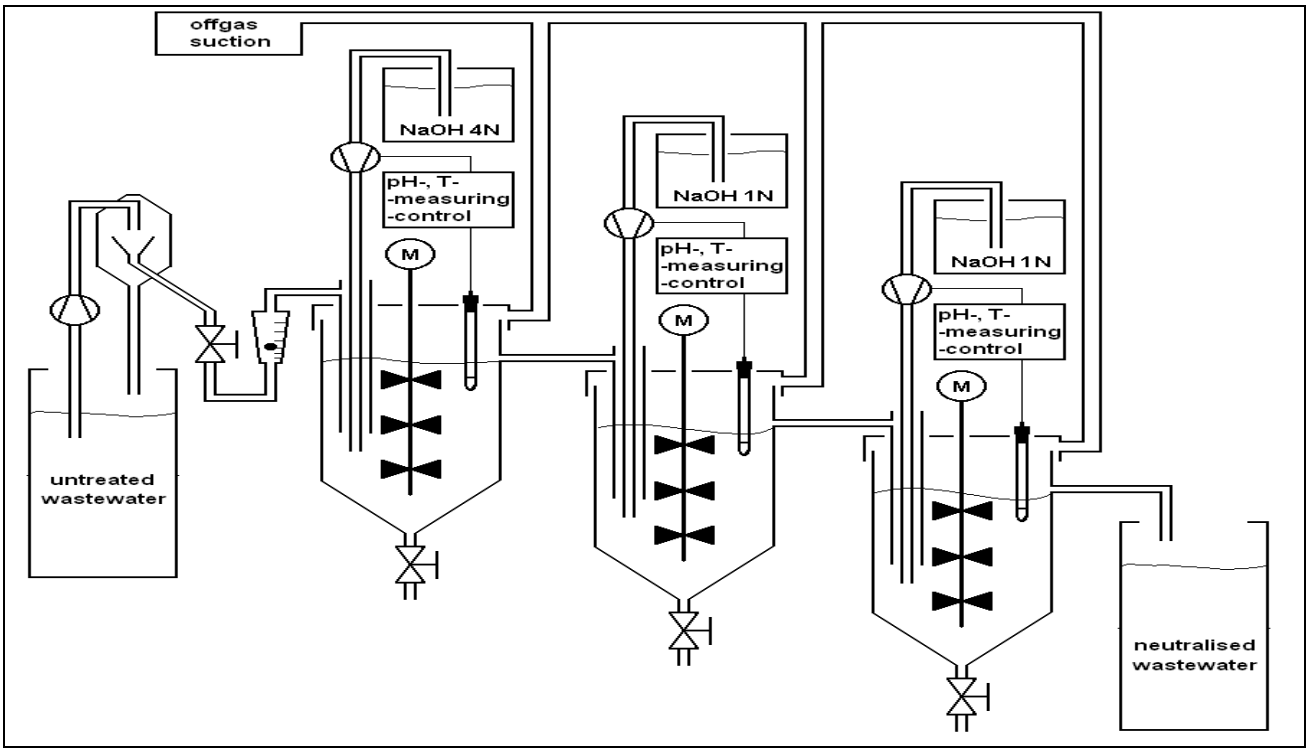

Figure 2: Sketch of the cascade line reactor for continuous neutralization/ precipitation

3. RESULTS

3.1. Electrolytic treatment of real waste water

Concerning the electrolytic treatment the performed experiments were conducted as shown in Table 1. The first five experiments are related to a synthetic solution as previous presented in [8]. The experiments from 6 to 10 were previously presented in [9] and discussed here in more detail. The obtained results are summarized in Figure 3.

Table 1: The performed experiments of an electrolytic treatment

Experiment No.	current density (A/m^2)	Volume flow (l/h)	solution type
1	240	0.5	Synthetic
2	80	0.5	Synthetic
3	50	0.5	Synthetic
4	80	1.0	Synthetic
5	80	2.0	Synthetic
6	50	0.5	Real
7	80	0.5	Real
8	100	0.5	Real
9	80	1.0	Real
10	80	2.0	Real

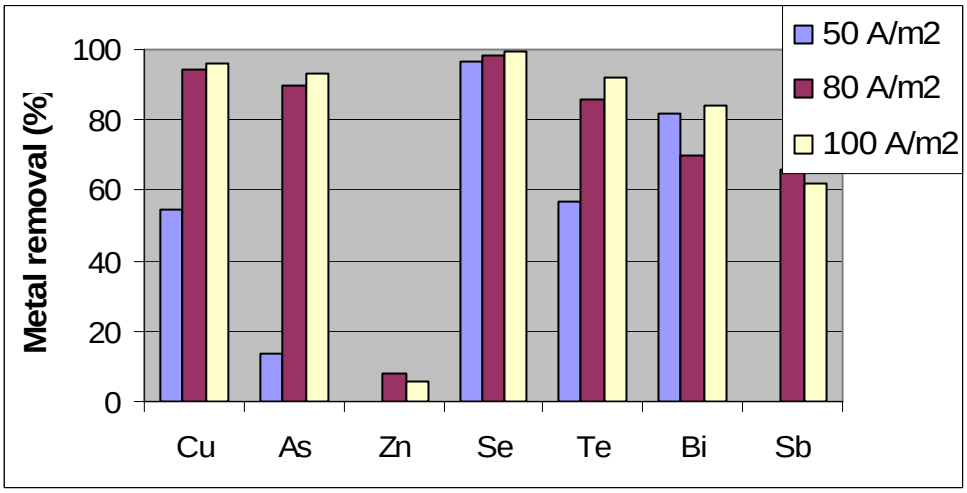

Figure 3: Metal removal as function of the current density

As easily can be seen the increase of the current density from 50 A/m^2 to 100 A/m^2 increases the metal removal for Cu, As, Te significantly. In the case of Se the removal degree was >95% for all three densities. In case the Zn the current has almost no influence on the metal removal due to its unnoble character. Due to the construction of our electrolytic cell (two separate cells see Figure 1) the increase of the current density has a limited influence on the final metal removal between 80 and 100 A/m^2.

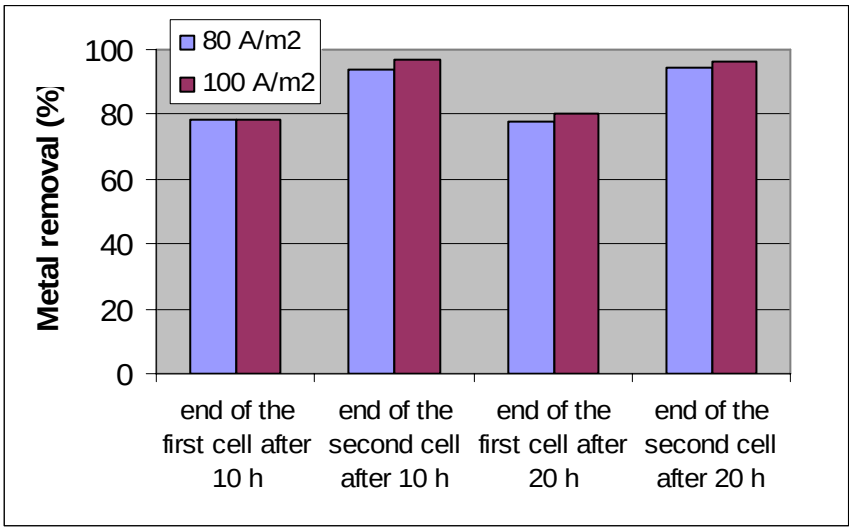

Figure 4: Copper removal in each of the two consecutive electrolytic cells

The obtained results show that this electrolytic treatment was successful in the case of copper and selenium. At the beginning of the electrolytic treatment the deposition of selenium took place. Then the deposition of copper was started after most of the selenium was extracted. The calculated current efficiencies for 80 and 100 A/m^2 are 44% and 58 %, respectively. The average values of the solution concentrations are shown in Table 2:

Table 2: Chemical composition of wastewater before an after the electrolytic treatment

mg/l	Al	As	Bi	Cd	Cu	Fe	Ni	Pb	Sb	Se	Si	Te	Zn
Initial solution	40	630	28	0,1	8330	86	660	3	75	260	21	68	34
After an electrolytic treatment	17	495	25	0.1	3400	3	725	3	73	50	29	44	32

3.2. Continuous treatment of waste water by chemical precipitation in a cascade line

First of all the real wastewater and previous treated synthetic wastewater are investigated in laboratory conditions using NaOH solution for neutralisation. The change of pH-value and temperature during a titration of 1l solution show the results presented in figure 5.

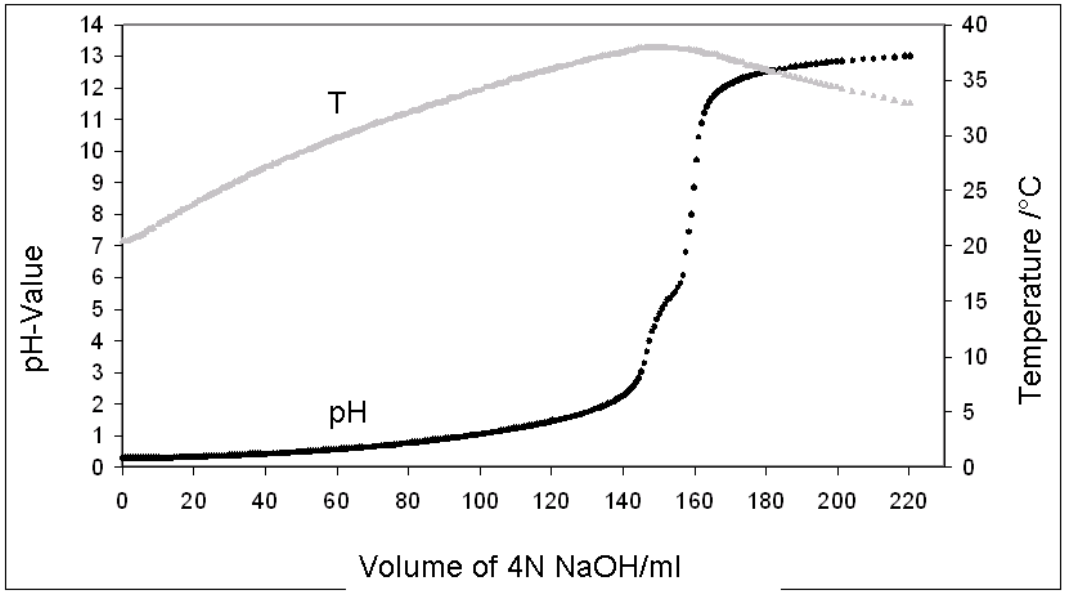

Figure 5: Change of pH-value and temperature during a titration of 1 litre real waste water

In comparison to the volume of 160 ml 4N NaOH needed for the titration of 1l real waste water a volume of 120 ml was consumed for the same volume of synthetic waste water up to pH value 7. The comparative analysis for titration curves is shown in Table 3. In both cases the titration showed an exothermic effect. The experimental conditions are presented in Table 4:

Table 3: Comparative analysis of a 1l titration test (three different regime of pH-changes)

waste water solution	Volume of 4N NaOH (ml) consumed for titration up to pH= 7	pH_1	pH_2	pH_3
Real	160	4.3	4.9	5.8
after an electrolytic treatment	120	3.2	4.6	5.4

Table 4. Experimental conditions for neutralization (t= 5 h, dV/dt = 6.5 l/h)

Reactor	Maximal Temperature (°C)	Stirring (revo-lutions) (rpm)	pH	Consumption of NaOH (l/h)
1	38	380	4.0	12,65 (4N)
2	41	338	7.0	7.36 (1N)
3	40	376	9.0	4.67 (1N)

Before the start of this experiment the calibration of an electrode was performed. During this neutralization experiment the sample of waste water were taken from three reactor and the collection tank (Table 5).

Table 5: Metal concentration in three reactors and the collection tank

Concentration (mg/l)	Al	As	Bi	Cd	Cu	Fe	Ni	Pb	Sb	Se	Si	Te	Zn
after an electrolytic treatment	17	495	25	0,1	3400	3	725	3	73	50	29	44	32
reactor 1, pH=4	5.0	21	25	0.1	2200	2	725	1	7	4	29	8	18
reactor 2, pH=7	0.7	<1	2.3	0.02	1100	0.6	615	0.5	0.5	1	18	<0,1	12
reactor 3, pH=9	0.4	<1	0.8	<0.01	<1	<1	1	<0,5	0.5	1	<1	<0,1	0.1
collection tank	0.4	<1	0,7	<0,01	<1	<1	1	<0,5	0.5	1	<1	<0,1	<0,1

The obtained results confirmed that the concentration of metals could be reduced under 1 mg/l, what was our main aim. The removal efficiency during a the treatment in the continuous cascade line is shown in Figure 6:

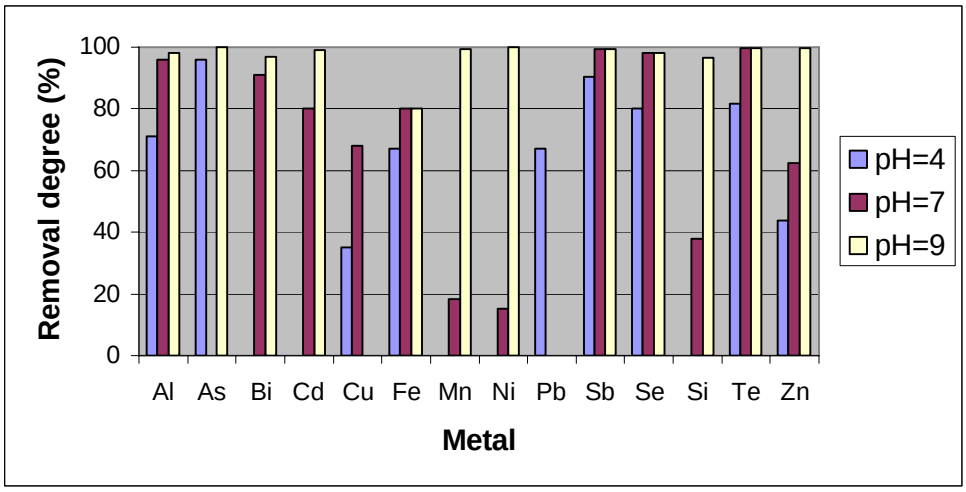

Fig. 6. Removal efficiency during a cascade line treatment with NaOH

Fig. 7 presents the precipitates, taken from the three reactors after stop of the stirring (for investigation reasons only) The content of the final dried precipitation sample with red-brown colour, is shown in Table 6:

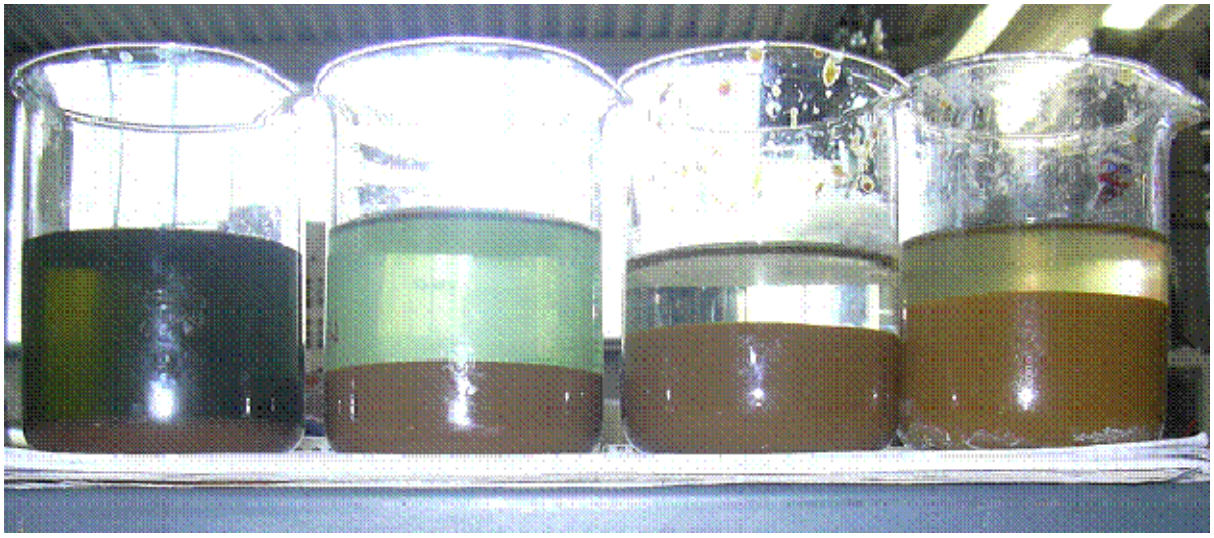

Figure 7: Samples from the first, second, third reactor (and collection tank)

Table 6. Composition of the final precipitate after a drying

Content (%)	Al	As	Bi	Cd	Cu	Fe	Ni	Pb	Sb	Se	Si	Te	Zn
Collection tank	0,17	1,21	0,03	<0,01	9,46	11,1	3,85	0,01	0,17	<0,01	0,20	0,19	0,11

The calculated value for the produced precipitate amount to 31.5 kg/m^3 and 30 kg NaOH/m^3 for the waste water treatment was consumed.

4 Conclusions

The rotating cathode electrolysis is suitable for a partially removal/recovery of Cu and Se without extracting Zn, and Ni from the waste water. But a following chemical precipitation treatment e.g in a continuous cascade line is required. Such the obtained solution after electrolytic treatment was used for a cascade neutralization treatment in order to decrease of copper concentration down to 1mg/l. After this treatment the concentrations of all metals (Al, As, Bi, Cd, Cu, Fe, Mn, Ni, Pb, Sb, Se, Si, Te, Zn) reached values below 1mg/l. The expected exothermic effect is present in all three reactors. The calculated values for the produced precipitate and the consumption of NaOH amount to 31.5 kg/m^3 respectively to 30 kg NaOH/m^3 waste water. An integrated treatment (electrolytic recovery and cascade line) of highly contaminated wastewaters might be a successful solution for the cleaning the waste water from smelters.

5 Acknowledgments

We would like to thank the European Commission for the financial support on the project INTREAT, INCO-CT-2003-509167, as well as Dipl.-Ing. Mario Schweda and Dieter Leimbach for their kind and valuable scientific support. Regarding the experimental part for the electrolytic treatment we would like to thank Mr. Anugerah Widigdo.

6 References

[1] NIKOLIC, B, VUCUROVIC, D., OSTOJIC, S., (2002): Obojena Metalurgija Jugoslavije na kraju 20 veka, Institut za hemiju, tehnologiju i metalurgiju, Beograd, pp. 90, (in Serbian language)

[2] ĆIRKOVIĆ, M,. MARINKOVIĆ, J., D. VUČUROVIĆ, D. STOPIĆ, S (1999): Kinetics of Copper Concentrates Oxidation in Fluidized Bed Reactor. In: Extraction & Processing Division, ed. Mishra, B., TMS**,** Warrendale,, pp. 933-944.

[3] LOW, J., de LEON, C., WALSH, F (2005): The Rotating Cylinder Electrode (RCE) and its Application to the Electrodeposition of Metals, Aust. J. Chem., 58, pp. 246-262

[4] PAVLOVIĆ, J., STOPIĆ, S., FRIEDRICH, B., KAMBEROVIC, Z. (2006): Selective removal of heavy metals from Metal-Bearing wastewater in a cascade line reactor", Environmental Science and Pollution Research, 5, (online), http//www.scientificjournals.com/sj/espr/Pdf/ald/8329

[5] STOPIĆ, S., PAVLOVIĆ, J., FRIEDRICH, B., et. al. (2007):Treatment of high contaminated wastewaters in cascade line reactor, Erzmetall World of Metallurgy, submitted for publication

[6] CECW-ET (2001): Engineering and Design – Precipitation, Coagulation, Flocculation. US Army Corp of Engineers EM1110-1-4012

[7] WETTER, C., PÖPPINGHAUS, K. (1992): Literaturstudie über Verfahren zur Schwermetallentfernung aus Abwasserschlämmen. FiW Forschungsbericht AZ, pp. 279-285

[8] STOPIĆ, S., FRIEDRICH, B., WIDIGDO, A. (2006): Electrolytic recovery of copper from highly contaminated wastewaters, Proceeding for Fourth Balkan Conference on Metallurgy, September 27-29, 2006, Zlatibor, Serbia, pp. 353-360.

[9] STOPIĆ, S., FRIEDRICH, B., WIDIGDO, A. (2007): Electrolytic treatment of highly contaminated effluents from copper smelters, Cu2007, Toronto, Canada, in print

[10] SCHWEDA, M., (2007): Kinetik der Neutralisation von Schwermetallen aus dem Abwasser einer Kupferhütte in einer Kaskadenanlage, diplome-thesis, IME Process Metallurgy and Metal Recycling, RWTH Aachen University, pp. 77.