Treatment of Highly Contaminated Waste Waters in a Continuous Cascade Line Reactor

Srećko Stopić, Jelena Pavlović, Bernd Friedrich et al.

This paper presents research work done on complex copper bearing effluents from the Serbian RTB-Bor plant. The INTREAT project, funded by the European community, addresses environmental pollution problems associated with solid and liquid wastes produced by complex sulphide ore mining and metallurgical activities. In order to offer a cost-effective and environmentally sound technology, a continuous precipitation system for selective neutralization and chemical precipitation was designed as cascade line reactor. However, since the minimum solubility for the dissolved metals occurs at different pH-values and the hydroxide precipitates are amphoteric in nature, the highest removal efficiency cannot be achieved at a single precipitation pH level, respectively in one reactor. Thermochemical analysis predicted three effective pH ranges: 4 to 4.5 (mainly iron hydroxides), 7 to 7.5 (mainly copper hydroxide/sulfate-mix), and > 10 (mainly nickel hydroxide). For this reason, the waste water was treated in multiple stages. During the testwork the influence of temperature and such pH-values on the metal removal degree was investigated in a continuous operation mode. The consumption of NaOH was monitored in dependence of its feed concentration. Obtained results show that the metal removal efficiency is very satisfactory and the recovered purified solution meets international discharge water standards.

Keywords:

Waste water purification – Continuous cascade line reactor – Selective neutralization – Chemical precipitation – Heavy metals removal – Copper

Behandlung hochkontaminierter Industrieabwässer durch Neutralisation in einer kontinuierlichen Fällungskaskade

Diese Veröffentlichung beschreibt die Forschungsergebnisse im Zusammenhang mit der Behandlung kupferhaltiger Abwässer aus der serbischen Kupferhütte in Bor. Das von der EU-Kommission finanzierte INTREAT-Projekt beschäftigt sich mit Umweltschutzproblemen, bedingt durch Feststoffe und Flüssigkeiten, die im Bergbau und bei der metallurgischen Behandlung eines sulfidischen Erzes anfallen. Es wurde ein kontinuierliches Fällungssystem zur selektiven Neutralisierung und chemischen Präzipitation in Form eines Kaskadenreaktors vorgeschlagen, welches Fragen der Wirtschaftlichkeit und des Umweltschutzes berücksichtigt. Da die minimale Löslichkeit der Metallionen bei unterschiedlichen pH-Werten liegt und das entstandene Hydroxid eine amphotere Verbindung ist, kann die maximale Fällungsausbeute nicht bei einem pH-Wert, bzw. in einem Reaktor, erreicht werden. Einer thermochemischen Analyse zur Folge wurden drei unterschiedliche pH-Bereiche der Fällung vorgesehen: 4 bis 4,5 (überwiegend Eisenhydroxid), 7 bis 7,5 (überwiegend eine Mischung aus Kupferhydroxid/Kupfersulfat), und > 10 (vor allem Nickelhydroxid). Daher fand die Abwasserbehandlung in mehreren Reaktoren statt. Der Einfluss der Temperatur und des pH-Wertes auf die Metallentfernungseffizienz wurde im kontinuierlichen Betrieb untersucht. Die erzielten Ergebnisse wiesen die ausreichende Entfernungseffizienz der Metalle auf.

Schlüsselwörter:

Abwasserbehandlung – Kontinuierlicher Kaskadenreaktor – Selektive Neutralisierung – Chemische Fällung – Entfernung von Schwermetallen – Kupfer

Traitement des eaux usées hautement contaminées dans un réacteur en ligne en cascade continue

Tratamiento de aguas residuales altamente contaminadas por neutralización en una cascada de precipitación

Paper presented on the occasion of the meeting of GDMB Special Metals Committee, November 23 to 24, 2005 in Hanau.

1 Introduction

Exploitation of complex sulphide ores is one of the dynamic industrial sectors in Serbia. Actually, sulphide ores are the most important copper bearing resources that are commercially available. Their exploitation is accomplished either by open pit or underground mining. During the whole copper production cycle, large amounts of solid, liquid and gaseous wastes are generated. These wastes interact with the local environment resulting in serious impacts for the local eco-system [1]. Many types of waste waters/effluents are produced from pyrometallurgical treatment of copper bearing mixed sulphide ores [2]. These waste waters are characterized by a low pH-value due to a high content of residual sulphuric acid and heavy metals, such as Cu, Fe, Ni, Mn, Zn etc. The majority of these waste waters are released untreated into the natural waste water streams and through the network of the existing rivers, contaminants end up to the River Danube [3].

Industrial uses of water generally lead to deterioration in quality and, in most instances, waste water must be collected and given effective treatment before being released to the environment. The conventional method for heavy metal removal from industrial waste water generally involves a chemical precipitation process of the various treatment methods employed to remove heavy metals [4, 5]. Hydroxide precipitation is the most common and economically sound treatment technology. Metal precipitation is primarily dependent upon two factors: the concentration of metals in waste water and the pH of the water [6]. Heavy metals are typically removed by adding alkali such as caustic, lime or soda ash to adjust the waste water pH to points where the individual metals exhibit their minimum solubility. Then the precipitates are removed by a proper solid-liquid separation technique such as sedimentation and filtration.

A basic knowledge of precipitation phenomena and of the characteristics of typical precipitates provides useful guidelines for process development. Obtaining a precipitate with desirable physical characteristics is a problem which often causes difficulties in pilot-scale development of new hydrometallurgical processes [7]. Removing metals via hydroxide precipitation has several advantages. Hydroxide precipitation is a well-established, simple technology, which is relatively inexpensive. It has proven its ability to achieve regulatory effluent limits for several metals, and it is well suited for automation [8, 9]. The main drawbacks are: the generation of big sludge volumes that are usually unstable in terms of heavy metals mobilization and require either safe land filling responding disposal or a further treatment to meet the disposal criteria and to reduce valuable metal losses [10-12].

In this paper a continuous process of chemical precipitation was carried out in a cascade line reactor in order to achieve selective precipitation of different metals present in waste water. In order to define the process parameters a synthetic metal-bearing solution with a chemical composition similar to the waste water formed after mixing of the streams from Copper Refining, Precious Metals Plant and Electrolyte Regeneration (5.33 m^3/d at RTB-Bor, Serbia) was used. Afterwards the tests were extended to real solutions from the plant. The main aim of this paper was to study the influence of the pH value on the selectivity of precipitation during a continuous process and the investigation of the precipitate behavior in subsequent steps working at elevated pH-values.

2 Thermochemical analysis of waste water neutralization

Regarding the thermochemical analysis of waste water neutralization all aqueous metal species (sulphate, chloride, hydroxide) have been taken into account (Figure 1). Parallel checks of the formed hydroxide and sulfide precipitates were performed to verify this. Three different areas can be proposed: the first: pH = 3-5; the second: pH = 5-7.0, and the third: pH = 7-9.5. In the area between pH values from 7 and 10 a significant decrease of Zn, As, Ni-concentration

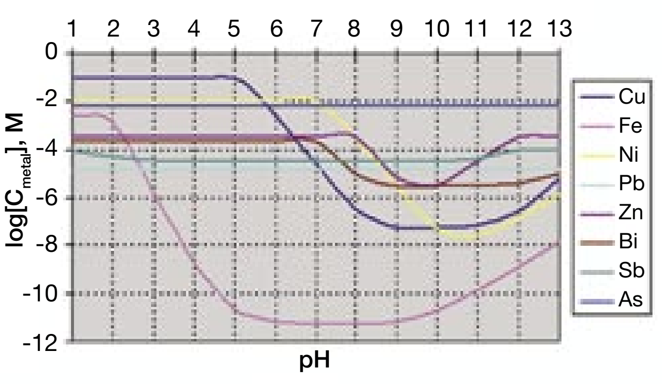


Fig. 1: Thermochemical analysis of waste water neutralization at room temperature

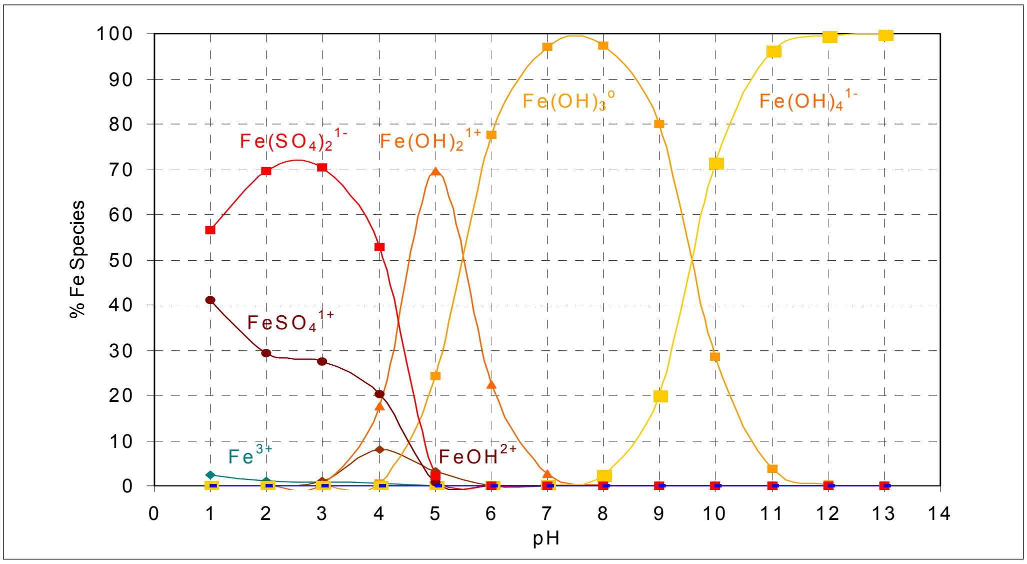


Fig. 2: Thermochemical analysis of iron species at room temperature

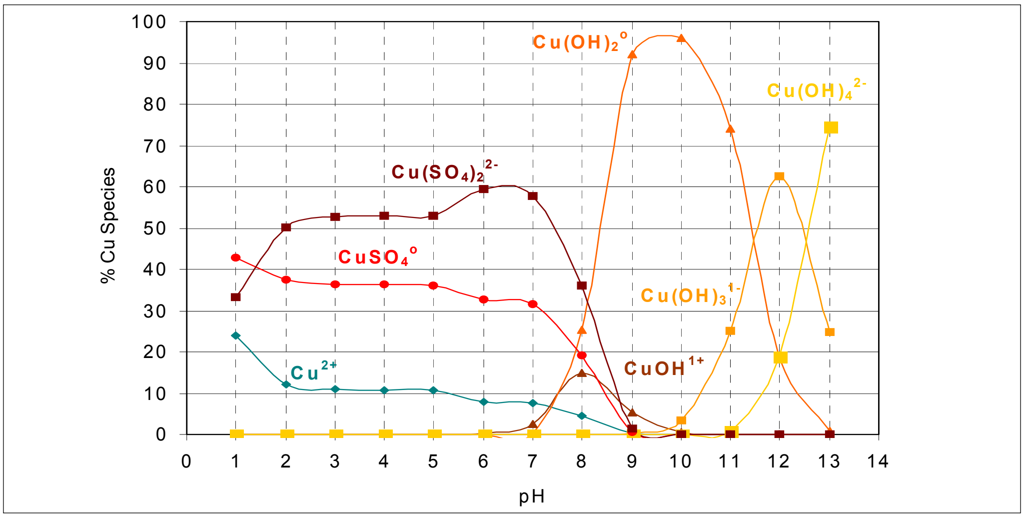


Fig. 3:
Thermochemical analysis of copper species at room temperature

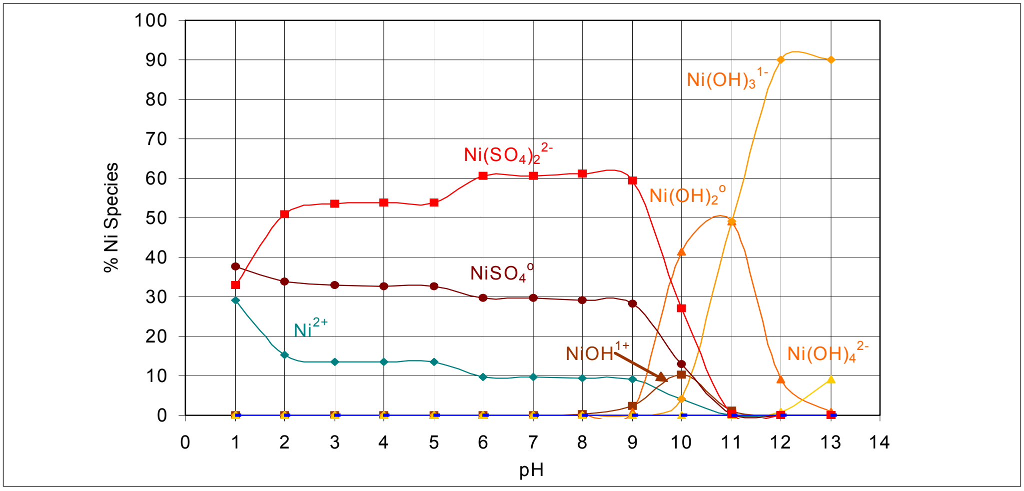


Fig. 4:
Thermochemical analysis of nickel species at room temperature

can be expected (formation of Zn-, As-, Ni-hydroxide). A further increase of pH-values above 10 leads again to increased concentrations of Zn, Ni and Cu (re-dissolution). For Pb there is no significant change of concentration in the whole range. Therefore the neutralization process will give only low possibility for the removal of these metals if not absorption methods will parallel be effective.

Figures 2 to 4 additionally present a more detailed thermodynamic analysis for Fe, Cu, Ni. In the pH-area between 3 and 5 the content of iron hydroxide increases up to the maximum of 70 %. The following increase of pH-value from 5 to 7 decreases the content of Iron hydroxide. In this area of pH-values the content of iron sulphate is mostly decreased (Figure 2). For pH-values between 7.0 and 9.0, a significant decrease of Cu-concentration in form of copper sulphate is dominant. In same interval the content of copper hydroxide is increased up to 90 % (Figure 3). The content of nickel sulphate starts to fall at pH-value of 9 (Figure 4). At the same pH-value the content of $Ni(OH)_2$ increases.

The titration curve with NaOH-solution shows again the three clearly defined endpoints Fe precipitation, Cu precipitation and Ni, Zn, Bi precipitation (Figure 5).

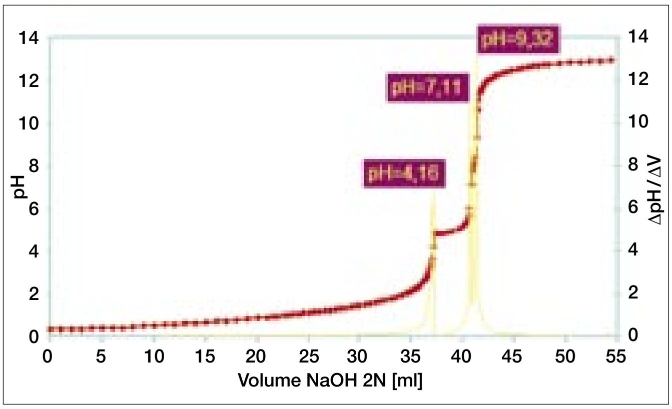


Fig. 5: Titration of a synthetic waste water with NaOH-solution at room temperature

3 Experimental method and equipment

All experiments were conducted in a continuously operating cascade line with three stirring 10 l glass reactors. A view of the equipment is given in Figure 6. The main components of the systems are:

- System for adjustment and continuous feed of waste water (9 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 9 l with three mixers and one thermostat)

Fig. 6: Detail of the cascade line reactor for continuous neutralization/precipitation

- 200 l storage tanks for waste water 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).

The chemical composition of the synthetic metal-bearing solution used in experiments, the compounds used for synthesis, their quantity needed to prepare 1 l solution and the discharge limits according to The Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances into the aquatic environment of the Community [8] are shown in Table 1. For synthesis the soluble chemical compounds (p.a. grade) of metals, were dissolved in distilled water.

Tab. 1: Chemical composition of the investigated waste water, required salt amounts for synthesis and EU discharge limits

Component	Concentration [g/l]	Compound	Discharge limit [mg/l]
Cu	6.0357	$CuSO_4 \cdot 5H_2O$	0.25-1.00
Ni	0.6128	$NiSO_4 \cdot 7H_2O$	0.20-1.00
As	0.5055	As_2O_3	0.125-1.00
Fe	0.1502	$FeSO_4 \cdot 7H_2O$	2.00-6.00
Bi	0.0448	Bi	–
Al	0.0033	$AlCl_3$	2.50-20.00
Sb	0.0123	$SbCl_3$	5.00
Mn	0.0002	$MnSO_4 \cdot 7H_2O$	1.00-4.00
Zn	0.0237	$ZnSO_4 \cdot 7H_2O$	2.5-10.00
Cr	< 0.0011	$CrCl_3 \cdot 6H_2O$	0.30-1.00
Co	0.0012	$CoCl_2 \cdot 6H_2O$	0.20
Mg	0.0078	$MgSO_4 \cdot 7H_2O$	–
Pb	0.0029	PbO	0.10-0.40
Sn	< 0.0031	$SnCl_2 \cdot 2H_2O$	–
H_2SO_4	83.2826	H_2SO_4	1500.00
Cl^-	0.0608	HCl	1.00

4 Results

4.1 Tests with synthetic solution

4.1.1 Required time to reach the equilibrium state of the experimental system – equivalent to a stable pH value in each reactor

During experiments the pH-value could be adjusted with time as illustrated in Figure 7. For the first reactor, it took about 40 min for neutralization with 4M NaOH in order to achieve the defined pH-value of 4. The required

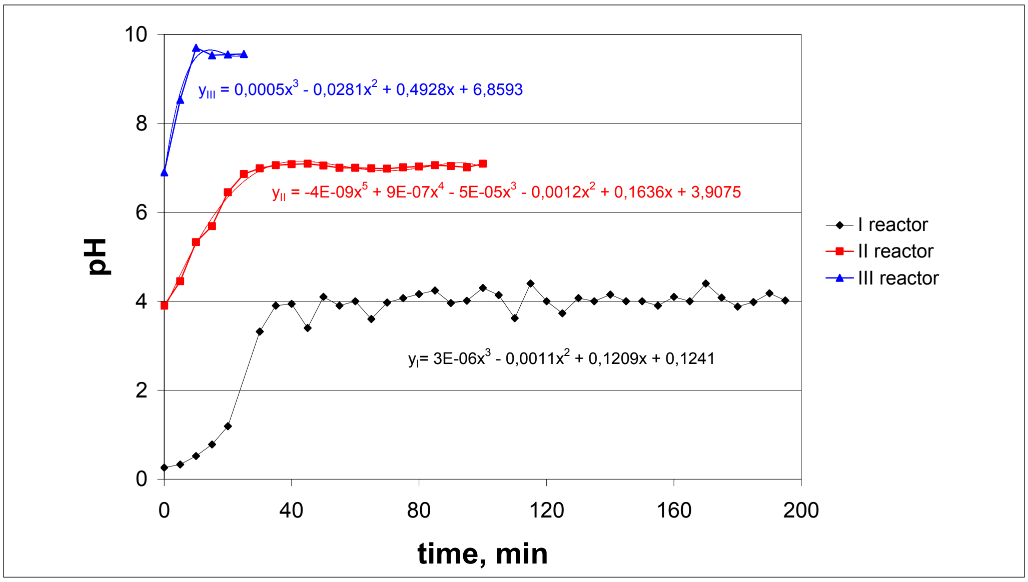


Fig. 7: Changing of pH-value in all three reactors of the continuous cascade line during time

time to reach a pH-value of 7 from an inlet pH-value of 4 amounted to approx. 30 min for the second reactor using a 1M NaOH solution for the neutralization. As expected in the third reactor the time to reach stable conditions was shortest (10 min for pH-value of 9.5 starting from 7). All together the system seems to be stable more or less immediately after filling the third reactor.

4.1.2 Metal removal during the neutralization with NaOH

In order to verify the efficiency of metals removal, chemical analyses was done. Samples were taken from the effluent of all three reactors at different pH-values after stabilization of the process. The neutralization was performed using NaOH with 4 mol/l concentration in the first reactor and 1 mol/l in the second and the third reactor. After the filling of the first reactor the solution flow was set to 5 l/h. The consumption of NaOH for a five hour tests (total flow of solution 35 l) is shown in Figure 8. As expected the highest consumption of NaOH is in the first reactor. The agitation speed of the stirrers was set to 340 to 380 rpm in the reactors.

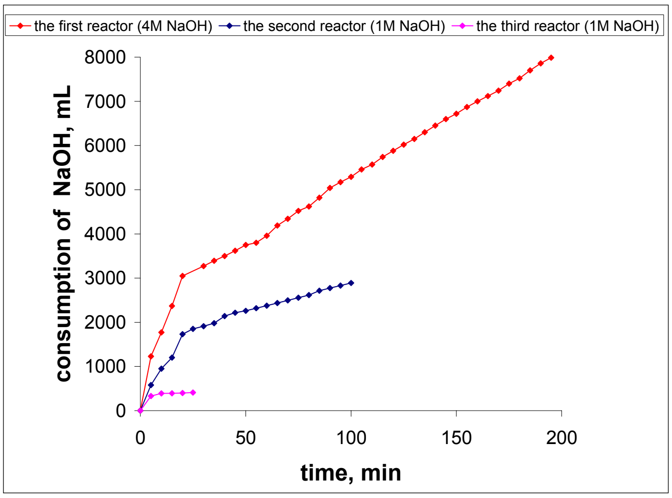


Fig. 8: Consumption of NaOH in all reactors to treat 40 l of synthetic waste water

The collected samples were filtered and subjected to AES-ICP analysis. The experiments were performed at room temperature allowing to determine possible exothermic effects. Some obtained solutions with solid residues are shown in the Figure 9.

The results based on the chemical analyses for the above mentioned samples are presented in Figs. 10a and 10b as metals removal efficiencies [%], calculated based on equation (1).

$$\%\ \text{metals removal} = \frac{\text{conc}_{\text{start}} - \text{conc}_{\text{end}}}{\text{conc}_{\text{start}}} \qquad (1)$$

The obtained results show that after neutralization with NaOH at optimal pH-values the following metal contents in solution can be reached, divided into three groups:

- Concentration ~ 3 mg/l for Ni, As, Mg
- Concentration below 1 mg/l for Cu
- Concentration below 0.1 mg/l for Mn, Sn, Al, Ca, Si, Co, Cr, Fe, Bi, Zn, Sb, Pb

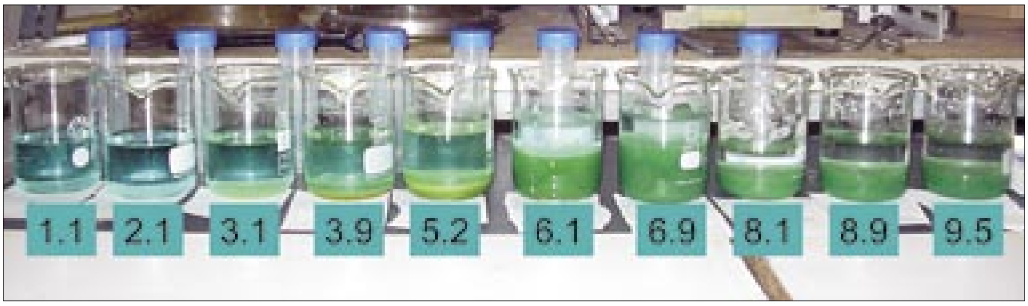


Fig. 9: Samples taken after neutralization of synthetic waste water from three reactors of the continuous cascade line at different pH-values (t = 25 °C)

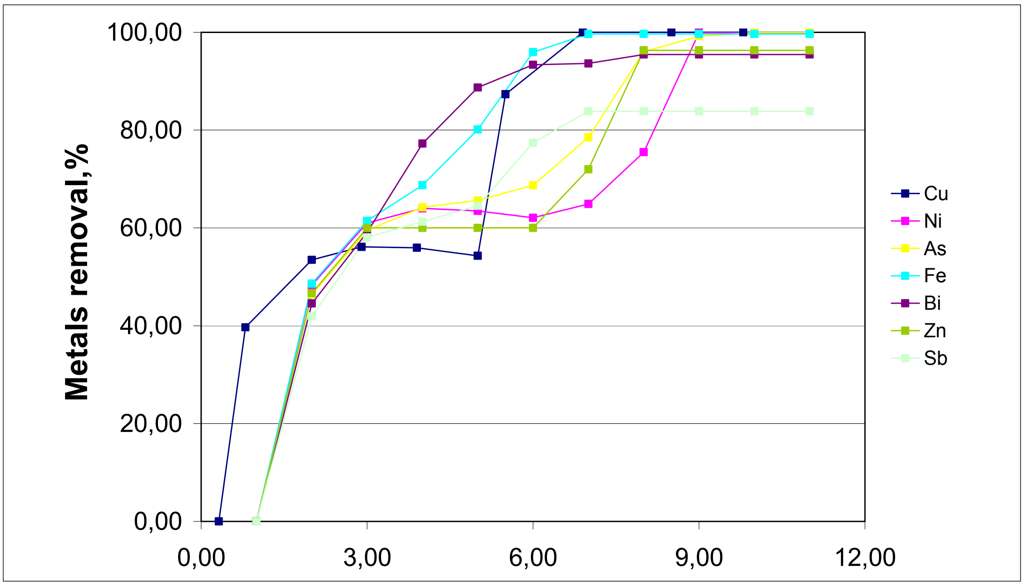


Fig. 10a: Removal of Cu, Ni, As, Fe, Bi, Zn, Sb depending on pH

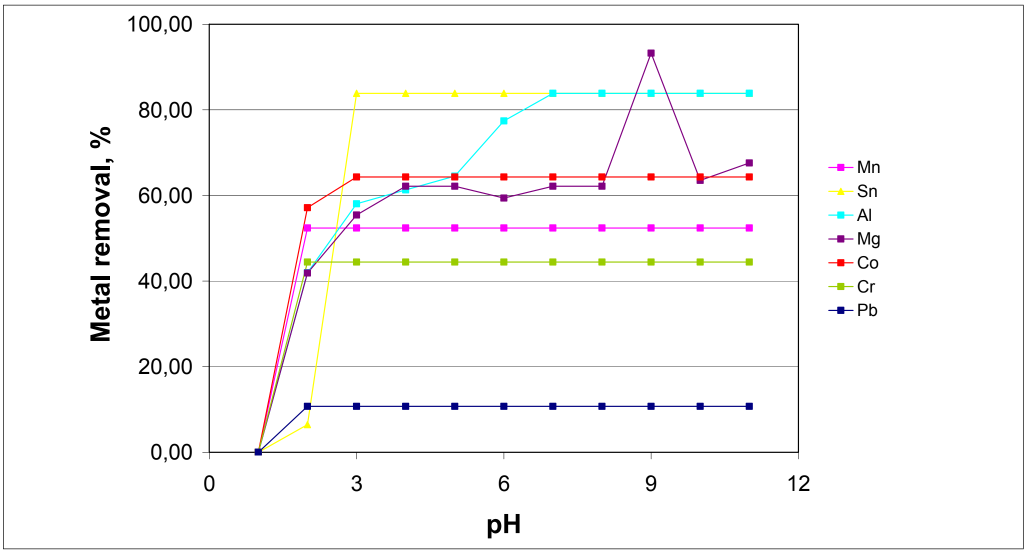


Fig. 10b:
Removal of Mn, Sn, Al, Mg, Co, Cr, Pb depending on pH

4.1.3 Solid residue after neutralization

It was the target, that the precipitates of each tank are transported by the waste water flow to the subsequent reactor forming one final solid product at the end of the procedure. Solid residues from each reactor were sampled and their compositions as well as that of the final product are shown in Table 2. For this investigation the individual reactor precipitates were taken from each reactor and analysis took place after neutralization, sedimentation, filtration, washing and drying (Table 2).

After experiment the measured mass of precipitates in each reactor amounted: reactor 1 = 9.3 g; reactor 2 = 368.8 g; reactor 3 = 284.7 g corresponding to a total metal removal during the entire test period. The high presence of sodium in the solid residue is a consequence of the formation of $Na_2SO_4 \cdot 10\,H_2O$ at temperatures below 32.4 °C:

$$Na_2SO_4 + 10\,H_2O \rightarrow Na_2SO_4 \cdot 10\,H_2O \qquad (2)$$

4.1.4 Temperature change during neutralization

The neutralization with 4M NaOH shows a temperature increase between 16 °C and 31 °C due to a strong chemical reaction with free acid and metal sulphates in solution. In the second and the third reactor the temperature change amounted only to about 2 °C. Because most of the sulphuric acid was neutralized in the first reactor the final neutralization (transformation of metal sulphates $CuSO_4$, $NiSO_4$, $ZnSO_4$, ... into oxide/hydroxide precipitates) followed in the second and the third reactor happened without a strong exothermic effect (Figure 11).

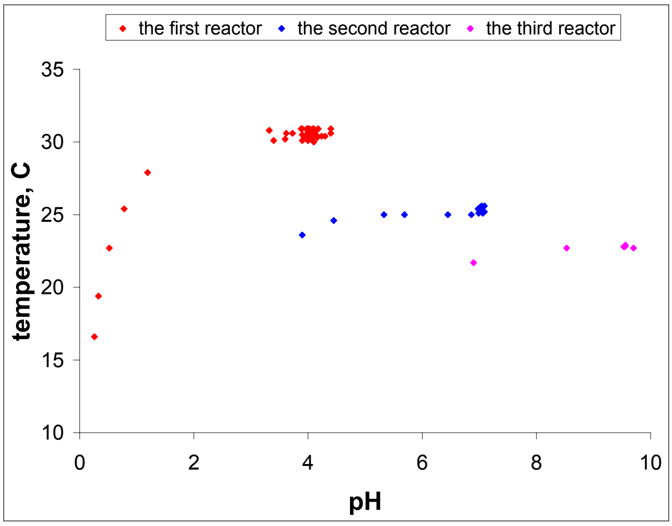


Fig. 11: Temperature change during neutralization in the three reactors

4.2 Tests with industrial waste water

The composition of real waste water obtained in Copper Mining and Smelting Complex Bor (RTB-Bor) after electrolysis amounts to 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 (values in g/l, Table 3). The neutralization was again performed using

Tab. 2:
Chemical composition of solid residues from the three reactors and the collection tank

Metal [%]	Al	Fe	Si	As	Cu	Ni	Na	Zn
Reactor 1 (pH = 3.9)	0.72	7.88	0.53	11.70	16.7	0.84	7.81	0.05
Reactor 2 (pH = 6.9)	0.09	0.53	1.92	3.46	24.3	1.74	12.30	0.13
Reactor 3 (pH = 9.5)	0.017	0.60	0.24	3.97	27.2	3.16	10.12	0.15
Collection tank	0.017	0.58	0.24	3.83	26.4	2.93	10.4	0.15
Metal [ppm]	**Mn**	**Sn**	**Mg**	**Co**	**Cr**	**Bi**	**Sb**	**Pb**
Reactor 1 (pH = 3.9)	85	3031	71	372	630	9215	6468	695
Reactor 2 (pH = 6.9)	< 5	97	< 5	216	8	392	196	188
Reactor 3 (pH = 7.9)	7	164	247	60	31	654	333	304
Collection tank	< 5	< 500	< 500	60	< 500	654	< 500	304

Tab. 3: Chemical composition (values in g/l) at different places in the continuous precipitation line, data measured on industrial copper waste water

pH	Cu	Ni	As	Fe	Bi	Zn	Pb	Mn	Al	Si	Sb	Ca	Mg
Initial solution (pH = 0)	8330	660	630	90	30	30	3	1	40	20	80	–	–
Reactor 1 (pH = 4.0)	4308	482	211	1.1	0.68	4.29	0.11	0.26	19.4	8.7	12.8	60.4	23
Reactor 2 (pH = 7.0)	14.7	265	1.27	< 0.1	0.1	0.92	0.04	0.19	0.03	1.8	2.1	52.1	20
Reactor 3 (pH = 9.5)	2.62	0.49	0.6	< 0.1	0.09	< 0.01	0.04	0.06	0.02	0.3	4.8	39.1	13

NaOH with 4 mol/l concentration in the first reactor and 1 mol/l in the second and the third reactor. After filling the first reactor the flow rate of waste water was set to 7 l/h. As expected the highest consumption of NaOH takes place in the first reactor (16.29 l in 5 h for 40 l of solution). The consumption of 1M NaOH in the second and the third reactor amounted to 3.97 l respectively 0.55 l.

The selected pH-values are confirmed as suitable for precipitation of metals: pH = 4.0 (Fe, Bi, Pb), pH = 7 (Cu, As, Al), pH = 9.5 (Ni, Zn). The flow of metals from reactor to reactor can cause deviations from thermodynamic prediction. The comparison of obtained precipitation efficiencies (% removed from individual reactor inflow) for synthetic and real solution are performed for Cu, Ni, As and Zn, shown in Table 4).

Tab. 4: Precipitation efficiencies for neutralization of a waste water

pH	Cu	Ni	As	Fe	Bi	Zn	Pb	Mn	Al	Si	Sb	Ca	Mg
4.0	48	27	67	99	98	86	96	74	52	57	84	–	–
7	99	45	99	–	–	79	–	27	100	79	84	14	13
9.5	–	100	–	–	–	100	–	68	–	83	-129	25	35

The negative value for antimony indicates the possibility of redissolution at the pH value of 9.5. The data are in very good agreement with prior synthetic solution results of removal of Cu, Ni, Zn, and As, as compared in Figure 12.

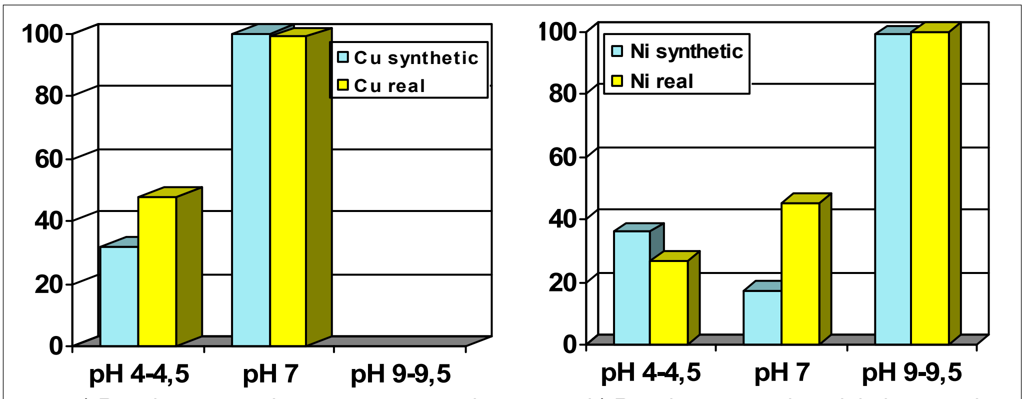
The chemical composition of the solid residue from a collection tank amounts to 26.5 Cu, 2.57 Ni, 1.58 As, 0.55 Fe, 0.93 Se, 0.24 Se, 0.22 Te, 0.13 Zn and Sb, 0.08 Al, 0.05 Bi, 0.02 Pb, < 0.01 Cd and Mn (values in weight-%). The total quantity of solid residue was determined as 608.67 g after a period of 5 h. The production rate of solid residue therefore can be calculated to 3.48 g/l h.

The neutralization of industrial waste water with 4M NaOH shows a temperature increase between 24 °C and 45 °C (synthetic solution between 16 °C and 31 °C) due to of a even stronger chemical reaction with free acid and metal sulphates in solution. In the second and the third reactor the temperature change amounted only to 2 °C as expected from previous tests.

5 Conclusions

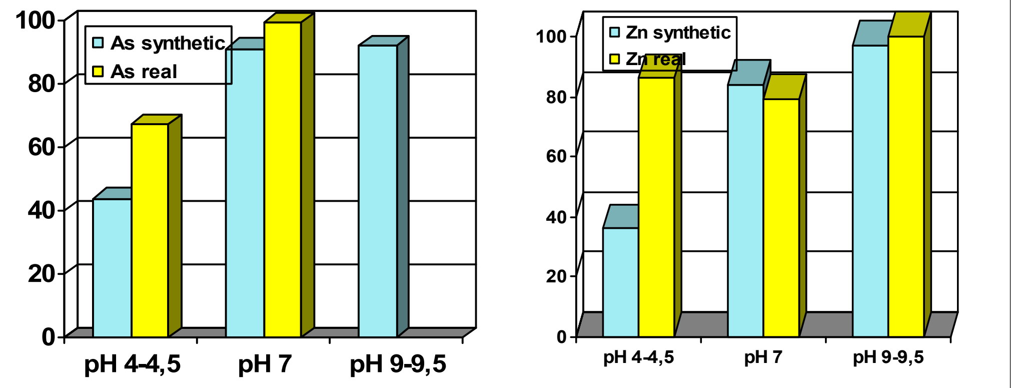
The following conclusions derive from the presented test results:

- Three effective pH-areas were proposed by thermochemical analysis – 3 to 5 (Fe, Bi, Pb), 5 to 7.0 (Cu, As, Al)



a) Results concerning copper removal

b) Results concerning nickel removal



c) Results concerning arsenic removal

d) Results concerning zinc removal

Fig. 12: Removal efficiencies [%], comparison of synthetic and real waste water tests

and pH = 7 to 9.5 (Ni, Zn) – in order to reach highest purification results for the metals contained in the waste water.

- In order to define the reaction parameters for the treatment of highly acidic and contaminated waste water from RTB Bor, Serbia, first experiments were done with synthetic solutions. Suitable parameters were established to be room temperature, concentration of NaOH: 4M in the first reactor, 1M in the second and the third reactor; minimal flow rate of 5 l/h, pH values: 3.9 to 4.5 in the first reactor, 6.5 to 7.0 in the second reactor, 9.0 to 9.5 in the third reactor.
- Because of the neutralization reaction with NaOH a strong exothermic effect is present in the first reactor, where of cause also the highest consumption of NaOH takes place.
- Operating in a continuous reactor, the overflow of metals/compounds from reactor to reactor cause slight deviations from thermochemical prediction.
- The comparison of the obtained precipitation efficiencies for synthetic and real solution regarding Cu, Ni, As and Zn show very good agreement and reach almost 100 % except for Mn (68 %), Si (83 %), Ca (25 %) and Mg (35 %)
- The specific quantity of the final solid (dried) residue amounts to 3.5 g/l h. The chemical composition was measured to be 26.5 Cu, 2.57 Ni, 1.58 As, 0.55 Fe, 0.93 Se, 0.24 Se, 0.22 Te, 0.13 Zn and Sb, 0.08 Al, 0.05 Bi, 0.02 Pb, < 0.01 Cd and Mn (values in weight-%).
- In the future work the investigation will be extended and experiments will be conducted with electrolytically pre-decopperized solutions, using a continuous cell with rotating disc cathodes.

Acknowledgments

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Literature

[1] Nikolic, B., Vucurovic, D. & Ostojic, S. (2002): Nonferrous Metallurgy in Yugoslavia on the End 20th century, 90 (in Serbian).

[2] Ćirković, M. et al. (1999): Kinetics of Copper Concentrates Oxidation in Fluidized Bed Reactor. – In: Mishra, B. (Ed.): Extraction & Processing Division; TMS, Warrendale, 933-944.

[3] Pavlović, J. et al. (2006): Selective chemical precipitation of heavy metals in cascade line reactor. – Environmental Science and Pollution Research, **9**: 1-5.

[4] Schäfer, H. & Rötlich, H. (2005): Arsenentfernung aus Prozesswasser. – WLB, **9**: 16-20.

[5] Stopić, S., Friedrich, B. & Panias, D. (2005): Hydrometallurgical Treatment of Solid Wastes and Wastewaters towards an Environmental Protection. Proc. of the Sixth European Meeting on Environmental Chemistry, Belgrade, Serbia and Montenegro, December 6 to 10, 2005: 34.

[6] Ayres, D. et al. (1994): Removing Heavy Metals from waste. Engineering Research Centre Report: 90.

[7] Burkhart, L. & Voigt, J. (1986): Aqueous Precipitation in Hydrometallurgy. – In: Bautista, R.G, Wesly, R.J. & Warren, G.W. Hydrometallurgical Reactor Design and Kinetic: 441-456. The Metallurgical Society of AIME, Warrendale.

[8] Regulation on hazardous substances in water – Off. Reg. of SRS, No. 53-426/31-04.

[9] www.wvu.edu/~agexten/landrec/2003TFS/Rose03.pdf

[10] www.ams.usda.gov/nop/NationalList/TAPreviews/CalHydrox.pdf

[11] Lee, C., Wang, I. & Hsieh, C. (2004): Removal of Cu (II) from aqueous solution in a fluidized-bed reactor. – Chemosphere, **57**: 1173-1180.

[12] Santos, S. et al. (2004): Treatment of acid mining waters. – Minerals Engineering, **17**: 225-232.

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