Short Research Communications

Selective Removal of Heavy Metals from Metal-Bearing Wastewater in a Cascade Line Reactor

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Abstract

Goal, Scope and Background. This paper is a part of the research work on 'Integrated treatment of industrial wastes towards prevention of regional water resources contamination – INTREAT' the project. It addresses the environmental pollution problems associated with solid and liquid waste/effluents produced by sulfide ore mining and metallurgical activities in the Copper Mining and Smelting Complex Bor (RTB-BOR), Serbia. 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, selective removal of mixed metals could be achieved as the multiple stage precipitation. For this reason, acid mine water had to be treated in multiple stages in a continuous precipitation system-cascade line reactor.

Materials and Methods. All experiments were performed using synthetic metal-bearing effluent with chemical a composition similar to the effluent from open pit, Copper Mining and Smelting Complex Bor (RTB-BOR). That effluent is characterized by low pH (1.78) due to the content of sulfuric acid and heavy metals, such as Cu, Fe, Ni, Mn, Zn with concentrations of 76.680, 26.130, 0.113, 11.490, 1.020 mg/dm^3, respectively. The cascade line reactor is equipped with the following components: for feeding of effluents, for injection of the precipitation agent, for pH measurements and control, and for removal of the process gases. The precipitation agent was 1M NaOH. In each of the three reactors, a changing of pH and temperature was observed. In order to verify efficiency of heavy metals removal, chemical analyses of samples taken at different pH was done using AES-ICP.

Results. Consumption of NaOH in reactors was 370 cm^3, 40 cm^3 and 80 cm^3, respectively. Total time of the experiment was 4 h including feeding of the first reactor. The time necessary to achieve the defined pH value was 25 min for the first reactor and 13 min for both second and third reactors. Taking into account the complete process in the cascade line reactor, the difference between maximum and minimum temperature was as low as 6°C. The quantity of solid residue in reactors respectively was 0.62 g, 2.05 g and 3.91 g. In the case of copper, minimum achieved concentration was 0.62 mg/dm^3 at pH = 10.4. At pH = 4.50 content of iron has rapidly decreased to < 0.1 mg/dm^3 and maintained constant at all higher pH values. That means that precipitation has already ended at pH=4.5 and maximum efficiency of iron removal was 99.53%. The concentration of manganese was minimum at pH value of 11.0. Minimum obtained concentration of Zn was 2.18 mg/dm^3 at a pH value of 11. If pH value is higher than 11, Zn can be re-dissolved. The maximum efficiency of Ni removal reached 76.30% at a pH value of 10.4.

Discussion. Obtained results show that efficiency of copper, iron and manganese removal is very satisfactory (higher than 90%). The obtained efficiency of Zn and Ni removal is lower (72.30% and 76.31%, respectively). The treated effluent met discharge water standard according to The Council Directive 76/464/EEC on pollution caused by certain dangerous substances into the aquatic environment of the Community. Maximum changing of temperature during the whole process was 6°C.

Conclusion. This technology, which was based on inducing chemical precipitation of heavy metals is viable for selective removal of heavy metals from metal-bearing effluents in three reactor systems in a cascade line.

Recommendations and Perspectives. The worldwide increasing concern for the environment and guidelines regarding effluent discharge make their treatment necessary for safe discharge in water receivers. In the case where the effluents contain valuable metals, there is also an additional economic interest to recover these metals and to recycle them as secondary raw materials in different production routes.

Keywords: Cascade line reactor; chemical precipitation; effluent, metal-bearing; heavy metals removal; selective precipitation

Introduction

During the whole copper production cycle, large amounts of solid, liquid and gaseous wastes are generated. These wastes interact with the local environment, thus resulting in serious impacts for the local eco-system [1]. Many types of effluents are produced from pyrometallurgical treatment of copper bearing sulphide ores [2]. These effluents are characterized by low pH due to the high content of residual sulphuric acid and heavy metals, such as Cu, Fe, Ni, Mn, Zn, etc. [3]. The conventional method for heavy metals removal from effluent generally involves chemical precipitation [4,5]. Hydroxide precipitation is the most common treatment technology. Metal precipitation is primarily dependent upon two factors: the concentration of the metal in effluent and the pH of the effluent [6]. Heavy metals are removed by adding alkali such as sodium hydroxide, lime or soda ash to adjust the effluent pH to the point where the metals exhibit a minimum solubility. Hydroxide precipitation is a well-established, simple technology and relatively inexpensive treatment of effluents. It has proven its ability to achieve regulatory effluent limits for several metals, and it is well suited for automation [7–9]. The main drawbacks are: the generation of big sludge volumes that are usually hazardous or unstable in terms of heavy metals mobilization and require either safe land filling or disposal, the further treatment of sludge to meet the disposal criteria, and the valuable metal losses.

In this work a continuous process of chemical precipitation was carried out in cascade line reactor in order to achieve selective precipitation of different metals present in effluent. The main aim of this paper was to study the influence of pH value on the selectivity of precipitation during a continuous process.

1 Theoretical Aspects of Hydroxide Precipitation

Precipitation is a physical–chemical process, in which soluble metals and inorganics are converted to almost insoluble metal and inorganic salts (precipitates) by the addition of a precipitating agent. Most often, an alkaline reagent is used to raise the solution pH, lower the solubility of the metallic constituent, and, thus, bring precipitation about. To effectively precipitate metals, control of pH is essential. Hydroxide precipitation effectively removes cadmium, chromium (3+), copper, iron, manganese, Ni, lead and Zn. Solubility is defined as the number of moles (or milligrams) of solid (precipitate) that will dissolve in a liter of solution. This is an important concept to the process designer, as it dictates the concentration of soluble metals that will be present in the treated effluent after precipitation and clarification [10]. Precipitation alters the ionic equilibrium of a metallic compound to produce a relatively insoluble precipitate. In other words, it induces supersaturated conditions (i.e., the solubility-product constant, typically denoted as K_{SP}, is exceeded). For the solid precipitate C_aA_b (*s*), the following general solubility expression can be written:

$$C_aA_b\ (s) = aC + bA(1) \qquad (1)$$

where

$$K_{SP} = [C]^a[A]^b(2)$$

and [*A*] and [*C*] are in moles per liter. K_{SP} represents the maximum value that the product of the molar concentrations of ions can have at equilibrium conditions for a given temperature. Supersaturated conditions (non-equilibrium, by definition) must be present for precipitation to take place. In a supersaturated solution, the product of the molar concentrations of the ions is greater than the solubility-product constant, or $[Me^{2+}]\ [OH^-]_2 > K_{SP}$.

Removal efficiencies (or solubilities) observed in industrial practice will often differ considerably from theoretical solubility. In most cases, the actual solubility will be higher than the theoretical solubility due to incomplete reactions, poor separation of colloidal precipitates, and the formation of soluble metal-complexes (e.g. metal-chelates) not considered in the equilibrium model. However, the actual solubility may also be lower than theoretical solubility because of co-precipitation [16,17].

As previously discussed, the concentration of heavy metals in solution is strongly dependent on the pH value. Especially the iron concentration decreases in a pH-range between 2 and 5. The precipitation of copper initiates at around a pH of 6, while for other metals, like Ni, Zn, As, Pb and Sb, this pH value is reached in the pH-range between 7 and 10. Re-solubility of Zn occurs in pH-range between 10 and 12. That means the precipitation with NaOH could be a selective process if used in few different pH-steps. The Cu chemical behavior should be clearly differentiated from the chemical behavior of Fe, Ni, Zn and Mn. For the given wastewater, three different steps can be anticipated: a) pH = 4-4.5 (mainly Fe hydroxides); b) pH = 7 (mainly mixed Cu hydroxide - Cu sulfate); c) pH > 10 (Zn, Mn and Ni hydroxide).

2 Materials and Methods

All experiments were conducted in a cascade line reactor at the IME Process Metallurgy and Metal Recycling of the RWTH University Aachen (**Fig. 1**). The main features of the system are:

- adjusted and continuous feeding of effluents,
- injection of the precipitation agent,
- pH measurements and control,
- removal of process gases,
- three reactors, identical in structure and capacity of 10 dm^3.

2.1 Synthetic metal-bearing effluent

The chemical composition of the synthetic metal-bearing effluent, similar to the effluent from open pit, Copper Mining and Smelting Complex Bor (RTB-BOR), used in experiments, is shown in the **Table 1**. The compounds used for synthesis of 1dm^3 of effluent including its quantity (column 4) and discharge limits (according to The Council Directive 76/464/EEC on pollution caused by certain dangerous substances into the aquatic environment of the Community [8]) are noticed in Table 1. Soluble chemical compounds, p. a. grade, carriers of metals, were used for synthesis. All compounds used for synthesis of effluent were dissolved in distilled water. In order to prevent the sedimentation of heavy metals, 2416 mg/dm^3 of H_2SO_4 was added in the water and the pH reached a value of 1.78. Components, such as Cr, As, Pb, Cd, also present in real effluent, were not added because of their very low concentration (lower than discharge limit).

2.2 pH measurement and control

Measurement and control of pH were conducted using a pH Transmitter (2100e, Mettler-Toledo, Germany) with glass electrode InPro 4250 SG (ISM). There is typically a control panel with indicator, starters and control for chemical dos-

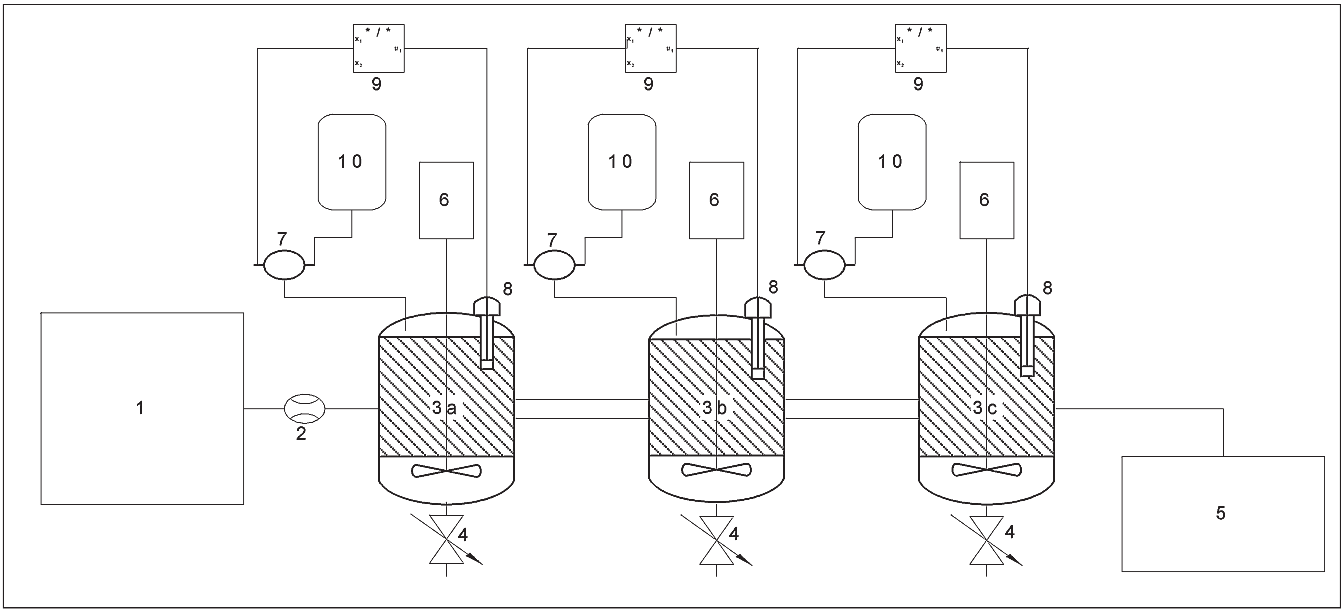

Fig. 1: Cascade line reactor for continuous process of precipitation/chemical precipitation. 1. tank with wastewater (200 dm³); 2. flow meter; 10 dm³ vessel for feed adjustment of solution; 3. three 10 dm³ reactors; 4. valve for regulation of wastewater injection; 5. tank (200 dm³) for purified solution; 6. mixers; 7. solenoid metering pumps; 8. protected electrodes; 9. pH transmitters; 10. tank with precipitation agent

Table 1: Chemical composition of representative contaminated groundwater with average flow rate of 3802 m³/day and required amounts for the used synthesized liquid

Component	Compound	Concentration	Quantity for 1 dm^3	Discharge limit
		mg/dm^3		
Cu	$CuSO_4 \times 5H_2O$	76.68	301.30	0.25–1.0
Ni	$NiCl_2 \times 7H_2O$	0.11	0.46	0.20–1.00
Zn	$ZnSO_4 \times 7H_2O$	1.02	4.63	2.50–10.0
Mn	$MnCl_2 \times 4H_2O$	11.49	41.39	1.00–4.00
Fe	$Fe_2(SO_4)_3 \times 7H_2O$	26.13	80.06	2.00–6.00
	$FeCl_3 \times 6H_2O$		18.20	
Cr	–	0.002	–	0.30–1.00
As	–	0.004	–	0.125–1.00
Pb	–	0.009	–	0.03
Cd	–	0.011	–	0.01
SO_4	H_2SO_4	132.51	2416	1500.00
PO_4	H_3PO_4	1.08	1.08	–
NO_3	HNO_3	1.14	1.14	–
Cl	–	22.14	–	1.00

ing pump. Based on the specific pH set point, which is defined for each reactor, the analyzer transmits signals to a recorder or control system that activates (or deactivates) dosing pumps automatically.

2.3 System for injection of precipitation agent

The precipitation agent was 1M NaOH, which was injected into all three reactors using a solenoid diaphragm-dosing pump (BT4a 1005 ProMinent) with self-dosing head and a maximum capacity of 4.5 dm³/h. Consumption of 1M NaOH in reactors was 370 cm³, 40 cm³ and 80 cm³, respectively.

2.4 Determination of metal content

The samples were taken from the effluent of all three reactors at different pH value (1.80; 4.50; 6.00; 7.00; 8.05; 9.10; 10.40; 11.00). The filtration of samples was performed in filters that did not retain the metals. In order to verify the efficiency of heavy metals removal, chemical analysis was done using the AES-ICP method (**Fig. 2**).

2.5 Other parameters

Total duration of the experiment was 4 h including dosing of the first reactor. The sludge quantity per treated effluent

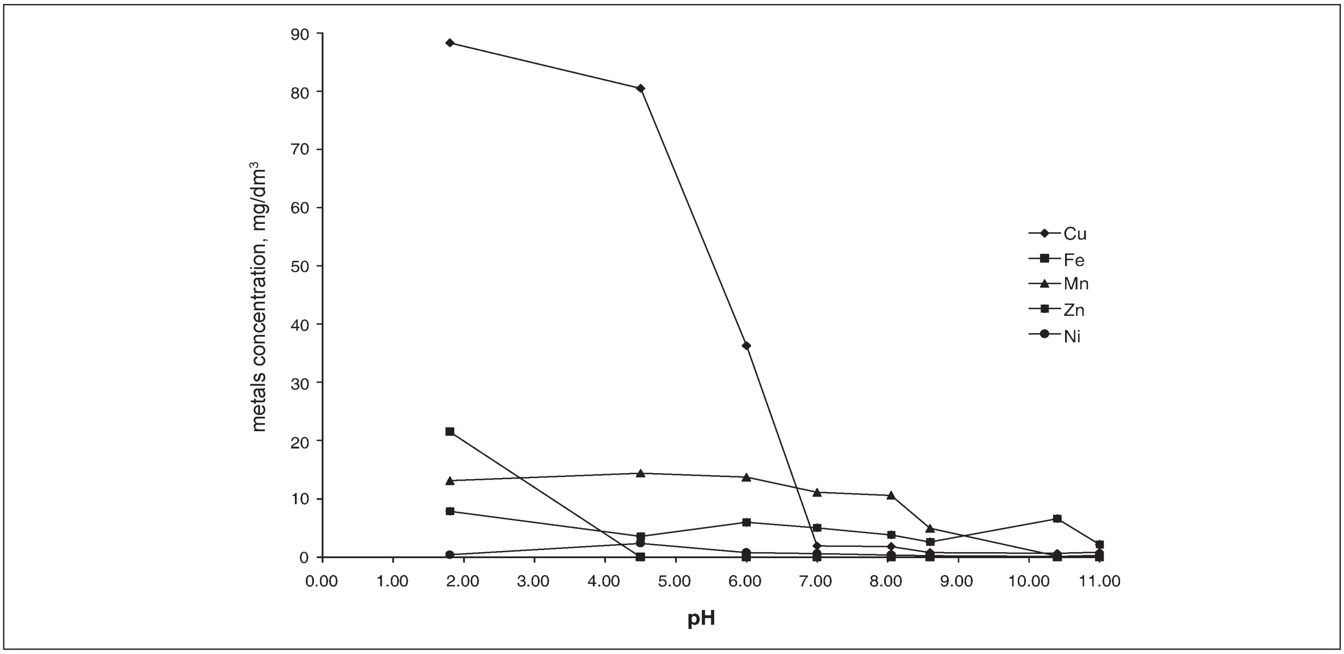

Fig. 2: Effect of pH solution of heavy metals concentration

volume was 0.25 kg/m^3. The quantity of solid residue in reactors was 0.62 g, 2.05 g and 3.91 g, respectively.

3 Results

3.1 Efficiency of copper removal

In the case of Cu, a significant decrease of concentration in effluent was observed at pH values higher than 6.0. In Fig. 2, the concentration of heavy metals as a function of effluent pH is shown. It could be seen that minimum achieved concentration of Cu was 0.62 mg/dm^3 at pH = 10.4, which is lower than the discharge limit [8]. At this pH value, the efficiency of Cu removal reached its maximum of 99.30%. According to the thermodynamical data obtained in Facts age [12], Cu at that pH value was present in effluent in the form of the following species: $Cu(OH)_2$ and $Cu(OH)^+$.

3.2 Efficiency of iron removal

The concentration of Fe in untreated effluent was 21.50 mg/dm^3. At pH = 4.50, content of Fe has rapidly decreased to values < 0.1 mg/dm^3 and maintained constant at all higher pH values. It means that Fe can be precipitated completely at pH=4.5 with a maximum efficiency of Fe removal (99.53%). Thermodynamic data, at that pH value, show that iron can be present in effluent as following species: $FeOH^{2+}$, $Fe(OH)_3$, $FeSO_4{}^{1+}$, $Fe(OH)_2{}^+$, $Fe(SO)_2{}^{4-}$. At pH values higher than 4.5 the amount of insoluble $Fe(OH)_3$ has increased and reached a maximum value (99.99%) at pH of 7.5.

3.3 Efficiency of manganese removal

Maximum efficiency of Mn removal was 99.24% at a pH value of 11. Using thermodynamic data, it can be noticed that Mn was present in solution in the form of $Mn(OH)_2$ at that pH value [13].

3.4 Efficiency of zinc removal

Thermodynamic analysis of the system indicates that complete Zn removal is impossible. The behavior of Zn comparing with other metals present in effluent is more complicated, as is illustrated in Fig.2. It could be noticed that the concentration of Zn did not decrease in the whole pH range. Minimum obtained concentration of Zn was 2.18 mg/dm^3, leading to a maximum efficiency of Zn removal of 72.30% obtained at pH values of 11. In this case, Zn existed generally as $Zn(OH)_2$. If pH value is higher than 11, Zn can be re-dissolved. That means that a stable species of Zn, $Zn(OH)_4{}^{2-}$, occurs in effluent. Taking into account the Zn re-dissolution, the maximum pH value in the third reactor was kept lower than 11 [13].

3.5 Efficiency of nickel removal

As shown in Fig. 2, the concentration of Ni decreased continuously, from an initial concentration of 0.38 mg/dm^3 (pH = 1.80) to its minimum concentration of 0.09 mg/dm^3 (pH = 10.4). This Ni concentration of 0.09 mg/dm^3 is close to the discharge limit for Ni (see Table 1). The maximum efficiency of Ni removal reached 76.30% at a pH value of 10.4. The existing Ni species were: Ni^{2+}, $NiSO_4$, $Ni(OH)^{1+}$, $Ni(SO_4)^{2-}$ and almost 50% of $Ni(OH)_2$.

3.6 Required time to reach the aimed pH value in each reactor

In this experimental study, changing of pH value with time is investigated. Necessary time to reach the targeted pH value in each reactor was determined. The time necessary to achieve the defined pH value was 25 min for the first reactor and 13 min for both the second and third reactors. Based on the obtained results, correlations between pH and time for each reactor were fitted (eq. (3), (4), (5)). For the first and second reactor polynomial expressions of the fifth degree express the relationship between pH and time. The polynomial expression of the third degree describes the relationship between pH and time for the third reactor.

$$y(I) = 0.02x^5 - 0.46x^4 + 0.98x^3 - 1.47x^2 + 1.90x + 1.69 \quad (3)$$

$$y(II) = -0.003x^5 + 0.06x^4 - 0.56x^3 + 2.05x^2 - 2.43x + 4.20 \quad (4)$$

$$y(III) = -0.01x^3 + 0.17x^2 - 0.14x + 6.71 \quad (5)$$

3.7 The effect of pH value change on the temperature in reactors

The temperature in the first reactor was changing over the entire range of pH [1.78–4.5]. In the first reactor, temperature was 21.3°C at the beginning of the process and the maximum temperature reached was 27.1°C at pH = 4.25. There was no difference between initial and final temperature in the second and the third reactor. In whole range of pH value in the second reactor [4.5–7.0], the temperature was constant, 24.8°C. Temperature was decreased in the third reactor to 21.9°C and maintained constant in the entire range of pH [7.0–11]. Taking into account the complete process in a cascade line reactor, the difference between maximum and minimum temperature was as low as 6°C. This indicates that chemical process in cascade line reactor took place without significant heat effect.

4 Conclusions

Based on the findings of this work, the following conclusions can be drawn:

This technology, which was based on inducing chemical precipitation of heavy metals, is applicable for removal of heavy metals from metal-bearing effluents in a three-reactor system in the cascade line. The results presented in this work allowed one to conclude that chemical precipitation could be performed as a two-stage process for representative effluent. In view of the Fe precipitation, the optimal pH value for Fe removal was 4.5 with a maximum efficiency of 99.53%. It means that Fe precipitation occurs completely in the first reactor. Simultaneous removal of Cu, Ni, Zn and Mn, with efficiency of 99.30%, 76.30%, 72.30% and 99.24%, respectively, occurred in the third reactor at pH value in the range of pH 10–11. Finally, it is important to emphasize that the quality of obtained filtrates met the discharge water standards.

5 Recommendations and Perspectives

The worldwide increasing concern for the environment and regulations regarding effluent discharge make their treatment necessary for safe discharge in water streams. In the case where the effluents contain valuable metals, there is also an additional economic interest to recover these metals and to recycle them as secondary raw materials in different production routes.

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