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TECHNICAL ARTICLE

A Process for Advanced Recycling of Water Originating from Mining Operations, with Metal Recovery

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Abstract Water associated with mines and mineral processing, as well as other industrial processes, often contains significant levels of potentially recoverable metals. For example, mineralized water associated with a mining complex in the southern Urals contains high levels of non-ferrous metals (up to 1.1 g/L of Cu and up to 1.8 g/L of Zn). A process has been developed to treat such wastewater as a hydro-mineral resource. Selective extraction of Cu and Zn was incorporated into a proposed water treatment operation by combining techniques such as galvanocoagulation, sorption, and hydrolytic precipitation.

Keywords Copper · Galvanocoagulation · Industrial wastes · Recycling · Technology · Zinc

Introduction

For the non-ferrous mining industry, the problem of treating mine drainage water poses a special challenge due to the formation of wastewater at practically all stages of production. Mining allows ore losses beyond the mine boundaries, operational losses in the underground workings, and moderately saline rock and cut-off grade ore in surface dumps, all of which are a potential source of contamination. Areas of oxidizing ore promote formation of poly-component acidic, high sulphate water with mineralization (of varied cationic composition) levels up to 8–12 g/L. Moreover, this water contamination continues after mining is no longer viable.

Mine dumps (tailings) can discharge highly contaminated water for many decades. Mine dump drainage can be extremely aggressive and acidic (pH 1.5–3.2), with high concentrations of copper, iron, zinc, sulphate (over 30,000 mg/L), and hardness (over 100 mmol/L), and metal concentration ratios that are unfavourable for recycling. In addition, there can be significant seasonal changes in water quality and quantity. The quantities of contaminated water can be huge; mine and dump waters from the South Ural copper and zinc mining plants produce an estimated 0.9 million m^3 of water a day, all of which must be treated. The drainage waters there contain up to 1.1 g/L of Cu and up to 1.8 g/L of Zn. Metal losses (waste) associated with these metalliferous waters are comparable to the metal loss that occurs during the flotation process. Such factors make it possible to consider these wastewaters as a potential hydro-mineral raw material and to necessitate resource recovery.

Most mines employ water treatment processes that produce complex sediments that have a low weight content of non-ferrous metals and are not suitable for effective metal recovery. Dividing the treatment process into stages would allow one to obtain selective products, but would make treatment costlier. In other words, it is generally not considered economically feasible to selectively extract potentially valuable components.

An option being considered is to combine conventional water treatment with hydrometallurgical methods. Recent efforts along this line led to experimental treatment of mine wastewater to produce metal-bearing products suitable for

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further use and water that could be recycled. Processes tested include: hydrolytic precipitation (Shidlovskaya et al. 2005), sulphide precipitation (Khalezov 2009), cementation (Khalezov 2009; Medianik et al. 2012), and ionic floatation (Medianik et al. 2012). However, these processes have not been applied at mine sites, mainly because they would be difficult and expensive to implement, requiring the construction of new treatment facilities. Alternatively, they involve the use of reagents that are expensive and pose an environmental risk, their productivity of a marketable material is low, or the water that is produced fails to meet regulatory requirements.

An analysis of mining operations and its inter-relation with ore beneficiation and metal-making operations has allowed us to conclude that in treating acidic mine waters, it is best to aim at selective recovery of Cu and Zn and to produce a metal-enriched product whose matrix corresponds to the concentrates or charge components used in melting furnaces (Chanturia et al. 2011). Moreover, the metals must be recovered at an early stage of water treatment, the process must not add additional contaminants to the water, and the approach must be compatible with existing treatment facilities. Finally, the approach must be economical.

Following an analysis of various Cu and Zn recovery methods, we developed a technology to process mine and dump waters using a traditional galvanocoagulator charging mix (iron chips and coke) (Chanturia et al. 2011) and an Fe-containing waste product of Cu production, Zn clinker (Orekhova et al. 2012; Shadrunova et al. 2011). The theoretical foundations of galvanocoagulation are described in detail in monographs (e.g. Solozhenkin et al. 2001), but it is based on reactions that result from the formation of a short-circuited galvanic element with intermittent contact between the components of a galvanic couple. Solid wastes containing a galvanic couple can be used as the charge for the galvanocoagulator; the most common galvanic couple is iron–carbon. Galvanocoagulation is characterized by a number of physical and chemical processes, including: electrochemical dissolution of the anode, cathodic reduction of metals, and formation of dissolved complexes. Distinct from cementation, galvanocoagulation involves the transfer of Fe to the sediment, together with the metals that are being recovered, as a result of the anodic dissolution of the charged particles. The inter-electrode space generates magnetite (Fe_3O_4), goethite (FeOOH), and ferrites ($MeFe_2O_4$). The process forms sediment that contains amorphous and crystalline phases of variable composition with enhanced settling properties that can likely be dehydrated in a magnetic field. Moreover, it allows for the selective recovery of Cu and Zn.

Experimental Methods

The development of the process was carried out in the following stages:

- Theoretical validation of the possibility of selective recovery of Cu and Zn;
- Laboratory study of the mechanism of selective recovery of Cu and Zn by sedimentation;
- Parameter optimization, and;
- Industrial testing.

Theoretical validation was carried out using special software (Selector S; Karpov et al. 1997) for simulating physical and chemical processes in natural and man-made systems by free energy minimization. An equilibrium composition was calculated for the heterogeneous multicomponent system: "$CuSO_4$, $Cu(OH)_2$–$ZnSO_4$, $Zn(OH)_2$–Fe–C–O_2–H_2SO_4–H_2O". The matrix consisted of seven independent components, 125 dependent components, 39 solid phases, and 77 electrolyte components. The simulation scope included: C_{Cu}, $C_{Zn} = 10^{-2}$–2×10^{-2} mol/L, $C_{Cu}/C_{Zn} = 1{:}1, 1{:}2$, $Fe/C = 3{:}1$, pH 2–7, $Fe/O_2 = 0.5$–1.5 $Fe/Cu = 1{:}1$–$1{:}10$, overall pressures of 100 kPa, and a temperature of 298 K. A range of Cu and Zn concentrations was selected based on the chemical composition of a mine dump water at a copper mine.

The theoretical results were verified using a laboratory galvanocoagulation unit comprising a gravity supply tank, a solution flow rate control unit, a drum-type galvanocoagulator, and a sediment tank. The galvanocoagulator had a 350 mm long drum with a diameter of 110 mm and a working space volume of 180 cm^3 and was made of 4 mm thick polypropylene. Installed inside the drum were four agitator shelves 300 mm long and 15 mm wide, positioned circumferentially at an interval of 90° from each other. The drum rotation speed was 12 rpm. The charge for the galvanocoagulator consisted of: a mixture of steel chips (St3 ps steel grade) and blast furnace coke (+5 to 10 mm fraction), with a weight ratio of 3:1, and a mixture of magnetic and non-magnetic fractions of Cu clinker waste (+2 to 7 mm fraction) from the Waelz Zn process, with a weight ratio of 3:1.

The liquid-to-solid ratio was 1:5. To avoid accidental errors, prior to each series of experiments, the galvanocoagulator was filled with a new charge that was prepared by passing industrial water through it for 5–8 h until the drainage showed a marked reaction for Fe(III) and the sediment had clear magnetic properties. The experiment was carried out under dynamic conditions; the liquid phase was analysed as it exited the galvanocoagulator, while the charge was analysed both before and after it was exposed to the solution.

The study involved standardized test solutions that accurately simulated actual mine dump water that were prepared using distilled water and by dissolving the required quantities of the following analytical quality reagents: $CuSO_4·5H_2O$, $ZnSO_4·7H_2O$, $FeSO_4·7H_2O$, $Fe_2(SO_4)_3$·$9H_2O$, $Mg(SO_4)$, $Ca(SO_4)$ (within the solubility range), and H_2SO_4. The solutions were analysed using photometric methods, while the sediment was analysed chemically and examined using electronic microscopy.

Results and Discussion

Simulated Experiments

The simulation results indicated that once the system reached equilibrium, within the studied range of input parameters and depending on the acidity, redox conditions, and sulphate and iron concentrations, Cu can be recovered from sulphate solutions, mainly as ferrite, hydroxosulphates, Cu oxide (I), and elemental Cu, while Zn is precipitated as ferrite. Selective Cu recovery should be possible from sulphate solutions with Cu(II) and Zn(II) concentrations of 0.01 mol/L and a Fe/O_2 ratio $n = 1.0$ at a pH of 2.6–4.1 and an Eh of 0.42–0.48 V (Fig. 1a). Zn should stay in solution while Cu is deposited as ferrite (Fig. 1b).

Insoluble Zn-containing compounds are most probable when the pH of equilibrium solutions is above 6.2, over an Eh range of 0.57–0.60 V, with sulphate concentrations below 0.02 mol/L. Selective Zn extraction is only possible when Cu is preliminarily removed from solution. Theoretically, mass concentrations of Cu and Zn in selective precipitates should be possible within an optimal parameter range of 10.67–13.49 and 6.28–11.78 %, respectively.

Laboratory Experiments

Using a traditional charging mix (iron chips-coke) in a galvanocoagulator produces efficient Cu extraction from model sulphate solutions with Cu concentrations of 50–500 mg/L (simulating mine dump water), with extractions occurring quickly: up to 50, 75, and 92 % Cu extraction at 1, 2, and 5 min, respectively (Fig. 2). The high speed of Cu recovery is caused by the kinetics of the cementation electrochemical reaction, which occurs under the conditions of a microgalvanic couple on the Fe-containing charged particle. The proportions of cemented Cu and ferrite Cu in the sediments are approximately equal.

Zinc is efficiently removed after a longer treatment. During 10 min of contact with the galvanic couple, the Zn concentration at the outlet is reduced by 30–50 %. With Zn

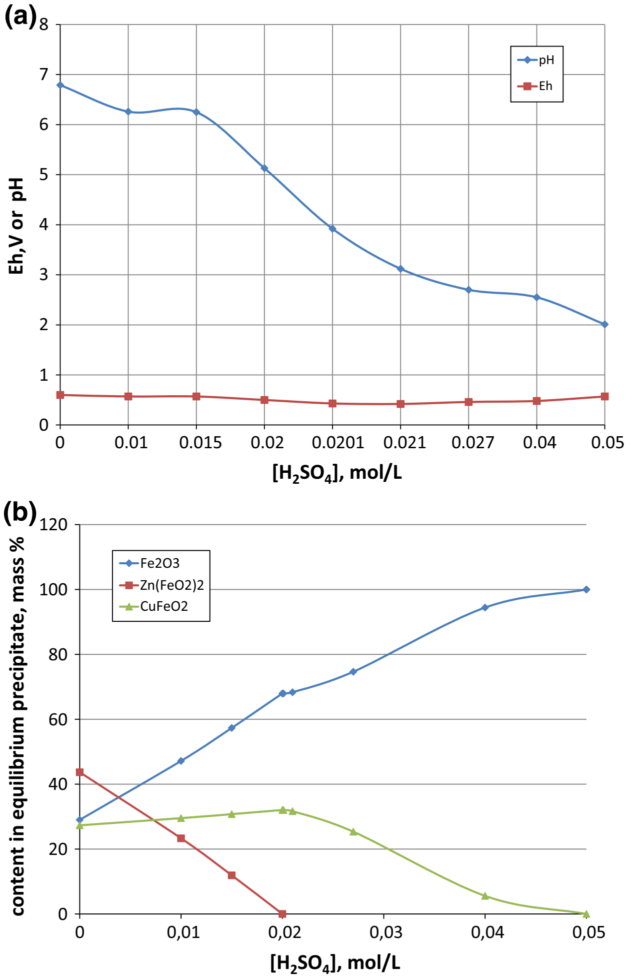

Fig. 1 Main equilibrium parameters of the system $CuSO_4$, $Cu(OH)_2$–$ZnSO_4$, $Zn(OH)_2$–Fe–C–O_2–H_2SO_4–H_2O with $Fe/O_2 = 1.0$ and $C_{cu} = C_{zn} = 0.01$ mol/L; **a** Eh, pH; **b** sediment phase composition

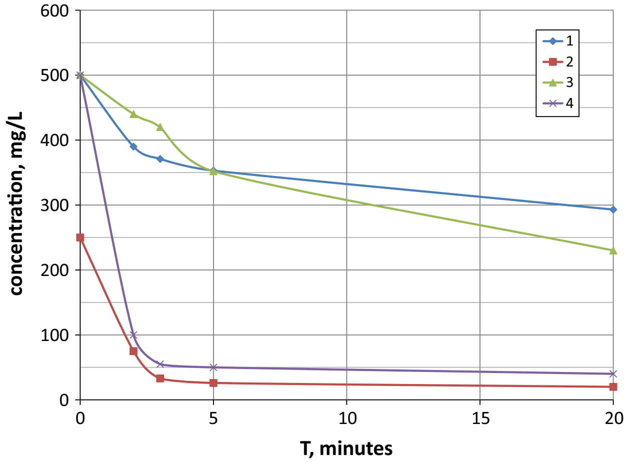

Fig. 2 Kinetics of metal recovery from a two component solution: Cu: *lines 2* and *4*; Zn: *lines 1* and *3*; $C_{cu}/C_{zn} = 1:2$, *lines 1* and *2*; $C_{cu}/C_{zn} = 1:1$, *lines 3* and *4*; Cu: *lines 2* and *3*; Zn: *lines 1* and *4*; $C_{cu}/C_{zn} = 1:2$, *lines 1* and *2*; $C_{cu}/C_{zn} = 1:1$, *lines 2* and *3*

and Cu concentrations in the original solution of 1:1 and 2:1 and a pH of 2.5, significant selection occurs in 2–5 min (Fig. 2). The residual Zn concentration is 3–4 times higher than the Cu concentration. From the efficiency and productivity point of view, the effective range was accepted as 8–12 min. The pH has a strong impact on Zn extraction and mass concentration in the precipitate. After 5 min of treatment, the strongest contrast of Cu and Zn content in the precipitates ($\beta Cu/\beta Zn = 4.25$, where β is a mass fraction of metal in sediment as a percentage; this ratio shows the selectivity of Cu and Zn precipitation) was achieved at a pH of 5.5 of the treated solution, which could be due to Cu being present as a hydroxide in the original solution. In the acidic environment (pH 2.5) at which Cu was extracted at the greatest rate, the Zn content in the precipitate was one-third of the Cu content (Fig. 3).

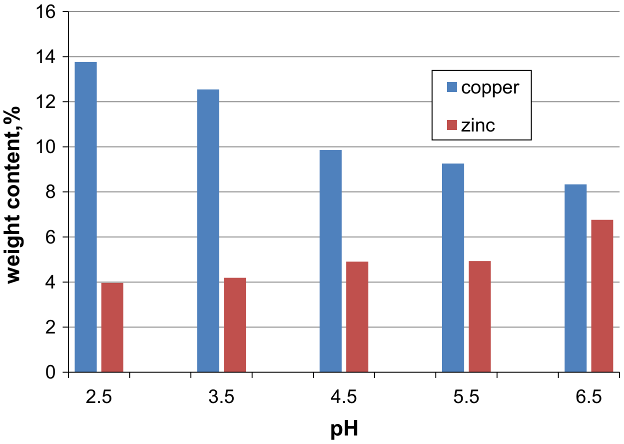

Fig. 3 Effect of pH of the solution on the weight content of metals in the sediment

Table 1 Phase composition of the copper clinker

Description	Weight content, %
Magnetite	14.5
Metallic iron	11
Feldspar	5
Carbonates (Ca, Mg)	5–6
Coke breeze	20–35
Glass (Fe, Mg, Al, Si) O_2	21–22
Mullite (Al_2SiO_5)	7
Cubanite + bornite + chalcocite + tenorite + cuprite (Cu…)	3.8–4.5
Metallic copper	0.1
Jacobsonite ($MnFe_2O_4$)	5
Franklinite + sphalerite + willemite (Zn…)	4.5–5.5
Wollostanite ($CaSiO_3$)	4.5
Kaolinite ($Al_4Si_4O_{10}$) $(OH)_8$	4.3

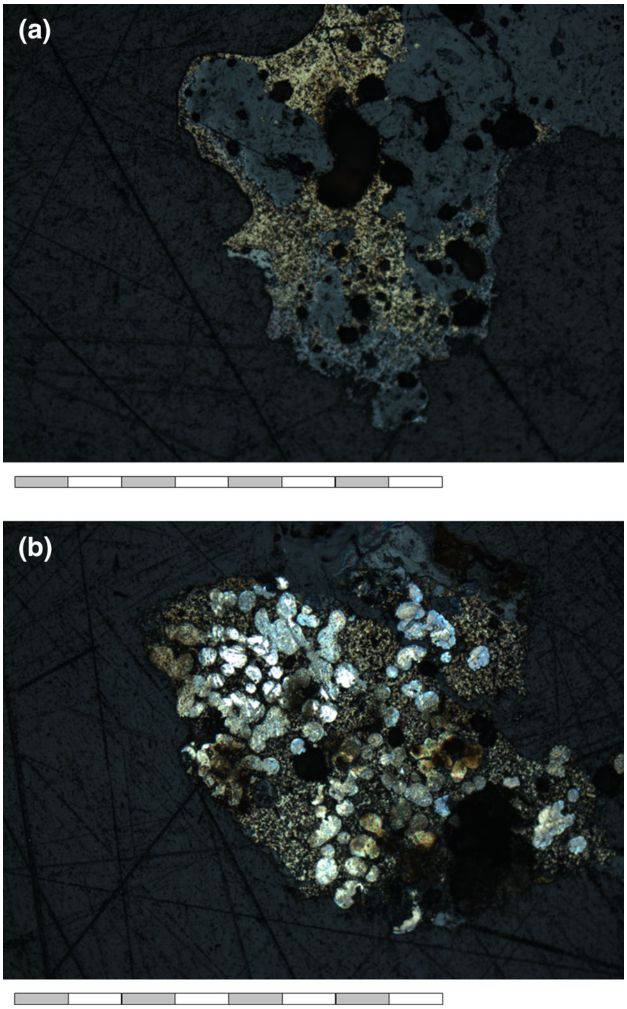

Fig. 4 Microphotographs of **a** non-magnetic and **b** magnetic particles of the charge (one scale division represents 0.5 mm)

Copper clinker was used as a substitute for the steel chips plus coke charge. The phase composition of the clinker is shown in Table 1. The weight contents of Cu, Zn, and Fe were 3.05, 2.18, and 28.65 %, respectively.

Crushing this material down to ≤7 mm, and screening out the finer fraction of ≥2 mm produced magnetic and non-magnetic fractions contrasted by their Fe and carbon content. Non-magnetic fraction lumps contained coke (Fig. 4a), while the magnetic fraction contained globular iron (Fig. 4b).

Factorial experiments using Cu clinker from Waelz processing as the charging mix for galvanocoagulation produced >90 % Cu extraction in all test conditions within 4–6 min of solution contact with the clinker. Higher Zn concentrations in the effluent were observed at treatment times <10–12 min (Fig. 5) and in the acidic pH range (up to 5; Fig. 6). Longer treatment times caused Zn to precipitate (Figs. 5, 6b). When the initial Cu concentration in the wastewater was reduced and/or contact time of the

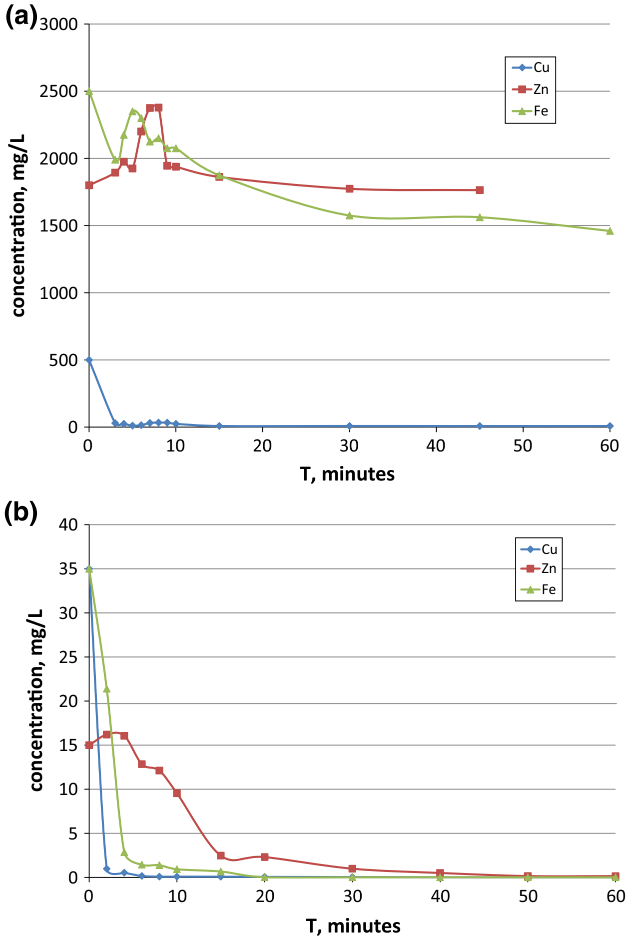

Fig. 5 Dependence of metal content changes in the solution with high (**a**) and low (**b**) concentration on the clinker charge contact duration

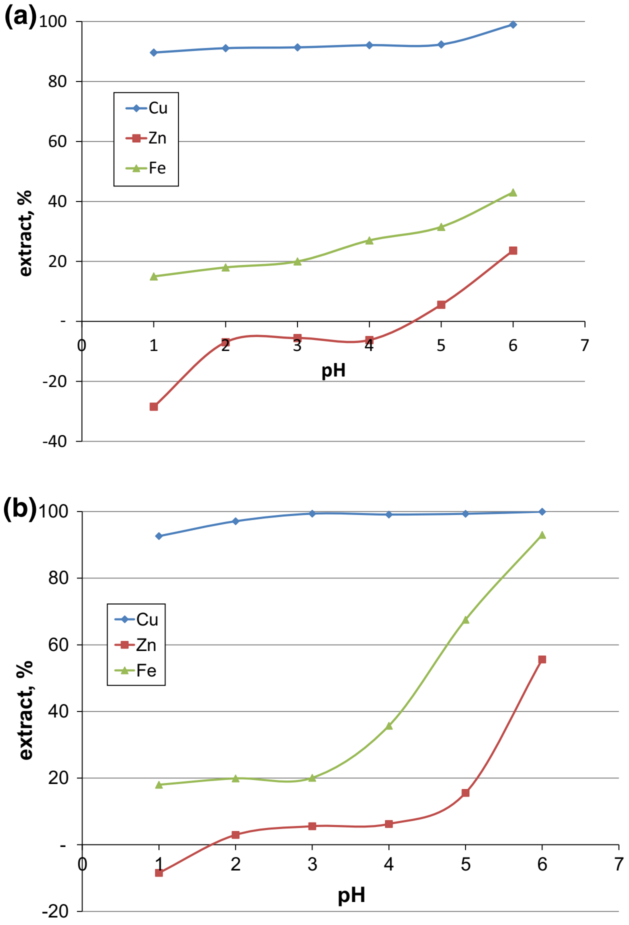

Fig. 6 Effect of pH on metal recovery effectiveness (E), a negative percentage means that Zn dissolved in the acidic pH **a** 5 min, **b** 15 min)

solution with the charge was extended and/or the pH level of the original solution was increased, the Cu mass concentration in the precipitate was reduced.

The optimum ratio of magnetic and non-magnetic fractions of clinker to be used as the galvanocoagulator charging mix was determined to range from 4:1 to 3:2 (20–40 % of the non-magnetic fraction). The optimal treatment time to produce a precipitate with the highest Cu concentration from the acidic solutions was 4–6 min. The Cu mass concentration in the precipitate was 4.44–6.83 %. Longer treatment times caused the Cu content in the precipitate to decrease and the Fe content to increase.

A study of kinetic dependencies on the distribution of Cu and Zn between the liquid and solid phases revealed that with a treatment time of <10–12 min and an acidic pH (up to 5), the Zn concentration in the drainage increased (Fig. 6a). This probably was associated with zinc sulphide entering the clinker, both as a result of direct leaching of Zn, according to the reaction $ZnS + H_2SO_4 + 0.5\ O_2 \leftrightarrow ZnSO_4 + S^0$ (Maslenetsky et al. 1969), and the reaction $ZnS + Fe_2(SO_4)_3^{2-} > ZnSO_4 + FeSO_4 + S$ (Takala 1999). Thus, galvanocoagulation using a Cu-containing clinker as the charge, with a contact time of up to 5 min, combined the processes of precipitating Cu from the solution and leaching of Zn from the clinker, redistributing, in a selective manner, the valuable component between the phases involved in the process.

With longer treatment times and higher pH values, the Zn settles to the sediment (Fig. 6b). However, to achieve Zn and Fe(II) removal rates >90 %, the pH had to be increased to 6–7 and the treatment time near the galvanic couple had to be increased up to 15–30 min.

The results of our theoretical and experimental studies have led to technological process parameters and high-level laboratory tests with water having various Zn and Cu concentrations. The tests were performed with dump water of the South Ural mine and metallurgical plants. Figure 7 shows the process flow. It includes two stages of galvanocoagulation with further settling after each stage and additional drain water purification after the second stage by sorption or hydrolytic precipitation.

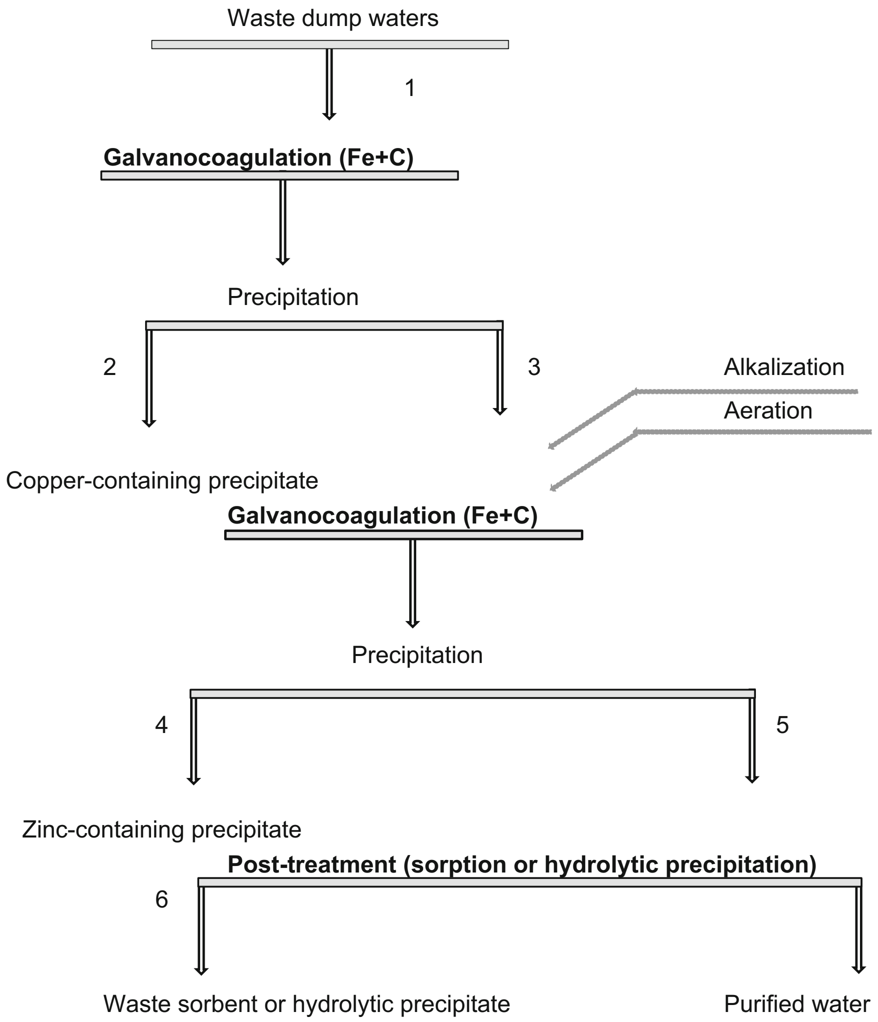

Fig. 7 Mine dump water treatment process flow chart

The water was aerated prior to the second stage and a double geochemical barrier was used for sorption. The upper barrier layer consisted of 0.5–0.1 mm zeolite-containing rocks with a zeolite mass concentration of 12.4 %; the bottom layer consisted of 0.5–0.1 mm of lime. The granular material-solution contact time was 20 min.

For hydrolytic settling, the drain water was treated with a 5 % lime suspension to achieve a pH of 9. Settling was intensified using Magnafloc M-338.

The treatment of mine dump waters using a conventional galvanocoagulator charge yielded Fe oxide products with an average weight content of Cu of 10.9 % after the first galvanocoagulation stage, and 6.78 % Zn after the second stage. The treatment process was continuous. However, as the ferrous anode dissolved, it was necessary to make up the ferrous component of the galvanic couple.

Using a clinker charge with an initial weight content of 3.05 % Cu and 2.18 % Zn, the first stage of mine dump water treatment produced sediment with an average weight content of 5.6 % Cu. The average recovery rate of Cu from the solution was 95.2 % (Table 2). The second stage of the galvanocoagulation produced sediment with more Zn than Cu. The average weight content of Zn was 3.45 %, with a Zn recovery rate of 87.5 %. Zinc transfer from the charge to the solution during the first stage raised the Zn content of the sediment.

Unlike the conventional galvanocoagulator charge, using the Cu clinker charge did not permit continuous recovery. How long the charge lasts depends on how fast the metallic Fe is depleted. Cu mass concentrations increased up to 9.03 % in the first galvanocoagulation stage waste charge after water throughput exceeded the clinker charge weight by 300, while the Zn mass concentration fell to almost 0.63 %. For the Zn recovery stage, with the solution pH brought up to 6.2 by an alkaline agent, the charge was changed simultaneously with the change at the first stage. The Cu and Zn content in the exhausted clinker was practically the same as in the initial charge, while the Fe content had decreased by 10–11 %.

Preliminary metal extraction based on galvanocoagulation resulted in generally smaller contaminant concentrations in the flow before the comprehensive post-treatment

Table 2 Test results

Type of water Type of charge (*Type of post-treatment*)	Parameter	Concentration in water, mg/L				Weight content in sediment, %	
		Initial	After 1st stage	After 2nd stage	After post-treatment	1st stage	2nd stage
Mine dump water							
Steel chips + coke (*sorption*)	Cu^{2+}	220.28	9.09	3.08	0.001	10.9	0.11
	Zn^{2+}	451.03	414.08	14.45	0.01	1.97	6.78
	Fe_{tot}	286.5	336.15	1.9	0.08	49.1	51.2
	pH	3	4.8	7.8	8.1		
Mine dump water							
Copper clinker (*hydrolytic precipitation*)	Cu^{2+}	157.3	11.44	0.029	0.07	5.6	2.16
	Zn^{2+}	208.64	412.93	15.32	0.06	1.69	3.45
	Fe_{tot}	1558.68	1082.42	74.69	0.43	30.71	33.11
	pH	2.8	3.7	6.3	8.97		

stage, and less residual metal concentrations after lime addition and flocculation, compared to precipitation from the original water. Average residual concentrations of Cu, Zn, and Fe fell from 0.16, 0.445, and 0.395 mg/L, respectively, to 0.07, 0.06, and 0.43 mg/L, respectively.

Conclusions

Metal-bearing water from mining and metal-making operations can be viewed as hydro-mineral raw materials. The development of processes to recover valuable components from such wastewater is an important challenge for nonferrous mining operations. The optimal strategy for recycling metal-bearing waste waters is selective recovery of valuable components to a metal-enriched product whose matrix corresponds to the composition of concentrates, fluxes, or other components of melting furnace charges.

The process discussed in this paper is based on the use of galvanocoagulation for selective recovery of Cu and Zn and produces selective enriched sediments with a weight content of metals suitable for metal production. Moreover, its use of solid waste from mining and metal-making operations provides additional ecological and economic benefits. Using Cu clinker from the Waelz process to treat mine dump water economically produced metal-bearing products suitable for use in metal-making, while decreasing water treatment costs (since the pH only had to be brought up to 9), and reduced the area required for waste storage. The mass concentrations of Cu and Zn in the produced sediment was 1.7–2.6 times the initial Cu mass concentration in the clinker and 1.55 times the initial Zn concentrations. The residual concentrations of Cu, Zn, and Fe fell an average 0.16, 0.445, and 0.395 mg/L respectively. The amount of clinker waste that would be used to treat 40×10^6 L of mine water during the process is estimated at 486 t per year. The profitability of this technology is estimated at 9.0 %.

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