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ORIGINAL PAPER

Electrodialytic remediation of copper mine tailings with sinusoidal electric field

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Abstract In this work an electrodialytic remediation cell for copper mine tailings using sinusoidal electric field was analyzed, in order to increase the removal efficiency. The sinusoidal electric field was obtained by applying simultaneously continuous-alternating voltages; in this work an alternating voltage of low frequency was applied. The system was tested considering the effect of: (1) the effective voltage applied to the cell, (2) the period for the alternating voltage, (3) remediation time, and (4) copper complexing capacity of citric acid. According to the conditions studied in this investigation, the laboratory results showed that decreasing the effective voltage improves the remediation action, due to polarity reversal of the system, which reduces polarization during the process, but in terms of the period for the alternating voltage there is no effect. As expected the remediation time and copper complexing capacity of citric acid improves the amount of remediated material and the remediation action in general.

Keywords Electroremediation · Electrodialysis · Alternating current · Direct current · Copper mine tailings

1 Introduction

Chile has the largest mineral reserves of copper and about 32% of the world production of this metal [1], from which 80% is obtained by grinding and flotation processes. Annually, this mineral processing generates large quantities of waste which are transported and disposed as pulps forms in conditioned sites called mine tailing ponds. In these places, mine tailings not only have a damaging effect on water resources by the natural leaching of heavy metals and chemicals, but also generate effects on flora, fauna and air quality by the generation of fugitive emissions of fine particles.

Originally in the mine tailings, heavy metals such as copper could be expected to be found as residual sulfide, which was not liberated in the grinding process prior to flotation. During the disposal in the ponds, the sulfide of the tailings becomes soluble and less stable with time as consequence of physical–chemical changes due to weathering and bacterial actions. In the case of copper, the content of soluble copper is variable due to the heterogeneous origin of the mine tailings in the ponds, such as copper grades which depend on the original characteristics of the tails disposed, and aging of the tailing in the ponds.

One solution to this environmental problem is the conversion of the waste into a chemically stable solid by remediation processes which use electrokinetic phenomena. In this case, the use of the electroremediation technology will imply the periodic application of the method in order to remove the soluble heavy metal such as copper that will be generated with time. Therefore, the remediation action for this heterogeneous solid waste is to remove the soluble copper in the tailings and in this way making the final residue more stable.

The electroremediation is a technique which has raised interest over the last 20 years. This type of remediation is based on the application of an electric field to a humid solid sample using two electrodes. Electro-kinetics remediation (EKR) has proven to be a good method to remove heavy metals in fine solid waste such as soils, clays, ashes and mud [2–4]. On the other hand, electrodialytic remediation (EDR) [5, 6] improves the process with the introduction of

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ionic exchange membranes, isolating the phenomena of remediation from electrode reactions.

The objective of this work is the application of a sinusoidal electric field obtained by applying simultaneously continuous-alternating (DC–AC) voltages, to enhance the behavior of an EDR cell for copper mine tailings. The application of DC–AC electric field as power source for electroremediation of organics contaminants in soils has been investigated lately [7]. In the case of EDR with copper mine tailings, according to the magnitude of DC–AC voltages a periodic reversal of polarity of the system can be produced. This periodic phenomenon improves the efficiency of EDR technique with copper mine tailings [8], mainly because it reduces the polarization in the cell. In this work an alternating voltage of low frequency was applied.

2 Experimental

2.1 Experimental tailings

The mine tailing used for remediation experiments were sampled from the Caren impoundment at Codelco-El Teniente copper mine in VI Region of Chile. Table 1 gives characteristics of the mine tailings used, determined by X-ray Diffraction Analysis.

2.2 Analytical methods

2.2.1 Copper concentration

The total and soluble copper was determined according to the following methods. In both cases the analysis was done in triplicate, and an average was used.

The total copper content of the tailings was determined by adding 20 mL 1:1 HNO_3 to 1.0 g of dry material and treating the sample in autoclave, according to the Danish Standard DS 259:2003 (30 min at 200 kPa 120 °C). The liquid was separated from the solid particles by vacuum through a 0.45 µm filter and diluted to 100.0 mL. The metal content was determined by AAS in flame.

The soluble copper content of the tailings was determined by adding 50 mL H_2SO_4 5% (v/v) to 5.0 g of dry material, and stirring the sample in an 250 mL Erlenmeyer flask for 30 min. The liquid was separated from the solid particles by vacuum through a 0.45 µm filter and diluted to 100.0 mL by adding 10 mL concentrated HCl and distilled water. The metal content was determined by AAS in flame.

2.2.2 pH

pH was measured by mixing 5.0 g dry matter and 25.0 mL distilled water. After 1 h of contact time, pH was measured using a pH electrode.

2.3 Tailings pre-treatment

Before remediation experiments, the tailings were stove-dried for two days at 70 °C. Once dried, the material was pulverized in a mortar and sieved with meshes 4 and #20, until a homogeneous sample was obtained. Depending on the experiment, 1 M sulfuric or citric acid was added to the tailings until an average humidity of 20% was reached.

2.4 Experimental cell design

The principle of the remediation equipment is given in Fig. 1. Experiments were carried out in an acrylic cell; the length of the cylindrical central compartment II was 15 cm, and the inner diameter 8 cm. In order to separate the central compartment from the lateral ones, ion exchange

Table 1 Mineral composition in the mine tailings sample

Quartz	SiO_2
Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$
Ferric clinochlore	$(Mg,Fe)_6(Si,Al)_4\ O_{10}(OH)_8$
Calcic albite	$(Na,Ca)Al(Si,Al)_3\ O_8$
Anorthite	$CaAl_2Si_2O_8$
Hydrated calcium sulfate	$CaSO_4{\cdot}0.6H_2O$
Chalcocite	Cu_2S
Brochantite	$Cu_4SO_4(OH)_6$
Chalcopyrite	$CuFeS_2$
Ramsbeckite	$Cu_{15}(SO_4)_4(OH)_{22}{\cdot}6H_2O$
Wroewolfeite	$Cu_4(SO_4)(OH)_6{\cdot}2H_2O$
Guildite	$CuFe(SO_4)_2(OH){\cdot}4H_2O$

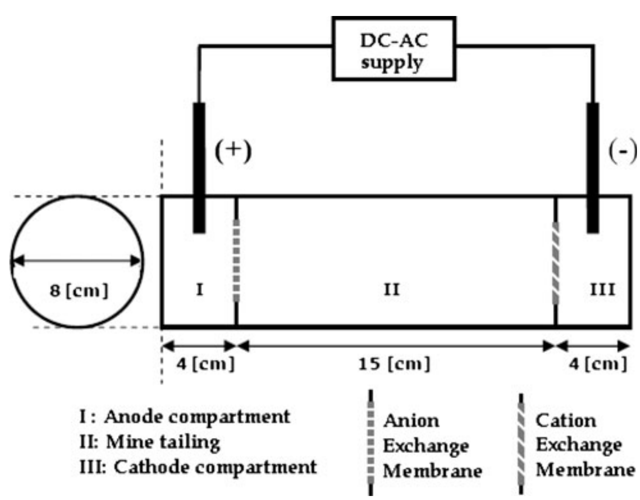

Fig. 1 Electrodialytic remediation cell

membranes were used: cationic CMI-7000 and anionic AMI-7001. The pre-treated mine tailings were placed in compartment II. The electrolytes were initially distilled water, and later sulfuric acid was added to the catholyte to keep the pH under 4.0 to avoid precipitation.

After the experiments were carried out, mine tailings remaining in the compartment II were segmented into three slices of equal size, where copper concentration was measured. In this work anode zone is defined as the slice closest to the anode, center zone the slice in the middle, and cathode zone the slice closest to the cathode.

2.5 Experimental plan

Nine EDR experiments were carried out with the conditions given in Table 2. In all experiments, a sample of approximately 1.3 kg solid dry weight of mine tailings was adjusted to an initial humidity of 20%, using either sulfuric or citric acid solutions.

The objective of the experiments was to evaluate the effect of: (i) the effective voltage applied to the cell, (ii) the period for the alternating voltage, (iii) remediation time, and (iv) copper complexing capacity of citric acid. A reference was conducted to compare these experiments with conventional EDR.

With a sinusoidal electric field obtained by applying simultaneously continuous-alternating (DC–AC) voltages, the effective voltage applied to the cell is determined by:

$$V = V_{DC} + V_{AC} \cdot \sin(2\pi f t)$$

$$V_{effective} = \sqrt{\frac{1}{T} \cdot \int_0^T V^2 dt}$$

where:

V_{DC} = continuous voltage [V]
V_{AC} = alternating voltage [V]
f = frequency [min^{-1}]
t = time [min]
T = period [min]
$V_{effective}$ = effective voltage [V]

3 Results and discussion

Table 3 includes general EDR results in terms of: (i) total and soluble copper concentration ratios, C_F/C_0 (final/initial) in the anode, center, and cathode zone, (ii) the total net electric charge passed through the mine tailing, and (iii) the effective current for the experiment. The net electric charge and effective current were calculated from current–time recording.

Tables 4, 5, 6 and 7 show the results obtained according to the effect of: (1) the effective voltage applied to the cell, (2) the period for the alternating voltage, (3) remediation time, and (4) copper complexing capacity of citric acid, respectively. In these tables the corresponding removal percentage of total and soluble copper were calculated from the concentration ratios of Table 3. As expected usually positive removal values in the anode zone were obtained, and according to the negative values there was accumulation of copper in the cathode zone.

It can be seen from Table 3, all experiments with sinusoidal electric field (experiments 2–9) show better results than the reference experiment (experiment 1) with continuous electric field applied to the cell, since in the case of anode zone the C_F/C_0 concentration ratios of total and soluble copper using sinusoidal electric field are always less than with continuous electric field. These show that the reduction of polarization by applying sinusoidal electric fields improves the remediation performance.

3.1 Effect of effective voltage

According to Table 4, with a remediation time of 7 days, a period for the alternating voltage of 120 (min) and sulfuric acid addition in the mine tailing pre-treatment, when

Table 2 EDR conditions

Exp	Pre-treatment (acid)	*t* time (days)	V_{DC} (V)	V_{AC} (V)	$V_{effective}$ (V)	T period AC (min)
1	Sulfuric	7	20	0	20	0
2	Sulfuric	7	15	20	20.6	120
3	Sulfuric	7	15	20	20.6	60
4	Sulfuric	7	20	20	24.5	120
5	Sulfuric	7	20	20	24.5	60
6	Sulfuric	7	10	20	17.3	30
7	Sulfuric	7	10	20	17.3	120
8	Sulfuric	14	10	20	17.3	120
9	Citric	7	10	20	17.3	120

Table 3 General remediation results in terms of concentration ratios (−)

Exp	Total copper				Soluble copper				Total net charge passed (C)	$I_{effective}$ (mA)
	C_0 (ppm)	Anode C_F/C_0	Center C_F/C_0	Cathode C_F/C_0	C_0 (ppm)	Anode C_F/C_0	Center C_F/C_0	Cathode C_F/C_0		
1	995	0.94	1.01	1.05	423	0.86	1.02	1.12	342	0.6
2	1070	0.90	0.97	1.13	427	0.75	0.92	1.33	3921	6.5
3	1070	0.90	1.00	1.16	443	0.76	1.00	1.39	5162	8.5
4	1080	0.92	0.95	1.13	470	0.82	0.89	1.30	6919	11.4
5	1075	0.92	1.02	1.14	451	0.81	1.05	1.33	7147	11.8
6	1030	0.83	1.14	1.23	457	0.62	1.32	1.52	3107	5.1
7	1060	0.83	1.15	1.18	515	0.65	1.31	1.37	2257	3.7
8	1100	0.82	1.18	1.21	530	0.63	1.37	1.44	3983	6.6
9	1100	0.79	1.02	1.27	482	0.52	1.05	1.62	10603	17.5

Table 4 Effect of the effective voltage applied to the cell in terms of metal removal (%)

Exp	$V_{effective}$ (V)	Total copper			Soluble copper			Net charge (C)	$I_{effective}$ (mA)
		Anode $(1 - C_F/C_0) \cdot 100$	Center $(1 - C_F/C_0) \cdot 100$	Cathode $(1 - C_F/C_0) \cdot 100$	Anode $(1 - C_F/C_0) \cdot 100$	Center $(1 - C_F/C_0) \cdot 100$	Cathode $(1 - C_F/C_0) \cdot 100$		
7	17.3	17.0	−15.0	−18.0	35.0	−30.9	−37.0	2257	3.7
2	20.6	10.0	3.0	−13.0	25.1	7.5	−32.6	3921	6.5
4	24.5	8.0	5.0	−13.0	18.4	11.5	−29.9	6919	11.4

Table 5 Effect of the period for the alternating voltage in terms of metal removal (%)

Exp	T period AC (min)	$V_{effective}$ (V)	Total copper			Soluble copper			Net charge (C)	$I_{effective}$ (mA)
			Anode $(1 - C_F/C_0) \cdot 100$	Center $(1 - C_F/C_0) \cdot 100$	Cathode $(1 - C_F/C_0) \cdot 100$	Anode $(1 - C_F/C_0) \cdot 100$	Center $(1 - C_F/C_0) \cdot 100$	Cathode $(1 - C_F/C_0) \cdot 100$		
6	30	17.3	17.0	−14.0	−23.0	38.3	−31.6	−51.8	3107	5.1
7	120		17.0	−15.0	−18.0	35.0	−30.9	−37.0	2257	3.7
3	60	20.6	10.0	0.0	−16.0	24.1	0.0	−38.6	5162	8.5
2	120		10.0	3.0	−13.0	25.1	7.5	−32.6	3921	6.5
5	60	24.5	8.0	−2.0	−14.0	19.1	−4.8	−33.4	7147	11.8
4	120		8.0	5.0	−13.0	18.4	11.5	−29.9	6919	11.4

Table 6 Effect of remediation time in terms of metal removal [%]

Exp	*t* time (days)	Total copper			Soluble copper			Net charge (C)	$I_{effective}$ (mA)
		Anode $(1 - C_F/C_0) \cdot 100$	Center $(1 - C_F/C_0) \cdot 100$	Cathode $(1 - C_F/C_0) \cdot 100$	Anode $(1 - C_F/C_0) \cdot 100$	Center $(1 - C_F/C_0) \cdot 100$	Cathode $(1 - C_F/C_0) \cdot 100$		
7	7	17.0	−15.0	−18.0	35.0	−30.9	−37.0	2257	3.7
8	14	18.0	−18.0	−21.0	37.3	−37.3	−43.6	3983	6.6

increasing the effective voltage, from 17.3 to 24.5 V, the total and soluble copper removal in the anode zone and the copper accumulation in the cathode zone decreases.

From the EDR results, the improvement could be explained by the positive effect of the polarity reversal, which allows the system to depolarize, for example in the

Table 7 Effect of copper complexing capacity in terms of metal removal (%)

Exp	Pre-treatment	Total copper			Soluble copper			Net charge (C)	$I_{effective}$ (mA)
		Anode $(1 - C_F/C_0) \cdot 100$	Center $(1 - C_F/C_0) \cdot 100$	Cathode $(1 - C_F/C_0) \cdot 100$	Anode $(1 - C_F/C_0) \cdot 100$	Center $(1 - C_F/C_0) \cdot 100$	Cathode $(1 - C_F/C_0) \cdot 100$		
7	Sulfuric	17.0	−15.0	−18.0	35.0	−30.9	−37.0	2257	3.7
9	Citric	21.0	−2.0	−27.0	47.9	−4.6	−61.6	10603	17.5

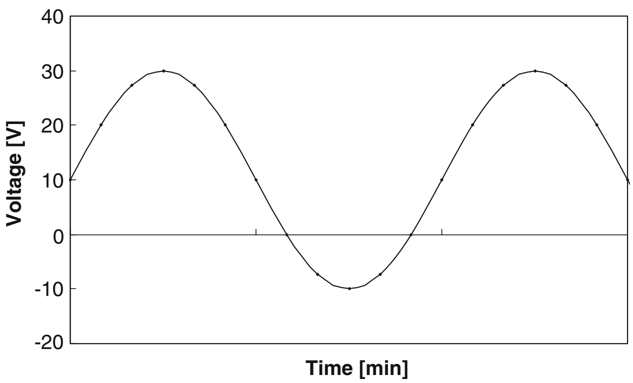

Fig. 2 Voltage–time experiment 7

experiment 7 for 40 min each period (see voltage–time in Fig. 2). In experiment 4, with the highest effective voltage, the polarity reversal phenomenon is not produced. The positive effect of depolarization during the polarity reversal of the system is obtained although in each period electrokinetic phenomena occur in the opposite direction with an energy consumption associated.

Certainly in this kind of process a lowest net charge trough the mine tailing is expected, and the best removal observed is produced by the better use of current through the tailings. In this context, the lowest effective voltage will be favorable in terms of current efficiency and energy consumption.

3.2 Effect of the period for the alternating voltage

In Table 5, the results are sorted in 3 comparable pairs of experiments with different effective voltage each, and the only difference in a pair is the period. In all cases, the total and soluble copper removal, for 7 days experiments with sulfuric pre-treated mine tailings, does not seem to be affected by changing the AC period from 30 (or 60) to 120 min.

However, it must be stated that all experiments were carried out at relative high periods—or low frequencies. It was chosen to work with low frequencies according to previous experiences applying pulsed electric fields with similar frequencies [8].

The total net electric charge and effective current obtained in each pairs are relative similar as expected due to effective voltage applied to the cell.

3.3 Effect of remediation time

From Table 6 it can be seen that higher remediation times would increase the total and soluble copper removal in the center and the accumulation in the cathode zone of the cell, and only a greater amount of remediated material is obtained. On the other hand, in the anode zone, the removal is only significant during the first 7 days.

As expected, the electrical parameters are almost duplicated with the remediation time.

3.4 Effect of copper complexing capacity

From Table 7 it can be observed that the total and soluble copper removal was higher using citric acid in the pre-treatment of the mine tailings. In addition, the copper accumulation is higher in the cathode zone for the citric acid experiment, indicating that copper has moved further than the similar experiment with sulfuric acid, where there is an equal accumulation in center and cathode zones. These findings correspond well with previous results [9].

Total charge and effective current was higher when pre-treating the mine tailings with citric acid, showing that citric acid not only enhance the copper complexation and removal but also increases the conductivity in this system.

4 Conclusions and recommendation

For the conditions studied in this investigation, the conclusions are:

- The EDR with sinusoidal electric field is more effective than the conventional method with continuous electric field applied to the cell.
- Polarity reversal of the system reduces polarization during the remediation, and by this way enhances the process mainly in terms of increasing the copper removal.

- The experimental condition that delivered the best result was when using V_{DC} = 10 V and V_{AC} = 20 V ($V_{effective}$ = 17.3 V), with citric acid, obtaining a 21% total copper removal (48% soluble copper) for a 7-day remediation in the anode zone.
- The remediation seems to be favored by low effective voltage in spite of the relatively long period of polarity reversal, which affects the power consumption.
- The disadvantage of higher power consumption, which normally is produced in processes with polarity reversal, seems to be compensated by increased net removal efficiency in EDR/EKR systems.
- These findings should be complemented with experiments applying sinusoidal electric fields with low periods—or high frequencies—since it could be expected that the depolarization processes, obtained with polarity reversal of the system, would be occurring at higher frequencies too.

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References

1. Chilean Copper Commission (COCHILCO) (2008) Yearbook: copper and other mineral statistics 1988–2007
2. Lageman R (1993) Electroreclamation. Environ Sci Technol 27: 2648–2650
3. Acar YB, Alshawabkeh AN (1993) Principles of electrokinetic remediation. Environ Sci Technol 27:2638–2647
4. Probstein RF, Hicks RE (1993) Removal of contaminants from soil by electric fields. Science 260:498–503
5. Hansen HK, Ottosen LM, Hansen L, Kliem BK, Villumsen A (1997) Electrodialytic soil remediation—a derivative from electrokinetic soil remediation. In: Proceeding of the workshop on electromigration applied to soils remediation, Albia, France, 15–16 May 1997
6. Ottosen LM, Hansen HK, Laursen S, Villumsen A (1997) Electrodialytic remediation of soil polluted with copper from wood preservation industry. Environ Sci Technol 31:1711–1715
7. Lageman R, Clarke RL, Pool W (2005) Electroreclamation, a versatile soil remediation solution. Eng Geol 77:191–201
8. Hansen HK, Rojo A (2007) Testing pulsed electric field in electroremediation of copper mine tailings. Electrochim Acta 52: 3399–3405
9. Rojo A, Hansen HK (2005) Electrodialytic remediation of copper mine tailings: sulphuric and citric acid addition. Sep Sci Technol 40(9):1947–1956