УДК 553.98:551.24

RESEARCHES CONCERNING THE INFLUENCE OF IONIC EXCHANGE COLUMN'S GEOMETRY ON COPPER RECOVERY EFFICIENCY FROM MINE WATERS

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Статья иллюстрирует возможность добычи меди из кислотных шахтных вод в области Cornu-Nedeil-Baia Borsa – Румыния.

Сначала, вода очищалась с использованием $Ca(OH)_2$ для распространения Fe^{2+}. После фильтрации, она отправлялась к ионным обменным колонам, содержащим катионнообменную смолу PUROLITE S-930 для отделения меди.

Изучалось влияние скорости потока на ионнообменную способность и продуктивность определенной колонны как отношение ионнообменной способности на пределе прочности к общей ионнообменной способности.

Для экспериментов использовалось три ионнообменных колонны с одинаковым объемом смолы, но имеющие разные отношения (R) между высотой/диаметром ионнообменного слоя.

Главные заключения, базирующиеся на экспериментальных данных, есть следующие:

влияние R и скорости водного потока на степень использования ионнообменных колонн на пределе прочности есть противоположным

влияние скорости потока более значимо, так как значения R есть меньше.

The paper presents a possibility for copper recovery from acid mine waters from Cornu-Nedeii - Baia Borsa area - Romania.

Initially, the water has been treated using $Ca(OH)_2$ for advanced remove of Fe^{2+}. After filtering, she has been sent to the ionic exchange columns, containing PUROLITE S-930 a copper selective cations exchange resin.

Has been studied the influence of water flow rate on ionic exchange capacity and efficiency of column defined as the ration of ionic exchange capacity on break point and complete ionic exchange capacity

For experiments has been used three ionic exchange columns, charged with the same volume of resin, but having a different ration (R) between height/diameter of ionic exchange bed.

The main conclusions that we can noticed, based on experimental data, are followed:

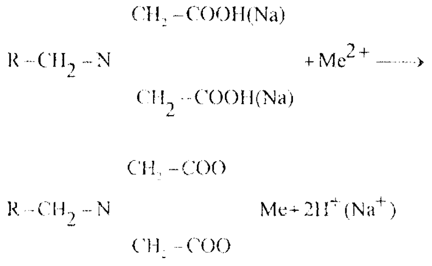
- *the influence of R and water flow rate on utilization degree of ionic exchange columns on break point is opposite;*
- *the influence of flow rate is most significant as value of R is lower.*

Introduction

Mine waters produced by non-ferrous extractive industry having flow rates in range 0,1 – 150 L/s, are characterised by different contents of heavy metals. Usually, they are cleared by using cleaning collective methods, meaning remove of metallic impurities or, mixed with alkaline waters from gold-silver ores processing plants and sender to the tailing ponds. Most of the time, the method mentioned bellow didn't provide a depth cleaning of waters. To assure a concentration of pollutants under the maximum admitted limits, the wastewater are diluted by spilling in the running waters, contribute in this way to continuous degradation of environment. That is necessary an advanced clean up of wastewaters, an action difficult to realised because of high flow rates and a simultaneously presence of a large number of heavy metals cations. The paper present a technology for recovery of copper from acid mine waters using ionic exchange process. First, the waters are treated with $Ca(OH)_2$ 10% to remove the iron, as $Fe(OH)_3$. After the filtering, the solution is contacted with PUROLITE S-930, cations exchange resin, selective for copper. In Figure 1 is presented the technological process for copper ions recovery from acid mine waste waters.

Characterisation of purolite S-930 resin

PUROLITE S-930 is a macroporous polystyrene chelatic resin, containing inside, iminodiacetics groups who retain the heavy metals ions from waste waters[1, 2]. The functional groups of the resin, even she is as Na of H form, will co-ordinate the heavy metals ions, in a cycle, because of attraction between carboxylic function and ions, as follows:



$$R-CH_2-N\begin{matrix}CH_2-COOH(Na)\\ \\ CH_2-COOH(Na)\end{matrix} + Me^{2+} \longrightarrow$$

$$R-CH_2-N\begin{matrix}CH_2-COO\\ \\ CH_2-COO\end{matrix} Me + 2H^{+}(Na^{+})$$

The selectivity of PUROLITE S – 930 is:

$$Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > \\ > Fe^{2+} > Mn^{2+} > Ca^{2+}$$

In Table 1 are presented the main characteriste of PUROLITE S-930 and in Table 2, the standard conditions of work for copper recovery from acid wastewaters [3].

Experimental

The water used for experiments were collected from Cornu-Nedeii Mine, placed in Baia Borsa area, Romania.

Have been used three ionic exchange columns containing the same volume of resin PUROLITE S-930, almost 100 ml. In Table 3 are presented the geometrical characteristic of used columns.

For each column has been studied the efficiency of resin PUROLITE S-930 to retain the copper ions from defferized mine waste water. Each column has been charged by three time, using different flows, as 8V/h, 10V/h and 12V/h, where V is the volume of the resin from the used column. Every charge has been followed by elutions with 250 ml H_2SO_4 200 g/l solution and ablution of column until value pH = 7 in flushing waters.

In each experiment have determined the concentration of copper ions in evacuated water

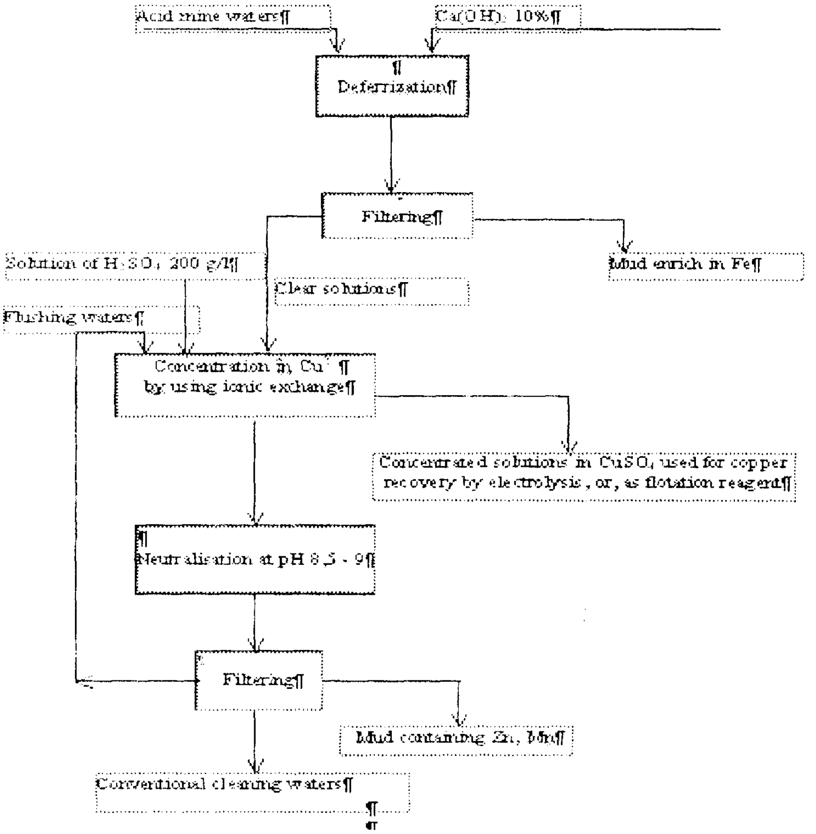


Figure 1. Technological process for copper recovery from acid mine waters

Table 1 - The main characteristics of cationic exchange resin PUROLITE S – 930

Nr. crt.	Property	Value
1	The structure of the matrix of polymer	macroporous divinil-benzen-stiren
2	Physic shape, aspect	opaque, beige spheres
3	Size of particles	+1,2 mm < 2% - 0,3 mm < 1%
4	Active functional groups	iminodiacetics
5	Exchange ionic capacity	H-form (wet) 77 mg Cu^{2+}/g Na-form (wet) 62 mg Cu^{2+}/g
6	Maximum work temperature	70°C
7	The work pH	3 – 6 for H-form 2 – 3 for Na-form

from ionic exchange column. Quantitative analysis of copper ions concentrations have been made using a RADELKIS 110 polarograph.

In Figure 2-4 are presented the results obtained.

Starting from data presented below, have been calculated, for each column, the follow parameters:

- ionic exchange capacity at break point, CBP;

$$CBP = \frac{V \cdot C_{Cu}}{V_r} \quad mg/ml \qquad (1)$$

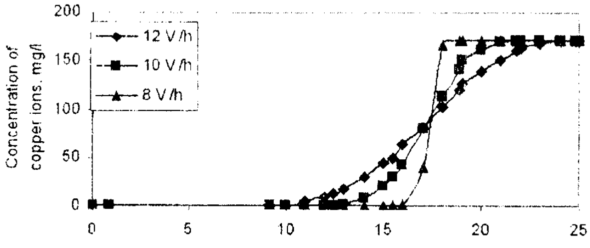


Figure 2 - Variation of copper ions concentration with flow of waste water evacuated from ionic exchange column, R = 7.69

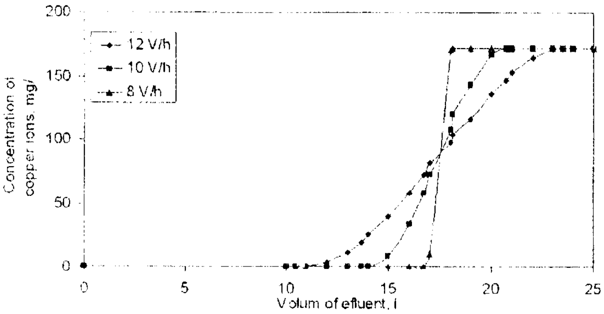


Figure 3 - Variation of copper ions concentration with flow of waste water evacuated from ionic exchange column, R = 12

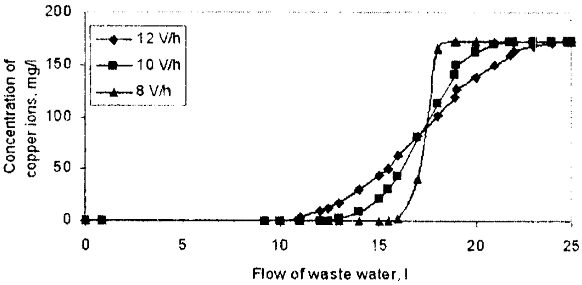


Figure 4 - Variation of copper ions concentration with flow of waste water evacuated from ionic exchange column, R = 16

- full ionic exchange capacity, FC;

$$FC = CBP + \frac{(V_W + V)}{2} \cdot \frac{C_{Cu}}{V_r} \quad mg/l. \qquad (2)$$

- efficiency of the column, EC, as the ration between CBP and FC.

$$EC = \frac{CBP}{FC} \cdot 100 \quad \%, \qquad (3)$$

where:

V – the volume of solution that contains copper ions who cross the column up to the break moment, [ml];

C_{Cu} - initial copper concentration in the solution, [mg/ml];

V_r – the volume of resin placed in the column, [ml];

V_w – the volume of the solution who cross the column until the column is exhausted (the final concentration of copper became equal to initial one), [ml];

The values obtained are presented in the table 4.

Table 2 - Work condition for cationit resin PUROLITE S – 930

Nr. crt.	Operation	Rate, V/h	Solution	Time minutes	Amount
1	Exhausted	8 – 16	work solution	-	-
2	Fluidisation	5 – 7	raw water	5 – 20	1,5 – 6 V
3	Regeneration	3 – 5	mineral acids	30 – 60	140 – 160 g/l HCl 200 – 300 g/l H_2SO_4
4	Ablution	3 – 5	raw water	30 – 40	2 – 3V

Table 3. Geometrical characteristic of ionic exchange used columns

Nr. crt.	Columns	High, H cm	Internal diameter d, cm	Ratio R = H/d
1	A	20	2.6	7.69
2	B	26.4	2.2	12
3	C	32	2	16

Table 4. Values of CBP, FC and EC

Parameter	Column A			Column B			Column C		
	6 V/h	10 V/h	12 V/h	6 V/h	10 V/h	12 V/h	6 V/h	10 V/h	12 V/h
CBP	24.62	18.95	13.12	26.56	21.25	15.77	28.57	23.44	17.96
FC	29.23	29.15	28.91	29.47	29.30	29.14	29.76	29.43	29.08
EC	84.22	65.10	45.38	90.12	72.52	54.11	96.00	79.64	61.72

In Figure 5 is presented the influence of R on efficiency of columns at different flows and in Figure 6, the influence of flows on efficiency of columns at different values of R.

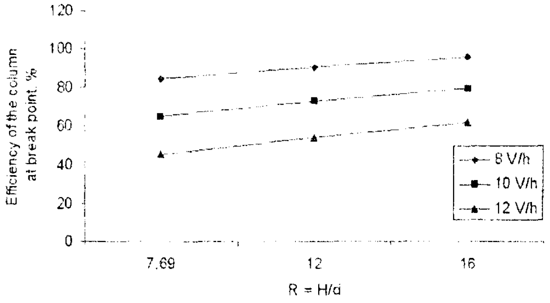


Figure 5. The influence of R on efficiency of the column at break point, for different flows

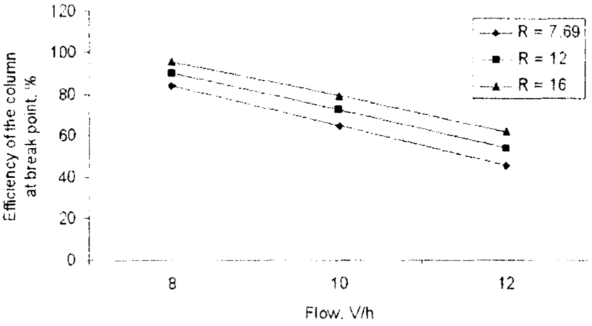


Figure 6 The influence of flows on efficiency of the column at break point for different values of R

Conclusions

Based on experimental data, we can conclude the follows:

- For each studied column, no matter of geometrical size, rise of flows leads to decrease of the efficiency of the column at break point.
- The influence of flows on recovery copper ions efficiency is more important as ratio R is lower. Thus, at ratio R = 7.69, the increase of flow from 8V/h to 12V/h determined a decrease of column efficiency by 38.84% (from 84.22% to 45.38%). In the same time, at ratio R = 16, the same increase as flow, leads to decrease of column efficiency by 34.24% (from 96% to 61.76%).
- The parameters R and flow of defferized mine water have an opposite action on efficiency of columns at break point. Between they, the flow of mine water has the most significant influence.

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