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SOME PROBLEMS IN THE SEPARATION OF COPPER AND IRON FROM MINE WATERS

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SUMMARY

Some copper mine waste waters contain, in addition to copper, also iron ions, the presence of which makes it difficult to recover copper by ion-exchange methods, particularly as the high acidity of the water lowers the capacity of weakly acidic ion exchangers. Using the proposed method, mine water samples were completely freed from iron and the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ form was sorbed using the full capacity of the weakly acidic resin Ostion-KM (Na^+). After elution with sulphuric acid, we achieved a concentration of Cu^{2+} ions in solution, eliminating all of the iron present in the original sample.

INTRODUCTION

The isolation of copper from solutions, mainly from mine waters containing other metals, has always been a problem and remains so as far as ion-exchange methods are concerned. The most common metal in mine wastes is iron and its ions are simultaneously sorbed with copper ions, thus decreasing the capacity of the resin and hindering the concentration of copper ions. Therefore, in our studies on the behaviour of iron and copper ions in mine waters, we wished to decrease the amounts of iron and other metals present before treating the waters with resins. Common methods for the isolation of copper ions from low-grade copper ores and from copper wastes, such as leaching with dilute sulphuric acid and then winning the copper either by reduction with metal and electrolysis, or obtaining it in the form of crystalline copper sulphate or other forms¹, are useful also in the separation of copper from mine waters. However, with varying and low copper contents, and when other metals such as iron, magnesium, lead, manganese and zinc are present, the results are unsatisfactory.

The most commonly used and promising method for treating mine waters nowadays is the cementation method, which gives a 41% copper recovery², using the lower standard redox potentials of iron ions.

The use of ion-exchange methods for the separation of copper from mine waters on a laboratory scale was first used by Quarm³. Before the use of Amberlite IRC-5u, he pre-treated the water, containing 0.15–0.30 g/l of copper and 1.5–3.0 g/l of iron, by adding calcium carbonate. In this manner, he sorbed in the resin 84% of copper and 20.1% of iron.

Quarm³ also recovered similar amounts of copper and iron using a weakly acidic cation-exchange resin. Vránová⁴ studied the sorption of copper ions from mine waters from the Smolník locality and found that resin in the Mg^{2+} form was more useful than in the Na^+ or H^+ form.

We have treated samples of the same mine water containing lower contents of copper and also containing silica solids by sorption on a weakly acidic resin of Czechoslovak origin, namely Ostion KM (Na^+), and by floating the resin in order to separate it from the solids, recovering 66.7% of the copper, and later⁵ we treated waters without solids, with a 92.2% recovery of copper and a 20.53% recovery of iron.

We then treated samples of mine water containing higher copper contents, by pre-treatment with calcium carbonate, and separated 95.2% of the iron; we were then able to sorb 73.2% of the copper on the Na^+ form of the resin and subsequently all of the remaining iron content by sorption on the Mg^{2+} form of the resin⁶. By elution, we achieved a 4.8-fold concentration of copper-containing mine water.

It is evident that the main disadvantages of the cementation method are low recovery, a great dependence on the variation in copper content in wastes, and also the quality of the copper metal obtained which is not satisfactory without a pre-treatment step. Ion-exchange methods, involving the use of pre-treated resin to permit the selective sorption of copper from mine waters, do not eliminate the possible sorption of other metal ions present in waters, which decrease the sorption capacity of the resin. The capacity of weakly acidic ion exchangers is also not fully utilized owing to the acidity of mine waters. Therefore, in this work we have investigated a more sensitive method for the pre-treatment of resins and also of the samples of mine waters.

EXPERIMENTAL

The resin used was weakly acid Ostion KM (Na^+), 0.315–0.8 mm, in a column containing 26 ml of resin.

The mine waters from the Smolník locality represented two concentration ranges:

Sample 1:

Original pH 2.24: 98.0 mg/l Cu^{2+} ; 142.0 mg/l Fe^{3+}

After pre-treatment to pH 10.10: 89.0 mg/l Cu^{2+} ; 0 mg/l Fe^{3+}

Sample 2:

Original pH 2.24: 156.5 mg/l Cu^{2+} ; 205.8 mg/l Fe^{3+}

After pre-treatment to pH 10.12: 140.1 mg/l Cu^{2+} ; 0 mg/l Fe^{3+}

The water, after establishing the optimal pH range for pre-treatment, was pre-treated with 25% ammonia solution and, after filtering off the precipitate and all the Fe^{3+} formed, the solution with the remaining Cu^{2+} content was sorbed in the form

of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ on the resin in the Na^+ form at a flow-rate of 0.123 ml/min per millilitre of resin and then eluted with sulphuric acid.

RESULTS

The copper content in mine waters after pre-treatment with various amounts of 25% ammonia solution was as shown in Fig. 1. The optimal pH value was found to be 10.12. Sample 1, after pre-treatment with 25% ammonia solution to this pH value, contained 89.0 mg/l of Cu^{2+} , all Fe^{3+} present being filtered off, and sample 2 at this pH value contained 140.1 mg/l of Cu^{2+} .

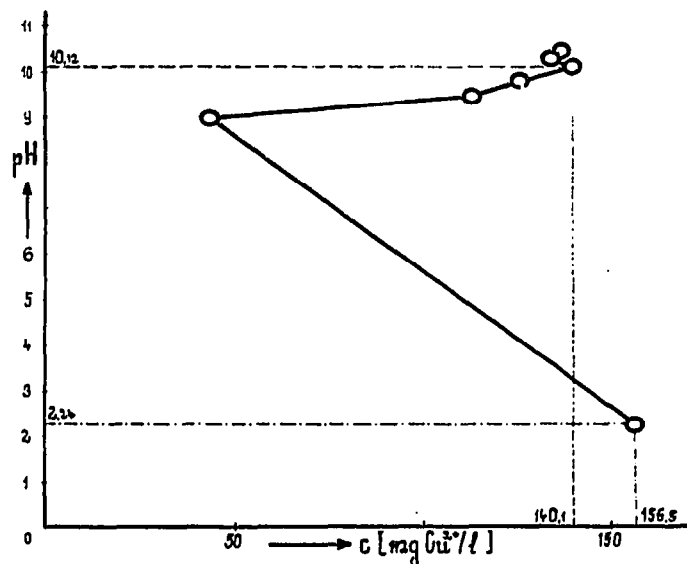


Fig. 1. Optimal value of pH after pre-treatment of mine water.

The sorption conditions of both samples are shown in Fig. 2. The amounts of copper sorbed were 74.6% in sample 1 and 71.3% in sample 2 and, after elution with the optimal⁶ concentration of 10% sulphuric acid, we achieved 9.5 and 5.3-fold concentrations, respectively, and recovered a solution of relatively pure copper sulphate.

A comparison of results from our previous methods with those from the proposed method is given in Table I.

DISCUSSION

For mine waters with varying copper and iron contents, we have developed a method of pre-treatment that eliminates the disadvantages of other methods with respect to the recovery grade, purity of isolated copper, time required and also the complete use of resin capacity. Pre-treatment of samples with ammonia solution to the optimal pH and subsequent sorption of the copper-containing solution on a weakly acidic resin in the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ form eliminates the other metals present and,

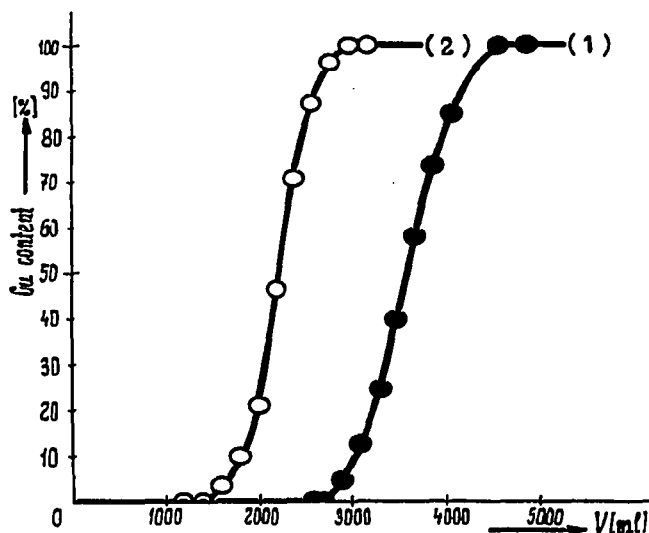


Fig. 2. Sorption of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ from mine waters. (1) 89 mg/l of Cu^{2+} ; pH = 10.10. (2) 140 mg/l of Cu^{2+} ; pH = 10.12.

after 100% elution of Cu^{2+} ions⁶, satisfactory 9.5 and 5.3-fold concentrations of relatively pure copper solutions are achieved. We obtained more complete results by studying mine waters in the Smolník locality after different periods of rain, and found mainly two ranges of copper and iron contents in the waters.

TABLE I

COMPARISON OF RESULTS OBTAINED BY DIFFERENT METHODS

	<i>Cementation²</i>	<i>Ion exchange</i>		<i>Ion exchange (this work)</i>			
	<i>Cu</i>	<i>Cu</i>	<i>Fe</i>	<i>Cu</i>	<i>Fe</i>	<i>Cu</i>	<i>Fe</i>
Water pretreated with to pH		CaCO_3		NH_4OH (1)		NH_4OH (2)	
Concentration of original sample (mg/l)	121.5	199.2	262.1	98.0	142.0	156.5	205.8
Concentration of pre-treated water (mg/l)		195.0	12.5	89.0	—	140.1	—
Volume of sorbed water (ml)		525		4.600		3.000	
Sorbed (mg)		102.4	6.6	409.4	—	420.3	—
(%)		75.04	6.56	305.0	—	298.1	—
Eluted with 10% H_2SO_4 (mg)		73.5	99.4	74.6	—	71.3	—
Recovery from original water (%)	41	70.28	0.05	304.9	—	297.9	—
(concentration)		93.7	0.76	100	—	100	—
Recovery from pre-treated water (%)		67.1	0.04	67.7	—	63.5	—
(concentration)		3.5	—	8.6	—	4.8	—
Recovery from pre-treated water (concentration)		68.7	0.77	74.5	—	70.9	—
		3.6	—	9.5	—	5.3	—

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