Selective Recovery of Copper and Cobalt from Mine Effluent

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Abstract

Adsorption is a powerful tool to remove contaminants ions from water. In here, two major limitations of adsorption technique (the accumulation of exhausted waste-adsorbent and poor selectivity) are overcome by time-dependent selectivity and cycling of adsorbent by selective desorption. Real mine effluent containing 917 ± 92 mg Cu/L and 36,9 ± 3,7 mg Co/L was used as a real-life sample to demonstrate the ability to separate Cu and Co by means of adsorption on MgO with subsequent recovery copper by leaching and cobalt as sulfide. A brief economic evaluation supports the suitability of the approach.

Keywords: selective adsorption, copper, cobalt, mine effluent, economic evaluation

Introduction

The fast-growing electric vehicle market has increased the need for efficient lithium, cobalt, and nickel containing batteries. It has been estimated, that the cobalt requirements will grow by 15-fold by 2030, as compared to 2019, while the trading of cobalt is often associated with human right violations (Claudiu 2018). However, cobalt, and other critical and valuable materials, can be recovered from industrial side streams and from acid mine drainage, or mine process water. While the concentration is usually low (5 – 40 mg/L for Co, for example) the large flow of water, often hundreds of cubic meters per hour, makes those a substantial source of valuable elements.

Commonly, mine water is treated by applying $CaCO_3$ or $Ca(OH)_2$ to co-precipitate the impurities as faulty cations within the lattice of the forming gypsum or as metal hydroxides by the increase in pH (Geldenhuys 2003). However, this approach has the valuable metals seized in a calcium-rich low metal matrix and requires large storage capacity for tailings. In here, the selective recovery of cobalt and copper from mine effluent is discussed (CCR).

Samples

Mine effluent was received from a mine in Zambia, taken before neutralization process and subsequent flow to environment. Initial parameters are a pH 2,52 and an electric conductivity of 6,82 mS. The samples were analyzed by ICP-OES from accredited laboratory and the results of initial mine effluent shown in Table 1. Synthetic waters with the main constituents was mimicked for initial selectivity tests and for the first eight cycles, with the concentrations depicted in Table 1. After establishing an efficient routine for the recovery path (CCR) the remaining four cycles were repeated with real mine water sample.

Methodology

AAS analysis were conducted with a Perkin Elmer 5000 spectrometer (air-acetylene flame). XRF data was collected with a Panalytical Minipal 4 XRF spectrometer utilizing semiquantitative Omnian parameter. The XRD diffractograms were collected on Panalytical Xpert PRO diffractometer with Co α-radiation at a wavelength of 1.79 Å. Diffractograms were interpreted with Highscore plus and commercial database.

UV-vis spectra were recorded with Specord 50 PLUS from Analytik Jena AG. Deionized water had an electric resistivity of 0.036 mΩ.

Initial tests were conducted with synthetic mine water, prepared according to the concentrations determined by ICP-OES from real mine water, containing the most important contaminants and target elements as shown in Table 1.

Adsorbents

Adsorbent was prepared by calcination of magnesite tailing from local Finnish talcum mine. The main constituents of adsorbent are MgO (58.8%), Fe_2O3 (13.5%), and SiO_2 (21.7%) residues, with MgO being in periclase form. The XRF data of new and copper loaded adsorbent after 10th adsorption cycle is gathered in Table 2.

Iron Removal

Iron is an interfering ion in adsorption and lowers the adsorption capacity by preferential adsorption. The iron in the mine water was removed by pretreatment procedure, without affecting the concentration of the desired cobalt and copper ions. As such, the pH was adjusted carefully to pH 5 by dropwise addition of 5 M NaOH. The precipitated iron hydroxides were filtered through glass powder on filter paper, by means of suction filtration.

Table 1 Initial concentration of elements from mine water sample and dissolved cobalt sulfide, ICE-OES in mg/L.

Element	mg/L mine water	synthetic mine water mg/L	mg/L dissolved CoS
Al	114,8		1,61
As	<0,75		< 0,075
B	<1		< 0,1
Ba	<0,25		0,781
Be	0,59		< 0,025
Ca	510	59	41
Cd	<0,1		0,025
Co	36,9	37,552	132
Cr	0,62		0,22
Cu	917	895,05	1,6
Fe	15,4	15,434	0,925
K	66,6		5,75
Mg	953	940	59,5
Mn	264	105,14	475
Mo	<0,25		< 0,025
Na	18,4		30,4
Ni	0,99		3,37
P	5,63		< 0,25
Pb	<0,75		< 0,075
S	2680		242
Sb	<0,75		< 0,075
Se	<0,75		< 0,075
Sn	<0,75		< 0,075
Ti	<0,75		< 0,075
V	<0,25		< 0,025
Zn	2,1	2,36	0,112

Table 2 Adsorbent XRF data.

Element	Adsorbent raw, %	after 10th adsorption, %
MgO	58,8	32,64
SiO$_2$	21,7	17,53
SO$_3$	1,28	8,13
K$_2$O	0,12	0,05
CaO	1,11	0,56
Cr	0,25	0,26
Mn	0,15	0,61
Fe$_2$O$_3$	13,58	19,62
Ni	0,16	0,12
Cu	-	11,66

Copper Adsorption and Recovery

To establish selectivity time dependent tests were performed. After iron removal, the solution was divided into 12 aliquots of 200 ml water. MgO-adsorbent was added to the complex water matrix at pH 5 with an overall adsorbent dose of 3 g/L. In appropriate time intervals, the adsorbent was filtered off and the copper and cobalt concentration measured by AAS method. The data from 5 min to 23.5 h is depicted in Figure 2. Copper adsorption is preferential over cobalt adsorption and starts only after complete removal of copper. The study was repeated at lower pH, without pretreatment, and the same overall trend however with slight time delay was observed, most likely due to the slow pH rising effect of MgO to pH 5 – 6, as depicted in Figure 2.

After filtration, copper was recovered by leaching with ammonia solution at 5 % (cycle 1–9) or 10 % (cycle 10–12). The treatment cycle was repeated twelve time and the copper, cobalt, and manganese removal percent is depicted in Figure 3, after each cycle adsorbent mass (loss from filtration, handling and dissolution, less than 10%) reconstituted to 3,00 g/L. Copper was removed selectively with very little effect on cobalt and manganese concentration as can be seen Figure 3. Copper was leached with 5% ammonia, and the adsorption capacity slowly declined to 50% copper removal at
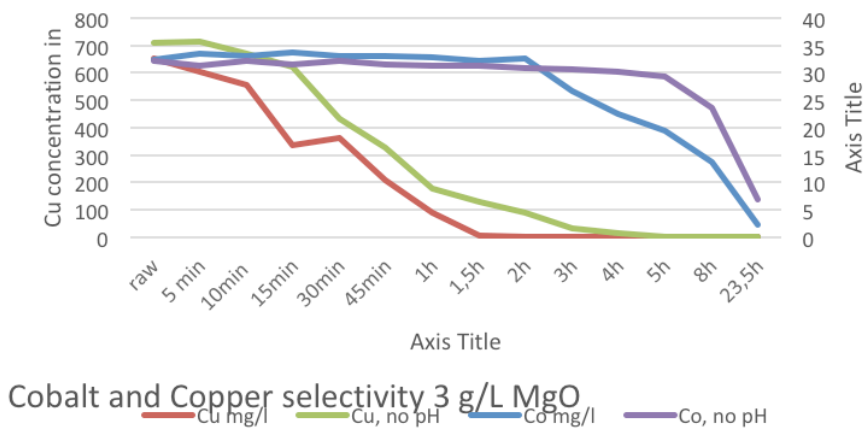

Figure 2 Time dependent adsorption of copper and cobalt onto MgO, at 3 g/L adsorbent dose at pH 5 and pH 2.5 (raw mine water, no pH and iron removal).
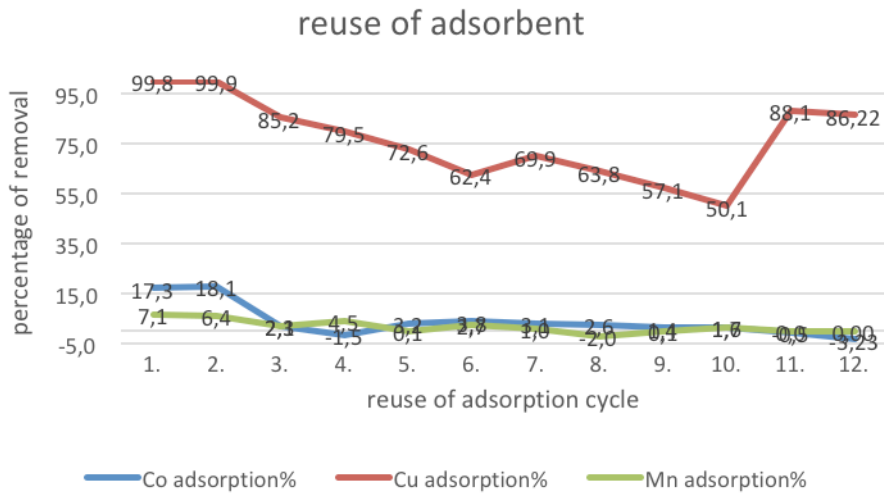
Figure 3 Sorption and desorption of MgO utilizing synthetic mine water, negative datapoints due to measure uncertainty.

tenth cycle, with initial concentration of 895 mg/L Cu and an adsorbent dose of 3 g/L. XRF spectroscopy, refer to Table 2, confirmed the visual analysis of 11% copper loading of adsorbent. Leaching with 10% ammonia removed copper and restored adsorbent capacity, as seen after 11th cycle.

Cobalt Recovery

After copper removal by adsorption, cobalt was precipitated as CoS by dropwise addition of Na_2S upon stirring. Black precipitate formed was filtered off, dissolved in HNO_3, and sent to accredited laboratory for quantitative analysis. The concentration of contaminants in dissolved CoS is combined in Table 1. Manganese (475 ± mg/L) precipitated with the cobalt (132 ± 13 mg/L) to give cobalt/manganese sulfide. Other impurities are coprecipitated magnesium and calcium, and enrichment of less than 1%

nickel (3,37 ± 3,4 mg/L). Copper is present in 1.6 ± 0,16 mg/L.

Proposed treatment scheme for copper and cobalt recovery (CCR)

To put the proposed CCR scheme into piloting stage, only mature and commercial technique is required for pH adjustments, filterings, and adsorbent dosage. The process can be overviewed in Figure 1.

Economic Considerations

Three main valuable contaminants are included in mine effluent from Zambian mine: copper, cobalt, and manganese. At the current flow of 800 m³/h and 19200 m³/d and the prices for copper, cobalt, and manganese being 4617 USD/t, 29500 USD/t, and 2000 USD/t, respectively, (infomine, June 2020) the mine is losing daily a potential revenue of 2768 USD per day or 1010203 USD per
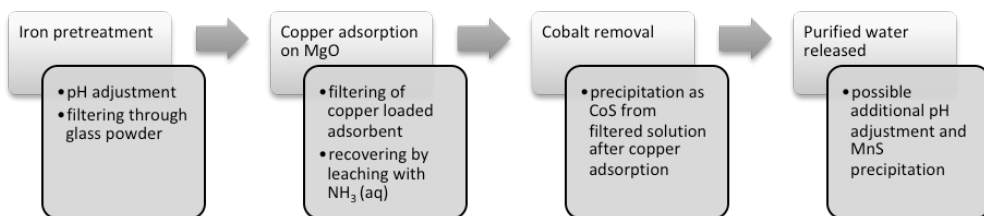

Figure 1 Process-flow of copper and cobalt recovery (CCR).

year, calculated from the metals currently precipitated as hydroxide into tailings, at 100% yield. The present gypsum precipitation has a cost of 12 to 18 USD per day and can be considered as the cheapest practice. Reagent costs in USD for the proposed CCR process (Figure 1) including pretreatment-copper adsorption/desorption-pH adjustment and CoS and MnS precipitation steps are considered in Table 3 and calculated as costs per day. To estimate the costs some assumptions were made, e.g. adsorbent cost was estimated to be 400 USD per ton, taking calcination costs of magnesite tailings into considerations. Reagent prices were averages from common retail vendors. Ammonia was reused 20 times at 10% concentration and the adsorbent 20 times. This results into combined costs of 21,890 USD per day. Certainly, the costs of sulfide concentrate must be correlated to metal prices taking smelting costs into account. At the current process shown, the process appears far from economical (10 times of revenue). Possible optimizations can be considered after breaking down the costs: the largest price was the use of NaOH for

pH adjustment, this could be cut by utilizing lime as currently also used, but only with the goal of pH adjustment until pH 5 not for full precipitation of metals. Calcium ions does not influence adsorption properties of MgO. The second largest price is adsorbent and ammonia leaching. Here, a piloting to find out the final number of re-usability of adsorbent and the re-use and optimization of ammonia amount. The left most column in Table 3 considers the optimization parameters such as reuse of adsorbent 40 times, reusing ammonia 40 times, and utilizing lime for pH adjustment.

Conclusions

Calcined magnesite can adsorb over 11% of its weight in copper as determined by XRF. Selectivity of copper over cobalt is obtained by time-dependency. Real mine effluent containing copper in over 10 times excess over cobalt was used as a real-life sample to demonstrate the ability to separate chosen elements by means of adsorption and to recover copper and cobalt, two commercially valuable elements (CCR process). The

Table 3 Chemical costs for proposed recovery scheme, in USD, 19200 m³/d.

treatment step	chemical	price USD/t	used for 1 m³ in kg	price per m³/USD	price per day	pos. optimization
adsorbent	MgO	400	3	0,06	1152	576
pH adjustment	NaOH	400	0,8	0,32	6144	12
filtration	sand or glass	80		0	0	0
ammonia desorption	ammonia 25%	200	30	0,12	5760	1440
Na₂S precipitation	Na2S	400	0,025	0,010	189	189
pH adjustment	NaOH	400	0,8	0,32	6144	12
Na₂S precipitation	Na2S	400	0,181	0,072	1390	1390
pH adjustment	H2SO4	200	0,006	0,001	21	21
Na₂S precipitation	Na2S	400	0,142	0,057	1091	1091
SUM					21890 USD/d	4730 USD/d
possible revenue					2768 USD/d	2768 USD/d

composition of sample was complex: iron, calcium, aluminium and magnesium were the major components in concentration $15 \pm 1,5$ mg/L Fe, 510 ± 51 mg/L Ca, 115 ± 12 mg/L Al, and 953 ± 95 mg/L Mg, respectively. In the first step, iron was removed by pre-treatment to reach maximum capacity of adsorbent and improve selectivity of adsorption. Then, copper was selectively adsorbed onto MgO-containing powdered adsorbent, and selectively removed by extraction. Cobalt was quantitatively precipitated as CoS. The adsorbent was then reused and has been cycled for twelve times. Based on comparison of reagent costs and loss of revenue, the approach is currently more expensive than lost revenue, however politic decisions, tailing storage problems, rising commodity prices and especially optimization of process by piloting and cycling of leaching solution could make CCR process easily feasible in the future.

Acknowledgements

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