SEQUENTIAL EXTRACTION TO PREDICT THE LEACHING POTENTIAL OF REFRACTORY BLACK COPPER ORES

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ABSTRACT. The micro chemical composition of mineraloids of variable composition, called "black copper phases", was related to sequential extraction of Cu, Mn and Fe in different redox conditions, to predict the copper recovery in the heap leaching process. The composition of this mineraloids, range between Cu-Mn to Cu-Fe rich phases, with great variability from one deposit to another and even in the same deposit. The industry normally apply the copper soluble test, by cool diluted sulfuric acid, to estimate the extraction of the oxide copper ores in general, but in these case the information is not agree with the recovery in the heap.

The mineral chemistry of the "black copper phases" was analyzed by EPMA in order to introduce the mineraloids in the SIP list of the Qemscan. Cu, Mn and Fe were determined by atomic absorption spectrometry in a sequential extraction procedure of five steps, including the first remotion of the elements by cation exchange, and the last total digestion by acids.

The extraction of Cu, Mn and Fe of the samples, by steps, permit to predict with more specific information the operational modifications for the leaching of these refractory phases at the general procedure apply to the oxide copper minerals, like chrysocolla, malachite, atacamite and azurite.

Keywords: Oxide copper ores; heap leaching; process mineralogy; leaching

INTRODUCTION

Secondary copper deposits in the first place consist of chrysocolla, malachite, azurite, atacamite, brochantite and antlerite, also known as green and blue "coppers". In some deposits an important part of the copper content is found in black mineraloids of varied texture. These have traditionally been described as copper pitch and copper wad (Pincheira *et al.*, 2003; Chávez, 2000; Münchmeyer, 1996). The "black copper" phases are mineralogically complex, difficult to recognize and display a low solubility in conventional hydrometallurgical systems when compared with carbonates, sulphates, chlorides and other copper silicates (Hernández *et al.*, 2011; Pincheira *et al.*, 2011). Furthermore information in main stream specialized publications is very scarce.

Based on the microchemistry and mineralogy, "black copper" phases are generically mineraloids (very low crystallinity) with a variable composition of Cu, Mn, Fe, Si and Al. This descriptor is based on Chilean deposits such as: El Tesoro, Gaby, Ministro Hales, Mina Sur, Radomiro Tomic, Huiquintipa and Rosario (Collahuasi district) (Pincheira *et al.*, 2012a and 2012b; Pincheira *et al.*, 2011; Pincheira *et al.*, 2003).

The wide compositional spread between phases with high respective Cu-Mn and Cu-Fe contents, is considered to be the cause for differences in solubility between various deposits and, for zones within a single deposit, product of rhythmic fluctuations of pH and Eh during formation.

Traditional optical microscopy does not allow a differentiation between Cu-Fe; Cu-Mn and Cu-Fe-Mn copper phases. Being amorphous or of very low crystallinity also limits the use of X-ray diffraction. Given this situation, different textural types are selected by optical microscopy to be analyzed by electron microprobe. This information together with the whole sample contents of Cu, Fe and Mn permit to adjust the database (SIP) of automated microanalyses equipment (Qemscan®, MLA, TIMA) to obtain the proportions of each of the "black copper" phases. To evaluate the leaching capacity of sulphuric acid for oxide copper ores, soluble copper is determined under standard conditions using dilute sulphuric acid at ambient temperature. This information does not allow to predict the comportment of all Minerals in the same fashion, as the test is not sensitive enough to distinguish between "black copper" phases with different solubilities (Jerez *et al.*, 2010). As an option to evaluate the conditions of solubility in deposits with important "black copper" contents, the sequential extraction is studied of Cu, Fe and Mn in different oxidative reductive agents and pH environments.

MATERIALS AND METHODS

Five samples with black copper mineralization form three different deposits (A-1, A-2, B-1, B-2 and C) were studied by quantitative mineralogy, Qemscan®-Tescan system, complemented with electron microprobe (JEOL 8600 M) and X-ray diffraction (Bruker D4). An atomic absorption spectrophotometer (Hitachi A-8100 Zeeman) was used for chemical analyses of Cu, Fe, and Mn, total (CuT) and soluble (CuS) and in the five step sequential extraction procedure. This consisted of element removal by ammonium acetate, hydrolylamine chlorhydrate, ammonium oxalate and total digestion by concentrated HCl, HNO$_3$ and HF.

RESULTS AND DISCUSSION

The contents of total and soluble Cu, Fe and Mn, as well as their solubility ratios of the five samples from three deposits with oxide mineralization are listed in Table 1. Total copper is in the range of 0.3 to 3.2 %, and the solubility ratios between 56 to 93% for Cu, 7 to 43% for Fe and 17 to 75% for Mn.

Tabl. 1 Total (T) and soluble (S) Cu, Fe and Mn and ratios of solubility for samples of the three different deposits

Element contents (%) and ratios	Samples				
	A -1	A -2	B - 1	B - 2	C
CuT	0.66	0.77	0.52	0.30	3.17
CuS	0.37	0.43	0.48	0.17	2.95
FeT	4.35	4.13	2.02	2.19	3.32
FeS	0.59	0.27	0.86	0.34	0.50
MnT	0.15	0.15	0.08	0.45	2.71
MnS	0.07	0.11	0.06	0.21	0.45
CuS/CuT	56.06	55.84	92.31	56.67	93.06
FeS/FeT	13.56	6.54	42.57	15.53	15.06
MnS/MnT	46.67	73.33	75.00	46.67	16.61

Table 2 shows the modal mineralogy with non-copper phases simplified as gangue, based on automated electron microscopy using a modified Qemscan® database as described above (Pincheira, 2012a and 2012b; Pincheira *et al.*, 2011).

Tabl. 2 Simplified modal mineralogy - Qemscan® (weight %)

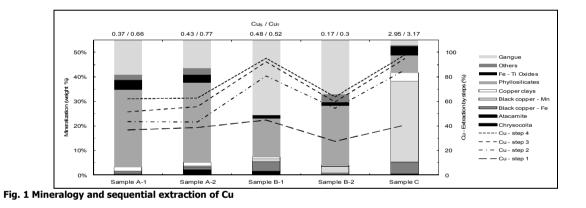| Qemscan® (weight %)	Samples				
	A -1	A -2	B - 1	B - 2	C
Chrysocolla	0.04	0.27	1.69	0.00	0.51
Atacamite	0.32	1.85	0.01	0.01	0.01
Black copper-Fe	1.28	1.40	3.81	0.82	4.87
Black copper-Mn	0.11	0.25	1.13	2.84	32.82
Copper clays	1.45	1.49	0.74	0.47	3.49
Phyllosilicates	31.61	32.45	15.65	24.10	6.95
Fe-Ti Oxides	3.89	3.07	1.42	1.35	3.86
Others	2.22	2.72	0.13	3.37	0.49
Gangue	59.06	56.47	75.42	67.03	47.00

Five step sequential extraction of Cu, Fe and Mn is shown in Table 3; results show the liberation of elements from their host phases in response to the different chemical reagents and pH. At step 1, water-soluble and exchangeable cations are extracted, e.g. Cu linked to clays. At step 2, Mn is preferentially extracted under acid reducing conditions, e.g. Mn from "black coppers". At step 3, conditions favor the extraction of Fe in amorphous iron phases, e.g. Fe linked to "black coppers"; for step 4, heat is added under the same conditions as in step 3 thus extracting Fe from more crystalline phases. At step 5 Cu, Fe, and Mn are extracted (amongst other elements) from

refractory phases during the previous steps using a mixed acid attack (HCl, HNO₃, HF). The sum of the five steps represents the total contents of the elements in the sample.

Tabl. 3 Five step sequential extraction of Cu, Fe and Mn.

Element extraction by steps (%)	Samples				
	A -1	A -2	B - 1	B - 2	C
Cu - step 1	36.84	38.64	44.99	27.63	40.55
Cu - step 2	6.73	4.49	35.82	26.98	44.87
Cu - step 3	8.04	12.71	11.58	4.87	9.56
Cu - step 4	10.67	6.80	2.86	4.42	2.85
Cu - step 5	37.72	37.36	4.74	36.10	2.16
Fe - step 1	3.10	1.29	8.33	2.49	2.67
Fe - step 2	1.39	0.89	8.25	2.86	4.68
Fe - step 3	5.35	2.45	8.55	3.10	5.55
Fe - step 4	13.14	6.83	15.34	8.01	13.44
Fe - step 5	77.02	88.54	59.53	83.54	73.66
Mn - step 1	13.53	28.30	44.58	5.82	1.62
Mn - step 2	62.35	48.43	16.03	88.14	92.30
Mn - step 3	5.29	4.40	3.54	2.84	3.57
Mn - step 4	4.12	1.89	5.58	0.15	0.66
Mn - step 5	14.71	16.98	30.28	3.05	1.86

Figure 1 contrasts Qemscan® mineralogy and sequential extractions, where step 5 represents 100% extraction. Copper bearing phases are chrysocolla, atacamite, Fe-rich "black copper", Mn-rich "black copper" and copper clays. The step 1 line shows the most soluble copper with about 40% extraction on all samples but G-20, which contains only traces of atacamite and minor copper clays. Step 2 line corresponds to Cu extracted from phases associated to Mn-rich "black copper"; A-1 and A-2 release 7 and 5 % respectively, whereas for B-1, B-2 and C between 27 and 45 % Cu are obtained. This is related to the low presence of Mn-rich "black copper" for A-1 and A-2 but more abundant for B-1, B-2 and C. Step 3 line adds the Cu linked to Fe-rich phases of low crystallinity; here B-2 comes last and coincides with its minor contents of Fe-rich "black copper". Step 4 line adds Cu from more crystalline iron-rich phases; here the contribution is largest for samples A-1 and A-2 with 11 and 7 % respectively. The difference between step 4 - line and 100% extraction represents the refractory copper during steps 1 to 4, which is almost impossible to recover in a conventional heap leach process or modified by the information obtained in this study. Samples A-1, A-2 and B-2 contain about 37% of extremely low solubility Cu phases. Figures 3 and 4 complement the information from Figure 1 with the partial extractions of Fe and Mn. They confirm the observations linking mineralogy to the solubility of Cu-bearing phases.
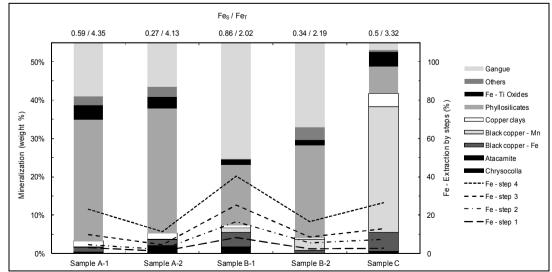

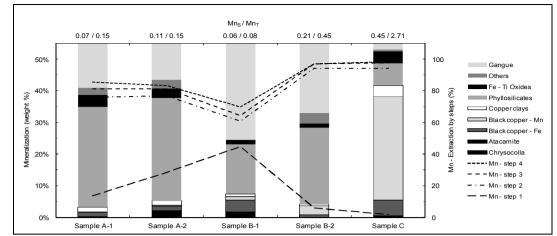**Fig. 1 Mineralogy and sequential extraction of Cu**

Fig. 2 Mineralogy and sequential extraction of Fe

Fig. 3 Mineralogy and sequential extraction of Mn.

CONCLUSIONS

The study of complex mineral phases and their comportment in industrial extraction has to be accompanied by an integrated use of different techniques of mineralogical characterization. The option to enhance the understanding of "black copper" phases by including their response to different extraction media, as presented in this study, is a recommendable option to predict the industrial process response and introduce modifications in the operating conditions.

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