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Copper Recovery VIA Non Conventional Techniques from Abu Swayeil Technological Ore Sample, East Desert, Egypt

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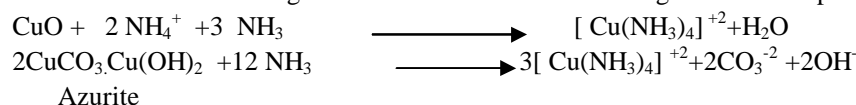
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ABSTRACT: A copper mineralization located in granite rocks of Abu Swayeil technological ore sample, East Desert, Egypt has been studied for the recovery of copper metal value. The relevant factors of acidic leaching of a technological sample of this material assaying 6.5% Cu were studied using non conventional technique. The latter by adipic acid. Under the optimum conditions, it was possible to realize a dissolution efficiency of about 77.7 % for Cu via this new technique respective. Recovery of the leached copper values was achieved using direct precipitation by formation of the blue CuSO₄ crystals by pH adjustment at 5.5.

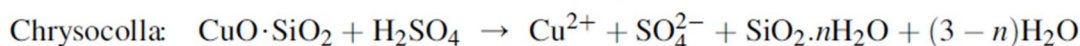
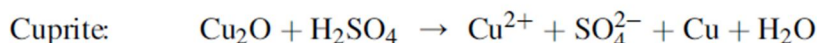
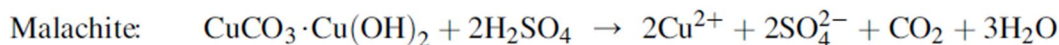
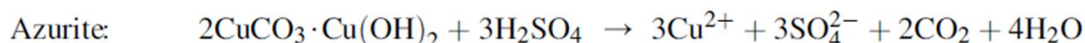
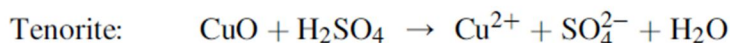
I. INTRODUCTION

Copper exist, naturally in the environment, the average content is about 50g/ton in the earth's crust. Copper commonly occurs as sulfide ores, e.g. CuFeS₂ (90%), but also as oxide ores, e.g. Cu₂O, (9%) and as pure copper (1%). In the primary copper producing industry it is mainly the sulfide ores that is used, although a large part of the produced copper comes from recycled materials (Elding et al., 2012). Half of the amount of produced copper is used in the electric component industry where its excellent conductivity is highly valued. Other industries that use copper are engineering industry (21%), building industry (11%), household articles (10%) and transport industry (8%). New materials have started to compete with copper in many of the common usages, this have accelerated the development of new copper materials with improved qualities (Elding et al., 2012).

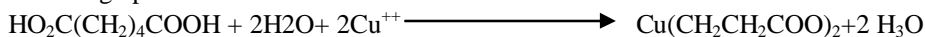
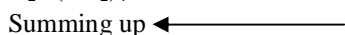
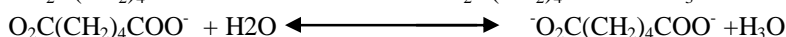
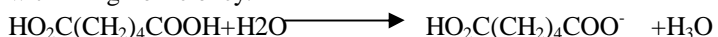
Apart from copper sulfide ores which are generally processed through pyrometallurgical techniques, the copper oxide or roasted ores are indeed amenable to either acid or alkaline leaching procedures. Choice among the latter techniques depends upon the gangue composition of the working ore. Thus, in case of ores containing abundant acid consuming gangue minerals like dolomite, calcite, etc, the alkaline leaching would be necessary. Also, in presence of abundant iron gangue minerals the alkaline leaching is also preferable in order not to contaminate the obtained leach liquor with iron which is partially soluble in acid media. Alkaline leaching of copper oxide ores can actually be realized by several alkali reagents; namely carbonate or bicarbonate of sodium or ammonium or else ammonium hydroxide. Ammonia leaching was first used at the Kennecott Plant, Alaska, since the processed copper ore was containing both the carbonate gangue minerals calcite and dolomite (Habashi, 1970, 1983; Alguacil, 1999). Copper dissolution reactions using ammonia and/or ammonium reagents can be represented by the following reactions:



Acidic leaching of copper Leaching involves dissolving Cu⁺² (or Cu⁺¹) from copper-containing minerals into an aqueous H₂SO₄ solution, known as the lixiviant, to produce a pregnant leach solution. In addition to copper, the leach solution will also contain other impurity species, such as Fe, Al, Co, Mn, Zn, Mg, Ca, etc., that may be present in the ore and are leached with the copper. The leach residue (solids remaining after leaching) contains gangue or waste minerals, such as alumina, silica, and insoluble iron oxides/hydroxides/sulfates. Cu can be dissolved as Cu⁺² under mildly acidic conditions (pH < 5). Examples of some copper minerals that leach in this manner are:



Suresh(2009) has been interested in the structural chemistry of Cu(II) and Co(II) ternary coordination polymers by utilizing the versatile coordination modes of carboxylate ligand with metal center and various N-donor ligands such as bipyridyl, imidazole, methyl imidazole etc. Typically, adipic acid [α -, ω -Dicarboxylate aliphatic acid $(\text{CH}_2)_4(\text{COOH})_2$] could react with copper to form Cu (II) adipate: $\text{Cu}(\text{CH}_2\text{CH}_2\text{COO})_2$. The latter has previously been prepared and reported by Burken (1950). In this regard, El-Sheikh et al, 2013 succeed in leaching of copper with adipic acid from carbonate rich latasol ore material of Abu Thor locality within high efficiency.



From the industrial perspective, adipic acid is indeed the most important dicarboxylic acid. About 2.5 billion kilograms of this white crystalline powder are annually produced, mainly as a precursor for the production of nylon. Adipic acid is a valuable raw material used in the production of fibers, lubricants, plasticizers, and food additives as well as in the production of intermediates for pharmaceuticals, insecticides, and bactericides. Conventionally, it is manufactured by oxidation of cyclohexanone / cyclohexanol, by hydrogenation of phenol, or more commonly, by oxidation of cyclohexane (Davis et al., 1991; Castellan et al., 1991).

According to, the hydrometallurgical characteristic of the studied metal values, for copper leaching several non conventional acid leaching processes technique using adipic acid to avoid excessive consumption of sulfuric acid were performed. Crushing and grinding processes (ore comminution) deal with, the reduction of grain size to the fineness suitable -200 mesh to be feed to the slurry in the leaching stages. Other technique or physical ore dressing not play any role in our work. For this goal, a technological sample assaying 6.5% CuO has been collected from Abu-Swayeil technological ore sample, East Desert, Egypt

II. EXPERIMENTAL

A. Material

The technological sample weighing about 5 kg was collected

B. Leaching procedures

After collection the mentioned technological sample, separately leached Cu with adipic acid (as non conventional techniques) and sulfuric acid as conventional techniques was applied.

1) *Adipic acid leaching of copper* : Several leaching experiments for copper have actually been performed using adipic acid to optimize the relevant leaching factors. In these experiments, a suitable weight of the working Cu ore ground to -200 mesh size was mixed with a suitable volume of adipic acid of various concentrations. The slurry was then agitated for a fixed time at a certain temperature after which the treated slurry was filtered and the residue left behind was thoroughly washed with distilled water and both filtrate and washings were made up to volume before analysis.

C. Analytical procedures

Proper quartering of the technological sample was performed after its grinding to less than 200 mesh size to obtain a representative sample which was subjected to complete chemical analysis of both major and trace elements content. (Shapiro and Brannock, 1962).

Whereas SiO_2 , Al_2O_3 , TiO_2 and P_2O_5 were determined using relevant spectrophotometric methods, the contents of Na and K were determined by a flame photometric technique. Total Fe as Fe_2O_3 , MgO and CaO were determined by titration methods. The loss on ignition (L.O.I) was determined gravimetrically. The estimated error for major constituents is not more than $\pm 1\%$.

The trace elements V, Cr, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Pb and Ba were analyzed at the laboratories of the by the X-ray fluorescence technique (XRF) using Philips Unique II unit with automatic sample changer PW 1510 (30 position), connected to a computer system using X-40 program for spectrometry. The detection limit of the measured elements by XRF technique was estimated to be 5 ppm.

To follow the leaching and recovery efficiency, the different stream solutions were subjected to Cu analysis, using an atomic absorption spectrophotometer (AAS) Unicam 969, England was used. Finally, the obtained products have been qualitatively analyzed using ESEM-EDX analysis.

III. RESULTS AND DISCUSSION

A. Chemical composition of the working technological sample

The complete chemical analysis of the working technological Abu-Swayeil ore sample is given in table (1) as well as its metal values Cu and Ni. From the latter, it is obviously evident that besides the high level of the loss on ignition, it contains a high Mg content beside Cu metal which exists as carbonate minerals; a matter that reflects a high carbonate content.

Table (1): The chemical analysis of the working Abu Swayeil technological ore sample

Component	wt. %	Component	wt. %
SiO_2	38.8	K_2O	0.85
TiO_2	0.14	Na_2O	0.03
Al_2O_3	4.36	P_2O_5	0.04
Fe_2O_3	22.45	L.O.I	9.10
MgO	14.67	CuO	6.5
CaO	1.8	NiO	1.89
		Total	100.63

*L.O.I. = loss on ignition

On the other hand, another part of technological sample was subjected to X-ray fluorescence for the analysis of some trace elements (table 2). The latter shows that there are some important values of Cr and Ba only.

Table (2): XRF analytical results of the interesting trace elements in the working technological ore sample.

Trace element	ppm	Trace element	ppm
Ba	583	Pb	7
V	40	Cr	1250
Y	24	Sr	2
Nb	8	Ga	2
Zn	79	Zr	49

B. Results of chemical processing

1) Copper recovery

a) Adipic acid leaching

i) *Effect of adipic acid concentration:* The effect of adipic acid concentration was studied between 0.1 and 0.9 mole, while the other leaching factors were fixed at -200 mesh size, an hour agitation time, 60°C leaching temperature, 50 rpm stirring speed and

1/3 solid-liquid (S/L) ratio. The leaching efficiency of copper given in table (3) indicate that the best conc. of adipic acid is 0.6 mole for copper leaching. Under these conditions, the leaching efficiency of copper has attained up to 69 %. Higher concentrations of adipic acid did not markedly affect the copper leaching efficiency. The obtained data are actually in agreement with the results obtained by (Bassi et al., 1988) who have reported that solid-solid reactions of basic copper carbonate with adipic acids gave the corresponding copper (II) carboxylate chelates. Formation of Cu adipate can be represented by the following successive equations (Fessenden and Fessenden, 1982; Bassi and Kalsi, 1977):

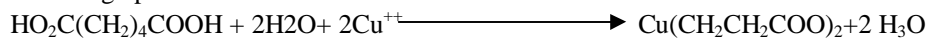
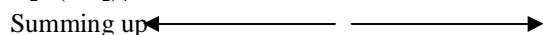
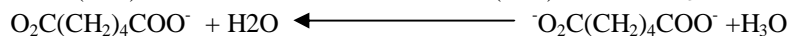
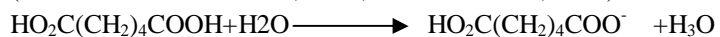


Table (3): Effect of adipic acid concentration on copper leaching efficiency from Abu Swayeil ore sample

Adipic acid concentration, mole	Copper leaching efficiency, %
0.1	52.2
0.2	57.8
0.3	64.4
0.4	64.5
0.5	67.4
0.6	69.1
0.7	70.4
0.8	71.3
0.9	71.3

ii) Effect of agitation Time: The effect of leaching time upon Cu leaching efficiency was studied in the range from 30 to 180 minute while the other leaching conditions were fixed at 0.6 mole adipic acid concentration, -200 mesh size ore material, a leaching temperature of 60 C⁰ and using a solid / liquid ratio of 1/3 with 50 rpm stirring speed. The obtained data shown in table (4) revealed that a high copper leaching efficiency exceeding 77% occurs within 120 min.. Therefore, it can be concluded that 120 minutes are acceptable to Cu leaching using 0.6 mole adipic acid concentration.

Table (4): Effect of leaching time upon copper leaching efficiency from Abu Swayeil technological ore sample

Time/minutes	Copper leaching efficiency, %
30	50.18
60	69.10
90	73.30
120	77.70
180	77.98

iii) Effect of round per mint : For studying the effect of round per min. upon Cu leaching efficiency, four experiments have been performed from 50 to 200 rpm. In these Experiments, the other leaching conditions were fixed at 0.6 mole adipic acid concentration, -200 mesh size ore material, a leaching temperature of 60 C⁰ and using a solid / liquid ratio of 1/3 with agitation times of 120 min. The obtained results tabulated in Table (5). From the obtained results, it was clear that, stirring is quite important for attaining a high copper leaching efficiency and 50 rpm recorded the best leaching efficiency.

Table (5): Effect of round per mint upon copper leaching efficiency from Abu Swayeil technological ore sample

Round per mint	Copper leaching efficiency,%
50	77.7
100	78.20
150	78.80
200	78.70

iv) Effect of temperature: Four adipic acid leaching experiments have been performed to investigate the effect of leaching temperature in the range from room (about 25 °C) up to 100 °C. In these experiments, the other leaching conditions were fixed at -200 mesh size ore material, 0.6 mole adipic acid concentration for 120 min. agitation time with 50 rpm and using a 1/3 S/L ratio. The obtained data were given in table (6) and reveal actually the importance of temperature to obtain a high leaching efficiency of copper. Working at room temperature under the mentioned conditions did not leach more than 20% of Cu. Increasing the leaching temperature to 50°C has increased the leaching efficiency of copper to 43.3% and its further increase to 60°C increased the Cu leaching efficiency to 77.7% and after which there has been only a slight increase in the leaching efficiency. It can thus be mentioned that the optimum leaching temperature of Cu using 0.6 mole of adipic acid under the above mentioned condition would be 60°C.

Table (6): Effect of leaching temperature upon copper efficiency from Abu Swayeil technological ore sample

Temperature, °C	Copper leaching efficiency,%
25	20.00
40	43.30
60	77.7
80	77.8
100	88.2

v) Effect of the solid/liquid ratio: The effect of the solid/liquid ratio upon copper leaching efficiency was studied between 1/3 and 1/5. In these experiments, the fixed leaching conditions involved -200 mesh size ore material, 0.6 mole adipic acid concentration for 120 min within 50 rpm . agitation time at 60 °C as leaching temperature.. From the obtained leaching efficiency given in table (7), it was found that beyond 1/3 S/L ratio, only a slight steady increase in the leaching efficiency of copper has been achieved. Accordingly, a solid ratio of 1/3 would be considered as optimum at which the leaching efficiency of copper attained 77.7.

Table (7): Effect of solid/liquid ratio upon copper efficiency from Abu Swayeil technological ore sample

Solid/liquid ratio	Copper leaching efficiency%
1/3	77.7
1/4	78.90
1/5	78.92

From the above studied leaching factors of copper from Abu Swayeil technological ore sample, it can be concluded that the optimum leaching conditions for dissolving about 77.7 % of copper would be summarized as follows:

Grain size : -200 mesh.
 Acid concentration : 0.6 mole
 Leaching time : 120 minute
 Leaching temperature : 60 °C.
 Solid/liquid ratio : 1/3

vi) *Preparation of copper product:* For studying the recovery procedures for copper from the working sample, a proper 3 liter adipate leach liquor was prepared from 1 Kg of the working ore sample using the above mentioned determined optimum leaching conditions. Chemical analysis of Cu in this liquor was found to attained 16.80 g/l. From this liquor, blue copper adipate crystals have been obtained by its proper cooling for half an hour. To prepare a marketable Cu product, the obtained copper adipate was easily converted to hydroxide or oxide by dissolution in one excess ammonia solution followed by precipitation of CuSO_4 using ammonia solution at pH 5.5. The obtained hydroxide product have been subjected to proper analysis using the ESEM-EDX technique (Fig. 1).

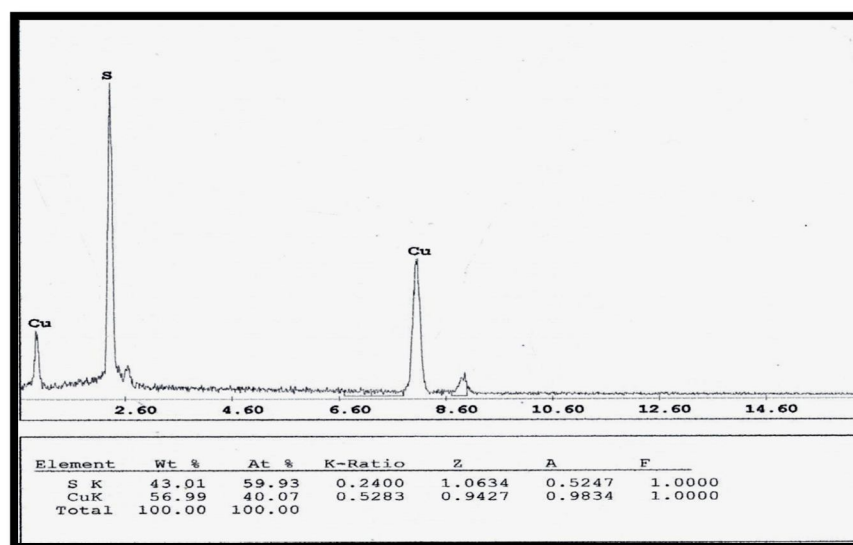


Fig. (1): ESEM with EDX analysis of the prepared copper hydroxide product

IV. CONCLUSIONS

Proper processing has been achieved for the Abu Swayeil mineralization hosted in... technological ore sample, East Desert, Egypt. Thus, to avoid excessive sulfuric acid consumption in the classical leaching procedure. An selective Cu leaching has first been performed using adipic acid as non conventional technique. In this techniques, the optimum working conditions have been determined using on ore ground to-200 mesh size. Accordingly, for Cu leaching, 0.6 mole adipic acid was used at 60 °C for 120 min. in a S/l ratio of 1/3 resulting in leaching efficiency exceeding 77.7%. Accordingly, thus can be concluded adipic acid as environmental method could be a proper reagent for copper leaching.

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