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# Engineering Science and Technology, an International Journal

journal homepage: <http://ees.elsevier.com/jestch/default.asp>

## Dissolution of copper and iron from malachite ore and precipitation of copper sulfate pentahydrate by chemical process



H. Kokes, M.H. Morcali\*, E. Acma

Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering, Maslak, 34469 Istanbul, Turkey

### ARTICLE INFO

#### Article history:

Received 23 December 2013

Received in revised form

7 March 2014

Accepted 8 March 2014

Available online 3 April 2014

#### Keywords:

Malachite ore

Copper

Iron

Leaching

Precipitation

### ABSTRACT

The present work describes an investigation of a chemical process for the recovery of copper and iron from malachite ore. For the dissolution of copper and iron,  $H_2SO_4$  was employed as well as  $H_2O_2$  as an oxidizing agent. The effects of reaction temperature and time, acid concentration, liquid-to-solid ratio and agitation rate on the copper and iron percentage were investigated. Following the steps of dissolving the copper and iron sulfate and filtering, iron (III) hydroxide was precipitated by adjusting the pH level of the solution. Subsequently, copper sulfate pentahydrate was obtained by using various precipitants (i.e. ethanol, methanol and sulfuric acid).

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### 1. Introduction

Copper has many application areas in both metallic form and its various components, such as metallurgy, chemistry, paint and agriculture industries [9,11].

Copper oxide minerals, such as malachite ( $Cu_2(OH)_2CO_3$ ), azurite ( $Cu_3(OH)_2(CO_3)_2$ ), tenorite (CuO) and chrysocolla ( $CuSiO_3 \cdot 2H_2O$ ), are easily soluble in either acid or alkaline media [9,11,17]. In hydrometallurgical extraction, many leaching agents have been used such as sulfuric acid [5,6], hydrochloric acid, nitric acid [10], citric acid [17] and ammonium acetate [12] and ammonium nitrate [8]. The citric acid (Organic acid), the ammonium acetate (neutral salt) and the ammonium nitrate (weakly acidic salt) can be attractive leachant as the leaching is carried out at moderate acidic conditions. However, due to their low boiling temperatures and decompositions cannot be used as leaching agents for hard dissolving compounds. For that reason sulfuric acid is generally preferred as leaching agent for oxidized copper ore in the scientific literature [5,6].

In general, the methods reported for the recovery of copper from ores involve two steps: the first involves dissolving the copper

from the ores while the second one is the recovery of the dissolved copper by solvent extraction [3,9,12], cementation [4,7,9,19] or precipitation as copper compounds [1].

Ethanol, or ethyl alcohol, with the formula  $C_2H_5OH$ , is the second member of the aliphatic alcohol series. With the exception of alcoholic beverages, nearly all the ethanol produced and used industrially is a mixture of 95% ethanol and 5% water (known simply as 95% alcohol); it is prepared by distilling the solution that results from the fermentation of sugars [13]. Ethanol is also used as a solvent for paint, varnish and drugs, as a fluid in thermometers, and in the preservation of biological specimens [13]. Despite all of these applications, its properties as a precipitating agent have not been extensively investigated.

Methanol can be produced chemically from both biomass and fossil fuels [18] and is a primary feedstock for a wide array of chemicals. It is a constituent of many consumer products and is used widely in the treatment of wastewater and sewage. Additionally, methanol has been employed as an alternative fuel for motor vehicles, where it is considered to be a primary hydrogen carrier for fuel cells because it is easier to transport and store than hydrogen.

A common ion precipitation method, which is so-called as acidic precipitation in the industry, is an application of Le-Chatelier's Principle [16]. The common ion added in saturated solution will lead to the decrease of salt's solubility. The basis of this method is the common ion effect in which a reaction product, present as an

\* Corresponding author. Tel.: +90 5437696715.

E-mail address: [hakanmorcali@gmail.com](mailto:hakanmorcali@gmail.com) (M.H. Morcali).

Peer review under responsibility of Karabuk University

anion, is forced out of solution by addition of excess quantities of a counter cation. This method is widely used to precipitate metal salts (e.g. Cu, Fe, Ni, Co, Na, K, Mg, Al, Zn etc.) [2,14]. The main purpose of the present study is to outline an effective chemical process for the production of copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) from malachite ore and describe the optimal conditions and parameters for this chemical process.

## 2. Materials and methods

In this study, the malachite ore was obtained from an ore dressing plant in Tunceli region, Turkey. The ore was dried, crushed, grounded and sieved to minus 90  $\mu\text{m}$ . The obtained powder was homogenized using a three dimensional shaker (Turbula T2C, USA) after drying in an oven at 105  $^\circ\text{C}$ . The chemical composition and X-ray diffraction (XRD) (Panalytical, Netherlands) pattern are shown in Table 1 and Fig. 1, respectively.

As can be seen from Fig. 1, malachite, albite, enstatite, riebeckite, cebollite and quartz, were the major mineral phases in the malachite ore. All chemical reagents used in this study were of analytical grade. The dissolution experiments were performed inside a 400 mL Pyrex beaker in a temperature-controlled shaking bath to ensure uniform heat convection at the surface of the beaker. The copper content was determined using 0.1 M EDTA as the titrant in the presence of murexide. Other elements present in the solution were measured using atomic absorption spectrometer (AAS) (AAnalyst 800, Perkin Elmer Inc., USA). Total iron concentration was determined in all experiments.

The dissolution parameters were determined by evaluating the effects of the following factors: temperature and time, acid concentration, liquid-to-solid ratio and stirring speed. For each experiment, 40 mL of various sulfuric acid solutions of 0.4–2.0 M and 10 g of ore sample were employed to dissolve the copper and iron incorporated in the malachite ore. Then, the impure copper solution was treated with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to ensure that all iron (II) ions were converted to iron (III). Subsequently,  $\text{Fe}^{3+}$  ions were precipitated in the form of  $\text{Fe}(\text{OH})_3$  by using sodium hydroxide. After the filtration, the copper sulfate solution was treated with ethanol, methanol and sulfuric acid to precipitate all copper ions as copper sulfate pentahydrate. It was performed by XRD and Thermal Gravimetric Analysis (TGA) (TGA 4000, Perkin Elmer Inc., USA). The proposed process for the production of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  from malachite ore is shown in Fig. 2.

## 3. Results and discussion

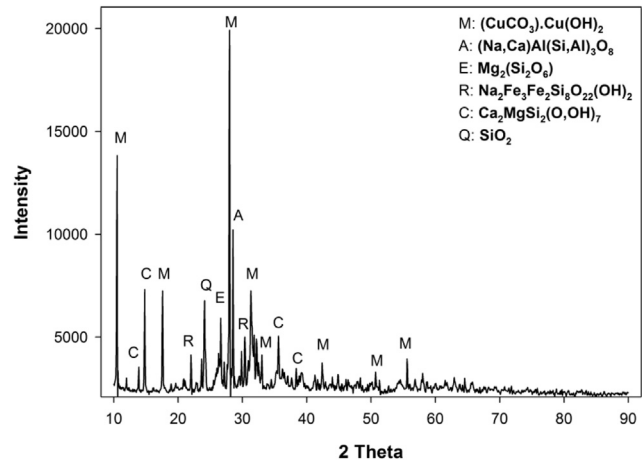
The process outlined in this paper can be used to dissolve almost all of the copper present in the malachite ore employed. Table 2 displays experimental conditions. By simply treating with  $\text{H}_2\text{O}_2$  and then adjusting the pH of the solution,  $\text{Fe}(\text{OH})_3$  was produced. Then, copper ions were precipitated as copper sulfate pentahydrate.

### 3.1. Effect of time and temperature on the dissolution of copper and iron from ore

Fig. 3a and b displays the variation in the dissolution of copper and iron percentage as a function of time at various temperatures.

**Table 1**  
The chemical composition of the malachite ore.

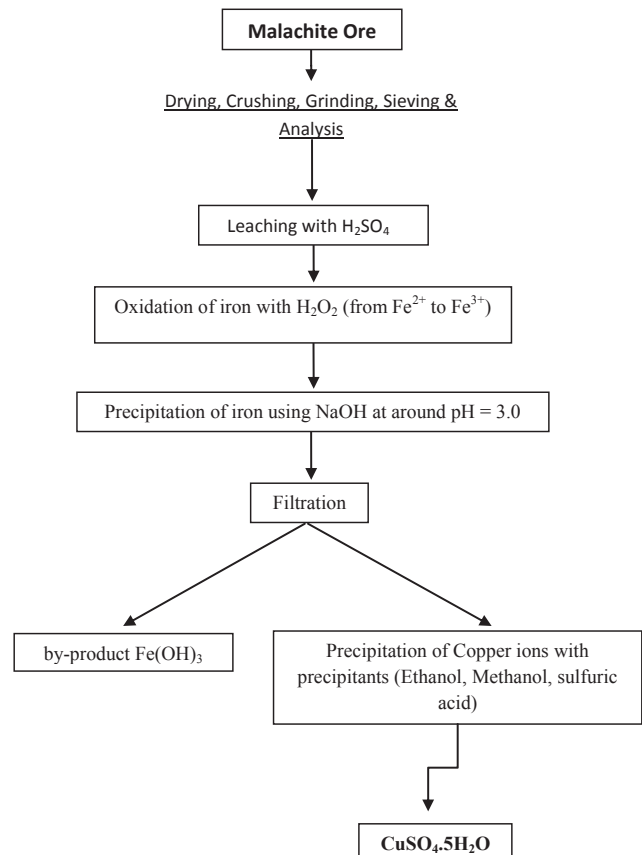
Wt., %									
CuO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Other oxides	LOI	
26.85	7.20	23.49	7.53	4.49	5.57	2.89	0.62	21.36	



**Fig. 1.** XRD patterns of malachite ore.

Fig. 3a presents the dissolution of copper as a function of temperatures and shows that increasing temperature results in an increase in the dissolution of copper [6,17].

At 25  $^\circ\text{C}$  and 30 min, a dissolution percentage of 84 were obtained while a dissolution percentage of 99 were obtained at 80  $^\circ\text{C}$ . After 30 min at 80  $^\circ\text{C}$  there is no significant change in dissolution percentage of copper. However, extending the time has an important effect on dissolution of copper at low temperatures. It can be concluded that, if there is no possibility of heating until 80  $^\circ\text{C}$ , dissolution percentage can be attained by just extending the time, because the interaction between sulfuric acid and malachite ore increases in time [17].



**Fig. 2.** The chemical process scheme.

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