EXTRACTION AND PURIFICATION OF MAGNESIUM SULPHATE FROM IRAQI DOLOMITE

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ABSTRACT

In this research, the magnesium sulfate was extracted and purified from Iraqi dolomite after dissolving the later in industrial sulfuric acid. The iron was removed completely as complex precipitation by hydrogen peroxide and ammonium acetate, and then removed the calcium as oxalate. The magnesium was precipitated as sulfate after cooling the filtrate to 5^0C and then purified by recrystalization from ethanol and deionized water mixture.

All the samples were identified and elemental analyses by X-ray diffraction and fluorescence, atomic absorption spectroscopy flame and flameless and light element.

INTRODUCTION

Magnesium compounds were confused with calcium compounds until 1754, when J.Black of Edinburgh showed that magnesia and lime was different materials. In 1808, Sir Humphy Davy should that magnesium oxide was the oxide of a new metal. In 1841, magnesium oxide and magnesium carbonate were produced synthetically by using kiln gives to separate lime from the magnesium compounds in dolomite. By the latter part of the nineteenth century, a flourishing business in magnesium compounds had been established in Europe, based on the production of magnesium sulphate, magnesium chloride, magnesium hydroxide, etc. at Sassfrut and the widespread use of magnesite in production of refractory linings of Bessemer and open- hearth furnaces.

Magnesium sulfate used as pharmaceuticals, fertilizers, and chemical treatments. Of the more than sixty significant magnesium-bearing minerals, the only ones used in the commercial production of magnesium compounds are magnesite ($MgCO_3$, 29% Mg), dolomite ($CaCO_3$ $MgCO_3$, 13% Mg), brucite ($Mg(OH)_2$, 42% Mg), Olivine ($Mg_2Fe_2SiO_2$, 19 Mg) and the various salts of oceanic deposits. The most important magnesium minerals can be conveniently divided into four groups:

1. The carbonates, magnesite and dolomite.
2. The chloride and sulfate salts and double salts found in oceanic deposits, such as carnallite ($KCl.MgCl_2.6H_2O$), kieserite ($MgSO_4.H_2O$), epsomite($MgSO_4.7H_2O$), langbeinite (K_2SO_4 $MgSO_4$), schoenite (K_2SO_4. $MgSO_4$. $6H_2O$), polyhalite ($2CaSO_4$. $MgSO_4$. $2H_2O$), and vanthoffite ($3Na_2SO_4$. $MgSO_4$).
3. The silicates, such as olivine (or chrysolite), serpentine ($H_4MgSi_2O_9$), talc (steatite or soapstone, approx $4MgSiO_3$. H_2SiO_3) ,forsterite (Mg_2SiO_4), and sepiolite ($Mg_2Si_3O_8$ $.2H_2O$). One of the most important members of this group is asbestos, a magnesium silicate of varying composition but commonly found as the serpentine type.
4. The oxides and hydroxides such as brucite and spinel (MgO. Al_2O_3). (The name spinel has also been applied more generally to a class of double oxides MO. M_2O_3, containing one bivalent metal and one less electropositive trivalent metal).

Traces of calcium and magnesium may be separated from matrices of metals forming cyanide complexes (e.g. Ni, Zn and Mn) by precipitation as phosphate with a lanthanium collector in alkaline cyanide medium [1].

Small amounts of calcium can be separated from magnesium by coprecipitation with strontium sulfate from aqueous ethanol [2].

In 1963 Fritz and Waki [3] studied the separation of magnesium and calcium by anion exchange, using dilute nitric acid in a medium containing a high proportion of water-miscible alcohol. A column separation factor is proposed and used selecting the best eluting medium. A solution of 0.5 M nitric acid in 90% isopropyl

alcohol is the eluent. Amberlyst XN 1002 resin is recommended for the separation.

A number of papers have been published on the ion exchange separation of magnesium and calcium. This separation has been done on a cation exchange resin merely by eluting with hydrogen ions [4,5]; although the difference in affinity for the resin is not very large. In this paper, extraction and purification will be achieved and discussed.

EXPERIMENTAL WORK

Purification and Drying of Ethanol

Ethanol has been used for purification of magnesium sulfate. The purification and drying of ethanol is described as in our previous research [6,7].

Extraction of iron

20 grams of dolomite are dissolved in 40% sulfuric acid (25 ml), heated at temperature between 60-70 °C with stirring. The solid was separated from filter by filtration. The hydrogen peroxide (3 ml) was dissolved in deionized water (10 ml) and added slowly with ammonium acetate (1 gram dissolved in 10 ml deionized water) to the filtrate at room temperature, which immediately turned reddish-brown. Boiling the solution until preparation of the reddish-brown solid was complete. The solid was then collected by filtration, dried between 80-100 °C for one hour.

Extraction of calcium

A saturated ammonium sulfate solution (2 ml) was added to the filtrate, followed by 0.2 gram of sodium thiosulphate. Heat the mixture in the beaker of boiling deionized water for 5 minutes, and to stand for a short time. The ammonium oxalate (1 gram) was dissolved in deionized water (10 ml) 1 ml was added slowly and warmed on a water bath until precipitation of calcium oxalate is obtain.

Extraction of magnesium sulfate

The filtrate was treated with ethanol until a precipitation of the white solid was complete. The white powder was collected by filtration. And then recrystallized from 20% ethanol and 80% deionized water mixture, and then collected by filtration and transferred to a glass watch, heated at temperature 100 °C for two hours.

RESULTS AND DISCUSSION

The X-ray fluorescence (XRF) technique was used for inspecting the elemental analysis for three samples (red and white color). We had carried out the qualitative analysis by using wavelength disperse spectrometry (WDS) of Siemense type SRS-200 Sequential X-ray spectrometer with the following specifications: X-ray tube target Nb-Mo, power: 22KV, 16mA for calcium, 28KV, 20mA for iron, filter: AL-foil, analyzing crystal:Lif (100) with 2d=4.03 °ADP with 2d=10.648°A, detector: Scintillation counter, and vacuum: 18-3 mbar in both samples and analyzing chambers.

The phase identification of the samples has been achieved by using Philips PW 1965/50 diffract meter (XRD). The X-ray target was copper with monochrometer for Kα1 radiation operated at 40 kV and 30 mA. The 2θ ranged was taken from 15 up to 500 . The scanned diffraction patterns were analyzed by using the power diffraction files (JCPPS).

Rapid oxidation of iron is affected by hydrogen peroxide [8,9]. Sodium acetate was added to ferric ion. Reddish –brown coloration attributed variously to complex ion [Fe $(OC_2H_3O_2)_6]^{-3}$ and boiling the solution, the iron was precipitated as basic ferric acetate, [Fe (OH) $.C2H_2O_2$]. The latter heated to 600°C for one hour to obtain red color which identified ferric oxide.Fe_2O_3 phase.

The calcium was separated from dolomite by precipitation as calcium oxalate at pH_{3-4}. Two white solids were identified calcium oxalate and magnesium sulfate phases. X-ray fluorescence. Atomic absorption flame (Shimadzu 670AA), atomic absorption flameless (Shimadzu) 680G AA) and light element techniques were used for elemental analysis, see tables and 2. Show the purification results. Tables (3-5) and figures (1-3) represent X-ray diffraction patterns for ferric oxide, calcium oxalate and magnesium sulfate. Because X-ray diffraction techniques cannot identify impurities of less than 2%, XRF and atomic absorption technique were also conducted in this work, except the iron because it has high diffraction and fluorescence [10].

Table-1- Results of solid samples after extraction and purification from dolomite

Sample No.	Sample Color	XRD	XRF	Atomic Absorption	Light Elements
1		Dolomite	70%Ca - 1.35%Fe 6.00%Si	26.5%Ca 16.00%Mg 1.32%Fe 6.05%Si	7.90%C 42.22%O
2	Reddish-Brown	-	100%Fe	37.5%Fe	16.12%C 43%O 3.34%H
3	Red	Fe_2O_3	100%Fe	70%Fe	29.8%O
4	White	CaC_2O_4	100%Ca	31.27%Ca	18.7%C 49.9%O
5	White	$MgSO_4.4H_2O$	-	20.1%Mg after ignited at 200^{0}C for 2 hr	26.0%S 53.6%O

Table –2- The analysis of magnesium sulfate at different techniques, carried out at atomic energy commission, Analytical Chemistry Center

Type of analysis	Typical analysis in this work in	Specification [11]
Color	A white crystal powder	A white crystal powder
Identification	+V	+V
Assay	99.7%	98-101.0%
As	Nil	2 ppm
Fe	0.1 ppm (0.00001%)	10 ppm
K	1.0 ppm (0.0001%)	500 ppm
Heavy metals	<0.1 ppm (<0.00001%)	10 ppm

Table-3- The X-ray diffraction analysis for ferric oxide

I(C/S)	2θ	d
400	33.1	2.70
370	35.7	2.52

Where I=Intensity (Count/Second), 2θ=Brag angle, (degree) and d=Plane spacing

Table –4- The X-ray diffraction analysis for calcium oxalate

I(C/S)	2θ	d
70	23.5	3.72
450	24.3	3.66
175	30.0	2.97
50	30.6	2.91
40	31.35	2.85
70	35.8	2.50
120	38.1	2.36
40	39.65	2.27
39	34.5	2.07
30	45.7	1.98*
29	46.4	1.95*
27	46.8	1.94*
15	47.9	1.89*

Table –5 The X- ray diffraction analysis for magnesium sulfate

I(C/S)	2θ	d
230	22.5	3.95
180	24.35	3.65
160	25.75	3.46
120	26.15	3.40
260	27.40	3.23
122	27.7	3.22
120	28.25	3.16
160	29.40	3.03
170	29.75	3.00
302	30.25	2.95
90	30.70	2.91
130	32.00	2.79
110	33.20	2.69
105	33.40	2.68
66	35.10	2.56
138	37.35	2.40
60	38.30	2.35
65	39.70	2.27

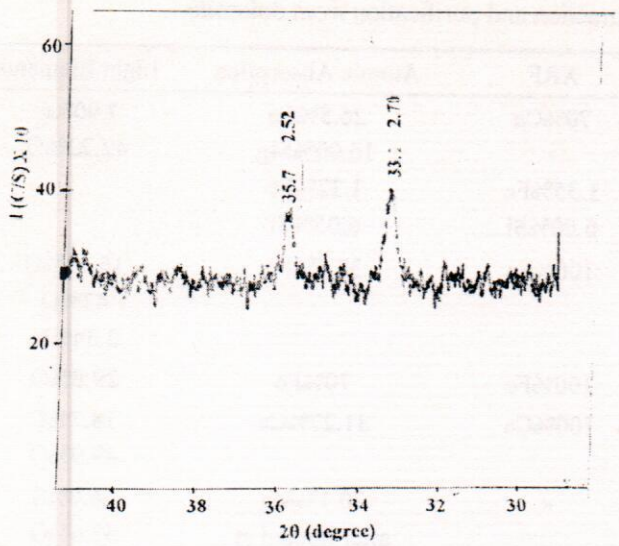

Fig. (1) X-ray diffraction of pure ferric oxide (Fe_2O_3)

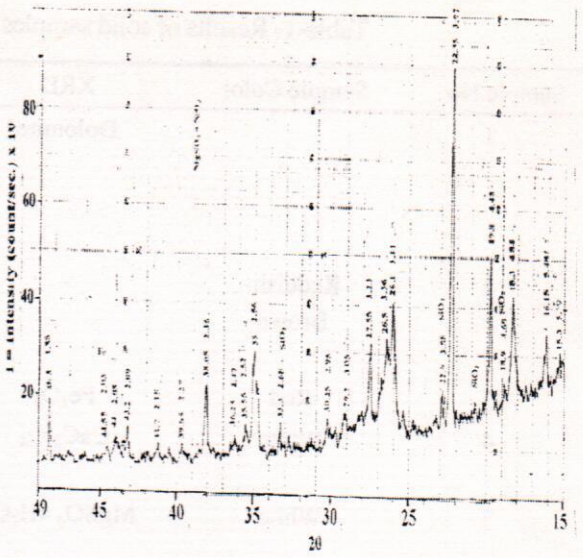

Fig. (4) X-ray diffraction mixture of ($MgSO_4$+SiO_2)

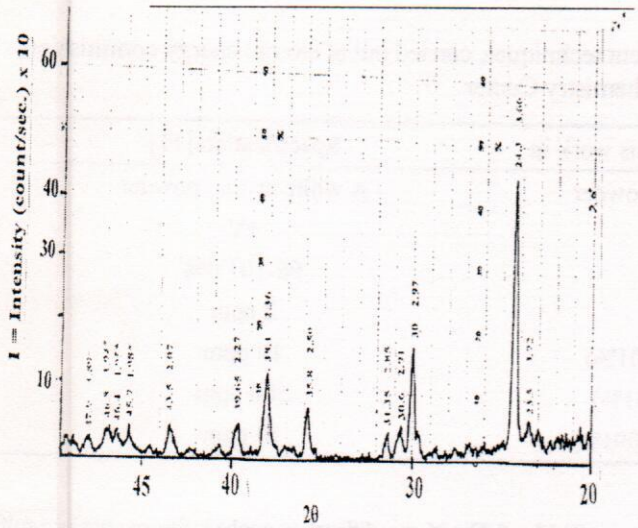

Fig. (2) X-ray diffraction of calcium oxalate (CaC_2O_4)

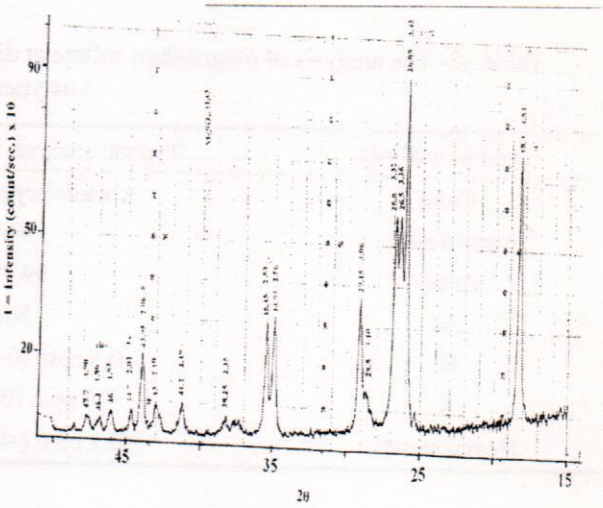

Fig. (5) X-ray diffraction of magnesium sulfate hydrated ($MgSO_4.H_2O$) after purification by recrystallization from ethanol and deionized water mixture for one time

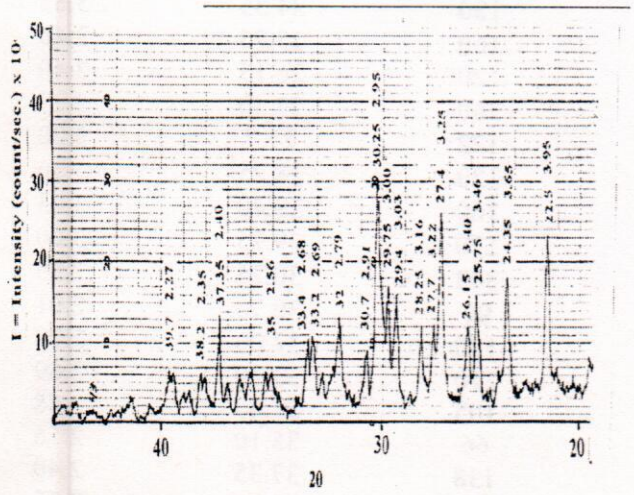

Fig. (3) X-ray diffraction of magnesium sulfate hydrated ($MgSO_4.4H_2O_4$)

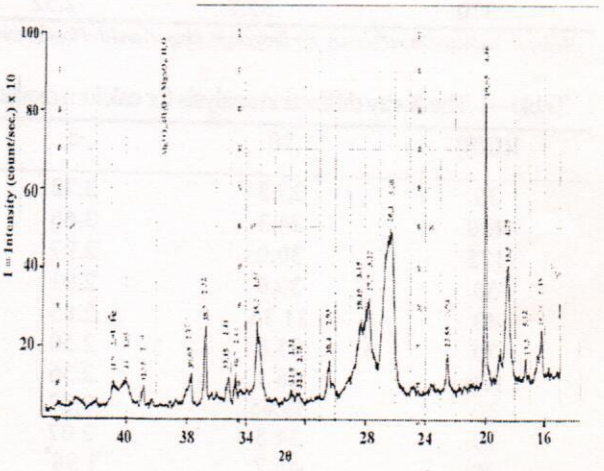

Fig. (6) X-ray diffraction of magnesium sulfate hydrated ($MgSO_4.H_2O$+$MgSO_4.4H_2O$) after purification by recrystallization from ethanol and deionized water mixture for more than one time

CONCLUSIONS

1-These methods which described in this work for extraction and purification of calcium oxalate, iron as ferric complex and then converted the later to ferric oxide, and separation the magnesium sulfate have many applications.

2-The extraction and purification of magnesium from dolomite can be considered as an excellent method for obtaining high purity magnesium sulfate.

3-More than 500 millions tons are distributed in different areas in this country, which contain high percentage of magnesium, calcium and iron can be extracted and purified economically by this method.

4-In this work, the iron showed (at d ranged 2.01-2.03) in figures (4-6) and it was extracted completely from dolomite, which has shown no iron with magnesium sulfate, see figure 3. Figure 4 represents magnesium sulfate before purification, Fig.5 after purification by recrystallization for one time from ethanol and deionized water mixture, while figure 6 represents purification of magnesium sulfate by recrystallization from the same mixture two times

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