



# PRODUCTION OF MAGNESIUM OXALATE FROM SEA BITTERN

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## ABSTRACT

The present study illustrates the details for precipitation of magnesium from Bittern as magnesium oxalate. The target of study is to prepare magnesium oxalate as a precursor for high purity MgO production. Bittern solution is considered as a byproduct in saline, but it is an ore reserve for many useful elements commercially produced at present based on dolomite, sea water. Its rich composition in various elements; especially magnesium salts gives bittern increasing economical concern for different industrial applications. In the present study, the mechanism of magnesium oxalate precipitation from bittern was investigated using oxalic acid. The global reaction kinetics of magnesium oxalate precipitation from seawater was determined using different molar ratios and varied pH (1-6). The effect of temperature on system kinetics was examined at temperatures between 15 to 80 °C. The effect of molar ratio on reaction conversion was investigated from 1:1 to 1:1.8 (magnesium to oxalic acid). The optimized parameters were found to be feasible to produce pure magnesium oxalate with 99% conversion at stoichiometric molar ratio at room temperature with pH=4. The effect of different calcinations temperature was studied from 450 °C to 1100 °C. All necessary instrumentation and chemical analysis needed for final products characterization have been executed including, XRD, XRF, and SEM analysis.

**Keywords:** magnesium oxalate, precipitation, sea bittern, liquid-liquid reaction.

## 1. INTRODUCTION

The future world-wide production of magnesium metal is projected to increase substantially over the next decade and beyond, basically as a response to the perceived requirement to reduce the on-street weight of a scope of vehicles as a major way in which fuel consumption can be improved with a simultaneous reduction in the generation of greenhouse gases. Magnesium is one of light metals having a density of 1783 kg/m<sup>3</sup>. This is 66% of aluminum and one sixth of steel. The strength to weight proportion of metal is 158 kNm/kg, which is higher than 130 kNm/kg for immaculate aluminum. Magnesium metal of high quality when compared to its weight proportion, these phenomena drives a focusing interest to this metal. The business required for magnesium according to ASTM B92 (2007) for 9980A is at least 99.80 wt% Mg with impurities, for example Fe, Si, Al and Ca below 0.05wt% each [1]. The metal has various industrial uses, for example, magnesium compounds are widely used in the automobiles industry [2], an alloying component in aluminum alloys (41%), die casting (32%), steel desulphurization (13%), and different applications as an industrial chemical (14%) [3]. Aluminum industry uses magnesium as alloying to improve the ductility, strength and consumption resistance of aluminum combinations [4]. Magnesium's use in both aluminum and steel production strongly links its demand to these two other metal commodities. The use of magnesium has generally been constrained by moderately high cost of production and related energy costs. There have likewise been logical issues around alloy improvement, specifically, expanding creep resistance for drive train applications and enhancing corrosion resistance. [5]. Magnesium and its salts have been utilized in many applications for example, agriculture, insulation,

construction, in compound and different industries[3]. High purity MgO is particularly utilized in food and manufacture of pharmaceutical while Mg(OH)<sub>2</sub> is a mainly component in the manufacture of flame retarding reagents[6]. Magnesium is found in minerals such as dolomite, magnesite, serpentinite, brucite, etc. It is the most part recovered from seawater, saline solutions and bitters. Sea water contains about 1.3 g/L while the asset of magnesium-bearing saline around the global is evaluated to be in the billions of tones [7]. High contents of magnesium have been found in solar brines located in South America[8]and other salt lakes around the world. The production of magnesium is technically challenging, as well as having relatively high capital and operating costs. In their simplest form, the two principal methods of producing magnesium metal involve (a) high-temperature reduction of magnesium oxide and (b) electrolysis of molten magnesium chloride. Both options are characterized by having high energy requirements [9]. Alternative technologies have been studied such as Cabothermic process, Magnethermic process and SOM process. In previous study[8] two processes were proposed to remove Mg from the bittern by precipitation using sodium hydroxide and ammonium hydroxide solution. Such a step produces a mixture of Mg(OH)<sub>2</sub>and some impurities which requires further processing to recover valuable Mg metal. The high level of Ca in the brine would contaminate the Mg products if not removed first.

In this work, it was required, to recover highly pure magnesium oxide from bittern through magnesium oxalate optimization process. The study was carried out experimentally in lab scale. The effect of different parameters on Mg oxalate precipitation were studied. The parameters varied included MR, pH and reaction



temperature. The parameters should result highly pure Mg oxalate which in turn results in pure MgO.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Bittern(100 L) having density of about 1.3325 g/cm<sup>3</sup> (36 °Be) was obtained from EMSC, Egypt (received May, 2014), the raw material used in this work is known as the richest source of Mg<sup>2+</sup> ions containing > 85 g/L magnesium.

Starting with Sea Water of 3.5°Be and passes through many stages to reach 36°Be during the evaporation process as shown in figure (2) as follows:

#### a) Concentration ponds

The concentration ponds are consisted of four stages shown in Figure-1 where in the first stage at concentration (3.5-8°Be) organic matter will be precipitated. In the second stage the sea water reached (8-

14°Be) and calcium carbonate and bicarbonate will be precipitated. In the third stage sea water reached (14-18°Be) calcium sulfate dehydrate will be precipitated. In the fourth stage sea water converted to mother liquor at (18-24°Be) and Gypsum will be precipitated and sodium chloride starting to precipitate.

#### b) Precipitation ponds:

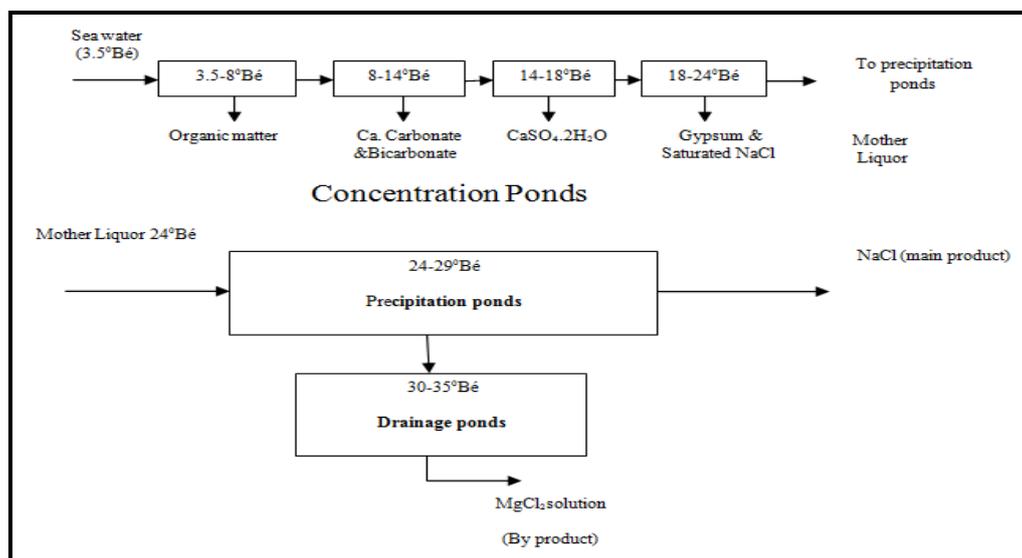
Precipitation ponds are consisted of 28 ponds where all sodium chloride had been precipitated at 24-29°Be (the desired product for the saline company) and residual solution went to drainage ponds.

#### c) Drainage ponds:

These ponds consisted of two ponds where the bittern will be concentrated at (30-36°Be) this bittern full of magnesium salts. The main chemical composition of bittern was analyzed by atomic adsorption and reproducibility of bittern by complex metric titration method as shown in Table-1.

**Table-1.** Main chemical composition of bittern.

Composition	Mg <sup>++</sup>	Ca <sup>++</sup>	pH	SO <sub>4</sub> <sup>-</sup>	TDS	Conductivity
Bittern(36°Be)	85.7 g/L	0.12 g/L	6.24	56.9 g/L	449533 ppm	513 mS/cm, at 25°C



**Figure-1.** Stages of bittern preparation.

## 2.2 Chemicals

### 2.2.1 Purchased chemicals

From Fluka Chemika company, C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, oxalic acid M<sub>wt</sub>126 g/mol, mp 100-102°C, Assay≥99.0% were supplied, commercial sodium hydroxide, NaOH, Mwt= 40 was also used. Hydrochloric acid and Ammonia solution 25%, Pure reagent were supplied from ADWIC Co., Assay 30-34%. Magnesium sulfate (Heptahydrate) MgSO<sub>4</sub>·7H<sub>2</sub>O, was supplied from EL NASR PHARMACEUTICAL CHEMICALS Co., assay 99%. Ammonium chloride, finely supplied from

Rasayan Co., with a molecular weight of 53.49, purity 99.0%. for analysis. Calcium carbonate was supplied from EL NASR Pharmaceutical Chemicals Co., not less than 99% purity and dried for 4 hr at 105°C before use.

### 2.2.2 Prepared reagent

All reagents and indicators were prepared according to method No. 2340 C and 3500Ca D[95], calcium Standard solution (0.01022M): method No.2340 as stated in (Standard Methods for The Examination of Water and Waste Water). EDTA (0.1M): method No.2340, Ethylenediaminetetraacetic Acid Disodium salt 2-



hydrate  $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$  Mwt=327, Assay $\geq$ 99.0% and is prepared by dissolving 3.7 gm (dried for 2 hrs at 80°C before use) in 1 liter volumetric flask and diluted to the mark with distilled water and stored in a polyethylene bottle.

### 2.3. Methods

Figure-2 shows the experimental set-up for preparation of magnesium oxalate and consists of:

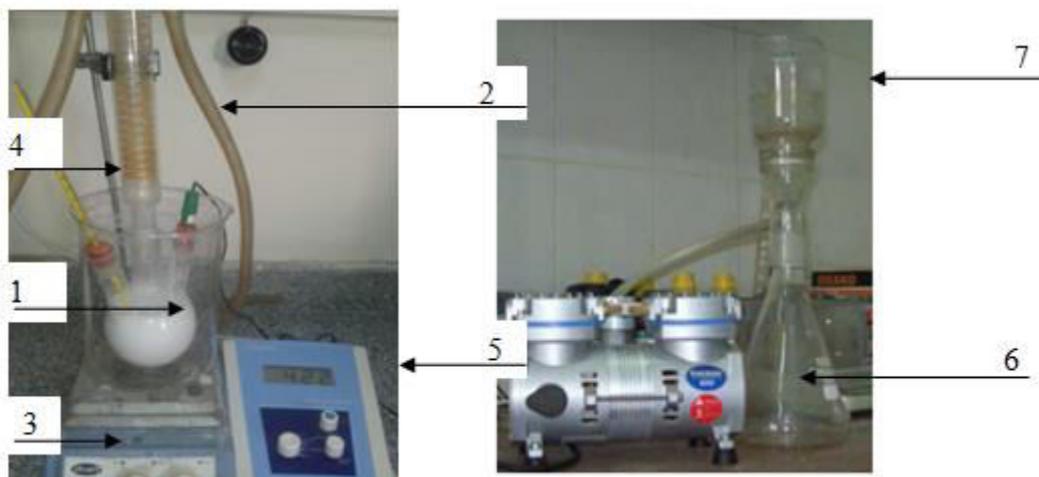


Figure-2. Laboratory set-up of magnesium oxalate preparation.

#### 2.3.1 Description of the laboratory experiment

Batch experiments were carried out in one liter three-neck round bottom flask, one side connected to reflux condenser, the second side opening for inserting pH and temperature probes and the third side opening for sample withdrawal intervals. The 3-necked flask is filled with calculated volume of bittern, a known amount of oxalic acid as precipitant. Sodium hydroxide was used to adjust pH of reaction.

The precipitation of magnesium oxide from bittern was carried out using different precipitants such as oxalic acid, ammonia solution and sodium hydroxide.

#### 2.3.2 Precipitation using oxalic acid

100 ml of bittern in each experiment at different reaction temperature (15 to 80°C), Hot plate was set at constant stirring rate of 210 rpm. to homogenize the solution. Oxalic acid is added to the stirred solution and 6.25M NaOH was continuously added for controlling pH. (10 ml) samples were taken at interval time to evaluate state of reaction. The total amount of sodium hydroxide added was measured through reaction to calculate the molar ratio of NaOH used with respect to Mg ions in bittern and Oxalic acid in reaction media. After reaction completion, the precipitate was by a vacuum filtration. Further the solid was washed with distilled water followed by ethanol. The final precipitate (magnesium oxalate) was dried at 100 °C for 2 hr before analysis. It was also calcined at 650°C for 2 hrs. The products were subjected to XRD analysis. EDTA titration was used to

- one liter three-neck round flask, acts as reactor.
- Water –cooled vertical reflux condenser.
- Electrically hot plate and magnetic stirrer to allow heating and agitation of reaction mixture.
- Digital thermometer, (5) Digital pH meter, (6) Vacuum filtration pump, (7) Buchner flask.

evaluate the unreacted magnesium in the residual solution.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Effect of different parameters on reaction conversion

The effect of different parameters such as reactant molar ratio, pH and temperature were studied on the reaction conversion of oxalic acid at different time interval as follows:

#### 3.1.1 Effect of reactants molar ratio (MR)

The molar ratio of the reactants (magnesium to oxalic acid) greatly influences the rate of batch process. To reach the optimum magnesium to oxalic acid molar ratio, the reaction was carried out at fixed temperature 25°C, pH=4 and different RMR (1:1, 1:1.2, 1:1.4, 1:1.6 and 1:1.8). For each molar ratio the magnesium conversion was calculated and plotted versus time and full product characterization was fulfilled for precipitated solids as XRD, XRF, and SEM.

#### 3.1.2 Effect of pH

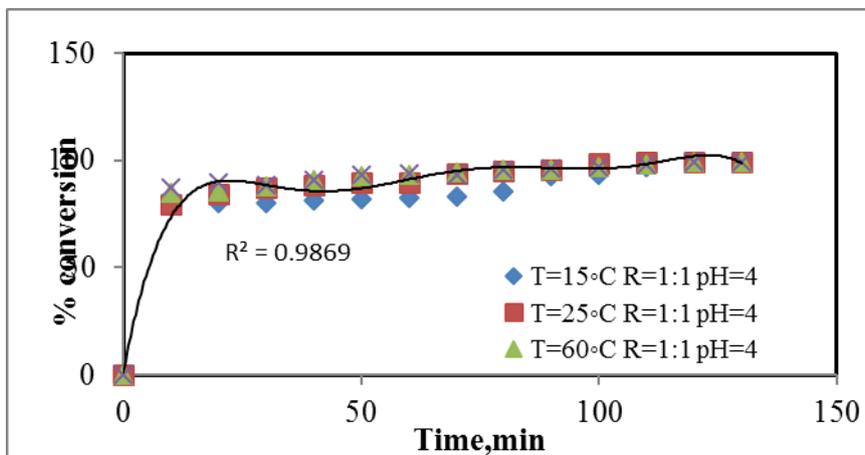
Effect of pH was studied at constant MR (1:1) and constant reaction temperature at 25°C. Different pH was used (1, 3, 4 and 6). Magnesium conversion percentage was plotted versus time and subjected to XRD, XRF, and SEM analysis.



### 3.1.3 Effect of temperature

Influence of temperature on each batch process was studied at various temperatures 15, 25, 60, and 80 °C as. The optimum temperature that provides the highest

conversion was detected at 25 °C. The batch process was carried out at MR=1:1, pH=4. The reaction conversion calculated was plotted versus time Figure (3) and Table (2).



**Figure-3.** Effect of reaction conversion at different time, temperature, MR=1:1 and pH=4.

**Table-2.** Effect of reaction temperature on magnesium oxalate purity.

Element	15 °C	25 °C	60 °C	80 °C
% C	18.36	20.86	22.81	32.75
% O	61.43	63.55	61.49	54.26
% Na	5.07	0.78	0	2.68
% Mg	14.47	13.57	13.11	7.98
% Al	0.34	0.82	1.5	0
% K	0	0.41	0	0
% Cl	0.33	0	0	2.33

### 3.2 Instrumentation analysis

**3.2.1** The content of magnesium in residual solution was determined by Complexometric titration method using murexide indicator and NaOH to adjust pH up to 12 as mentioned before.

**3.2.2.** Figure-4 illustrates the XRD patterns of magnesium oxalate under this condition, where all peaks in the pattern could be clearly indexed on the basis of a monoclinic cell reported for magnesium oxalate.

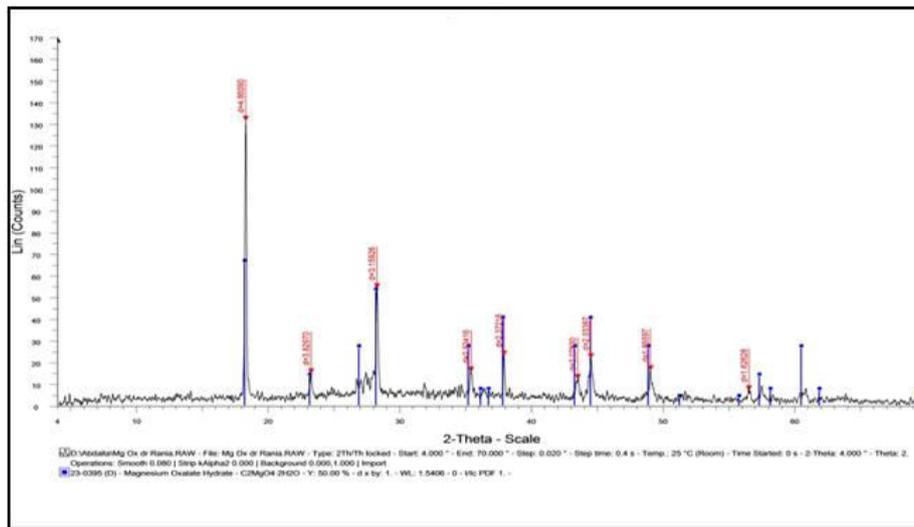


Figure-4. XRD patterns of Mg oxalate product.

Reaction time is one of the most important factors that affect precipitation of magnesium oxalate. At the end of reaction, most magnesium ions were converted to pure magnesium oxalate. Complete specification of product was confirmed by XRD pattern.

### 3.2.3 Effect of pH on reaction conversion

The influence of pH on the precipitation of magnesium oxalate at MR 1:1 at ambient temperature is

shown in Figure-5. Results have shown that all magnesium concentration profiles seem to be close at constant molar ratio and temperature. Equilibrium was reached within the first 90 min. The removal of bittern containing magnesium ions as magnesium oxalate with highest conversion during 2 hours with conversion of 90-98%. Above pH=4, magnesium oxalate decomposes to magnesium hydroxide.

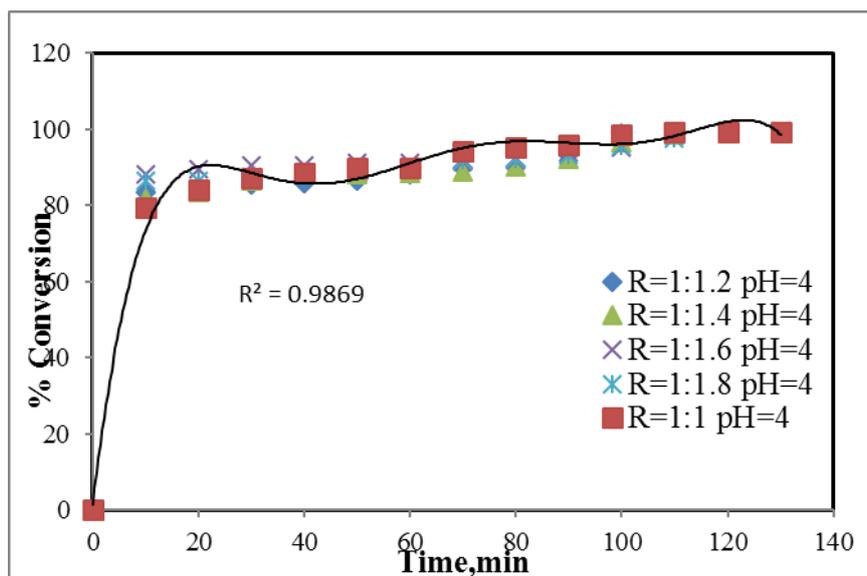


Figure-5. Conversion of magnesium at MR 1:1 to 1:1.8, temperature (25 °C) and pH= 4.

### 3.2.4 SEM and EDX analysis of magnesium oxalate

The morphology of magnesium oxalate is shown at 80 °C as shown in Figure-6<sub>a</sub> to Figure-6<sub>h</sub>. EDX analysis at these temperatures shows percentage of all elements

precipitated. Not only magnesium oxalate precipitated, but also sodium and chlorine were present too. EDX shows that main peaks are of magnesium oxalate indicating pure precipitation.

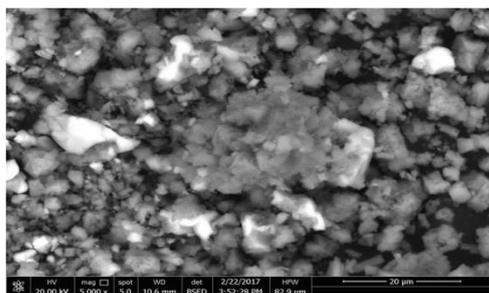


Figure-6a. SEM of Mg oxalate prepared at 15°C

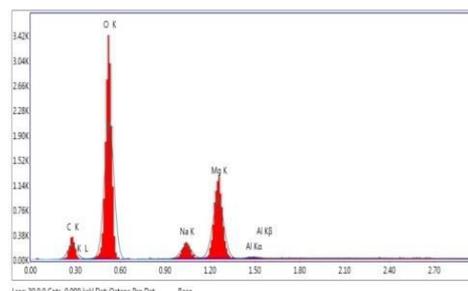


Figure-6b. EDX of Mg oxalate prepared at 15°C.

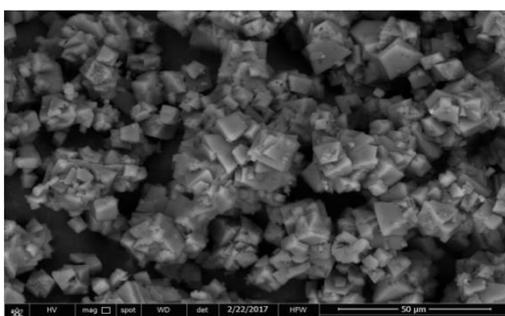


Figure-6c. SEM of Mg oxalate prepared at 25°C

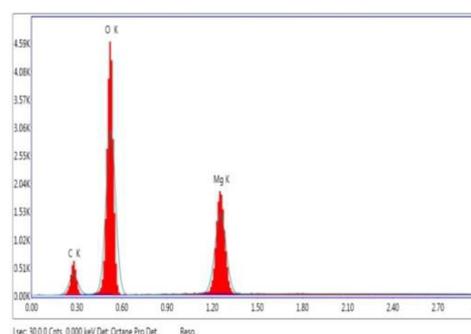


Figure-6d. EDX of Mg oxalate prepared at 25°C.

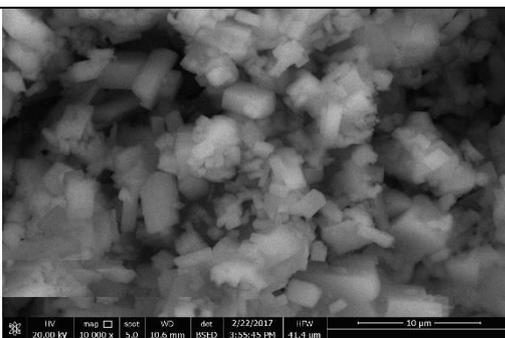


Figure-6e. SEM of Mg oxalate prepared at 60°C.

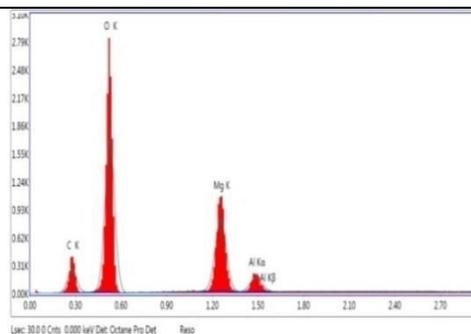


Figure-6f. EDX of Mg oxalate prepared at 60°C.

The purity of magnesium oxalate was calculated from the above charts at different reaction temperature. It was obvious from Table-3 highest purity of magnesium oxalate was fulfilled at 25 °C.

**Table-3.** XRF Data for before and after washing magnesium oxalate salts.

Concentration of main constituents	Before washing (wt, %)	After washing (wt, %)
SiO <sub>3</sub>	0.06	0.08
Al <sub>2</sub> O <sub>3</sub>	0.04	0.04
Fe <sub>2</sub> O <sub>3</sub>	0.002	--
MgO	26.36	25.45
CaO	0.05	0.05
Na <sub>2</sub> O	0.39	0.37
K <sub>2</sub> O	0.5	0.48

P <sub>2</sub> O	--	0.002
SO <sub>3</sub>	0.02	0.02
Cl	0.03	0.02
LOI	72.56	73.48
CuO	0.001	--
NiO	0.002	0.002
ZnO	0.002	--

From Table-3 magnesium oxide is stable and is more purified when washed with water as some oxides decreased by washing indicating its dissolution in water.

### 3.2.5 Effect of calcinations temperature on magnesium oxalate

The different calcination temperatures were studied for magnesium oxalate to optimize magnesium oxide salts for maximum conversion. Products under study were subjected to SEM and EDX tests. The tests of MgO



powder obtained at different calcinations temperatures were carried out at (500 °C, 650 °C and 1100 °C). The results are shown in Figure-7.a, Figure-7b, Figure-7c, Figure-7d, Figure-7e and Figure-7f. The best calcinations temperature detected is 650 °C to produce high purity MgO. The morphology of MgO was more regular at calcinations temperature of 1100 °C as shown in Figure-7g. The percentage of the elements associated with magnesium oxide at different calcinations temperatures was explained in the following Tables (4), (5), (6) and (7).

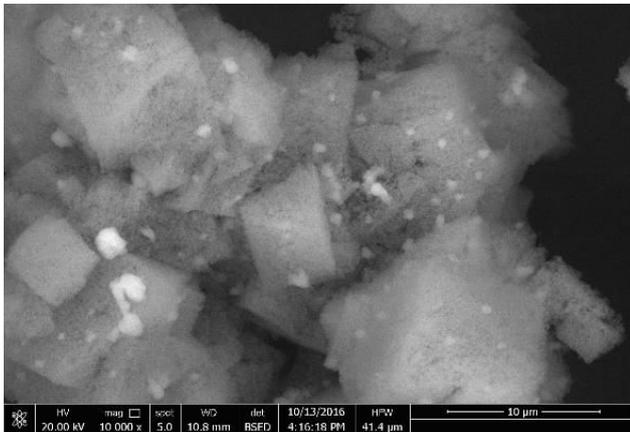


Figure-7a. SEM of MgO prepared at 450 °C.

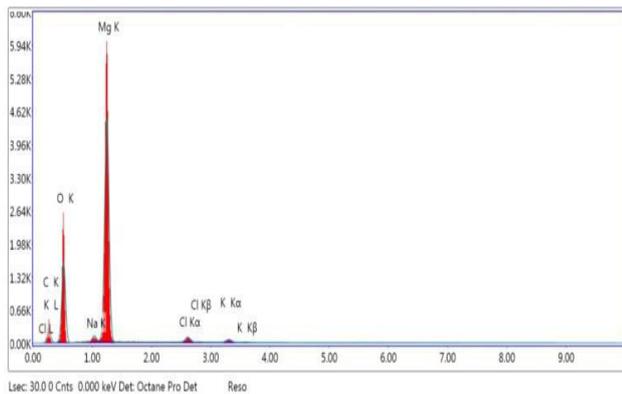


Figure-7b. EDX of MgO prepared at 450 °C.

Table-4. Composition of MgO calcined at 450 °C.

Element	Weight %	Atomic %	Net Int.	Error %
C	13.53	19.23	69.46	11.48
Na	1.36	1.01	35.67	11.98
Mg	28.46	19.99	1345.64	6.07
Cl	0.67	0.32	35.05	11.94
K	0.48	0.21	22.25	13.77
Oxygen	55.5	59.23	0	0

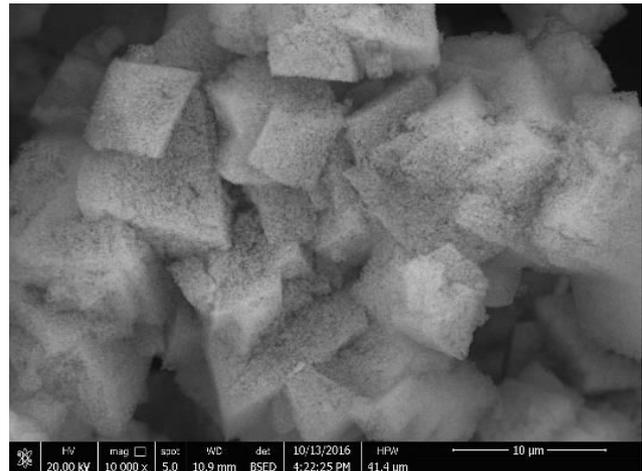


Figure-7c. SEM of MgO calcined at 650 °C.

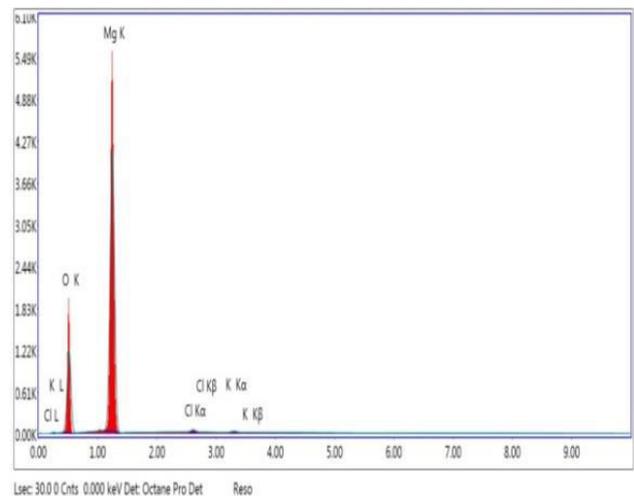


Figure-7d. EDX of MgO prepared at 650 °C.

Table-5. Composition of MgO calcined at 650 °C.

Element	Weight %	Atomic %	Net Int.	Error %
Mg	59.48	49.53	1231.18	4.83
Cl	0.68	0.39	11.36	24.84
K	0.44	0.23	6.77	37.64
Oxygen	39.4	49.85	0	0

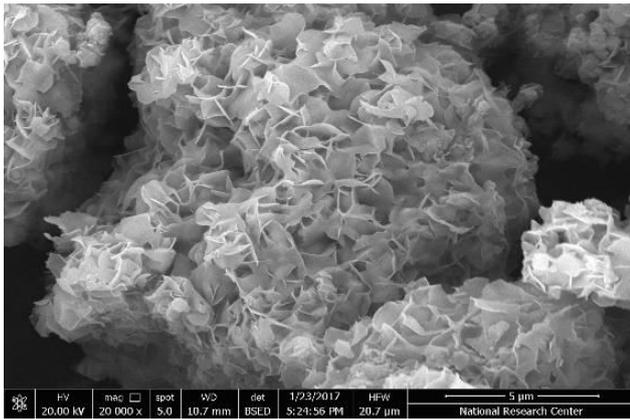


Figure-7e. SEM of MgO calcined at 1100°C.

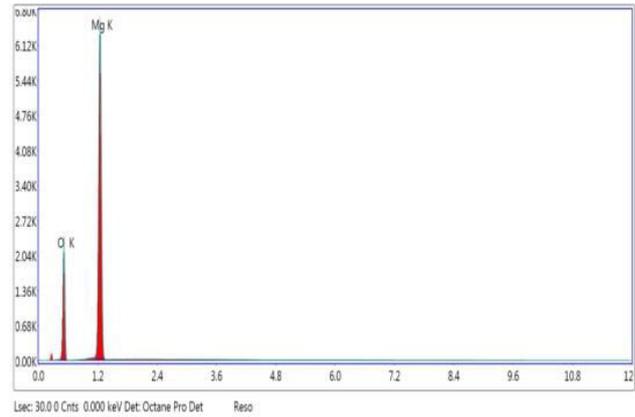


Figure-7f. SEM of MgO calcined at 1100°C.

Table-6. Composition of MgO calcined at 1100°C.

Element	Weight %	Atomic %	Net Int.	Error %
O	37.72	47.93	333.73	7.29
Mg	62.28	52.07	1344.14	4.64

Percentage of loss in weight of magnesium oxalate after burning at different temperatures is shown in Table-7.

Table-7. Percentage weight loss before and after calcination.

Calcination temperature(°C)	Weight before calcination (g)	Weight after calcination (g)	% Weight loss	% Purity
450	5	1.412	71.76 %	83.96
650	5	1.394	72.12 %	98.88
1100	5	1.385	72.3 %	99

#### 4. CONCLUSIONS

It can be concluded that the best optimum operating conditions for precipitating pure magnesium oxalate are confirmed at MR=1:1, pH=4, ambient temperature and time of reaction for 2 hr. The yield was 51.662 g with conversion 98.7%. The observed high yield and conversion data were due to using purified concentrated bittern solution of 36 Baume'.

No other peaks were detected in the spectrum within the detection limit of the X-ray diffraction instrument, indicating the purity of the synthesise powder.

#### ACKNOWLEDGEMENT

Our work was supported by the National Research Centre, Chemical Engineering Department and El Max Saline Company in Alexandria. The authors thanks the team colleagues in Cairo University and assistance with XRD, SEM, and XRF studies.

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