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Research Paper

# Preparation and Characterization of Magnesia Precipitated from Waste Liquid Bittern

**Engineering**

**KEYWORDS :** Magnesia, Bittern, X-ray diffraction, SEM, crystallinity, high purity, economic study

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## ABSTRACT

*The characterization of physical properties for MgO powders precipitated from Alexandria Salt company waste liquid Bittern and that precipitated from industrial wastewater rich with ammonia was studied. The decomposition of precipitated Mg(OH)2 from sea liquid Bittern was analyzed by TGA and crystallization process was observed by XRD for both Mg(OH)2 and MgO. The SEM analysis and EDX, shows the platelet morphology of Mg(OH)2 and hexagonal MgO powders originating from different calcinations temperatures. The XRF analysis showed the increase in Magnesia % purity from 35% up to 96.6 % by water wash of MgO prepared after calcination at 900oC. A techno-economic pre-feasibility study has been revealed conducted and high product profitability-potentials with respect to: (i) the expected percent annual return on investment 400% and (ii) payout-period (0.19 year) based on lower price than imported pure source of MgO with 7000 EGP per ton as a selling price.*

## INTRODUCTION

The largest single use of magnesium is alloying aluminum to provide strength and corrosion resistance. Significant quantities of magnesium are present in almost every structural use of aluminum ranging from window frames to aircraft components. The largest use of magnesium die-casting is in the automotive industry where magnesium's strength and light weight are being used in an ever-increasing volume to improve fuel economy. Another important use of magnesium die cast parts is the manufacture of manual and power hand tools where magnesium's lightweight improve safety and operator performance [1].

Precipitation of magnesium hydroxide from liquid bittern is the final step in the production of various magnesium compounds [2]. The availability of inexpensive starting materials and the high purity of the product make precipitating liquid bittern magnesia an economically significant process [3].

Indian patent (20100172812) proposes a process which comprises: the use of bittern having specific gravity =1.3 and chemical composition Ca = 0.5 % (w/v), Mg =11.5 %, Na = 0.4%, K=0.4% & $B_2O_3$= 0.032, was mixed under stirring with 123.8 g ammonia. The mixture was allowed to stand several hours. The result slurry was filtered and cake obtained was subjected to chemical analysis (Ca, Mg &Cl). The wet cake was dried and calcined at 900˚C to obtain MgO (magnesia) of high purity 98.5% and good quality [4].

European patent (80304524.4) with publication number (0038891) proposed a process which comprises: commercial bittern containing Mg $Cl_2$ of 34° Be was mixed with light calcined magnesite and light calcined dolomite in molar ratio $MgCl_2$ (calcined dolomite) 0.03: 1 and calcined magnesite: $MgCl_2$ = 0.04: 1. The mixture was stirred and solid mass was formed in less than 24 h dried and calcined at 900°C.The obtained fine MgO powder was washed with water and possessed a purity of 98% MgO [5].

Crystalline magnesium hydroxide, the so-called brucite, belongs to the bivalent metal hydroxides group, whose crystal structure is layered $CdI_2$ – type arrangement [6]. Successive hexagonal $Mg^{2+}$ ions layers and $OH^-$ ions layers are stacked one upon another. The magnesium cation is six- fold coordinated by hydroxyl groups, thus forming Mg $(OH)_6$ octahedral. Such layered crystal structure is an advantage for platelet- shaped crystallization of the compound [7].

Magnesium hydroxide can be obtained by several methods [8]. Magnesium (MgO) is the most important product of the magnesium compound industry. It is usually produced for commerce from magnesium hydroxide $Mg(OH)_2$ obtained from magnesium rich-bitterns [9]. The most important process for the production of MgO from brine or sea is based on the fact that $Mg(OH)_2$ can be precipitated bittern from solutions of magnesium salts by the addition of strong base. The $Mg(OH)_2$precipitated is washed, filtered and then calcined to produce MgO. The calcined MgO is produced at temperatures <$900^0$c and characterized by its moderate to high chemical reactivity [10]. Magnesia has numerous applications as mineral supplement for animal feeds, in fertilizers, as a raw material for various MgO chemicals, manufacture ceramics, cements, paper, petroleum additives and superconductor product [11].

The aim of this research work is to study and characterize the physical properties of MgO powders obtained by chemical precipitation from chemical compound (MgCl) to be compared with that precipitated from natural sea Bittern. DTG decomposition study of $Mg(OH)_2$ (brucite) and magnesia MgO were first performed. After that, XRD, EDX results were used to study the impact of calcination temperature. Development of the morphology was observed by SEM.XRF analysis shows the purity 96.6 % of the products.

## 2- EXPERIMENTAL

2.1 MgO powders were synthesized by chemical precipitation singly, from both natural bittern containing 30 g/L Mg ions and reagent-grade Mg $Cl_2.6H_2O$.

The chemical analysis of liquid bittern is shown in Table (1).

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**Table (1): Characteristics of liquid bittern used as source of Magnesium ions:**

| Element | Value mg/L |
|---|---|
| TDS | 292 |
| Ca | 1600 |
| Mg | 73.84 |
| Na | 21.76 |
| Cl | 218.63 |
| $SO_2$ | 3.2 |
| Carbonates | 0.5 |
| K | 9.81 |
| Bicarbonate | 1.73 |
| Br | 12 |
| I | 5 |
| Li | 0.31 |
| conductivity | 583 mS/cm |

2.2 The calcium in Bittern was eliminated by anhydrous sodium bicarbonate before precipitating the hydroxide.

2.3 The chemical grade (250g) $MgCl_2.6H_2O$ was added to (190.8g) ammonia solution, stirred 15 min at room temperature. The resulted slurry was filtered and washed with (280) ml distilled water. The wet cake was dried at $110^0$C and calcined at $900^o$C for 2hr in air to prepare MgO with 98% purity.

2.4 123.8 g ammonia solution was added , mixed to 200 ml Bittern containing 33g $Mg^{++}$ ions and stand 7hrs. The white precipitate was filtered then washed with (500ml D.W.). The cake was dried at $110^0$C and calcined at different temperatures, $700^o$C, $900^o$C & $1100^o$C 2hrs in air. The Mg OH powder before calcination was subjected to XRD and TGA anal SEM analysis.

2.5 The MgO powders after calcinations was subjected to XRF, XRD, EDX and SEM.

The (XRD) and crystallite size was calculated using the scherrer's formula using KCL as an internal standard, A Cu $k_\alpha$ radiation (ɧ = 1.5405 $^0$A) and Ni filter was used. The difractograms were registered in a range of 10-100 (30KV, 20 mA), in a step-scan mode of 0.0f2ϴ per step counting for 5 s/ step (model Siemens).

2.6 The thermal analysis Fig(1) was done by means of Schimadzu TGA /50H. The heating rate of the sample was $10^0$C min$^{-1}$up to $1000^0$C. Temperature, weight and change in weight of the sample recorded on chart. The morphology of $Mg(OH)_2$ and MgO agglomerates at different temperatures were examined by SEM (Leica S440). EDX was performed to confirm the Mg % in MgO crystals.

## 3. RESULTS AND DISCUSION

3.1 The thermal decomposition path of the precipitated $Mg(OH)_2$ from Bittern was studied by TGA analysis . A very small and a strong endothermic peak was observed; the first peak is related to the dehydration process at temperatures < $200^0$C and the second to the decomposition of magnesium hydroxide at the temperature of 310 $^0$ C, The chart shows a continuous weight loss of 8% between $100^0$C – 800 $^0$C. The total weight loss was around 40 % and $CO_2$evaporation occurred finally at $700^0$C. Therefore, the complete decomposition of $Mg(OH)_2$ can be achieved at low temperature ( < $400^0$C) up to 800 $^0$C Fig (1).

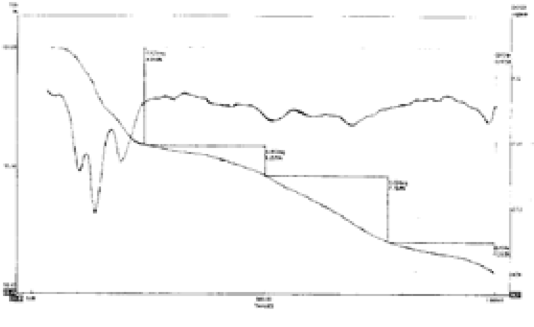


**Fig (1) TGA Chart for Mg OH prepared from bittern only**

3.2 The X-ray diffraction studies at different temperature on the crystallization process for the magnesia formed and showed no formation or very poor crystallinity at $700^0$C, although stronger diffraction peaks can be seen in Fig(2). At higher temperature, crystals of Pericles 26.2nm and 52.8 nm (MgO) were detected at 900 $^0$C Fig (3)and Fig (5)for proposed as standard from pure chemicals and became sharp, nice highest crystallinity were detected at > $1100^0$C ,Fig(6) i.e. the higher temperature improved purity and crystallinity of prepared magnesia priceless ( cubic MgO).

The peaks shown in XRD pattern around $40^0$C -$50^0$C 2ϴ position ascribed to percales (MgO).

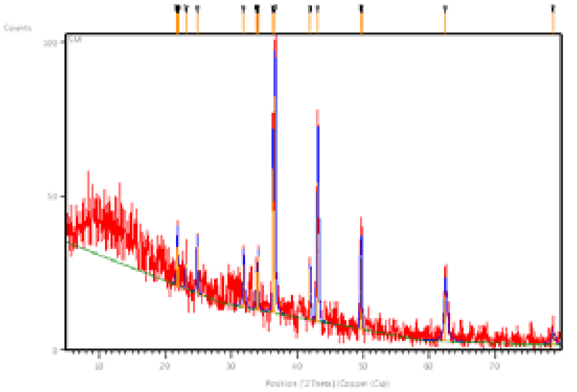


**Fig (2) XRD chart of Mg O sample prepared from bittern and calcined at $700^0$C 2h**

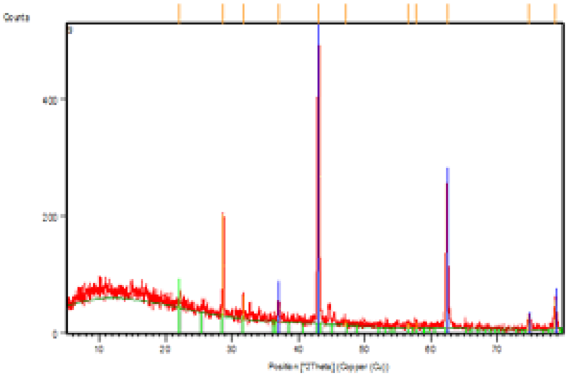


**Fig (3) XRD pattern of Mg O sample prepared from bittern calcined at $900^0$C 2h**

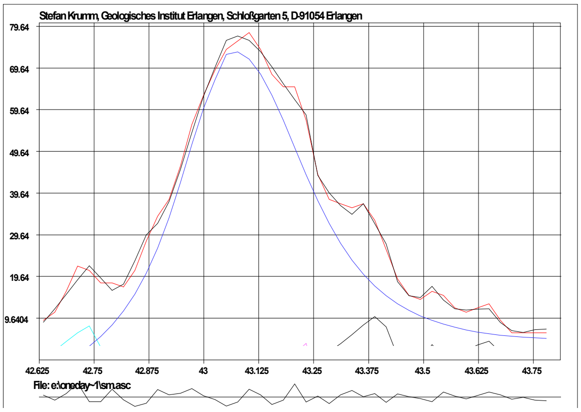


**Fig (4) particle size in nm distribution in volume % for Mg O sample from bittern calcined at $900^0$C 2h**

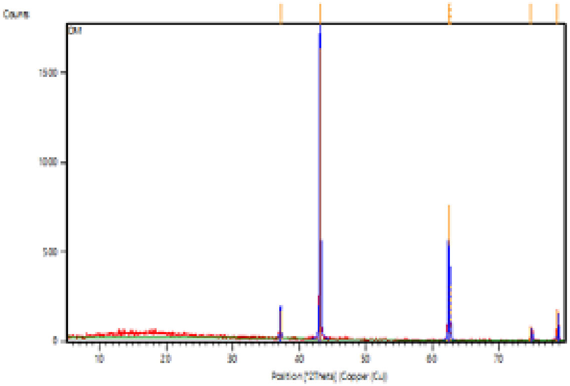


**Fig (5 ) XRD chart of Mg O sample prepared standard from pure chemicals (MgCl) and calcined at 900⁰C 2h**

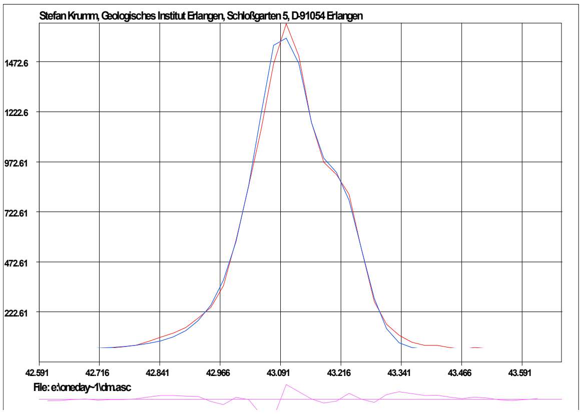


**Fig (6) Particle size distribution in volume % for Mg O as standard sample**

3.3 The Low crystallinity of magnesia calcined at 900⁰C was improved by washing the MgO prepared after calcinations with water [3]. Thus we achieved improvement in our yield from 35% purity up to 96% purity as shown in the XRF results Table (2).

**Table (2) XRF of magnesia obtained from Industrial wastewater, bittern, washed product, and pure chemicals respectively:**

| Reference MgO composition | % weight for Yield from WW | % weight for Yield from L.B. | % weight for Water washed yield | % weight for Standard yield |
|---|---|---|---|---|
| MgO | 33.84 | 35.09 | 96.08 | 92.65 |
| $SiO_2$ | 0.69 | 0.17 | 1.34 | 0.18 |
| $Al_2O_3$ | 0.28 | 0.08 | 0.32 | 0.12 |
| $Fe_2O_3$ | 0.99 | 0.01 | 0.02 | 0.01 |
| $Ca_2$ O | 0.21 | 0.27 | 0.19 | 0.25 |
| NaO | 4.8 | 4.53 | 0.33 | ND |
| $K_2O$ | 8.44 | 3.64 | 0.07 | ND |
| $P_2O_5$ | 0.02 | 0.01 | 0.01 | 0.01 |
| $SO_3$ | 12.94 | 8.07 | 0.88 | 0.03 |
| Cl | 35.69 | 17.64 | 0.66 | 0.77 |
| LOI | 0.2 | 30.5 | 0.01 | 5.95 |
| NiO | 0.07 | 0.004 | 0.01 | 0.007 |
| CuO | | 0.004 | | 0.006 |

Table (2) gives the chemical composition of the (MgO) prepared from Industrial wastewater rich with ammonia and dolomite & Bittern , (MgO) prepared from Bittern only, (MgO) prepared from bittern only and washed product with water, and(MgO) prepared from MgCl as pure standardproduct, respectively. The XRF analysis indicated MgO content 35% and loss on ignition (LOI) 30.50%.

MgO content 96% was achieved after washing the product and drying at 110⁰C .

The MgO content 98% was obtained from the pure MgCl as standard product for the preparation condition with 5.95% (LOI).

3.4 The morphology of MgOH powders obtained from precipitation reaction

**$MgCL_2$+ $2NH_4$ OH -------->$Mg(OH)_2$ + 2 $NH_4CL$**

Is shown by SEM High resolution micrograph Fig(7) and Fig (8) showing platelet –like arranged sample. The EDX chart confirmed the high Mg% Fig (9).

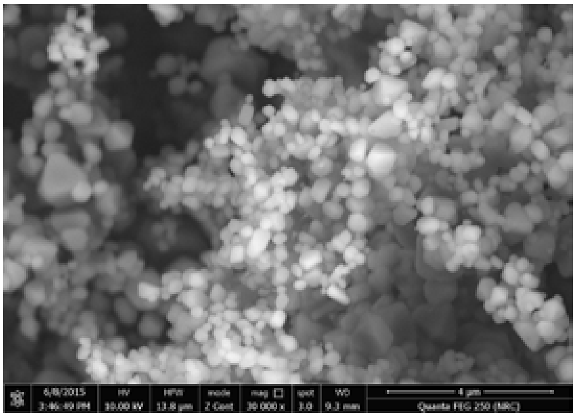


**Fig (7) SEM micrograph of $Mg(OH)_2$ showing arranged like platelet morphology.**

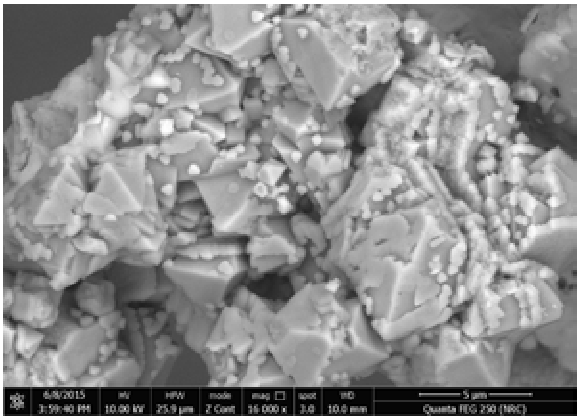


**Fig (8)SEM micrograph of Mg $(OH)_2$ showing platelet with high resolution**

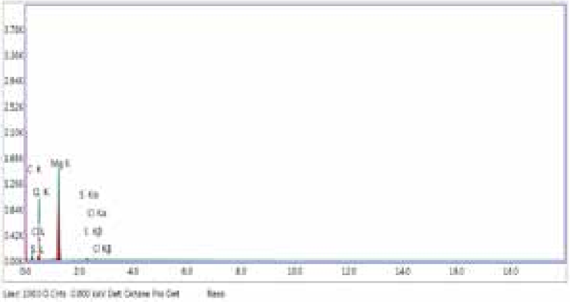


**Fig (9) EDX chart for Mg $(OH)_2$ The high Mg % in the precipitated product.**

| Element | Weight % | Atomic % | Net Int. | Error % |
|---|---|---|---|---|
| C K | 22.13 | 30.13 | 6.95 | 12.42 |
| O K | 50.28 | 51.38 | 45.75 | 9.78 |
| MgK | 27.17 | 18.27 | 96.96 | 7.78 |
| S K | 0.29 | 0.15 | 1.73 | 22.78 |
| ClK | 0.13 | 0.06 | 0.8 | 44.7 |

SEM of Magnesia powders obtained at different calcination temperatures($700^0$C, $900^0$C, $1100^0$C) is shown in Fig (10), Fig (11) and Fig (12).

The SEM Confirms that increasing calcination temperature achieved significant difference in Magnesia morphology. EDX chart for magnesia achieved at $900^0$C calcination temperature Fig (13). The EDX shows highest improvement for calcination of magnesia at $1100^0$C where the hexagonal crystals are nice and sharpFig (14).

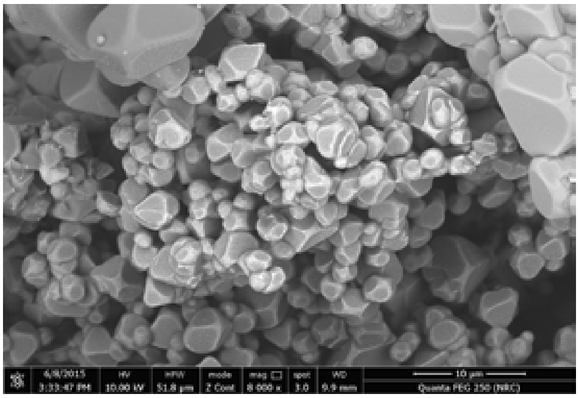


**Fig (10) SEM micrograph of Mg O calcined at 700 ° C showing platelet morphology**

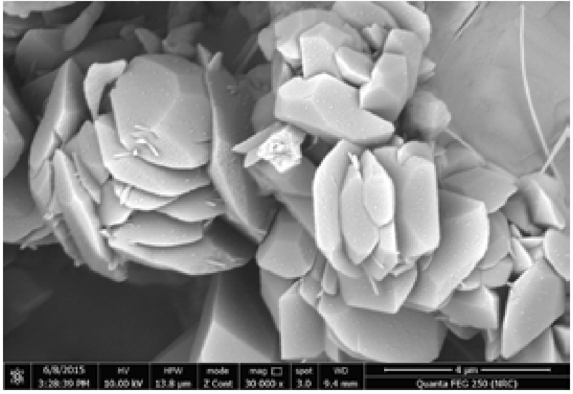


**Fig (11) SEM micrograph of Mg O calcined at 900 ° C showing arranged like platelet morphology.**

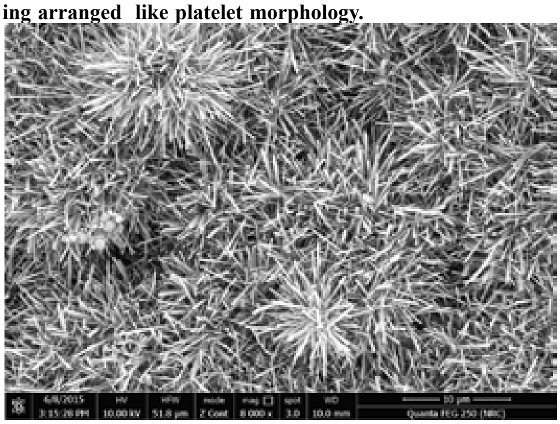
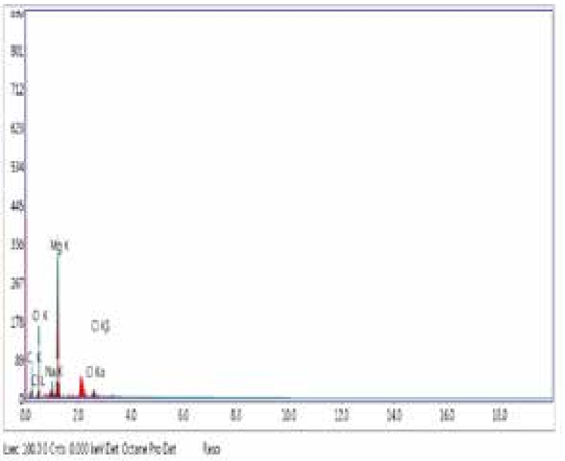
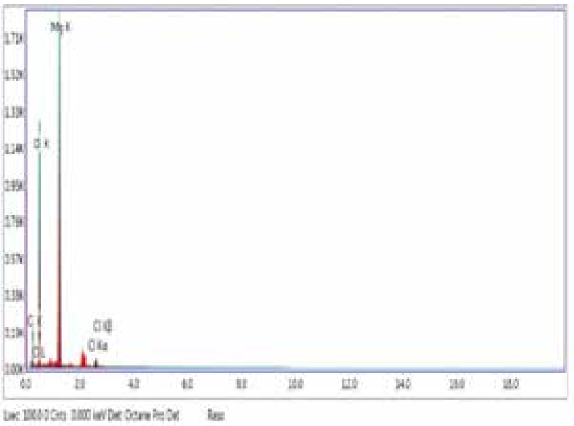


**Fig (12) SEM micrograph of Mg O calcined at 1100 ° C showing sharp hexagonal morphology.**



**Fig(13)EDX chart for Mg O calcined at 900 ° C with lower Mg % in the precipitated products**



| Element | Weight % | Atomic % | Net Int. | Error % |
|---|---|---|---|---|
| C K | 20.81 | 28.57 | 7.16 | 12.56 |
| O K | 50.63 | 52.18 | 53.13 | 9.6 |
| MgK | 28.04 | 19.02 | 112.51 | 7.71 |
| ClK | 0.52 | 0.24 | 3.62 | 15.1 |

**Fig(14) EDX chart for Mg O calcined at 110 ° C shows the higher Mg % in the precipitated products**

| Element | Weight % | Atomic % | Net Int. | Error % |
|---|---|---|---|---|
| C K | 30.82 | 41.16 | 2.4 | 15.99 |
| O K | 38.47 | 38.57 | 6.9 | 13.35 |
| NaK | 4.47 | 3.12 | 2.09 | 16.85 |
| MgK | 25.44 | 16.78 | 22.43 | 9.11 |
| ClK | 0.8 | 0.36 | 1.26 | 25.04 |

**4-Feasibility study for magnesium oxide preparation from bittern and ammonia:**

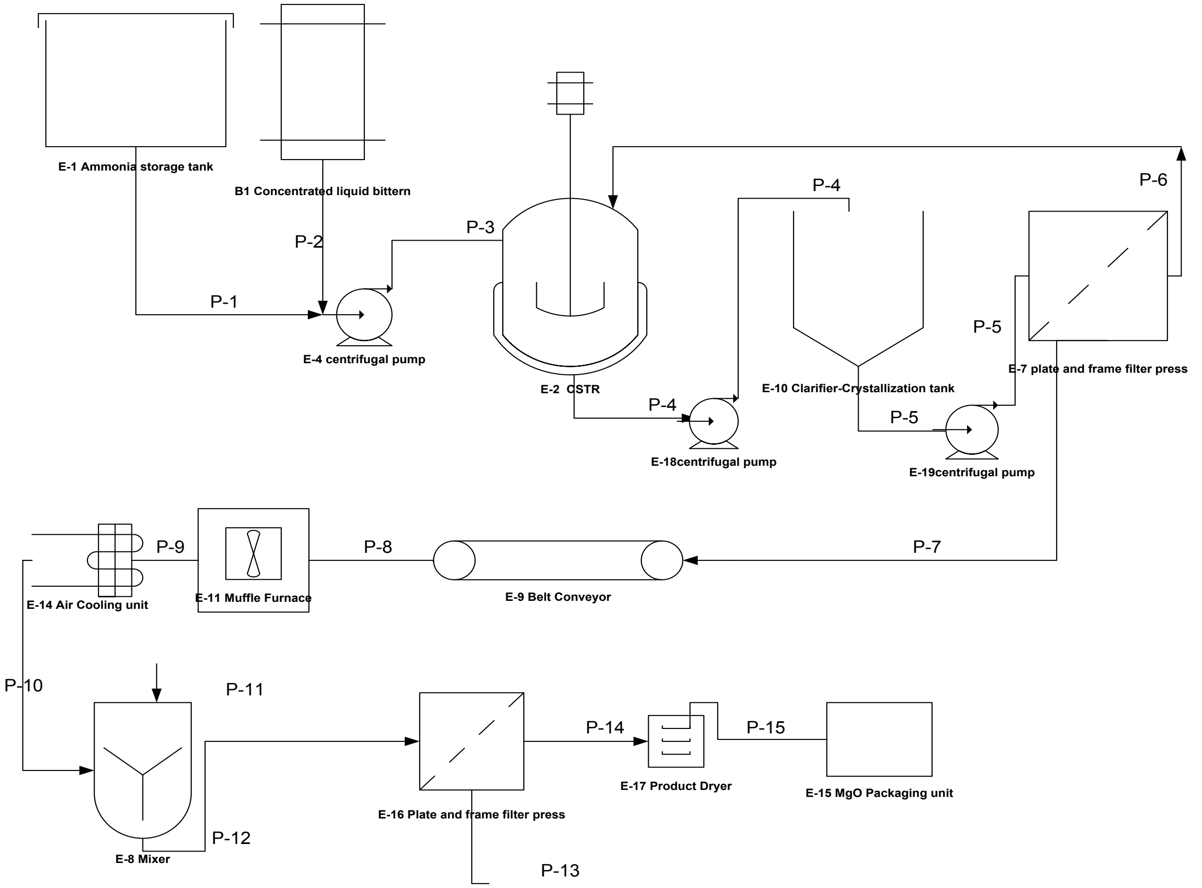


**Fig (15): Industrial process flow diagram of MgO precipitation from concentrated liquid bittern with ammonia solution With capacity 2000 ton/day.**

**Table (3): Overall mass balance for Magnesium Oxide production Unit**

| Stream No. | Mass Balance over process streams , Kg/hr |
|---|---|
| P-1 | 111.06 |
| P-2 | 1582.5 |
| P-3 | 1693.56 |
| P-4 | 1693.56 |
| P-5 | 1693.56 |
| P-6 | 280.61 |
| P-7 | 1412.95 |
| P-8 | 1239.43 |
| P-9 | 351.04 |
| P-10 | 351.04 |
| P-11 | 500 |
| P-12 | 851.04 |
| P-13 | 542.46 |
| P-14 | 308.58 |
| P-15 | 278 |

**Table (4): Estimation of Total Processing Costs**
**Basis: 2000 ton of Magnesium Oxide/ year**

| 1. Manufacturing cost = direct production costs + fixed charges + plant overhead costs. | |
|---|---|
| 1.1. Direct production costs | Cost, EGP |
| Annual Raw Materials<br>Operating labors (20% of TPC)<br>Direct supervision (0.05% of OL)<br>Utilities (0.2% of TPC)<br>Maintenance (5% of FCI)<br>Operating supplies (1% of FCI)<br>Laboratory charges (0.05% of OL)<br>Patents & Royalties (0.06% of TPC) | 800,000<br>99,490<br>100<br>1559<br>139,376<br>27875<br>-<br>-<br>- |
| 1.2. Fixed Charges | |
| Depreciation (10% of FCI)<br>Local Taxes (4% of FCI)<br>Insurance (1% of FCI)<br>Rent | 278,753<br>-<br>27875<br>- |
| 1.3. Plant overhead costs | |
| 2. General expenses = administrative costs + distribution and selling costs + research and development costs | |
| Administration Cost (4% of TPC)<br>Distribution & Selling Cost (10% of TPC)<br>Research & Development (5% of TPC)<br>Financing (1% of FCI) | 31181<br>77953<br>38977<br>- |
| 3. Total product cost* (TPC) | 1,597,534 |
| 4. Gross earning cost | 14,000,000 |

Assuming Selling cost of 1 ton of Pure MgO= 7000 EGP = 1000 USD

**Profitability Evaluation**

The most commonly used methods for profitability evaluation are :

Rate of return on investment.

Payout period.

**Table (4) presents the estimation of total processing costs based on 2000ton of pure magnesium oxide.**

**Rate of Return on Investment (R)**

The yearly profit divided by the total initial necessary investment represents the fractional return on investment.

The rate of return on investment (r) for the developed processing plant is calculated as follows:

| | |
|---|---|
| (a) Service life of the plant =<br>(b) Fixed capital investment =<br>(c) Working capital investment = | 25 Years<br>LE 2,787,531<br>LE 278,753 |
| (d) Annual equipment depreciation assuming the application straight line. method and zero salvage value= | LE 11,150 |
| (e) Annual expenses including depreciation and any interest on borrowed capital = | LE1,597,534 |
| (f) Annual sales = | LE 14,000,000 |
| (g) Annual net profit (excluding income taxes) = | LE 12,402,466 |
| (h) Annual percent return on the total initial investment (excluding income taxes) | r =400 % |
| r= (annual net profit) / (fixed capital investment + working capital) | |

Payout Period ( $\tau$ ):

$$\tau = \frac{FCI}{x + y}$$

Where:

x = average profit per year, LE

y = average depreciation per year, LE

$\tau$ = 0.19 year = 2.38 months.

**Conclusion for economic study:**

Scaling –up of experimental results has been executed through carrying out a series of semi-pilot plant experiments. A process flow diagram for the manufacturing plant is developed together with its sizing and total material balances.

Based on former results, a techno-economic pre-feasibility study has been revealed conducted and high product profitability-potentials with respect to: (i) the expected percent annual return on investment 400% and (ii) payout-period (0.19 year) based on lower price than imported pure source of MgO with 7000 EGP per ton as a selling price. Higher profitability potentials are frequently expected due to the fact that the manufacturing plant –during its service life- is capable for the production of higher capacity with respect to market demand.

## COCLUSION

This study shows that synthesis of $Mg(OH)_2$ with aqueous ammonia promotes the formation of platelet-shaped particles at room temperature (25$^0$C). This temperature indicated the presence of circular plates with high diameter but desired morphology.

MgO shows different crystal size, shape and SEM morphology . The calcination temperature for MgO crystallinity ranges between 900$^0$C – 1100 $^0$C.

Finally the washed MgO approached the standard product purity and confirmed by X-ray diffraction and XRF analysis of > 96% magnesia of high purity.

## ACKNOLEGMENT

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