



ENVIRONMENTAL FRIENDLIER MAGNESIUM FUEL FROM LIQUID WASTE BITTERN

M. S. Shalaby¹, Shakinaz A. El-Sherbini², Rania Ramadan¹, Shadia A. El-Rafie¹ and Hanem A. Sibak²

¹Pilot Plant Department, EL Bohouth St. (former EL Tahrir st.) Dokki, Giza, Egypt

²Chemical Engineering, Faculty of Engineering, Cairo University, Egypt

E-Mail: shelrafie0000@yahoo.com

ABSTRACT

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 fossil fuel consumption with a simultaneous reduction in the generation of greenhouse gases. Bittern is considered as a hazardous liquid waste to the environment, causes massive environmental problems; but it also has many uses in industry and agriculture, as well as being used for the production of magnesium and other chemicals. Technology processes combining both were proposed to recover pure magnesium oxide from bittern by precipitation techniques using solutions of sodium, or ammonium hydroxide, or oxalic acid. The production of magnesium metal is technically challenging, as well as having relatively high production costs. There are recent methods of producing magnesium metal from oxides that involve high temperature reduction, and electrolysis of molten magnesium chloride and other applying laser with solar energy.

Keywords: magnesium, bittern, magnesium oxalate, precipitation, magnesium fuel.

1. INTRODUCTION

Salt industry was known in Egypt since long time ago. The ancient Egyptians produce their salt requirements from salty water, salt containing rocks or salty stems of plants. The Bittern solution is available in Mex-saline amounting to 2,214,000 metric tons per year (i.e.: 1,800,000 m³) while the quantity required to produce 75,000 tons of MgO and 5,000 tons of Mg metals per year is about 1,500,000 metric tons (i.e. 1,220,000) of bittern solution. El-Mex Saline, Located west Alexandria- Egypt whereas, each one ton of raw salt recovered from Sea water utilizing solar energy at Marine saline to be salted out from about 65 m³ of Sea water [1]. The most widely practiced technique for the separation of salts present in sea water is a fractional crystallization by solar evaporation [1-3].

Magnesium and its salts have been used in numerous applications for instance, horticulture, protection, development, in compound and distinctive industries [3,4]. High purity MgO is especially used in nourishment and make of pharmaceutical while Mg(OH)₂ is the most part segment in the maker of fire hindering reagents [5]. The ecological employments of magnesium oxide incorporate waste water and sewage treatment, for example, accelerating silica and overwhelming metals from mechanical effluents [6,7]. Additionally it is utilized for cleaning of sulfur dioxide and sulfur trioxide from modern pipe gases [7].

New power sources could be made using magnesium metal; it is exceedingly responsive and stores a huge amount of imperativeness [8]. To be sure, even a little measure of magnesium strip expends in a fire with a magnificent white warmth [9]. Analysts are currently conceiving approaches to remove vitality from magnesium in a more controlled manner [10]. It would be perfect for putting away power from sustainable sources, it is created a route for autos to produce hydrogen on board by responding magnesium fuel with steam [11,12]. The

response creates an unadulterated type of hydrogen reasonable for power devices, desiring just magnesium oxide, a generally amiable material, as a result [13,14]. The substance response between magnesium (in a powder frame) and water at room temperature in nearness of natural corrosive delivers high-vitality, steam and hydrogen gas [13]. The hydrogen is scorched in the meantime to create extra high-vitality steam. These two steam sources control the motor and may drive turbines to give power [15]. The vitality cycle delivers no carbon dioxide or other hurtful outflows. The main side-effects of this response are water and magnesium oxide or magnesium hydroxide [16-18]. The magnesium metal is isolated from magnesium oxide through breaking the Mg-O bond utilizing sunlight based controlled laser process (the improvement of which is as of now all around cutting edge) and is reused again and again as green natural fuel and creates sustainable power source that can be changed over to power [19-21].

The aim of this work is to evaluate the techno-economic prefeasibility study for the production of magnesium oxide from bittern and its influence as a profitable tool for saving environment and as being a way for producing clean fuel.

2. Materials and Methods

2.1 Stages of Sea Bittern formation

These stages include the preparation of bittern from sea water of (3.5°Be). 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-1.

Bittern(100 L) having density of about 1.3325 g.cm⁻³ (36 °Be) was obtained from EMSC, Egypt (received May, 2014), the raw material used in this work is known as the richest source of Mg²⁺ ions containing > 85 g.l⁻¹ magnesium.



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°Bé) organic matter will be precipitated. In the second stage the sea water reached (8-14°Bé) and calcium carbonate and bicarbonate will be precipitated. In the third stage sea water reached (14-18°Bé) calcium sulfate dehydrate will be precipitated. In the fourth stage sea water converted to mother liquor at (18-24°Bé) 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°Bé (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°Bé) this bittern full of magnesium salts. The main chemical composition of bittern was analyzed by ICP, atomic adsorption and reproducibility of bittern by Complexometric titration method as shown in Table-1.

Table-1. Chemical Composition of Bittern.

Composition	Mg ⁺⁺	Ca ⁺⁺	pH	SO ₄ ⁻	TDS	Conductivity
Bittern(36°Be)	85.7 g.L ⁻¹	<0.12 g.L ⁻¹	6.24	56.9 ppm	449*10 ³ ppm	513 mS.cm ⁻¹ , at 25° C

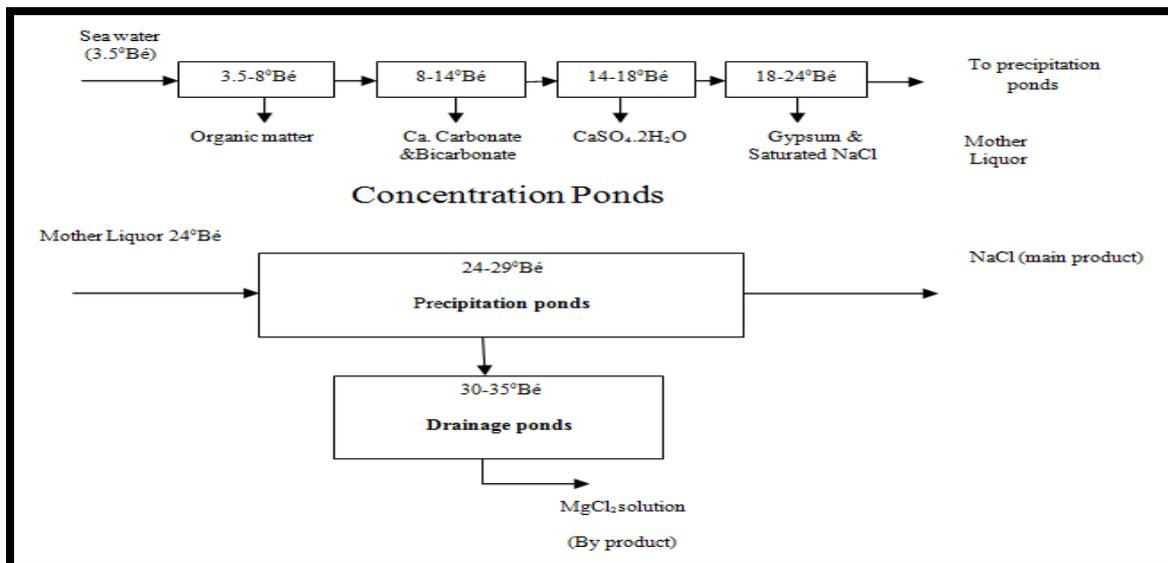


Figure-1. Stages of Bittern Formation.

3. Experimental Technique

Internationally, there are two main technological processes to produce periclase “MgO” from sea water, brines, bittern solution and magnesium bearing solutions all over the world. These methods are:

a) Conventional method “chemical treatment precipitation process”

b) Thermal decomposition process.

A new technological process which combines the two aforementioned processes called the combined technological process. The main features of optimized technological processes of magnesium oxide from oxalic acid are shown in the following block diagram.

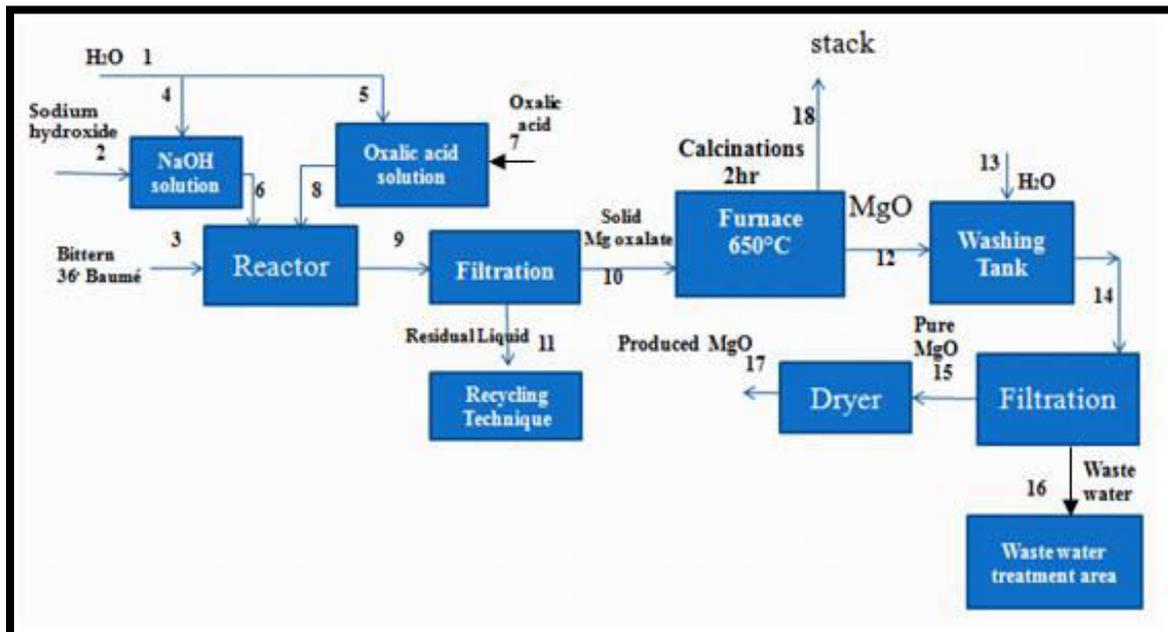


Figure-2. Block flow diagram for Magnesium Oxide production plant.

The process depends on recycling technique to decrease adverse impacts on environment on chemical disposal. Wastewater treatment area was scheduled to be built upon optimizing various pollutant lines to extract valuable elements and recycle water.

4. RESULTS AND DISCUSSIONS

A block flow diagram presented in Figure-2 and preliminary mass balance as shown in Table-2 are showing the sequential industrial units required for the production of 100,000 ton / year of magnesium oxide through precipitation of magnesium salts from bittern with oxalic acid. The purchased cost of equipment was estimated according to vendor prices in January 2016.

**Table-2.** Preliminary mass balance for MgO production. All amounts in tons/day.

No. Ofstreams	Bittern m ³ /d	NaOH	H ₂ O	Oxalic acid	Mg oxalate	Residual liquid	Gases in solution Co+CO ₂ +H ₂ O	MgO
1			9930					
2		63.27						
3	2724 *10 ³							
4			2530					
5			7400					
6		2593						
7				1023				
8		8423						
9					14046			
10					1190			
11						11823		
12								334
13								600
14								333.5
15								333.3
16								600.7
17								333
18							857	

The capacity of the proposed plant is 100,000 ton magnesium oxide /year (300 days, 24 hrs, and 3 shifts). The time per batch is about 8 hours.

The fixed capital investment was build upon classical method of calculation for vendor price of year 2014. The fixed - capital investment needed to supply the necessary manufacturing and plant facilities and the working capital necessary for the operation of the proposed preliminary design of magnesium oxide production plant are estimated below. Table-3 illustrates the items taken into consideration in the estimation of the fixed capital investment of the preliminary plant design. The following cost analysis is accomplished to get an estimation of the fixed capital investment. The purchased equipment cost was estimated based on official offers issued by specialized vendors and presented in Table-3. The installation of equipment involves costs for labor, foundations, supports, platforms, construction expenses and other factors directly related to the erection of purchased equipment. The installation costs for equipment are estimated as 10% of the purchased - equipment cost. Instrument costs, installation labor - costs and expenses for auxiliary equipment and materials constitute a major portion of the capital investment required for instrumentation. The costs or instrumentation and controls (including service, additional charges for installation and accessories) are estimated as 5% of the purchased - equipment cost.

The cost for piping covers labor, valves, fittings, pipes, supports, and other items involved in the complete erection of all piping used directly in the process. The cost of piping (installed) was estimated as 10% of the purchased equipment cost.

The cost for electrical installations consists primarily of installation labor and materials for power and lighting. Electrical installation costs (including installation costs) are estimated as 10% of the value of all purchased equipment.

The costs for building including services estimated as 10% of the value of all purchased equipment. Yard improvement cost for the manufacturing plant is estimated as 2.5% of value of all purchased equipment cost. Utilities for supplying steam, water are part of the service facilities of proposed plant is estimated as 10% of purchased equipment cost.

The cost for land and the accompanying surveys and fees is estimated as 2.5% of the purchased equipment cost. The costs for construction design and engineering, drafting, purchasing, accounting, construction and cost engineering, travel, reproduction, communications and home office expenses is estimated as 5% of the purchased equipment cost.

It includes temporary construction and operation, construction tools and rentals, home office personnel located at the construction site, construction payroll, travel and living, taxes and insurance and other construction overhead. This expense item is included, however, under



engineering and supervision cost item. A contingency factor is included in the estimate of capital investment. A 5% of the direct and indirect plant costs are considered as a contingency factor.

However, the working capital was estimated as 10% of the fixed capital investment taking all items to be considered into account.

Table-3. Breakdown of fixed - capital investment items for Magnesium Oxide production plant.

Item	Cost. L.E.
1-Purchased Equipment (PCE)	11,250,000
2- Purchased Equipment Installation (10%PCE)	1,125,000
3-Instrumentation and Controls(5% PCE)	562,500
4- Piping (10% PCE)	1,125,000
5- Electrical (10% PCE)	1,125,000
6-Building Including Services (10%PCE)	1,125,000
7-Yard Improvements (2.5% PCE)	281,250
8-Service Facilities (5% PCE)	562,500
9-Land (2.5%PCE)	-
Total Direct Plant Cost (DPC)	17,156,250
10-Engineering and Supervision (5%PCE)	562,500
11-Construction Expenses(5%PCE)	562,500
Total Direct and Indirect Plant Cost	18,281,250
12-Contractors Fee	500,000
13-Contingency	500,000
Fixed Capital Investment (FCI)	19,281,250

Table-4 presents the estimation of total production costs based on 1 ton of pure magnesium oxide.

**Table-4.** Estimation of total production cost Basis: 1ton of magnesium oxide.

1. Manufacturing cost = direct production costs + fixed charges + plant overhead costs.	
1.1. Direct production costs	Cost, LE
1.1.1. Raw materials	48,190
1.1.2. Operating labor	5650
1.1.3. Direct supervisory and clerical labor	1000
1.1.4. Utilities	2900
1.1.5. Maintenance and repairs	25
1.1.6. Operating supplies	2.5
1.1.7. Laboratory charges	265
1.1.8. Patents and royalties	-
1.2. Fixed Charges	
1.2.1. Depreciation	700
1.2.2. Local taxes	-
1.2.3. Insurance	25
1.2.4. Rent	-
1.3. Plant overhead costs	1450
2. General expenses = administrative costs + distribution and selling costs + research and development costs	
2.1. Administrative costs	580
2.2. Distribution and selling costs	580
2.3. Research and development costs	1450
2.4. Financing	-
3. Total product cost* (TPC)	62817.5
4. Gross earning cost	82.5

* TPC/ ton was taken = 62,900 LE

4.1 Profitability Evaluation

The most commonly used methods for profitability evaluation are:

4.1.1 Rate of return on investment.

4.1.2 Payout period

4.1.1 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 = 25 Years
- (b) Fixed capital investment = LE 19,281,250
- (c) Working capital investment = LE 1,928,125
- (d) Annual equipment depreciation assuming the application of straight line method and zero salvage value = LE 450,000
- (e) Annual expenses including depreciation and any interest on borrowed capital = LE 6.28*10⁹
- (f) Annual sales = LE 6.29*10⁹
- (g) Annual net profit (excluding income taxes) = LE 10,000,000
- (h) Annual percent return on the total initial investment (excluding income taxes) r = 47 %
 $r = (\text{annual net profit}) / (\text{fixed capital investment} + \text{working capital})$

Payout period,
$$\tau = \frac{FCI}{x + y}$$

where:

x = average profit per year, LE
 y = average depreciation per year, LE

$$\tau = 1.845 \text{ years.}$$

5. CONCLUSIONS

Although bitter liquid, by-product of Mex saline, causes many problems as discussed above, it can be exploited in the production of beneficial elements. The bitter solution represents a typical valuable resource for magnesium and other economical salts which could be produced as by-products in the processing of Magnesite. Preliminary techno-economic feasibility was presented showing profitable promising study for the production of magnesium oxide as a pure source of Magnesium fuel as future fuel alternative of glooming concern with a better solution for saving environment all over the world.

REFERENCES

- [1] Mohamed R. 2005. Improving Mex Salines Co. Economics By producing Magnesium Metal, Chlorine Gas and Magnesium Chloride from Mex Saline



- Bittern. MSc. Thesis, Arab Academy for Science and Technology and Maritime Transport. Alexandria.
- [2] Wulandari W., Geoffrey A.B., Muhammad A. R. and Brian J. M. 2010. Magnesium: Current and alternative production route. Chemeca, Engineering at the Edge; 26-29 September 2010, Hilton Adelaide, South Australia. Barton, A.C.T.: Engineers Australia. pp. 347-357.
- [3] Mordike B.L. and Ebert T. 2001. Magnesium. Properties - Applications - Potential. Materials Science and Engineering A. A302(1): 37-45.
- [4] USGS. 2007. Annual Yearbook Magnesium. [Online]. Available: <http://minerals.usgs.gov/minerals/pubs/commodity/magnesium/myb1-mgmet.pdf>.
- [5] Hull T.R., Witkowski A. and Hollingbery L. 2011. Fire retardant action of mineral fillers. Polymer Degradation and Stability. 96(8): 1462-1469.
- [6] Slade S. 2010. Magnesium: Bridging Diverse Metal Markets. Magnesium Technology, TMS (The Minerals, Metals & Materials Society). 10: 91-95.
- [7] Zang J.C. and Ding W. 2001. The Pidgeon Process in China and Its Future. Magnesium technology, Warrendale, PA, TMS. pp. 7-10.
- [8] Tran K. T., Han K. S., Kim J., Kim, M. J. and Tran T., 2016. Recovery of magnesium from Uyuni solar brines hydrated magnesium carbonate. Hydrometallurgy. 160: 106-114.
- [9] An J.W., Kang D.J., Tran K.T., Kim M.J., Lim T. and Tran T. 2012. Recovery of lithium from Uyuni solar brine. Hydrometallurgy. 30: 117-118, 64-70.
- [10] Anon. and *et al.* 2010. Carbothermic magnesium production. Chemical Metallurgical Engineering. 51(6): 128-131.
- [11] Fergusson J.E. 1982. Salt for New Zealand. Inorganic Chemistry and the Earth, Pergamon Press.
- [12] Tandon H.L.S. 1993. Fertilizers, organic manures, recyclable wastes and Bio fertilizers, fertilizer Development and consultation organization. 1st edition 3 New Delhi.
- [13] Yade T., Bagheri B., Ohkubo T. and Funatsu T. 2008. 100 W-class solar pumped laser for sustainable magnesium-hydrogen energy cycle. Journal of applied physics. 104: 19-25.
- [14] Kumaresan A. and Vaithyanathan C. 2016. Synthesis of magnesium based fertilizer from bittern of the salt-pans of Kanyakumari district and its applications to magnesium demanding crop Allium cepa. Journal of Chemical Pharmaceutical Research. 8(7): 689-93.
- [15] Lee. S.I., Weon S.Y., Lee C.W. and Koopman B. 2003. Removal of nitrogen and phosphate from wastewater by addition of bittern. Chemosphere. 51: 265, p. 271.
- [16] Bouropoulos N.C. and Koutsoukos P.G. 2000. Spontaneous precipitation of struvite from aqueous solutions. Journal of Crystal Growth. 213(3-4): 381-388.
- [17] Abdel-Aal H.K. 2006. From solar energy to hydrogen via magnesium: challenging approach. WHEC. 16: 13-16.
- [18] Zhao J.M., Shen X.Y., Deng F.L., Wang F.C., Wu Y. and Liu H.Z. 2011. Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A. Separation and Purification Technology. 78(3): 345-351.
- [19] Chitnis U. V. and Shanghavi J.R. 1992. Operational checks during solar evaporation of sea bittern. Proceeding 7th international Symposium on Salt, April 6-9, Kyoto, Amsterdam.
- [20] Zheng L., Sheng Y.J., Huiyuan Y. and Zhou G.D. 1992. New method of preparing potassium sulphate with mixed salts and potassium chloride. Proceeding of the 7th International. Symposium on Salt, April 6-9, Kyoto, Amsterdam.
- [21] Ayoub G. M., Semerjian L., Acra A., El-Fadel M. E. and Koopman B. 2001. Heavy metal removal by coagulation with seawater liquid bittern. Journal of Environmental Engineering. 127(3): 196-207.