

Seawater Bittern a Precursor for Magnesium Chloride Separation: Discussion and Assessment of Case Studies

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Abstract

Sea water bitterns (SWB) are encountered in the processes of desalination and sea-salt production where large quantities of bitterns and brines are produced, either as by-products, or as waste products. They could be described as “exhausted brines”. In theory, for every ton of sea-salt produced about one cubic meter of bittern is produced and is available for further processing. To exploit valuable salt products, in particular MgCl₂ from sea water in desalination plants and/or salt production, various methods were carried out, in particular by the author and his colleagues. Mainly they consist in applying the physical concept of preferential-type of salt separation, where Mg Cl₂ is the most soluble salt, will separate at the very end. An experimental work was initiated by Kettani and Abdel-Aal and extended by Abdel-Aal et al. Two case studies are presented and discussed in this paper.

Keywords: Desalination; Exhausted brines; Magnesium chloride

Introduction

Reject brines and carbon dioxide are two forms of environmental pollutants that we are facing in the course of obtaining fresh water from sea water. The common practice in dealing with these huge amounts of reject brine is to discharge back into the sea affecting seriously the aquatic life. To recover and extract valuable minerals found in these rejects is the prime objective of this work. In particular, magnesium chloride is targeted as a raw material to produce magnesium metal. Magnesium is the eighth most abundant element in the earth's crust but does not occur uncombined in nature. One cubic kilometer of sea water contains a minimum of one million tons magnesium, which makes the sea a “storehouse” of about 1.7×10^{24} tons.

In addition, magnesium chloride is found in seawater, brines, and salt wells. Magnesium (Mg) exists in sea water as ions of magnesium. It is a constituent of the chlorophyll in green plants and is necessary in the diet of animals and humans ions of magnesium. Figure 1, depicts the concentration of magnesium and magnesium chloride in sea water. When it comes to the mineral salts found in sea water, the major components of natural sea water determining their solubility properties are: Na⁺, K⁺, Mg⁺⁺, Cl⁻ and SO₄⁻. According to C Balarew [1] it is usually assumed that the major constituents present in the sea show constant relative proportions. He further added that the variations in the composition of waters from different seas are due only to the changes in the amount of water present. Accordingly, one can conclude that the composition-density diagram shown in Figure 2 for the initial composition of Black Sea-Water is valid for every sea water type.

Separation sequence of salts during sea water evaporation

When seawater (composition is given in Table 1) is evaporated soluble salts will be formed, at different stages during the evaporation. The crystallization of the salts dissolved in seawater is governed by their solubility products and occurs at different concentration levels. When seawater is concentrated gradually, brine concentration increases leading to the successive precipitation of the least soluble salts first. For example, iron oxide and calcium carbonate start to crystallize first, in very small quantities, followed by calcium sulfate (known as gypsum). It is reported that about 30-50 kg of gypsum comes out for every ton of salt produced. Right at this stage, sodium chloride starts to crystallize

out, yielding about 75% of the available sodium chloride (known as halide) in solution. Reaching this stage would correspond to the evaporation of about 97% of the total water. Next, magnesium chloride

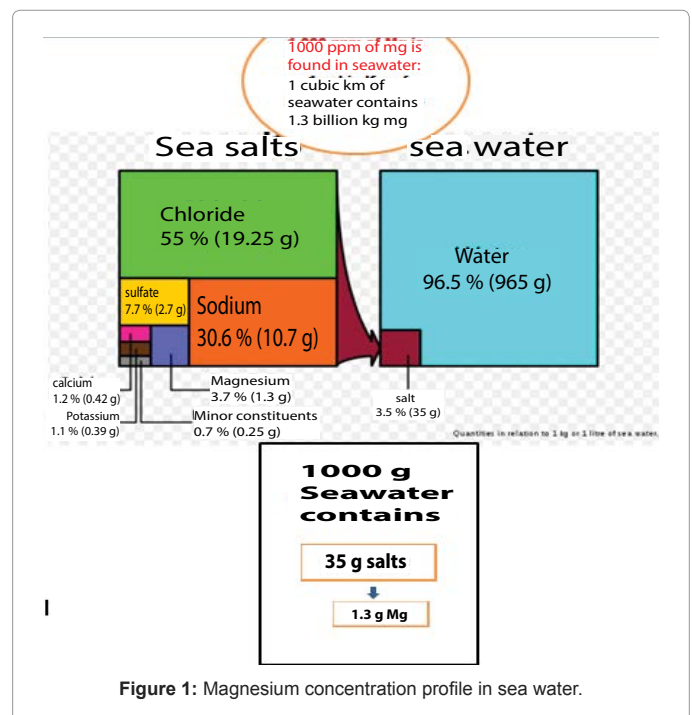


Figure 1: Magnesium concentration profile in sea water.

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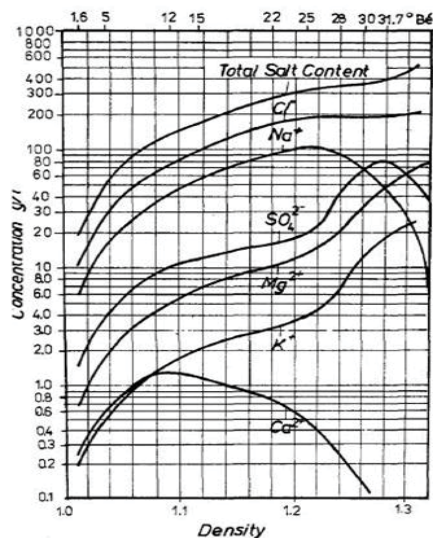


Figure 2: Composition-density changes during evaporation of sea water at 250°C (the density of the black sea water is 1.011) [1].

Component amount present (g/ 1000 g Seawater)	
Ca	0.408
SO4	2.643
Mg	1.265
Cl	18.95
K	0.38
Na	10.48
Br	0.065
Total	34.19

Table 1: Composition of sea water.

Fresh Water	Brackish Water	Saline Water	Brine
<0.05%	0.05-3%	3-5%	>5%

Table 2: Levels of concentration of salt in water and given different names.

will start to crystallize as a solid solution along with sodium chloride forming what is called “bitterns”. Detailed description is given next.

Sea water bitterns (SWB) and brines: A source for magnesium

SWB are encountered in the processes of desalination and sea-salt production where large quantities of bitterns and brines are produced as by-products. The term “bitterns” refers to the very bitter-tasting solution that remains after evaporation and crystallization of sodium chloride (table salt) from brines and seawater. It is a concentrated form of a collection of magnesium, potassium, sulfate and chloride salts, such as KCl, MgCl₂, MgSO₄ and double salts. SWB could be described as “exhausted brines”. Brine on the other hand, designates a solution of salt (usually sodium chloride) in water. In a different context, brine may refer to salt solutions ranging from about 3.5% (a typical concentration of seawater, or the lower end of solutions used for brining foods) up to about 26% (a typical saturated solution, depending on temperature). Other levels of concentration of salt in water are identified and given different names in Table 2.

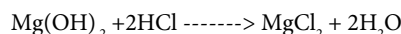
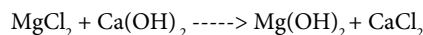
In salt-works, brines can represent a rich and promising source of raw materials, especially when they are very concentrated. In particular, magnesium concentration can reach values up to 30-40 kg/m³ of brine,

which is 20–30 times that of typical seawater. In theory, for every ton of sea salt produced, about one m³ of bittern is produced. Chemicals found in the bittern corresponding to 10 million tons of salt produced are classified into the different types in Table 3.

It is conclusive from the above, that bitterns are rich in chemicals and can be described as a ‘precursor for the production of magnesium metal.

Present state of art

Historically, the significance of evaporative concentration of marine brines as indicators of the chemical evolution of seawater with time is given in reference [2], and as shown in Figure 3. The precipitation of salts from evaporating seawater was thoroughly presented, as shown in Figure 4 [3], where the composition changes in the following order: First, calcite precipitates, followed by gypsum, halite and various chlorides and sulfates. When it comes to the extraction of magnesium chloride from sea water, it is produced commercially by the well-known Dow process [4]. It involves the “chemical options” that consists of the following chemical reactions:



To obtain dissolved MgCl₂ from sea water by using the “physical option”, the basic phenomena for the separation of MgCl₂ from seawater, is based on the physical and chemical natural phenomena occurring when seawater evaporates. In addition to pure distilled water (main product of co-generation plant, used as potable water), seawater evaporation products include NaCl, MgCl₂ and other mineral salts. As shown in Figure 5, the whole sequence of different salt separation is identified including MgCl₂. The concentration factor for the different salts can be deduced from the cumulative amount of water evaporated, which is also given in the Figure 5. To exploit valuable salt products,

	Tonnes
NaCl	1,500,000
MgCl ₂	1,200,000
MgSO ₄	700,000
KCl	238,000
Bromine	20,000

Table 3: Chemicals found in the bittern corresponding to 10 million tons of salt produced are classified above.

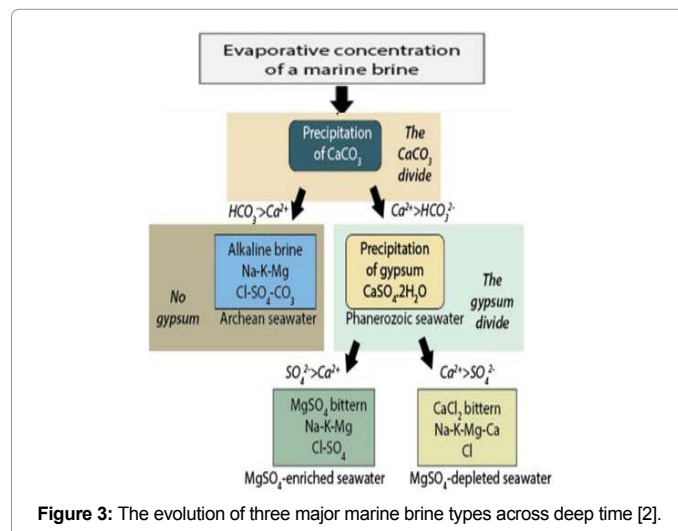


Figure 3: The evolution of three major marine brine types across deep time [2].

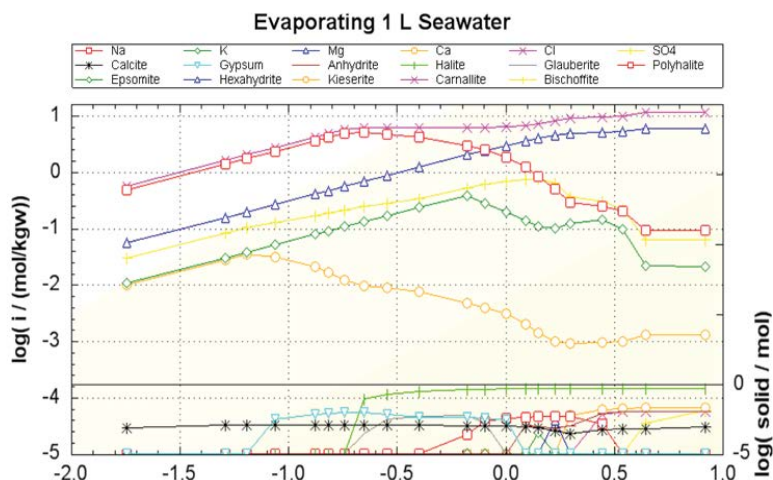


Figure 4: Evaporating seawater and precipitating salts [3].

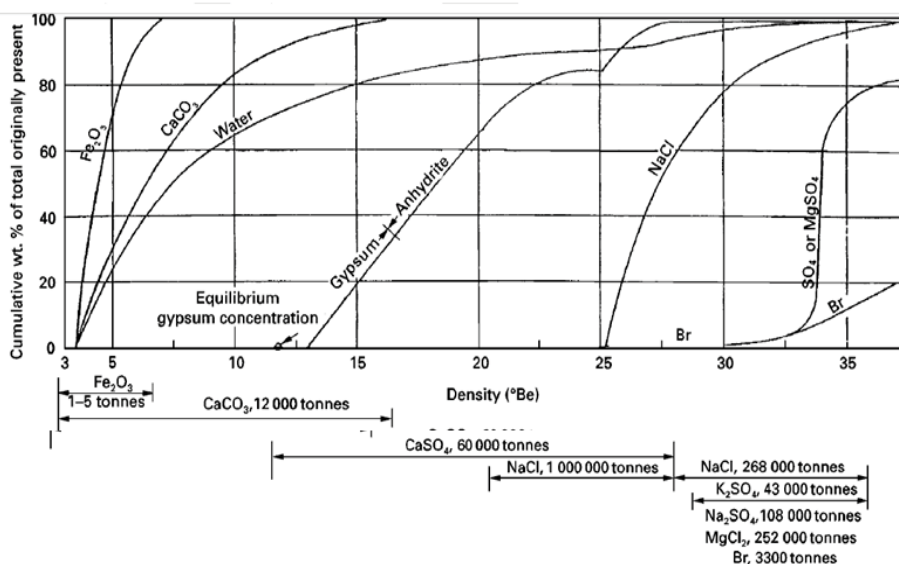


Figure 5: Deposition of salts during seawater evaporation [4].

in particular $MgCl_2$ from sea water in desalination plants and/or salt production, various methods were carried out, in particular by the author and his colleagues. Mainly they consist in applying the physical concept of preferential type of separation, with the understanding that $MgCl_2$ is the most soluble salt will separate at the very end. An experimental work was carried out to recover $MgCl_2$ by MA Kettani and HK Abdel-Aal [5]. The separation utilized the physical preferential technique to obtain a dense magnesium chloride solution or, a bittern, by vaporizing sea water. Work was further extended by running a simulation program for Al-Khobar Desalination Plant in Saudi Arabia. Real data was used through a 32 repeated cycles of 4 stages each. Additional potable water, NaCl, and a highly concentrated $MgCl_2$ bittern were obtained from the brines by Abdel-Aal et al. [6,7]. A theoretical study on the economics of a new magnesium production-process, carried out by Abdel-Aal [8,9], stimulated interest in the subject. Experimental work was resumed by Abdel-Aal and Al-Naafa [10] to build a multipurpose solar desalination pilot unit (MPSDU) for the enhanced evaporation of saline water.

Another experiment was carried out for the selective separation of $MgCl_2$ bittern from sea water by Abdel-Aal et al. [11], using a batch model. This model of evaporation utilizes the same principle of fractional separation, but using a batch operation.

Review of Case Studies for $MgCl_2$ Recovery

1st case: Preferential salt separation (PSS) - dynamic flow model

Kettani and Abdel-Aal [5], proposed a physical separation method known as the Preferential Salt Separation (PSS) to obtain magnesium chloride directly from sea water. In principle, the PSS concept is based on the selective separation of salts during the evaporation process of a dynamic flow of a fluid of brines. The model was experimentally tested for the first time on a semi pilot scale. Solar energy was simulated by using infrared light source mounted along the evaporator, as shown in Figure 6. The evaporation process could take place by direct solar

radiation or by using a heating system powered by a photovoltaic source. Magnesium chloride salts soluble in sea water precipitate as end product. Fresh water is produced as a byproduct.

Experimental results: The progress of the separation of salts along the channel evaporator that consists of 20 channels is given in Figure 7.

The separation sequence of these salts is best described by assigning the concentration of the salts, in ppm as follows:

Calcium: Concentration increases from 550 ppm to 2100 ppm, then it decreases steadily to 2100 ppm indicating the separation of CaCO_3 and gypsum CaSO_4 .

Sodium: Increases from 15300 ppm at the inlet, up to a maximum of 87000 ppm this corresponds to sp. gravity=1.215 at which NaCl starts to precipitate. With further evaporation, the concentration tends to remain constant in spite of the continuous evaporation of the flowing water. This means that the precipitation of Na in the form of halide, matches the amount of water evaporated. With further evaporation across the channels, the concentration decreases sharply from 85,000

to 59,000 ppm. This will lead to partial separation of Na element in the remaining concentrated brine.

Magnesium: Its concentration increases steadily from 1,850 ppm at the inlet up to 14,400 ppm, corresponding to a sp. gravity=1.215. With further evaporation along the evaporator, it drops to 10,000 ppm; this signals the precipitation of $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$. Further progress with more channels, Mg concentration shoots to a peak of about 29,000 ppm, indicating that MgSO_4 precipitation is coming to an end. The peak itself shows that the new salt (bittern) consisting partly of Mg is reaching maximum saturation (probably Carnalite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)); hence, precipitation occurs once saturation is reached. On channel 17, precipitation reaches its maximum corresponding to Mg concentration of 14,000 ppm in the remaining brine. Further evaporation leads to a sharp increase in Mg concentration to a value of 42,000 ppm almost at the end of the evaporator. This indicates that the brine is highly concentrated in Mg; or be described as a bittern or magnesium-rich-brine.

Comparing the ratio of Mg concentration in the finally obtained brine to that in the intake sea water, it is found to be $=42000 / 1850 \approx 23$ times.

2nd case: Preferential salt separation (PSS) – ‘Static-flow’ or batch model

This model of evaporation utilizes the same principle of fractional separation, but using a batch operation [10]. The evaporation takes place in a tank using solar-heated water jacket. When salts start to precipitate, evaporation is stopped and salts are separated by filtration. Chemical analysis is carried out to mark the first sample of salts. Evaporation is resumed, and the procedure is repeated for additional salt precipitates, until the stage of magnesium-rich-brine (bittern) is reached.

Experimental results: The batch model was implemented as described above. A preliminary experiment was carried out on a lab scale using a sample of 2 liters of sea water. Results are shown in Table 4.

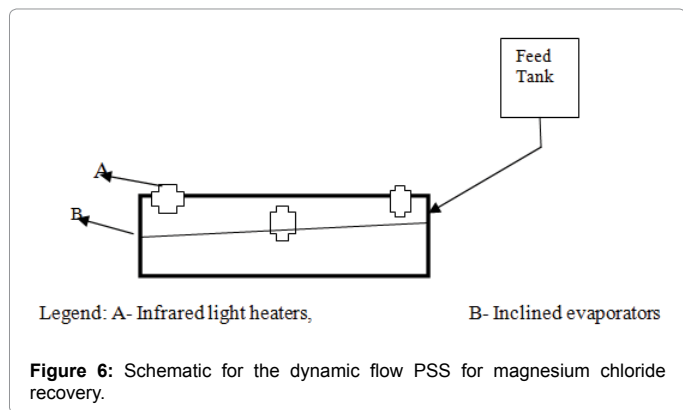


Figure 6: Schematic for the dynamic flow PSS for magnesium chloride recovery.

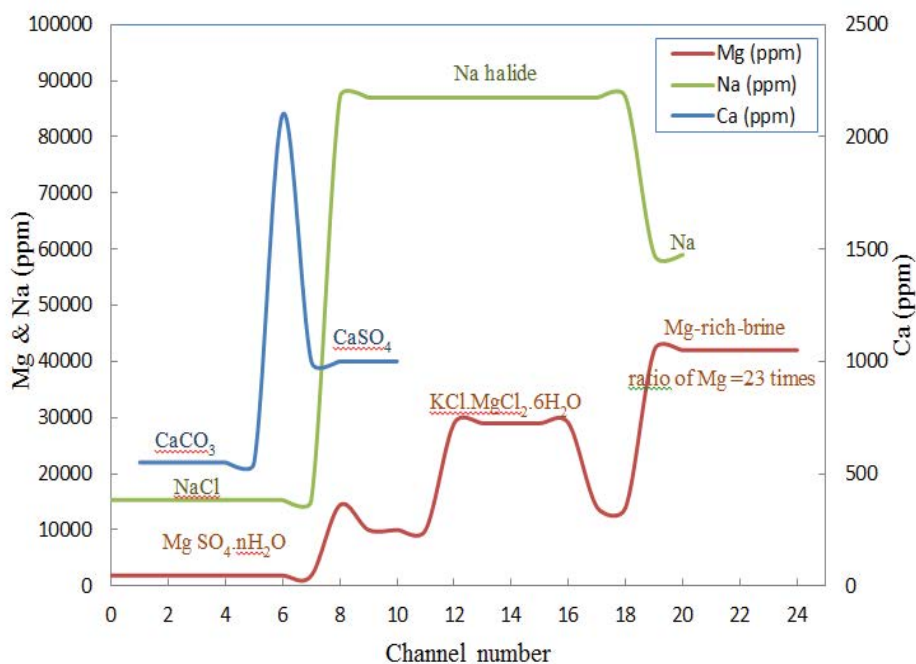


Figure 7: Experimental results for preferential salt separation (PSS) of MgCl_2 [5].

Original water sea water			PPT 1	PPT 2	PPT 3	PPT 4	PPT 5	PPT 6	PPT 7	
	PH	8.42						7.1	7.1	6.5
	TDS	35 gm/l						5.423	5.498	4.865
	Conductivity	57.5 ms/cm								
	Density gm/ml	1.0264	1.04436	1.22125	1.22705	1.22905	1.21562	1.2122	1.217	
		Al, mg/l	<0.01	<0.01	<0.01	<0.01				
		Ba, mg/l	0.0046	0.0103	0.0058	0.0031				
		Ca, mg/l	106.4	47.25	14.17	8.613	41.8	8.8	19.8	
		Cd, mg/l	<0.001	<0.001	<0.001	<0.001				
		Co, mg/l	<0.0004	<0.0004	0.0005	0.0005				
		Cr, mg/l	<0.003	0.0045	<0.003	<0.003				
		Cu, mg/l	<0.003	0.0045	<0.003	<0.003				
		Fe, mg/l	<0.02	<0.02	<0.02	<0.02				
		Mg, mg/l	0.4536	24.76	21.38	5.198	2.41	0.8019	7.22	
		Mn, mg/l	<0.001	<0.001	<0.001	<0.001				
		Mo, mg/l	0.0013	<0.0005	<0.0005	0.0046				
		Ni, mg/l	<0.001	<0.001	<0.001	<0.001				
		Pb, mg/l	0.0093	<0.004	<0.004	<0.004				
		Sr, mg/l	3.027	0.8726	0.2141	0.2146				
		V, mg/l	0.0106	0.0205	0.0114	0.013				
		Zn, mg/l	<0.001	0.0064	0.008	<0.001				
		K, mg/l	5	24	32	38	3	2	3	
		Na, mg/l	32	110	1420	1480	1900	2100	1900	

Table 4: Experimental results for the separation of MgCl₂ using batch evaporator.

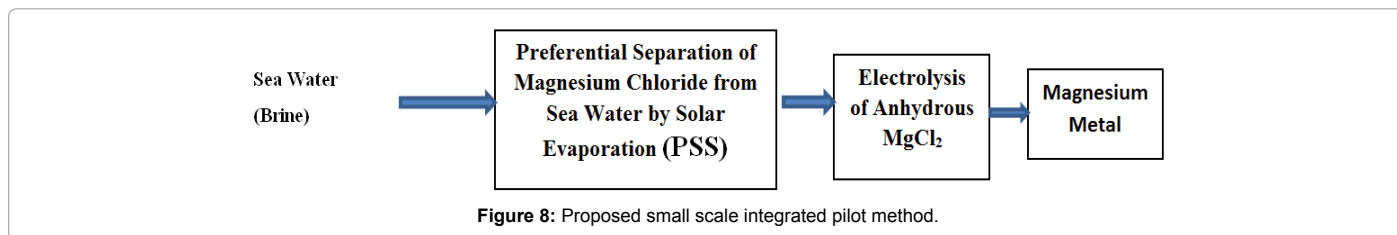


Figure 8: Proposed small scale integrated pilot method.

It is evident that a similar trend in salt separation is followed in this model as well. Magnesium chloride rich- brine is observed in terminal samples. Because of the limited scale of the initial volume used, very small quantity of separated salts was obtained.

Proposed small-scale integrated pilot model: Since the primary target is to produce magnesium metal, the overall scheme of such project could be simply represented which is shown in Figure 8.

The corner stone of such project is the PSS. The following features could be ascribed to build a more refined model for the PSS:

Solar energy is used to provide power for the pilot plant, via a photovoltaic system. It is needed first, to desalinate sea water and produce the brine-feed to PSS. Next, to supply heat for the PSS for evaporation, using an Ohmic resistance heating system.

A target small-scale capacity is to obtain MgCl₂ enough to produce say 5 kg/day of magnesium metal.

Surface area of the PSS has to be calculated based on the enhanced rate of evaporation and the quantity of MgCl₂ to be produced.

Discussion and Conclusion

To exploit valuable salt products, in particular Mg Cl₂ from sea water in desalination plants and/or salt production, various methods were carried out, in particular by the author and his colleagues. Mainly they consist in applying the physical concept of preferential type of separation, with the understanding that Mg Cl₂ is the most soluble

salt will separate at the very end. An experimental work was carried out to recover MgCl₂ by MA Kettani and HK Abdel-Aal [5]. The separation utilized the physical preferential technique to obtain a dense magnesium chloride solution or, a bittern, by vaporizing sea water. Solar energy is used as a source of energy to vaporize a dynamic stream of pre-concentrated sea water flowing along an inclined Preferential Salt Separator (P.S.S.). This evaporation process took place by direct solar radiation in an early experiment. The use of Joule Ohmic heating supplied by a photovoltaic system proves to be superior.

Magnesium chloride will separate as the very end product. Distilled water will be produced as a byproduct. Bitterns, which could be defined as “exhausted brines), will make an ideal feed stock for magnesium chloride as well.

For future work, anhydrous magnesium chloride is to be electrolyzed using energy generated by solar power in order to produce magnesium metal. Once produced, magnesium represents a reliable source of stored energy that could be exported by air, sea or other means of transportation to remote locations for power-generation. Magnesium could be used to construct a galvanic cells made of magnesium/iron electrodes to generate electricity for hydrogen production by water electrolysis.

Another option is to use magnesium as storage-medium to store hydrogen in the form of magnesium hydride.

The experiments demonstrated the feasibility of the recovery of magnesium chloride salt in the form of magnesium chloride-rich brine.

The concentration of magnesium chloride is reported in the final product was 23 times the initial concentration in the intake sea water. Further evaporation, would eventually lead to almost pure magnesium chloride. The full-fledge of the research work could really have a crucial impact when it comes to the production of magnesium metal, since magnesium metal is considered a -strategic metal.

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