

## A Fertilizer from bittern, Phosphoric Acid and Ammonia

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In recent years the fertilizer industry has recognized the potential advantages of low solubility fertilizer materials rich in ammonium magnesium phosphate. This salt can supply magnesium, nitrogen and phosphorus for plant growth over long periods of time. This compound has a solubility of about 0.02 grams per 100 grams of water. Intensive experimentation to produce these materials has, to the date, failed to yield a commercially attractive process.

Seawater bittern, a by-product from seawater solar salt plants, is rich, among other elements, in magnesium. A novel process for the recovery of this element as magnesium ammonium phosphate salt has been developed. The method consists, essentially, in mixing phosphoric acid with the bittern, followed by neutralization with ammonium hydroxide. Under appropriate operational conditions it was possible to produce a salt with the following composition:  $\text{NH}_4$  (11 %) + Mg (19 %) +  $\text{PO}_4$  (68 %). The recoveries were: Mg (99 %),  $\text{NH}_4$  (98 %) and  $\text{PO}_4$  (98 %). The exit ammoniacal solution is treated with lime for the liberation of ammonia in a distillation operation. X-ray powder diffraction analysis show the product to have a formule  $\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$ . SEM photographs of the crystalline products showed uniform crystals of grain size about 10 to 20  $\mu\text{m}$  of orthorhombic shape.

### 1. INTRODUCTION

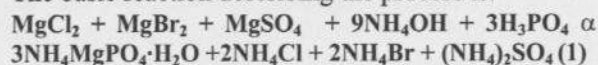
Attempts in recent years to develop and modernize the agriculture in the tropical regions have revealed great differences in soil types and nutrients, as well as in crop types and nutrients requirements. In addition, interest has raised in knowing what the correct level of water solubility for phosphatic base fertilizers should be, and what elements a multinutrient fertilizer should contain [1,2].

In recent years the fertilizer industry has recognized the potential advantages of long-term release ammonium magnesium phosphate salts. The efficiency of these materials for plants growth has been proved [3,4,5]. Intensive research to produce these type of fertilizer has been conducted [6,7,8,9,10].

#### 1.1. Formation of ammonium magnesium phosphate salt.

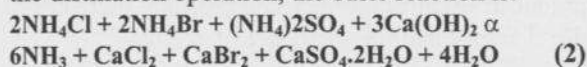
Seawater bittern, a by-product from sodium chloride plants, is a rich source of magnesium, the

recovery of which by conventional methods is made difficult by the presence of other elements. The research described here in concerns the fabrication of multinutrient salt rich in nitrogen, magnesium and phosphorus from seawater bittern and phosphoric acid by neutralization with ammoniacal solution. The basic reaction describing the process is:



#### 1.2. Recovery of ammonia from salt solutions

The exit ammoniacal solution from the process is treated with lime for the liberation of ammonia in the distillation operation, the basic reaction is:



This operation es well know, since it has been used in the solvay process for many years, therefore no major study of this operation was considered at this time.

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## 2. EXPERIMENTAL

### 2.1. Apparatus

The tests were conducted in a 1 litre stirred batch reactor. This was a cylindrical glass vessel, with a ratio of height to diameter of 1.5, equipped with four-blade propeller stirrer and two vertical evenly-spaced baffles. A Beckman pH meter, with slurry type electrodes installed into the reactor was used to follow the pH changes in the suspension. Another important unit was the injector, it consisted of a cylindrical glass vessel; this unit was used to feed the ammonium hydroxide solution through a graduated device into the reactor. The temperature in the system was maintained constant by cooling water circulating through the jackets from a constant temperature circulating unit.

### 2.2. Procedure

For each experimental run the coolant reservoir was set to the decreased temperature, with water circulation through vessel jacket. Seawater bittern was charged to the reactor and sufficient amount of phosphoric acid to react with all the magnesium present in the bittern, in accordance with reaction (1), was added and the ammoniacal solution was charged to the injector.

The bittern-phosphoric acid mixture was stirred; once the prefixed temperature was reached the ammoniacal solution was added from the injector until the desired pH was obtained. The rate of adding the ammoniacal solution was adjusted to give the desired neutralizing time. In some tests, after the prefixed pH was obtained, the suspension was stirred an additional time (digestion time). A Beckman pH meter with slurry type electrodes was utilized to follow the pH neutralizing operation. Tests were also conducted with bittern diluted with water, in this case the water was added to the reactor before the neutralizing operation. Chemical, X-ray powder diffraction and SEM analysis of the solids produced established their composition, recovery of the elements and form and size of crystals.

### 2.3. Materials

The reactants used in this work were: residual bittern from a local seawater solar salt plant, with density and composition given in Table 1, phosphoric acid of purity 85 % wt and ammonium hydroxide solution.

## 3. RESULTS AND DISCUSSION

### 3.1. Preliminary experiments

A series of preliminary experiments were carried out to assess the influence on reaction (1) of the following variables, the effects of which were then eliminated from later studies:

#### 3.1.1. Stirrer speed

The rate of reaction, yield and composition were found to be independent of the speed of agitation above 200 rpm. This appeared to be the minimum speed required to give a uniform suspension in the reactor. A speed of 300 rpm was chosen for all further runs.

#### 3.1.2. Reaction temperature

The influences of two different reaction temperature of 30 and 40 °C were evaluated. No significant influence on recovery and composition of the products was noted. The atmospheric temperature of 30 °C was used for all further test.

#### 3.1.3. Neutralization time

The influence of two different rates of adding the ammoniacal solution of 15 and 45 minutes were investigated. No significant influence on recovery and composition was noted. Therefore, the neutralizing time of 15 minutes was chosen for all further runs.

Table 1 : Composition of the residual seawater bittern used in this investigation.

Density g / ml	Composition, g/l								
	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>++</sup>	Ca <sup>++</sup>	SO <sub>4</sub> <sup>=</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	B <sup>-</sup>	H <sub>2</sub> O+O.E
1.258	56.09	11.70	45.90	0.20	57.72	180.59	2.06	0.13	903.61

Araya salt-field bittern, Venezuela. ; O.E.= other elements.

### 3.1.4. Dilution of the bittern

Trials with two different dilutions with water of 50% and 100 % by volume were conducted. The run with the higher dilution showed significant increase in the recovery of the reactants and the crystals were larger and easier to filter. Therefore, 100 % dilution was used in some tests.

### 3.2. Variation of pH

The neutralizing pH was found to be the main variable. The effects on the recovery and composition of products of changing the neutralizing pH were investigated by carrying out three runs with the following pH values: 8.0, 9.0 and 10.0, other variables which affect reaction (1) were maintained constant for these runs; these were neutralizing time 15 min, digestion time 60 min, stirrer speed 300 rpm, temperature 30 °C, and 100 % dilution. These results are presented in Table 2, showing that  $\text{NH}_4\text{MgPO}_4\cdot\text{H}_2\text{O}$  is the main component of the crystalline products. The recoveries of magnesium reach 99-100 % at pH 8.0. The recovery of ammonia in the product is higher at the lower pH; the rest of the ammonia is recovered by distillation. Phosphate recovery reaches a maximum of 98 % at pH 8.0 and then decreases to about 90 % at pH 10.0. The boron recovery increased with increase in pH.

### 3.3. Variation of digestion time

The effects on reaction (1) of changing the digestion time were investigated by carrying out three runs with the following values: zero min, 20 min and 60 min. Other variables which affect the reaction (1) were maintained constant for these runs, these included neutralizing time 15 min, neutralizing pH 8, reaction temperature 30 °C, dilution 100 % by volume, and stirrer speed 300 rpm. These results not shown here for the sake of brevity, revealed no significant changes in recovery and composition of product.

### 3.4. Form and size of the crystals formed

SEM photographs of the crystalline products, not shown here for the sake of brevity, show uniform orthorhombic shape crystals of similar size, about 10 to 20  $\mu\text{m}$ .

### 3.5. Purity of product

Chemical and x-ray powered diffraction analysis of the products obtained in the different runs show these to have the following formula:  $\text{NH}_4\text{MgPO}_4\cdot\text{H}_2\text{O}$ , small amounts of  $\text{Mg}_3(\text{PO}_4)_2\cdot 4\text{H}_2\text{O}$  were noted. Some boron, potassium and sodium were also present, but the products are almost chloride free.

**Table 2 : Composition of the salts produced and recovery of main elements from seawater bittern and phosphoric acid by neutralization with aqueous ammonia to three different pH**

pH	Products Composition, % wt								
	Na	K	Mg	$\text{NH}_4$	$\text{PO}_4$	$\text{SO}_4$	B	Cl	Ca
8.0	0.33	0.15	19.28	11.50	67.64	0.52	0.01	0.37	0.01
9.0	0.28	0.12	18.12	11.08	66.90	0.26	0.04	0.32	0.01
10.0	0.30	0.13	17.18	10.40	64.48	0.44	0.07	0.21	0.01

pH	Recovery, % wt				Main Phases
	$\text{NH}_4$	Mg	$\text{PO}_4$	B	
8.0	98.25	79.90	98.50	2.00	$\text{Mg}_3(\text{PO}_4)_2\cdot 4\text{H}_2\text{O}$ $\text{NH}_4\text{MgPO}_4\cdot\text{H}_2\text{O}$
9.0	98.10	99.97	94.00	45.15	
10.0	98.00	99.90	90.53	70.10	

- \* stoichiometry of reaction (1)
- \* bittern dilution 100 % by volume
- \* neutralizing time 15 min

- \* digestion time 60 min
- \* reaction temperature 30 °C
- \* stirrer speed 300 rpm



### 3.6. Solubility.

The salt produced can supply nitrogen, magnesium and phosphorus for plant growth over long periods of time. This compound has a water solubility of less than 0.02 grams per 100 grams of water, but is 100 % soluble in a 2 % wt solution of nitric acid, a method used to evaluate these type of fertilizers. It is important to note the efficiency of this product in terms of speed of plant response, of total plant yield and total recovery of nutrients.

### 3.7 Recovery of Ammonia.

It was quoted early in this paper that the recovery of ammonia from aqueous ammonia salty solutions is a well know operation in the traditional Solvay process; because of this previous knowledge, only preliminary tests were conducted following the stoichiometry of equation (2). The results, not shown here for the sake of brevity, demonstrated, as expected, the feasibility of this operation, with ammonia losses of less than 2 %.

## 4. THE PROPOSED PROCESS

A flow diagram of the process is given in figure 1. In brief the process comprises six major operations: mixing the bittern with the phosphoric acid; neutralizing the said mixture with ammoniacal solution resulting in the formation of crystalline ammonium magnesium phosphate product; separation of the said product by filtration, washing and drying and recovery of ammonia from the filtrates and washings by distillation. The process has several advantages: a) simplicity, b) high recovery efficiency, c) high purity of product, and d) the magnesium source, seawater bittern, is a by-product virtually inexhaustible.

The process produces a stripped suspension from the distillation operation rich in sodium, potassium and calcium chlorides, and solid gypsum.

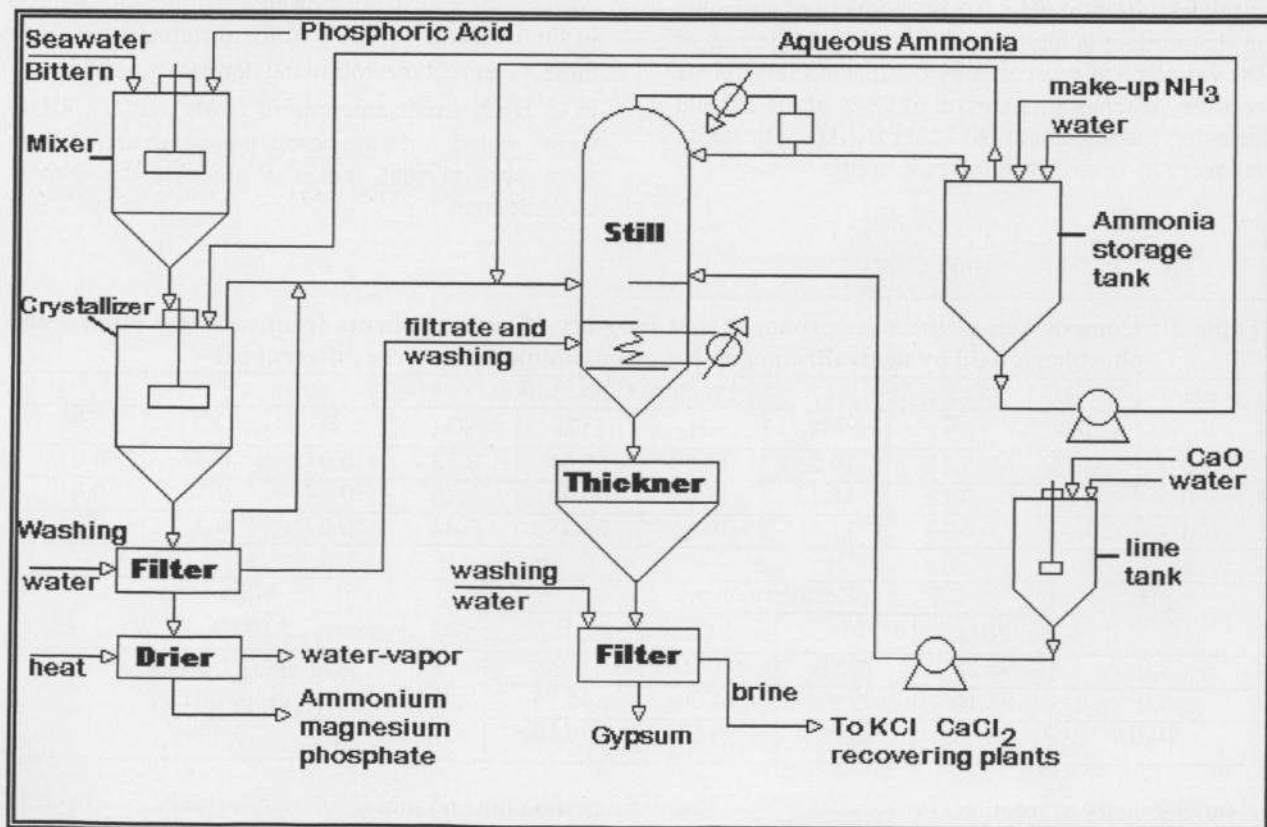


Figure 1 : Flow diagram of the proposed process for the fabrication of ammonium magnesium phosphate from Seawater Bittern.

## 5. CONCLUSIONS

The ammonium magnesium phosphate produced salt represents a chloride free multinutrient fertilizer with the following composition:  $\text{NH}_4$  (11 %) + Mg (18 %) +  $\text{PO}_4$  (68 %). The most promising conditions for possible industrial production are: neutralizing pH 8, neutralizing time 15 min, digestion time 60 min and reaction temperature 30 °C. Under these conditions the recoveries were:  $\text{NH}_4$  (98 %), Mg (99 %) and  $\text{PO}_4$  (98 %). The process produces as by-product high purity gypsum and a solution rich in potassium, sodium and calcium chloride from which these salts may be produced by known industrial processes.

## ACKNOWLEDGMENT

The authors are grateful to the Council for research of the University of Oriente for the financial assistance given for the realization of this investigation and to the National Salt Company of Venezuela, for providing the bittern.

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