

## Study on The Production of Ammonium Sulfate Fertilizer From Phosphogypsum

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### Abstract

The production of ammonium sulfate fertilizer from phosphogypsum is studied. The phosphogypsum is considered by product from extraction process of sulphuric acid. The mereseberg process is used a waste of phosphogypsum with ammonium carbonate to produce ammonium sulfate as a main product and calcium carbonate as a byproduct. It is a process could be used as a successful method in phosphate industry (AL-Qauim). The flow diagram is drawn to illustrate the mersberg process then material balance is done. The carbonation process is one of the stage of mereseberg method, then carried out at constant temperature ( $44C^{\circ}$ ) because of the reaction is exothermic and high temperature causes decomposition of ammonium carbonate and low temperature causes precipitate different kind of salts. From results of laboratory experiments the temperature of ammonium sulfate preparation is done in  $23C^{\circ}$  and the ratio of phosphogypsum to ammonium carbonate (400ml /192 gm phosphogypsum ) at reaction time( 4 ) hours. The aim of this work focus on making a process flow diagram which is used in dealing with waste of phosphogypsum and production a useful product.

**Keywords:** ammonium sulfate; phosphogypsum; fertilizer; meresberg

### دراسة استخدام الفوسفوجبسوم في إنتاج سماد كبريتات الأمونيوم

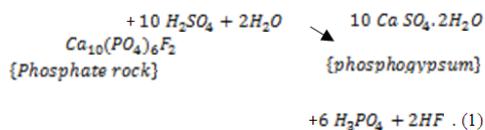
#### الخلاصة

تمت دراسة إنتاج سماد كبريتات الامونيوم من مادة الفوسفوجبسوم و الذي يعتبر ناتج عرضي من عملية استخلاص حامض الفسفوريك. وقد استخدمت طريقة (meresberg) والتي تتضمن تفاعل مادة الفسفوجبسوم مع الامونيوم كاربونيت لينتج كبريتات الامونيوم كنتاج رئيسي والكالسيوم كاربونيت كنتاج عرضي. وقد تبين ان طريقة (meresberg) ناجحة الاستخدام في مصنع الفوسفات في القائم، حيث ان عملية الكربنة وهي احد مراحل طريقة (meresberg) قد نفذت عند درجة حرارة ثابتة هي ( $44C^{\circ}$ ) بسبب ان التفاعل باعث للحرارة ودرجة الحرارة العالية تسبب تحلل لمادة كاربونات الامونيوم ودرجة الحرارة الواطئة تسبب ترسب أنواع مختلفة من الأملاح. وقد تم رسم مخطط كامل لعملية (meresberg) مع موازنة المادة . من النتائج العملية ان درجة حرارة تحضير كبريتات الامونيوم هي  $23C^{\circ}$  وان نسبة الفسفوجبسوم الواجب اضافته إلى كربونات الامونيوم هي (400ml/192 gm) من الفسفوجبسوم مع زمن تفاعل 4 ساعات . ان الهدف الرئيسي من هذا البحث هو رسم مخطط كامل لسير العمليات التي تجري في معالجة مخلفات الفسفوجبسوم وإنتاج مادة مفيدة هي س ماد كبريتات الاموني.

## Introduction

### Statement of The Problem

One of the most serious waste management problems in Al-Qa'im concerns the huge stockpiles of by-product gypsum produced by the phosphate industry. In fact, the phosphate industry, as it operates in Al-Qa'im as well as in many other parts of the world, could more accurately be termed as "gypsum" industry. During the wet process manufacture of phosphoric acid, the basic raw material from which most phosphate fertilizers are made, concentrated phosphate rock is reacted with sulfuric acid which results in the production of substantial quantities of by-product gypsum known as "phosphogypsum". A simplified chemical reaction for this process may be shown as follows:



gypsum and phosphoric acid is 5:3, the mass ratio is about 3:1, i.e., about 3 tons of gypsum are produced for every ton of acid. Phosphogypsum produced during this process is filtered off and pumped as

slurry to nearby storage areas, the so-called "gyp-stacks" [1]. The phosphate industry in Al-Qa'im produces approximately (2) million metric tons of by-product gypsum per year, almost million metric tons are stored near the phosphate industrial.

Although phosphogypsum is used in some countries for production of cement and other construction materials, its commercial use in the U.S. is currently limited to small quantities sold to farmers as a soil

amendment. One possibility for such a process is the large-scale conversion of phosphogypsum to the two end products (calcium carbonate and ammonium sulfate) of the so-called ammonocarbonation reaction. One of these products, ammonium sulfate, is an excellent fertilizer that adds both sulfur 60% and nitrogen 21% to the soil. The other reaction product, calcium carbonate, could be used for neutralizing acidic process water associated with the phosphate industry, or calcined to drive off the CO<sub>2</sub> which could be recycled for the production of the ammonium carbonate needed in the ammonocarbonation Process[2].

### The Methods of Ammonium Sulfate Production

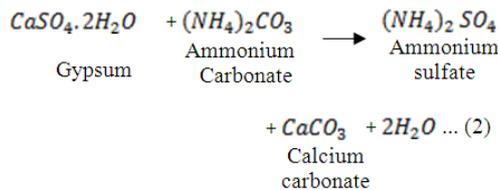
There are certain methods to produce ammonium sulfate, as follows:

1. Production from ammonia and sulfuric acid.
  2. Production from ammonia produced from gas coal and sulfuric acid.
  3. Production from SO<sub>2</sub> with organic solvent and converted to sulfur component then oxidized by air to sulfur and then treatment with ammonia to produce ammonia sulfate.
  4. From calcium sulfate with ammonium carbonate and this method use the waste of phosphogypsum with ammonium carbonate to produce ammonium sulfate. This fertilizer was imported by Iraq and manufacturing by limited amount in fertilizer factory nitrogenation (urea) in Basrah and Bejje, then the production is stopped for a numbers of years and method of production was depended on sulfuric acid and ammonia [2].
- Table (3) illustrated physical and

chemical properties for production ammonium sulfate and comparative with Egyptian result.

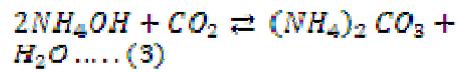
**Description of The Merseberg Process**

The manufacture of ammonium sulfate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, from gypsum (or anhydrite) is a very old technology, first developed by I.G. Farben Industries prior to 1914 [3]. According to Sacher (1968), it was actually used in Vienna as early as 1809 although not applied on an industrial scale until after the development of ammonia synthesis during World War II. Any type of gypsum, including by-product phosphogypsum, may be reacted with ammonium carbonate to form ammonium sulfate and calcium carbonate by the Merseberg process. Chemically, this process may be represented by the chemical reaction (2):

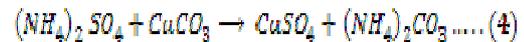


When by-product gypsum is used in the ammono carbonation process, the gypsum from the wet- process of phosphoric acid plant is purified by washing with water then treated with ammonium carbonate solution which, results in slurry of calcium carbonate in an ammonium sulfate solution. The ammonium carbonate solution is made from liquid ammonia and carbon dioxide, which can be derived from a variety of

sources, see equation (3). This reaction is exothermic and the temperature must be controlled to avoid Decomposition of ammonium carbonate with the temperature rise. Ammonium carbonate begins decomposition at temperature higher than 50°C and precipitates different kinds of salts and components of salts like ammonium bicarbonate with ammonium carbonate at temperatures lower than 40°C



ammonocarbonation process excess of ammonium carbonate solution must be used to avoid side gypsum reaction [4], this problem is illustrated in the following equation;



After separation the calcium carbonate and any excess ammonium carbonate is neutralized with sulfuric acid, the ammonium sulfate solution is concentrated and ammonium sulfate is crystallized. Several variations on this overall approach are possible and modifications have been made to suit the needs of a particular market. For example instead of crystallizing the ammonium sulfate it can be retained as a liquid for further processing into various mixed fertilizers such as ammonium sulfate phosphate. A flow chart for the industrial-scale Merseberg process, is shown in Figure (1) which illustrates some of the process factors which have been recognized as relating to the general quality and efficiency of ammonia carbonation[3]: (1) quality of the phosphogypsum (2) particle size (3) concentration of ammonium carbonate (4) conversion of calcium

sulfate (5) filtration of CaCO<sub>3</sub> and (6) evaporation and crystallization.

**The Experimental Work**

The experiments were conducted by treating phosphogypsum waste to produce ammonium sulfate fertilizer in multiple stages, as follows:

**1- The Carbonation**

The Carbonation process is carried out by blowing (CO<sub>2</sub>) gas in the ammonia solution (24% concentration) at 44°C at constant flow rate. The (CO<sub>2</sub>) gas passed through plastic distributor, see Figure (2). In this process the reaction is exothermic and the temperature must be controlled by keeping the solution under 44°C by cooling. For the optimum process, the following was studied:

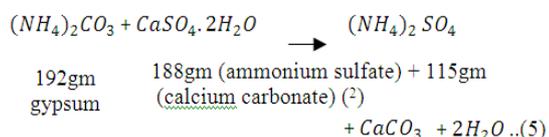
**2- Effect of Carbonation Time**

Carbonation experiment is done using different times by passing (CO<sub>2</sub>) gas through 500ml ammonia solution (24% concentration). The flow rate of (CO<sub>2</sub>) gas is 70 liter/hr at constant temperature (44°C). The results of experiments illustrated that, for the carbonation of solution by (CO<sub>2</sub>) gas for 1 hour is best time for this process. Any increase over 1 hour may cause precipitation carbonate and ammonium bicarbonate and this is undesired in other stage (reaction phosphogypsum with ammonium carbonate) on the other hand, the carbonation process is slow in time less than 1 hour (at constant flow rate of CO<sub>2</sub> gas 70 liter / hr). The pH meter is used to know when the carbonation process is over. Figure (3) shows pH reading vs. carbonation time. Ammonium sulfate was prepared from ammonium carbonate solution, when it was shown that ammonium sulfate increased by increasing carbonation time until the amount of ammonium

sulfate is constant after 1 hour, see figure (4).

**3- Phosphogypsum Reaction**

A numbers of experiments were carried out by reacting phosphogypsum with ammonium carbonate solution. Good mixing is obtained between the two materials by using mixer with suitable speed. The reacted amount of materials could be calculated by material balance on chemical equation eq. (2). Using (120%) excess amount of ammonium carbonate:



different time (2, 3, 4, 5, 6, 7 ) hours. The optimum reaction time was 4 hours to insure complete reaction; Figure (5) shows the relation between the amounts of ammonium sulfate vs. time of reaction

**5- Filtration and Washing**

After the reaction is complete, the solution is precipitated in order to separate calcium carbonate from filtrate ammonium sulfate solution. The Precipitate is washed and after first wash filtrate was taken to another stage while the precipitated (calcium carbonate) was washed well to remove sulfur residue. The calcium carbonate is considered as a side product and it could be used as a raw material in some other industry (paint industry, rubber industry, cement industry) [2]. Experiments were done to know amount of sulfur losses with washing water. After finishing every washing step a sample of solution was taken to measure percent of (SO<sub>3</sub>) in solution. The results are illustrated in table (1).

**6-The Neutralization**

Table (2) shows the effect of neutralization process on the amount of ammonium sulfate

**7- Evaporation and Drying**

Evaporation is done until white crystals of ammonium sulfate is precipitated. Drying is conducted at temperature between 120-130°C .After that milling can be conducted [4].

**8-The Results of Laboratory Experiments**

1 - Carbonation process (ammonocarbonation)

Carbonation of ammonia solution	24%
Reaction temperature	44°C
Carbonation time	1 hr
pH-meter	9.1
CO2 gas flow rate	70 liter / hr

sulfate Reaction temperature 23°C

The ratio of phosphogypsum to ammonium carbonate: 400 ml ammonium carbonate / 192 gm phosphogypsum The reaction time: 4 hour

3- Filtration process: washing the precipitate calcium carbonate to removal sulfur = 1 liter (washing with water)

4-The evaporation: Temperature = 110°C

5-Drying of crystals: Temperature = 120°C

**3-Conclusions**

1. The preparation method of ammonium sulfate fertilizer by ammonium carbonate with phosphogypsum (waste product from preparation of sulfuric acid) could be used as successful method in phosphate industry (Al-Qauim).
2. The phosphogypsum used does not require to purification before reacting with ammonium

carbonate because of fluorine and P<sub>2</sub>O<sub>5</sub> percents (F<sub>2</sub>=0.4%, P<sub>2</sub>O<sub>5</sub>=0.6%) are not significant i.e: the poison and radon element is very low.

3. The carbonation process is carried out at a constant temperature (44°C), because of the reaction is exothermic and at high temperature causes decomposition of ammonium carbonate and at low temperature causes precipitate different kind of salt.
4. The neutralization stage of ammonium sulfate solution by sulfuric acid could be omitted, where the removal of excess ammonia may be done by evaporation and recycled it to carbonation stage.

**References**

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[2]Wikkiam C. Burnett, Michael S., Carter H." Behavior of Radionuclides During Ammonocarbon of Phosphogypsum", Florida State Univ. email:bumett@ocean.fsu.edu (1970)

[3]Gopinath, N.D., 1968 Disposal or use of gypsum in production of ammonium sulfate. In: Phosphoric Acid, vol. 1, Part II, (ed. A.V. Slack), Marcel Dekker, New York, 541-566.

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**Table (1): No. of washing and amount of (SO<sub>3</sub>) for every washing**

No. of washing	SO <sub>3</sub> ppm
1	46400
2	2600
3	400
4	200

**Table (2): Amount of ammonium sulfate production with neutralized and with not neutralized solution.**

(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (gm)	Process method	Raw material (gm)
188	Neutralized	192
132	Not- Neutralized	192

**Table (3): physical and chemical properties for Production and comparative with Egyptian result.**

Component	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	CaCO <sub>3</sub>	Results of Egyptian* Ammonium Sulfate
N	21%	-	21%
CaO	0.06%	50.34%	-
P <sub>2</sub> O <sub>5</sub>	0.4%	0.3%	"
S	24%	0.24%	24%
Purity	99%	98%	98%
pH value	4.8%	-	5.1 ***
Solubility	Soluble **	-	Soluble **
Grain density	1.8gm/cm <sup>3</sup>	-	1.77 gm / Cm <sup>3</sup>
Grain size	-	50 Micron	-
Mineralogy	Amm-Sulfate	calc. carbonat	Amm. Sulfate

\* ReferenceNo. (1).

\*\* 82gm (ammonium sulfate) / 100gm water

\*\*\*10gm (ammonium sulfate)/gm wa

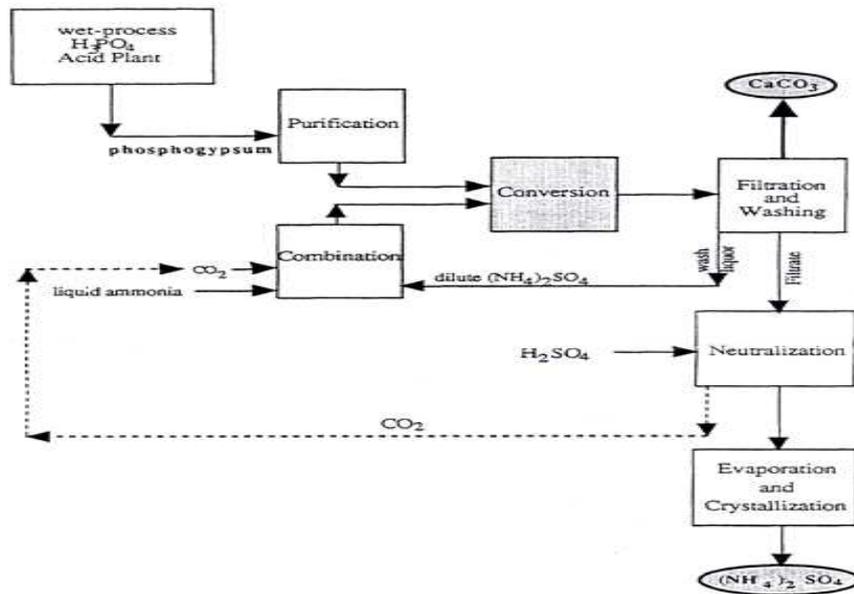


Figure (1): Simplified flow chart of the industrial-scale Merseberg process [4].

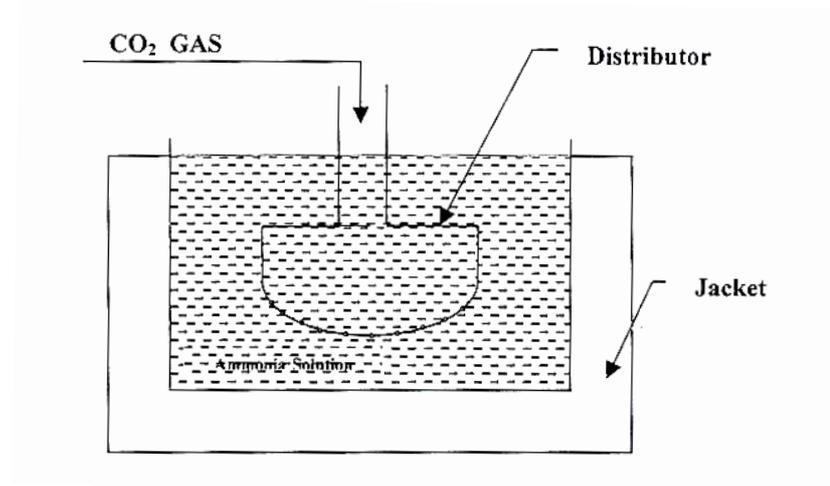


Figure (2): Carbonation Process [4]

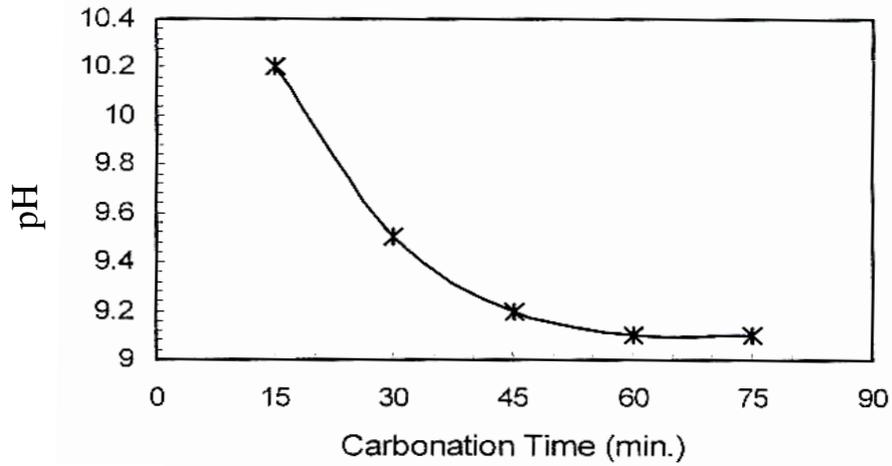


Figure (3): pH Vs. Carbonation time.

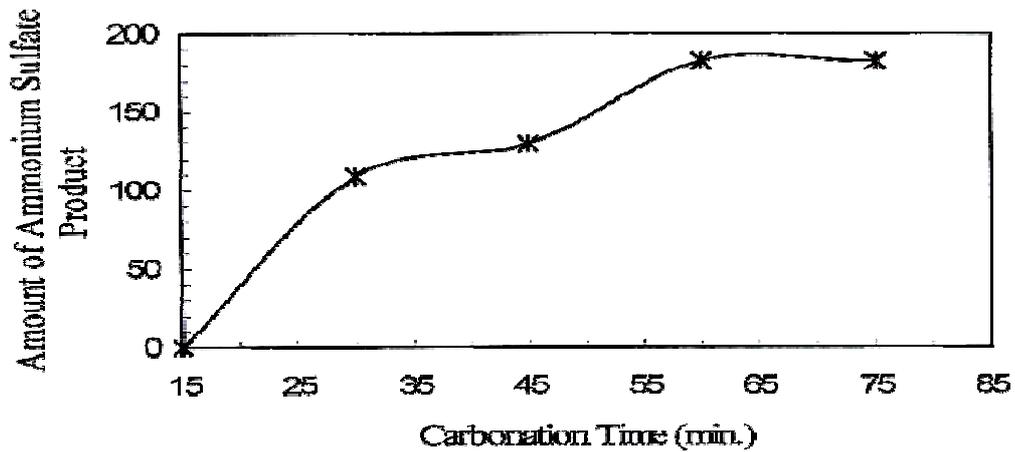


Figure (4): Production Behavior of Ammonium Sulfate

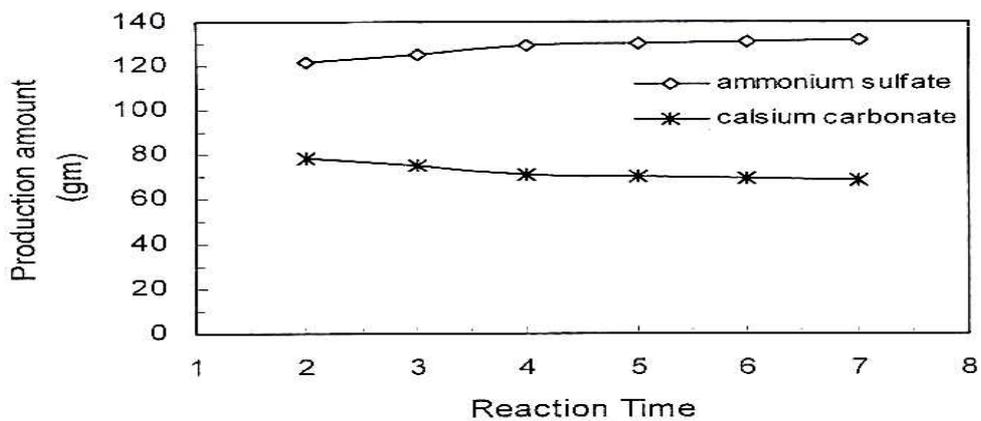


Figure ( 5): amount of ammonium sulfate Vs. Reaction time, Input Raw material (phosphogypsum =200 gm) and ml ammonia solution