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Chemical Processing of Phosphogypsum for Production of Ammonium Sulphate Fertilizer

Selim F. Estefan

National Research Centre, Dokki, Cairo, Egypt.

ABSTRACT. A safe and profitable method of utilizing phosphogypsum byproduct has been devised involving pretreatment of the sample to minimize impurity content, followed by reaction of the residual phosphogypsum with ammonium carbonate to produce ammonium sulphate fertilizer. The prepared fertilizer was subjected to some physico-chemical tests which proved it to be of good quality, suitable for modulating the pH of the highly alkaline Egyptian soil.

The safe disposal of solid wastes or byproducts from the fertilizer industry has been a serious problem in several countries. Phosphogypsum is by far the largest byproduct in the manufacture of wet-process phosphoric acid. Disposal of phosphogypsum has become of concern due to the construction of larger phosphoric acid plants which reject about 5 tons of phosphogypsum waste for every ton of P_2O_5 produced. Storage of this byproduct sludge will become more critical as the cost of land increases and public concern for solid pollution intensifies. Recycling and utilization of phosphogypsum will provide some benefit to the agro-chemicals industry.

In countries where land is relatively cheap and available, the phosphogypsum cake from the filter is mixed with water and discharged as a slurry to a gypsum pond. The calcium sulphate and calcium fluoride settle down and eventually fill the pond. Care must be taken to prevent groundwater contamination due to seepage from the pond. Alternatively, phosphoric acid plants located on sea shores usually discharge the slurried gypsum waste into the sea. Gypsum is soluble in seawater and is rapidly dissolved where the tidal currents are strong. However, this way of disposing of phosphogypsum may affect the aquatic life to some extent.

Processing of phosphogypsum for cement, building blocks, and plaster board, as well as the recovery of SO_2 from gypsum for production of sulphuric acid, has been practised by several fertilizer manufacturers in landlocked countries, where the lack of other disposal methods proved this process relatively economical. In 1978 the global utilization of byproduct gypsum was about 15 million tons compared with 60 million tons of natural gypsum (Roskill 1983). Market specifications for the recovered byproducts will determine, in each case, the economic viability and specific process to be adopted. Some other principal means for utilizing phosphogypsum include the following:

1. Production of ammonium sulphate by reaction of gypsum with ammonia and carbon dioxide.
2. Use of phosphogypsum as a fertilizer filler.
3. Direct application of phosphogypsum to farmland when the soil requires it.
4. Use of phosphogypsum to create off-shore recreational islands.

Recently, with the start of wet-process phosphoric acid plants in Egypt, the problem of safe disposal of phosphogypsum byproduct has attracted the attention of Egyptian scientists and technologists.

The aim of the present work was to investigate the utilization of phosphogypsum, rejected through chemical processing of Abu-Tartur phosphate rock, for the production of ammonium sulphate fertilizer which is greatly needed to modulate the pH of the highly alkaline soil in Egypt.

Process Technology

A technologically representative sample of Abu-Tartur phosphate rock was crushed, ground, and beneficiated through a combined classification/flotation process. A sample of the phosphoconcentrate was adapted to the dihydrate process in a single-tank reactor (Estefan *et al.* 1986). The phosphogypsum byproduct (−0.2 mm) was examined by X-Ray diffraction and by emission spectroscopy for detection of trace elements present. The fine phosphogypsum particles (30 microns), loaded with most of the impurities, were first removed by decantation after repulping the filtercake in an agitated vessel. The residual phosphogypsum had a significantly low radioactivity of 5 pCi/g (Weterings 1982) and was used for production of ammonium sulphate fertilizer. The sample was washed and filtered on a disc filter to get a good-quality gypsum with minimum moisture content and was reacted with ammonium carbonate solution (175 g/1), using 1.2 folds the stoichiometric amount, at 25°C for 4 hrs with continuous agitation. The slurry produced was filtered and the calcium carbonate cake was washed and dewatered on a continuous vacuum system. The liquor was neutralized with sulphuric acid and heated to 110°C to remove excess ammonia prior to concentration and crystallization. The ammonium sulphate crystals were dried at 120°C and were subjected to some physico-chemical tests.

Results and Discussion

Wet-process phosphoric acid is a profitable industry, and, considering the possibility of forward integration into agricultural and industrial chemicals, it seems probable that this industry may become one of the predominant elements of our Nation's economic well-being. Our phosphorus research programme is oriented toward assisting fertilizer manufacturers in Egypt to make better use of indigenous resources of Abu-Tartur phosphate rock which are estimated at one billion tonnes (Mineral Map 1979).

Recently, with the start of wet-process phosphoric acid plants in Egypt, manufacturers are facing a serious problem of the safe disposal of phosphogypsum byproduct. The land surrounding the phosphoric acid plant site in Cairo is too valuable to be used as a pond for dumping of phosphogypsum wastes. Dumping of phosphogypsum nearby the fertilizer complex would endanger groundwater supplies regardless of the possibility of environmental hazards which may interfere with recreational planning for a nearby new town. The groundwater is important for down-stream agricultural and human consumption. At the present time, a portion of the phosphogypsum byproduct is consumed by direct application on farmland. Nevertheless, when the Abu-Zaabal Fertilizers and Chemicals Complex in Cairo operates its wet-process phosphoric acid plant and reaches its full capacity of 120,000 tons of phosphoric acid per year, it is estimated that some 500,000 tons of phosphogypsum byproduct will be rejected annually. The safe disposal of such a huge amount of phosphogypsum waste will require intensive investigations in order to arrive at a relatively safe and economic solution.

Possibly, utilization of phosphogypsum byproduct as a starting material for production of ammonium sulphate fertilizer would be more logical from both technical and economical viewpoints. The role of ammonium sulphate in the fertilization process is to restore land suffering from high alkalinity. Ammonium sulphate simultaneously reduces the pH of the soil and provides a source of nitrogen for plants. It has additional value in sulphur-deficient soils or when particular plants, such as maize, require a source of sulphur for mobilizing the enzyme system. Ammonium sulphate, rather than urea, is the preferred fertilizer in irrigated lands (UNIDO 1985). Egypt has significant areas of irrigated lands and hopes to expand the number of acres under irrigation as part of its efforts to increase food production. In some cases, ammonium sulphate may be the most economical source of nitrogen when the transportation distance to the farm is short, when a credit can be taken for its sulphur content, or when it can be made available for the farmer at low cost. The main advantages of ammonium sulphate fertilizer are due to its low hygroscopicity, good physical properties, chemical stability, and good agronomic effectiveness. It is a good source of sulphur as well as nitrogen. Its reaction in the soil is strongly acid-forming which is a major advantage on the Egyptian alkaline soils. The majority of developing countries greatly depend for their agricultural success on ammonium sulphate as a source of nitrogen, especially those engaged in the cultivation of rice.

One of the simplest methods adopted for the manufacture of ammonium sulphate is the direct reaction of natural or byproduct gypsum with ammonium carbonate. The reaction stoichiometry is as follows:

$$CaSO_4.2H_2O + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4 + 2H_2O; \ \Delta H = 16.323 \ kJmole^{-1}$$

This method was originally developed in Germany and has long been used in Austria, India, Pakistan, and the United Kingdom (Gopinath 1968 and Rao 1977). This process has several advantages, for example, countries without indigenous sulphur supplies but having natural or byproduct gypsum or anhydrite can produce ammonium sulphate without importing sulphur from abroad. In addition, the byproduct calcium carbonate can be used for cement production (Ashburner 1968) or for other purposes such as in calcium ammonium nitrate manufacture or for agricultural lime when the soil requires it.

Table 1 presents the trace elements in Abu-Tartur phosphoconcentrate and the phosphogypsum byproduct, detected by emission spectroscopy. Fortunately, none of the toxic heavy metals Cd, Pb, or Hg could be detected in the phosphogypsum. X-ray diffraction patterns indicated that this phosphogypsum byproduct consists mainly of calcium sulphate associated with small amounts of aluminum phosphate and magnesium silicate fluoride (Humite) (Estefan *et al.* 1986).

Table 1. Spectroscopic detection of trace elements in Abu-Tartur phosphoconcentrate and phosphogypsum, in ppm unless otherwise stated.

Sample	Si	Al	Fe	Mg	Na	K	Mn	Cu	Cr	Zn	Ni	Mo	V	Cd	Pb	Hg
Phospho-concentrate	1%	1%	3%	100	100	–	30	10	30	ND	10	ND	5	ND	10	ND
Phospho-gypsum	1%	1%	1%	100	100	1000	30	30	30	ND	ND	ND	20	ND	ND	ND

In the present work, the purity of the recovered ammonium sulphate was 98.6%. The recovery of sulphate ion from phosphogypsum was 94%. 700 g of ammonium sulphate could be produced out of 1 kg of phosphogypsum. The nitrogen content in the ammonium sulphate produced was 21%. Physico-chemical studies of the product revealed that the solid ammonium sulphate has a density of 1.77 g/cm^3 at 25°C. It has a melting point of 510°C and has a good thermal stability as it decomposes at temperature above 280°C. It is highly soluble in water, its solubility is 82 g/100g of water at room temperature (25°C). When 10 g of ammonium sulphate crystals were dissolved in 100 g of water an acidic solution (pH = 5.1) was obtained. It has been reported that the use of acid-forming fertilizers on alkaline or calcareous soils may be practically helpful, although the effect of normal fertilizer application on soil pH usually is small in a single year. Therefore, application of ammonium sulphate fertilizer to the alkaline soil in Egypt would be beneficial as it improves the fertility of farmland.

On the industrial scale, the slurry from the reaction of phosphogypsum with ammonium carbonate is filtered on a two-stage drum filter installation provided with intermediate repulping. The evaporator feed-liquor usually contains about 500 g of ammonium sulphate per liter. Evaporation is carried out in continuous multiple-effect evaporator crystallizers. Crystals of the required size range are separated and washed in a centrifuge and dried in a vertical tray type of dryer at 120°C. The use of this type of dryer reduces crystal breakage and dust formation as compared with a rotary dryer and cooler. Figure 1 delineates a flowdiagram for the

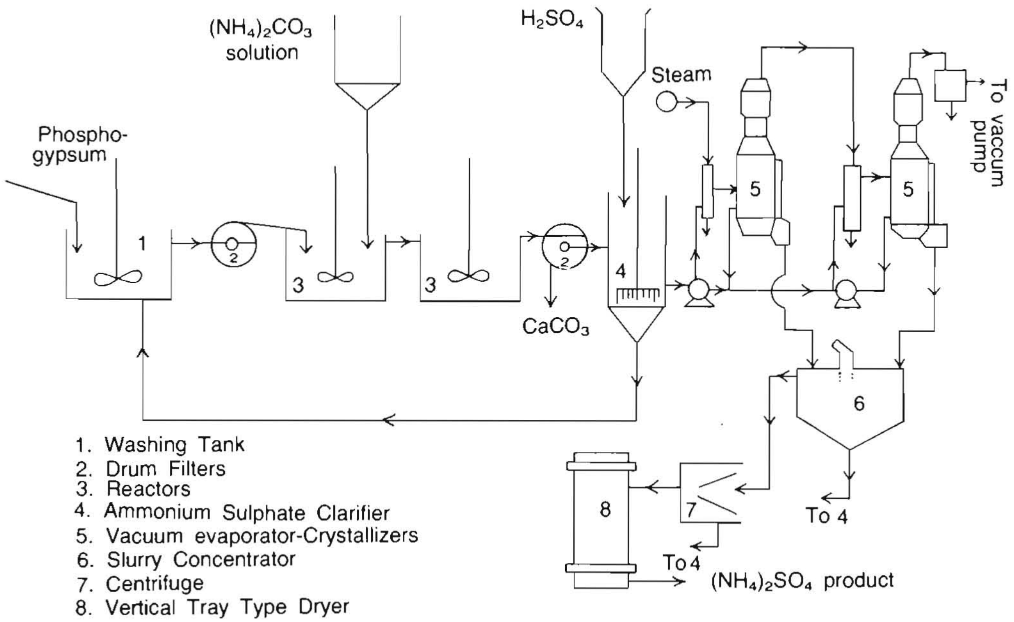

Fig. 1. Flowdiagram for production of ammonium sulphate fertilizer from phosphogypsum.

production of ammonium sulphate from phosphogypsum. The byproduct calcium carbonate, which is estimated to be about 600 kg per ton of phosphogypsum may be profitably utilized for the production of Portland cement (Ashburner 1968).

The phosphoric acid manufacturers in Egypt would no doubt welcome such a safe and profitable methodology of disposing all the phosphogypsum they generate for production of an important and cheap nitrogen fertilizer, ammonium sulphate, urgently needed for reclamation of the highly alkaline Egyptian soil.

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المعالجة الكيميائية للجبس الفسفوري لانتاج سماد كبريتات النشادر

سليم فهمي اسطفان

المركز القومي للبحوث - الدقي - القاهرة - مصر

تسبب مخلفات الجبس الفسفوري الناتجة عن تصنيع حامض الفسفوريك من خامات الفوسفات مشكلة كبيرة في كيفية التخلص منها بطريقة آمنة. وقد بدأت مصر تعاني من تلك المشكلة مع بداية تشييد وحدات لصناعة حامض الفسفوريك بالطريقة الرطبة. وقد أمكن التغلب جزئياً على هذه المشكلة بالاستخدام المباشر لبعض الكميات من الجبس الفسفوري في الأراضي الزراعية. إلا أنه عندما تستكمل وحدات تصنيع حامض الفسفوريك وتصل إلى كامل طاقتها الانتاجية التي تقدر بحوالي ١٢٠٠٠٠ طن من الحامض سنوياً يتخلف عنها حوالي ٥٠٠ ألف طن من الجبس الفسفوري، وعندها يكون من الصعب التخلص من تلك الكميات الكبيرة بطريقة إقتصادية وآمنة.

في هذه الدراسة أمكن استغلال مخلفات الجبس الفسفوري الناتجة من تحضير حامض الفسفوريك من خامات فوسفات أبو طرطور بالصحراء الغربية في تحضير سماد كبريتات النشادر وذلك بمعالجتها بمحلول كربونات النشادر حيث تترسب كربونات الكالسيوم وتبقي كبريتات النشادر ذائبة في المحلول. وقد تم فصل كربونات الكالسيوم بالترشيح، ثم أجريت عمليات تبلور لكبريتات النشادر بطريقة التبخر.

أجريت إختبارات معملية على كبريتات النشادر التي تم تحضيرها، وقد أكدت النتائج ان محاليلها في التربة حامضية التأثير، وهي لذلك تصلح لاستخدامها في استصلاح الأراضي الزراعية المصرية ذات القلوية العالية وفي زيادة خصوبتها. وتستهلك مصر في الوقت الحالي كميات كبيرة من سماد كبريتات النشادر، يتم تصنيع جزءا منها محلياً بينما تضطر إلى استيراد الجزء الباقي من الخارج.