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UTILIZATION OF THE PHOSPHOGYPSUM PRODUCED IN THE FERTILIZER INDUSTRY*

Prepared by the

Naomi Pena

Division for Industrial Studies

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I. Phosphogypsum - An Overview

A. Introduction

Phosphogypsum is a by-product of the manufacture of phosphoric acid from phosphate rock by the vet process.* The overall reaction is as follows:

 $Ca_{10}(PO_4)_{6}F_2 + 10 H_2SO_4 + 20 H_2O$ ------ 10 $CaSO_4$. 2 H_2O + 6 H_3P0_4 + 2 HF

Each ton of P_2O_5 in the acid is associated with the production of 4.5 to *5.5* tons of phosphogypsum. In other words, tor every ton of phosphate rock about 1.5 tons of phosphogypsum are formed. The exact quantity depends on the phosphate rock quality. (1)

Figure 1 shows, in schematic form, estimated and projected worldwide production of P_2O_5 and phosphogypsum for the period 1970-2000.⁽²⁾ As of 1983 some 120-150 million metric tons (mmt) of phosphogypsum were being produced annually. If historic trends continue, $150-200$ mmt of phosphogypsum will be produced annually by 1Q90, increasing to 220-280 mt by 2000.

B. Impurities in the phosphogypsum

The phosphogypsum as it comes from the phosphoric acid plant ma_j contain a number of undesirable iapurities, especially phosphates and fluorides. Typical levels of impurity for dihydrate processes are:

Phosphoric acid content, as $P_2O_5 = 0.663$ Fluoride content, as $CaF_2 = 1.442$

The quantity of impurities in the phosphogypsum depends primarily on the phosphoric acid process used, on the operation of the plant, and on the quality of the phosphate rock.

The terms phosphogypoun and by-product gypoun are used interchangeably in the technical literature. Waste gypsum is also a sy_', onym sometimes, but more often describes phosphogypsum which has been dumped or otherwise discarded.

Figure 1.

Phosphoric acid processes producing the dihydrate directly yield a phosphogypsum with a higher level of impurities than dihydrate/hemihydrate processes.

C. Uses for the phosphogypsum

Phosphogypsum can be used in many ways in the building materials industry. Its primary uses in the building industry are for plaster, plaster board, building blocks, and as an additive to cement. As an additive to cement it is used in two ways.

1. As an additive to cement before the clinker is prepared. The amount to be added may vary from 1.5% to 3.5% (calculated as SO_2). The clinker can be produced at a temperature about 100° C lower than normal. The resultant cement has quicker development of initial strength, higher long-term strength, and greater resistance to sulphate etching. Thus the product has better characteristics than normal Portland cement.

2. As an additive to cement after the clinker is prepared. The main purpose of Lhe added gypsum is to retard the setting time of the cement. It also tends to counteract the shrinkage which generally accompanies the setting of the concrete. Phosphogypsum has been widely used in Japan, the USSR, Belgium and Austria in this application. The phosphate and fluoride impurities should be low in the phosphogypsum or the strength of the cement will be reduced during the initial days of curing.

Phosphogypsum can also be used in agriculture either as a soil conditioner or to produce anmonium sulphate fertilizer. It can be used as a source of sulphuric acid and as land fill, and experiments are continuing for use of phosphogypsum as a roadbed material.

D. Potential pitfalls of utilization: the need to reduce trace amounts of radioactivity present

Trace amounts of certain radionuclides, especially radium-226, are present in the phosphate rock and released during the industrial processesing. If no measures are taken to reduce concentration of Radium-226, exposure to radiation would be expected to be up to 304

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higher than normal for persons living in houses with interior walls built from phosphogypsum. (3) A practical solution to the problem is hydrocycloning, as performed in the Donau Chemie process. The radioactivity of the phosphogypsum is thereby reduced by about 30%.

E. Disposal of phosphogypsum by dumping: environmental considerations

Host recent estimates indicate that approximately 85% of all (4) phosphogypsum is either stored or dumped rather than reused. Phosphogypsum is either dumped into water bodies or stored at land disposal sites.

Objections to dumping on land include rendering nearby areas unfit for recreational uses and possible leaching of acids into ground water supplies. In areas where land is at a premium there may also be a lack of adequate space for disposal.

Phosphogypsum land stockpiles are not toxic hazardous wastes according to U.S.EPA criteria. (5) Studies have shown that neither the radium nor the trace elements present in phosphogypsum disposal mounds leach into underlying soils. Although stored phosphogypsum has a very low Ph $$ samples ranged from 2.10 to 3.75 $-$ it is not sufficiently low to be classified as corrosive under U.S. EPA guidelines. (6) Ph must be 2.0 or less to qualify as corrosive under U.S. EPA guidelines.

Dumping of the slurried phosphogypsum into a holding pond is sometimes chosen because it is the least costly disposal solution. However, there are environmental objections based on the high acidity and high concentrations of various ions in the waste water. These are shown in Table 1. (7)

Objections to dumping in rivers and near-shore water bodies include destruction of aquatic life, rendering down-stream water unfit for industrial uses, hindering maintenance of water channels, and causing operational problems in equipment. Existing studies have concluded that the primary source of destruction of aquatic life is the suspended solids. Dumping of phosphogypsum has been cited as the cause of disappearance of shrimp, mussle and lobster populations.

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F. Phosphogypsum in 1970

The situation by 1970 was that nearly all the by-product gypsum was wasted. For example, by 1972 152 million tons of phosphogypsum had accumulated in Florida. This was supplemented by an annual generation rate of 21 million tons. (1) This represented three times the US production of natural gypsum in that year. World-wide, at least 50 million tons of waste gypsum were produced in 1970 *as* a by-product of the manufacture of phosphoric acid.

A case which attracted attention in Europe that year was the initial plan of Boliden AB of Sweden to dump 500,000 tons of waste gypsum from phosphoric acici production into the Oeresund between Sweden anc. Denmark. Although permission was obtained, the firm reversed its plan by autumn of that year and signed a contract with two producers of building materials to utilize 300,000 tons of the by-product gypsum for wallboard and cement production. (8)

G. Phosphogypsum in 1978

The world-wide estimated output of phosphogypsum was in the 120-150 mmt range by 1978. Only 10.5% of this amount was reused. (9) The reuse percentage for Eu1ope (22%) was double that of the world-wide average, and the regional reuse percentage for Asia approached 45%. A European country whose recycling record was about average for the region was Belgium. In 1977, about 25% of the production of 1,500 ktons of phosphogypsum were recycled. About 250 ktons were recovered for use in the cement industry (Liege area) and 120 ktons were utilized in the building industry (equally divided between Antwerp and Liege). < ⁷> Two countries from Eucope and Asia took the initiative to reuse essentially 100% of their waste gypsum; these were Japan and Austria. The case studies of these two countries will be discussed in more detail in Sections Ill and IV. In 1978 the global utilization of by-product gypsum was about 15 million tons compared with 60 million tons of natural gypsum. (9)

H. Phosphogypsum by the early 1980s

By 1980, annual production of phosphogypsum was estimated to have been in the 120-150 mmt range. A survey of companies producing phosphogypsum was carried out in 1981. Assuming these companies were representative, as of 1980 14% of all phosphogypsum was being reprocessed, 58% was stored, and 28% was being dumped. If at present 15% of all phosphogypsum is being recycled and 28% is being dumped, room for the storage of an additional $70-85$ million metric tons of phosphogypsum must be found every $\text{year.}^{(4)}$ The need to find suitable storage facilities for deposits of this magnitude is creating escalating pressure to explore reprocessing options. Results of recent efforts to solve the economic and technological problems of reprocessing phsophogypsum include a process for converting phosphogypsum into lime, sulphur dioxide and sulphuric acid, and a project to use phosphogypsum to create off-shore recreational islands.

I. New uses for phosphogypsum

Several new applications of phosphogypsum in the areas of building materials utilization and reprocessing as a chemical raw material came on stream in the late 1970s. In Brazil, SCIAG, a subsidiary of Rhone-Poulenc, was reported to be constructing three plants for the conversion of phosphogypsum into materials for the construction industry. Boliden AB in Sweden was reported to be using the Central Prayon process for the production of phosphoric acid which is claimed to produce a gypsum of sufficient purity for use in plasterboard and cement. Knagsack in West Germany was planning to use the Guilini process to produce 250 tons per day of by-product gypsum for building materials. Nitrigin Elrann Jecranta had similar plans for their plant at Arklow, Ireland.⁽⁹⁾ A potential American application of phosphogypsum is as a filler (up to 302) in asphalt. (1)

The TSP fertilizer plant in Chittagong, Bangladesh is also recycling phosphogypsum. First acids and other impurities are removed from the phosphogypsum. Then the recovered dihydrate is used to make plaster of Paris;

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$$
\text{Cas}_4.2 \text{ H}_2\text{O} \text{ -- } \text{Cas}_4.1/2 \text{ H}_2\text{O} + 1 \text{ I}/2 \text{ H}_2\text{O}
$$

The setting of the plaster of Paris $(CaSO_4, 1/2 H_2O + 1 1/2 H_2O)$ CaSO₄.2 H₂O) from phosphogypsum was too fast (2 min, 30 sec). However, experiments showed that solutions of borax and glue could be employed to retard the setting time. Solutions of $1\overline{2}$ and $0.1\overline{2}$, respectively, slow down the setting time to 5 minutes. (10)

J. Factors which determine the profitability of the recycling of phosphogypsum

The main factors governing reuse of phosphogypsum for existing fertilizer plants are (1) quality of the phosphogypsum resulting from phosphoric acid production, (2) the quantity of phosphogypsum produced, (3) cost of energy, (4) distance to the marketing site for the phosphogypsum, (5) distance from the natural gypsum site to the marketing site. For example, the transport cost in 1977 in Belgium was 140 BF/ton per 100 $km²$.

K. Summary

Interest in development of phosphate resources and in phosphoric acid processing facilities continues to run high in third-world countries. Table 2 lists third world countries which are major producers of phosphate rock and/or P_2O_5 . As can be seen from this table, almost all of these countries are both planning new P_2O_5 facilities and striving to increase domestic cement production. This combination presents a situation favorable to exploiting phosphogypsum to help meet building material requirements. Table 3 shows the level of cement production in these same countries as of 1981, as well as the rate at which cement production has increased over the past decade. Markets for phosphogypsum products can be expected to be particularly good in countries which have experienced rapid increases in cement production and which expect to continue to do so. Indonesia has been importing substantial amounts of gypsum and therefore might consider whether an import substitution based on reprocessed phosphogypsum would be technically feasible and cost effective.

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Table 2. Major Third World producers of phosphate rock and phosphoric acid (4) , (12), (13)

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Table 3 . Cement production for major Third World producers of phosphate rock and phosphoric acid (4) (000 t)

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II. Fly Ash/Phosphogypsum Concrete Masonry Blocks as *a* Construction Material in China

China is a country with a pressing need to construct large zmounts of low-cost housing. The growth of China's population and the relatively low amount of living space available per capita have sade the provision of increased housing a major national goal. Since the late 1970's in particular strenuous efforts have been made to construct new housing. China hopes to be able to provide each family with its own apartment by the year 2000. Achievement of this goal would require construction of 100 million square meters of housing annually, including 30 million units between 1981 and 1990.

For more than 20 years China has been investigating the feasibility of using fly-ash building blocks for residential construction. Several factors have contributed to this interest. China's domestic natural resources are limited, large amounts of industrial waste materials have become available, and it was recognized that in order to meet construction goals the construction industry would need to be mechanized.

Mechanization of the housing construction industry is necessary for China to meet its 100 million square meters per year target. This mechanization however must proceed at a pace in line with the country's existing technological skills. Both the manufacture of fly-ash building blocks and construction techniques based on use of fly-ash building blocks allow increased use of mechanized equipment. The technologies involved are relatively unsophisticated. These technologies were deemed well-suited to adoption by Chinese firms. In particular, construction with fly-ash blocks is better suited to use of mechanized hoisting equipment than brick-based construction. The use of mechanized hoisting equipme1t in particular reduces construction time and increases worker satisfaction. Both of these were important considerations for China.

China's relative scarcity of resources has meant that costs of materials play a significant role in total construction cost. In China 60% -70% of

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total construction cost is attributable to cost of materials. Consequently, in order to hold down costs for its massive housing construction program, China has been extremely interested in developing low cost materials. An excellent way to reduce costs of materials is to utilize waste products. Since these waste products have presented China with a major disposal problem, China has had an added incentive to search for productive uses of waste materials.

China has long been interested in finding a solution to the problem of disposing of its fly-ash from blast and industrial furnaces. Fly-ash building block& was one of the successes steming from research efforts to find productive uses for waste fly-ash. These fly-ash building blocks utilize not only waste fly-ash but two other industrial wastes; phosphogypsum and by-product lime from steel plants. In Shanghai alone it was estimated that the use of fly-ash for manufacture of building blocks resulted in a saving of 7 million Yuan in the period 1963-1981.

The fly ash blocks are not only an environmentally sound outlet for certain industrial wastes. Chinese officials have found the blocks are technically superior and can be produced at a lower cost than conventional clay bricks and brick masonry construction. (14)

The Chinese have established the following necessary quality requirements for the fly ash: (a) a loss of ignition of less than 15%, (b) an \sin^2 content of more than 4%, (c) an Al_2O_3 content of more than 15% and (d) the residue after passing through an 88 nm sieve should be less than 20%. The main procedures in the manufacturing process are grinding of raw materials, mixing, forming of the blocks, steam curing and stacking of finished blocks.

The fly ash blocks have sufficient strength to be used as load bearing structures. In fact, large blocks of apartments have been constructed using fly ash blocks. Sound engineering principles have been followed in designing structures especially suitable to this medium of construction. The Chinese have found that mechanized construction techniques are more suitable for fly-ash block construction than for brick walls.

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Observations of fly-ash block buildings constructed over the past ten years in many Chinese cities have not revealed any external deterioration or weathering. Even buildings constructed in the northern city of Qiqihaer, exposed to temperatures of -30 to 40° C, are still in good condition and the exterior wall surfaces are intact.

Economic advantages attributed to the use of fly-ash blocks include advantages at both the production and construction stages. Economic advantages at the production stage are a result of the fact that a fly-ash building-block manufacturing facility is approximately twice as productive as an ordinary kiln for baking bricks. The investment can be fully amortized, or paid back, in seven years as compared to the ten years required for a brick kiln. Of considerable importance to China is also the fact that 30% less energy is consumed in the manufacture of fly-ash blocks as compared to clay bricks.

During the construction stage economic advantages accrue in large measure due to the fact that building block construction allows more extensive use of mechanized equipment. This mechanized construction increases labor productivity by approximately one-third. It correspondingly decreases construction time by about 30%. In addition building-block construction reduces by 4.7 Kg the amount of cement required per square meter of construction. Since conservation of building materials is of primary importance in China this is also a signficant advantage.

The newest development in utilization of fly-ash, phosphogypsum and by-product lime in China is the production of concrete panels. The momentum for using these otherwise wasted materials is well established and other contributions may also be expected from the Chinese in the future.

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III. Japanese Developments in Phosphate Fertilizer Technology which Produce High-Qudlity By-Product Gypsum

A major exception to the accumulation of waste gypsum mountains was in Japan. By 1970 the Japanese construction industry was utilizing 1.5 million tons of phosphogypsum for the cement and plasterboard sectors. There were some twenty plants making gypsum plasterboard from by-product gypsum in that year. This activity contributed to a decline in the natural gypsum industry in Japan. In 1964, Japan produced 753,000 tons of natural gypsum, but only 550.000 tons by 1970 . (8)

A. The Nissan H-process

An important factor accounting for the substantial increase in utilization of by-product gypsum in Japan since 1959 has been the development of a hemihydrate-dihydrate phosphoric acid process which yields a phosphogypsum that is lower in impurities than that produced by the dihydrate process. The Japanese commercialization of the new process began in 1955, the year that the first Nissan Chemical Industries LTD phosphoric acid plant came on stream using the so-called Nissan (15) H-process.

One of the prime factors motivating the development of the H-process was stated to be the need to obtain the highest quality of by-product gypsum. Because of Japan's limited resources of natural gypsum, there is commercial value in the phosphogypsum which is produced as a by-product of phosphoric acid production.

In the H-process, ground phosphate rock is thoroughly mixed with a combination of sulfuric acid and recycled dilute phosphoric acid from the filter. The reaction takes place at a high temperature in order to decompose most of the phosphate rock and yield the hemihydrate form of calcium sulfate. Calcium sulfate dihydrate is stable under conditions of low acid concentration and low temperature, whereas calcium sulfate hemihydrate is stable at higher acid concentrations and temperatures.

Table 4. Typical properties and use characteristics of by-product gypsum obtained from the Nissan H-process using Florida phosphate rock

a Consistency, $\bar{x} = (100 \text{ g water/g planet required}) \times 100$

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The resulting slurry is cooled and recrystallized to dihydrate in the presence of seed crystals of calcium sulfate dihydrate. Recrystallizing calcium sulfate hemihydrate to form the dihydrate allows the crystals to grow to an easily filterable form and simultaneously completes the decomposition of residual phosphate rock. Nissan asserts that the quality of the gypsum discharged from the filter is sufficiently high that it can be utilized for various building materials without further treatment.

B. The by-product gypsum situation in Japan in 1978: applications in building materials

By 1978 over 90% of the Japanese supply of gypsum came from by-product gypsum. In 1972, 427,000 tons of natural gypsum were mined whereas about 4 million tons of by-product gypsum were utilized. In 1976, the mining of natural gypsum had declined to 65,000 tons while the amcunt of by-product gypsum used had increased to about *5* million tons. In each year throughout that period, Japan used internally more than 4 million tons of gypsum in various products, mostly associated with building materials. An average of about 2 million tons were used as a setting retarder for cement, between 1.3 and 1.7 million tons were used annually for gypsum board, and half a million tons were used as plaster of Paris.

The impact of the Nissan H process on the utilization of by-product gypsum in Japan has been substantial. According to the 1978 edition of "The Economics of Gypsum" two of the three largest producers of by-product gypsum in Japan were using the Nissan process (Nissan Chemical Industries Ltd, 330,000 tons per year and Rasa Industries, Ltd., 200,000 tons per year). Complete figures for Japanese producers for that year are shown in Table 5. (9) Most notable is that none of the by-product gypsum was stored or dumped. All of it found its way into useful products.

Table 5. Production and end **1.5es of by-product gypsum in Japan**, 1978

c. The Nissan C-process

In 1974, Nissan Chemical Industries Ltd. built the first plant based on new technology, the so-called C-process for manufacturing phosphoric acid. The process was described at the 1976 Technical Conference of ISMA Ltd. held in The Hague, Netherlands and the published report appeared in 1977. (16) At the time the paper was presented, units of 4? and 100 tons per day had been constructed and were operating. In the H-process, recrystallization of the gypsum takes place only by lowering the temperature of the hemihydrate slurry. However, in the C-process, recrystallizaticn takes place by changing both the temperature and the acid concentration. The C-process thus yields phosthoric acid of high concentration (45 to 50% P₂O₅) without evaporation. And even better quality by-product gypsum is obtained from the C-process than from the ff-process. Nissan states that the phosphogypsum can be used directly as plaster, for wallboard, and as cement retarder. Furthermore the C-process is able to use more coarsely ground rock than the H-process, so there is additionally an energy saving.

D. A summary of world-wide production operating using the Nissan processes

Nissan operates or has licensed 25 plants using the H-process. These are located in Japan, Australia, Ireland, France, Bangladesh, Belgium, India, Brazil, Morocco, the Netherlands, Taiwan, Turkey and Algeria. Three plants have been built by Nissan in Japan using the C-process and one plant is licensed in Indonesia. The total licensed capacity of plants using the ff-process (including the Nissan plants) is 8,090 tons per day. When the C-process plants are added to the total, the capacity for producing phosphoric acid fertilizer in the world using Nissan technology is nearly 9,000 tons (expressed as P_2O_5) per day. (17) The equivalent yearly generation of gypsum produced if all plants work up to capacity is more than 13 million tons. All of this gypsum can be recycled if the plants are properly operated.

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Table 6. Comparison of end use properties of phosphogypsum produced by the Nissan C- and H-processes

For gypsum wall board use

Source of phosphogypsum

For cement retarder

Source of phosphogypsum

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IV. Utilization of By-Product Gypsum - The Austrian Experiences

A. The Donau Chemie phosphogypsum process with end uses in building materials⁽¹⁸⁾

At Pischelsdorf, about 50 km west of Vienna, Donau Chemie AG operates a 50,000 tons per year phosphoric acid plant using tte Rhone-Poulenc dihydrate process. There is no convenient disposal area for the phosphogypsum and the plant was required to avoid environmental contamination. Therefore as early as 1970, Donau Chemie sought a new possibility for utilizing the large quantities of phosphogypsum which were being produced.

^Amarketing survey showed a demand for plaster in the building industry in Vienna and the surrounding area. It appeared at that time that sufficient demand existed within a 250 km perimeter of the plant to absorb the output of a 150,000 ton per year gypsum processing plant. In any event, marketing over a distance of more than 500 km was shown to be uneconomical due to high freight costs.

Phosphogypsum obtained in the Rhone-Poulenc dihydrate process contains some contaminants and cannot be utilized as a building material without further treatment. In Table 5 the average levels of contaminants in the phosphogypsum from Donau Chemie are shown. These are compared with the purity requirements according to Donau Chemie for the utilization of the phosphogypsum in plaster fabrication.

The small amounts of soluble impurities in phosphogypsum (free acids, phosphates, and fluorides) affect the quality of the gypsum to a much greater extent than, for example, the insoluble impurities which might be present in natural gypsum. Soluble phosphate influences the setting time and causes corrosion during burning of the gypsum to the hemihydrate. Fluoride affects the efficiency of the action of setting retarders. The presence of sodium and potassium cause efflorescence. Water-soluble salts in general reduce the strength of the hardened gypsum. Organic materials cauae discoloration, irregular setting times, and adversely affect the mechanical properties of the end-product. Silica particles and unreacted particles of phosphate rock usually have little influence on the quality of the gypsum but cause increased wear on the processing equipment.

Table 7. Comparison of average contaminaut levels in phosphogypsum from the Donau Chemie process with quality requirements for plaster fabrication

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Donau Chemie purifies its phosphogypsum through a series of washing steps, to remove water-soluble impurities, and hydrocycloning, to remove fine particles. Recycling of water through a countercurrent washing system reduces the demand for fresh process water. The purified gypsum slurry passes to a rotary filter. The resultant filter cake is further dried in a centrifuge.

From 1974 through 1981 the gypsum filter cake passed from the centrifuge into a fuel oil-fired flash dryer. Then it was burnt to the hemihydrate in a calciner indirectly heated by fuel combustion gases. The fuel expended in this process amounted to 50 kg per ton of hemihydrate produced.

Fortunately in 1981 Donau Chemie completed construction of a new sulfuric acid plant beside the phosphoric acid plant. In such a sulfuric acid plant, huge amounts of waste heat are available. Using special Lurgi technology called "Hot Absorption", the waste heat was obtained at a temperature of 120° C. This was sufficient for concentrating the phosphoric acid produced up to 54% $2₂0₅$ in a single stage vacuum unit. Steam heat produced in the sulphuric acid plant was channeled to the gypsum plant. The flash-dryer and calciner were replaced by steam heated equipment. The energy costs for drying and calcining the gypsum were reduced to one-third of the original costs per ton of hemihydrate.

The marketing of gypsum products at Donau Chemie became especially successful after the reduction of energy costs. Considering additional costs which would otherwise result from transport and safe disposal of the phosphogypsum, the profitability gained by Donau Chemie is even greater through the successful marketing of products from phosphogypsum.

Half of the gypsum production at Donau Chemie is sold as Plaster of Paris. Thirty per cent of the production is manufactured into gypsum partition panels. These panels are prepared by pouring plaster into moulds. The drying of the panels is also accomplished using waste heat from the sulphuric acid plant. The final twenty per cent of the production is marketed as joining plaster, mortar, and lime gauged gypsum plaster finish.

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Whereas the energy savings for gypsum production using waste heat were US\$ 600,000 per year, an additional US\$ 300,000 were saved through drying partition paaels using waste heat. Reduced production costs now allow Donau Chemie to profitably market gypsum products over distances up to 500 km. This may allow the plant to expand phosphoric acid and, concomitantly, gypsum production in the future.

B. Recycling of by-product gypsum via chemical conversions - the Chemie Linz processes

In order to recycle phosphogypsum, Chemie Linz has adapted chemical conversion schemes which were originally developed for natural gypsum. The phosphogypsum may be either processed to cement and sulphuric acid or to ammonium sulphate. In addition, the HF and Sif_{μ} in the tail gases are converted to hydrofluorosilicic acid through scrubbing the effluent gases. Subsequently, aluminum fluoride is produced.

1. Processing of phosphogypsum into cement and sulphuric acid via the Müller-Kühne plant⁽¹⁹⁾

The Müller-Kühne plant takes a feed mixture of dried and calcined (to approx. $6\text{\texttt{\^{2}}}$ H_{2} O content) phosphogypsum, clay, coke, and sand. There must be less than 0.5% P_2O_5 and 0.15% F present as impurities in the phosphogypsum. After preweighing the components, the mixture is preheated to 700[°] C using exhaust gases from the kiln, and then enters the rotary kiln. This utilization of waste heat reduces the fuel consumption requirement for the operation of the Müller-Kühne plant. In the rotary kiln the mixture, or raw meal, is burnt to Portland cement clinker at about 1400° C (The reaction temperature would be 1800° C except for the effect of adding silica to the meal). The exit gas from the rotary kiln contains about 9% $SO₂$. It is cleaned in a precipitator, scrubbed and cooled and then serves as feed gas for the sulfuric acid plant. A number of standard technologies may be utilized to convert the SO_2 to sulfuric acid.

The consumption figures shown below apply to the production of one ton of sulphuric acid and 0.9 tons of cement clinker: Waote gypsum (calculated as anhydrite, $CaSO_{\Lambda}$) - 1.65 tons; Fly ash (dry) - 0.11 tons; Sand $(dry) - 0.15$ tons; Clay $(dry) - 0.04$ tons; Coke $(dry) - 0.11$ tons; Natural gypsum to be added to clinker grinding - 0.03 tons; Natural gas (8400 Kcal/kg, dependent on moisture content of waste gypsum) - 90-100 m^3 ; Fuel oil (9500 Kcal/kg) - 156 kg; Electrical energy 320 kWh; Cooling water - 110 m³; Process water - 0.6 m³.

Figure 2 illustrates the closed cycle through which phosphoric acid is produced from phosphate rock and the by-products, phosphogypsum and hydrofluorosilicic acid, are utilized. The phos $_{\nu}$ hogypsum is converted into cement and sulfuric acid, the latter of which is then reused in the phosphoric acid plant. The hydrofluorosilicic acid is converted into aluminum fluorides.

2. Reaction of phosphogypsum with ammonium carbonate to form ammonium sub (20)

The value of ammoniun. sulfate in the fertilization process is to restore lands suffering from alkalinity. Ammonium sulfate simultaneously reduces the pH and provides a source of nitrogen for the plants. It has additional value in sulfur-deficient soils or when particular plants, such as maize, require a source of sulfur for mobilizing the enzyme system which converts nitrogen into protein.

Ammonium carbonate is prepared in a prior step through reaction of carbon dioxide and ammonia. The reaction with rhosphogypsum to form ammonium sulfate is shown below:

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(NH_{4})_{2}CO_{3}
$$
 + $CASO_{4}$ - 2 $H_{2}O$ --- $(NH_{4})_{2}SO_{4}$ + $CACO_{3}$ + 2 $H_{2}O$

The solution containing the product is neutralized and evaporated. Then the product is crystallized, centrifuged and dried.

The second product from this reaction is economically usable as well. Two possibilities exist: First, the CaCO₃ can be combined with ammonium nitrate to form an ammonium nitrate-limestone fertilizer which does not require grinding. Secondly, high quality calcium carbonate can be used for the manufacture of Portland cement. In fact the filtration and washing of the calcium carbonate cake, the most important step to assure quality, can be carried out by means of a rotary filter f the type used for filtering phosphoric acid (Prayon type filter). Waste heat from the cement plant can be used to dry the $CaCO_{3}$. A works in Pakistan has been able to use calcium carbonate obtained through reaction of natural gypsum for the manufacture of cement.⁽²⁰⁾ This alternative does not seem to have been extensively investigated for calcium carbonate obtained from the above reaction of phosphogypsum with ammonium carbonate.

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V. Phosphogypsum in France

France was producing 6.7 million tons of phosphogypsum in 1977. The phosphate rock was imported from Morocco, Togo, Israel and Florida. About 13% of the phosphogypsum was recovered. The preponderance of the recovered material was used in the building industry, chiefly as plaster or plaster board.

Host of the gypsum is disposed into seas, estuaries and rivers. Almost 10% of that disposed goes into dumps, excavations or settling ponds. The greatest single source of disposal is the Bay of the Seine River. In 1977 4,000 ktons of phosphogypsum were discharged into the bay of the Seine. This is the subject of some controversy. The fishermen in Normandy consider that the phosphogypsum reduces the fish population and spoils the mussels. Costs of disposal (FF/t dry gypsum) ranged from 10 for sedimentation followed by dumping to 100 for barging out to sea.

Three processes are used to prepare building materials:

(1) The Japanese Yoshino process is used to prepare a plaster for plaster boards. A plant in Alsace is producing wallboards to export to Germany using the Yoshino's research based on the Nissan phosphoric acid process. In 1977 the normal production capacity was 165 kt/year expressed as phosphogypsum utilized.

(2) Rhone-Poulenc prepares an anhydrite (burnt gypsum) after purification of the waste gypsum. A construction plaster is prepared consisting of a 60/40 mixture of hemihydrate and anhydrite.

(3) CdF Chimie and Air Industrie Process prepare purified hemihydrate suitable for making tiles. Purification is mainly through screening a phosphogypsum slurry. The coarse grains separated are mostly quartz and unreacted phosphate rock. After agitation traces of acid and soluble salts are left in solution. The purified gypsum is then dried and baked in a proprietary process to yield the hemihydrate.

Table 8. Phosphogypsum recovery in France, 1976-77, via plaster production

The abundance of natural gypsum in France has generally dampened enthusiasm for research and development in uses for phosphogypsum. However, in the region of Normandy, where 2/3 of the phosphogypsum in France is produced, an $R + D$ programme with annual outlays of 2.5 million FF had been established by 1976.

There is also potential for increased usage of phosphogypsum in the cement industry in northern France. These plants are presently supplied with natural gypsum from the region of Paris which is a long distance for transport.

Of these quantities of phosphogypsum, about 100 tons were exported as plasterboard in each year to Germany and Belgium. In 1976, about 100 tons of plaster were also exported. This figure rose to 200 tons in 1977. French phosphogypsum is best able to compete as a building material when it is produced in a region which has no exploitable reserves of natural gypsum. Production of plaster from phosphogypsum is only of interest far from Paris, for example, since the main source of natural gypsum in France is the Paris region.

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VI. Phosphogypsum in Belgium - the Classic Prayon Process and the New Central-Prayon Process

The classic Prayon process, or Prayon dihydrate process, and the Central-Prayon process are used in manufacturing processes in Belgium and licensed throughout the world by Societe Chimique Prayon-Rupel.⁽¹⁶⁾

The classic Prayon process is one producing gypsum dihydrate which requires further cleaning. The dihydrate is purified using a process such as used by Donau Chemie and described in Section IV.A., then dried and partially calcined to hemihydrate. The classic Prayon process has been in commercial use for more than 30 years. Improvements have been made during each decade which have focused on greater capacity, a better quality phosphoric acid product and effective utilization of lower grade phosphate rock as the raw material. The Central-Prayon process is carried out under an agreement between a Japanese firm, the Central Glass Company, and Societe Chimique Prayon-Rupel. The first commercial Central-Prayon process began production in 1965 in Belgium at the Engis plant of Societe Chimique Prayon-Rupel. The next plant was established by the Central Glass Company in 1967. In this process, the phosphoric acid plant produces gypsum in the hemihydrate state. Important features of the Central-Prayon process are outlined in Table 6. Gypsum coming from the Central-Prayon process requires no further purification. After curing in free-standing piles to the dihydrate form, the phosphogypsum is screened and ground. The gypsum is then suitable for direct use in the plaster industry or as a cement retarder.

The Societe Chimique Prayon-Rupel has sold 102 plants world-wide using the Prayon dihydrate process and 11 plants using the Central-Prayon process. On a world-wide scale, about 33,500 tons of P_2O_5 per day are produced from plants using the Prayon dihydrate process. For example. the Chemie Linz plant producing the by-product gypsum described in section IV.B, is a 60 ton P_2O_5 per day plant using the Prayon dihydrate process. Plants using the Central-Prayon process produce about 2300 tons of P_2O_5 per day.

Table 9. The Central-Prayon process for producing phosphoric acid and phosphogypsum hemihydrate

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First operation: Reaction of phosphate rock, sulphuric acid and recycled sulphophosphoric acid, with production of slurry A made up of phosphoric acid and phosphogypsum.

Second operation: Separation of slurry A into 2 fractions: (a) the phosphoric acid fraction, and (b) a thickened slurry B with a higher phosphogypsum concentration.

Second Stage

- Third operation: Conversion of the phosphogypsum in slurry B into hemihydrate by adding sulphuric acid and raising the temperature. Slurry C made up of hemihydrate in suspension in a sulphophosphoric acid is produced.
- Fourth operation: Separation of slurry C into 2 fractions: (a) the hemihydrate from which the sulphophosphoric acid has been extracted by counter-current washing, and (b) the extract which has accumulated the acid previously contained in slurry C. This extract is recycled to the first operation.
- Fifth operation: Storage of the hemihydrate in curing piles for subsequent utilization.

VII. Radiation Levels in Phosphogypsum

UNSCEAR $^{(3)}$ has ascertained that the bulk of the 226 Ra content of the phosphate ore is transferred to phosphogypsum. UNSCEAR has further estimated that, in view of the nuclide composition $(226_{Ra}$, 222_{Rn} and its short-lived decay products) and the conditions of irradiation (interior walls of residential buildings) exposure would be expected to be up to 30% higher for persons living in houses built using phosphogypsum. Man is exposed to 222 Rn and to its short-lived decay products mainly by inhalation.

Weterings⁽²²⁾ has summarized three methods for reducing the radioactivity level of phosphogypsum. In the examples given, the initial radioactivity of the phosphogypsum is 22 $pCi/g.*$

- (1) Treat with dilute $\text{H}_{2} \text{SO}_{4}$ + BaSO₄ at 98^OC. remove 70 micron particles (70 pCi/g). The residual gypsum has a radioactivity of 2 pCi/g.
- (2) Treat gypsum with 60 Z HNO_3 at 60^O C. The residual gypsum has a radioactivity of *5* pCi/g.
- (3) Physically remove the fine (and more highly radioactive) gypsum particles (30 microns) using a hydrocyclone. The residual gypsum has a radioactivity of 16 pCi/g.

The latter treatment is a means of reducing the radioactivity level of the phosphogypsum by 30%. It should be considered a minimum treatment method when the initial radioactivity of the phosphogypsum is greater than 16 pCi/g.

^{*} The curie is the standard unit of radioactivity, equivalent to 3.70 x 10^{10} disintegrations per second. A picocurie (pCi) is one trillionth of a curie.

VIII. Dalmar: A country with limited possibilities for environmentally acceptable disposal of a waste product such as phosphogypsum.

Dalmar is a socialist-oriented country where the government invests directly in production facilities through government controlled entities. During the 1970's Dalmar undertook a program of extensive investments in an attempt to achieve rapid industrialization. Both the cement and chemical industries were beneficiaries of this investment program. The magnitude of the investment program over-reached the ability of the public sector to deal with the enterprise management, staffing, and scheduling problems. As a consequence, in the 1980's Dalmar must concentrate on bringing the investment program to completion. The various manufacturing plants will need to be brought to full operating capacity and efficiency.

A. Need to Reprocess Phosphogypsum

As part of its investment in chemical industries, Dalmar built a major fertilizer production complex. Among other fertilizer products the complex produces phosphoric acid. During early planning stages it became apparent that dumping of phosphogypsum near the fertilizer complex would endanger groundwater supplies and interfere with recreational use of a near-by lake. Dalmar's water resources are limited. The ground water is important for down-stream agriculture and human consumption. The lake is an important recreational resource. Therefore Dalmar became interested in reprocessing options.

B. Prospects for Phosphogypsum Products: Building Materials and Fertilizers.

Dalmar's cement production should be double its late 1970 level by the mid-1980's. Domestic demand for all building materials grew strongly

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NOTE: The case studies have been prepared from actual field studies carried out by UNIDO in developing countries. The names of the countries have been fictionalized to respect *the* confidentiality of certain economic planning information and investment data.

during the 1970's and can be expected to continue to grow during the 1980's. In spite of the strong domestic demand, the doubling of cement production capacity should allow Dalmar to become a net exporter of cement. This is important for Dalmar because it has inordinately large balance-of-payment and budget deficits. Thus any excess cement can be expected to be absorbed through the export market.

Although Dalmar will not be undertaking any new investments in manufacturing plants in the near future, it will be making efforts to increase food production. This will take several forms including inc.eased education, restructuring of prices of agricultural goods and some extension of irrigated acreage. This effort will have high priority as uneven agricultural production levels have contributed significantly to Dalmar's budget and balance-oi-payments problems. As Dalmar seeks to increase per acre yields through improved farming techniques and to increase acreage under intensive cultiviation, demand for fertilizer products should grow strongly. In summary, the market for both building materials and fertilizer products should remain strong through the 1980's.

C. Economics of Phosphogypsum Disposition: Disposal Costs and "arket Prospects

As part of its investment program Dalmar undertook to develop a major fertilizer production complex. The complex was built at the site of an already existing facility. This facility has good road and railroad connections and was soon to be served by an additional rail line. The new rail line will connect the facility to a phosphate mining area at one end and to a port at the other end. Investigations soon showed that it would not be possible to dump the phosphogypsum resulting from phosphoric acid production near the fertilizer complex. This prompted the government of Dalmar to seek alternatives -- either alternative disposal sites or ways of reusing the phosphogypsum to produce marketable goods.

When the planned phosphoric acid plant reaches full capacity it is estimated that some 938,000 tons of phosphogypsum will be produced annually. A study was undertaken to determine (a) the costs for

disposing of this phosphogypsum in an environmentally acceptable manner and (b) the phosphogypsum-derived products which could be successfully marketed in Dalmar. The primary benefit of reusing the phosphogypsum was that it would solve the disposal problem. As the study investigated the range of goods which could be produced from the phosphogypsum it turned out that production of some of these would allow Dalmar to realize secondary benefits. The two most important secondary benefits were the achievement of import substitutions and opportunities to utilize other waste products. These secondary benefits increased the desirability of the reuse option.

l. Costs of environmentally sound dumping.

Two sites were located which provided suitable conditions for long term dumping and storage of the phosphogypsum. One of the sites was located approximately 45 km from the fertilizer complex. This site was not served by rail. The phosphogypsum would either have to be transported by truck or a special transportation system would have to be built. The investment costs for a special transportation system were estimated at 100 million Dalmar lira (DL). This was considered prohibitive. Use of trucks would have required the purchase of 30 trucks and a labor force of 150 persons. This was also considered prohibitive.

The second site was the phosphate rock mining area. Under this alternative the rail line from the phosphate mining area to the fertilizer complex could be used. The phosphogypsum would be loaded on the empty railroad cars and transported back to the mining area. This alternative would require construction of a loading station for the phosphogypsum at the fertilizer plant and an unloading station and distribution system for the phosphogypsum at the mines. Due to the greater bulk of phosphogypsum as compared to phosphate rock this alternative also required purchase of a few railroad cars.

Total investment costs for this alternative were estimated to amount to 9 million DL. Interest rates for long term loans were 9%. The interest rate for the construction loan was set at 7%. This resulted in a total annual financial burden -- payback of interest plus amortization -- of

1.5 million DL, or 16.67% of the total investment. Total operating costs for returning the phobphogypsum to the mining area are presented in Table 10 below:

Table 10. Total Annual Costs for Dumping

These total annual costs would provide for the removal and dumping of the 938,000 tons of phosphogypsum generated annually. The resultant per ton cost is 14.17 DL. As a consequence the study reconmended that any alternative that avoided dumping be given a 14 DL per ton credit.

2. Investigation of marketability of products.

Dalmar considered the feasibility of marketing a full range of goods which can be produced by reprocessing phosphogypsum. The list investigated was as follows:

- a. Soil Conditioner
- b. Plaster Board
- c. Sodium Sulfate
- d. Plaster of Paris, including use for building blocks
- e. Setting Retarder for cement
- f. Sulfuric Acid and Cement (Müller-Kühne process)
- g. Aamonium Sulfate

Dalmar concluded that the latter four were the best suited for local conditions. A brief review of the reasons for rejecting the first three products is presented prior to more detailed examinations of the economics of producing and marketing the four products favored by the report.

(a) Production of phosphogypsum-based soil conditioner was eliminated as the clay-type soils for which this conditioner is best suited do not occur in Dalmar.

(b) Wallboard was eliminattd both because its manufacture would require importation of a special cardboard used in its manufacture and because there is no existing market for wallboard in Dalmar. A market for wallboard would be difficult to create because wallboard offers neither economic nor other advantages over hand-plastering in Dalmar.

(ci Sodium sulfate was also eliminated for lack of an existing market. Unlike wallboard, however, it was foreseen that a market for sodium sulfate would soon develop. Both the pulp and paper and the detergent industries require sodium sulfate. Sodium suifate is not available in Dalmar. ht the time of the report the target industries were only in early development stages. However Dalmar believes sodium sulfate should be recongidered as an option as these industries reach full production. Use of phosphogypsum to manufacture the required sodium sulfate would then offer Dalmar an import-substitution opportunity.

(d) Plaster of Paris/Building Blocks: The study determined that plaster of Paris could be produced more cheaply from phosphogypsum than from natural gypsum at all production capacities. Under these circumstances the only limiting factor was the expected size of the market. Transportation costs account for a substantial part of the cost of plaster of Paris to the consumer. Consequently plaster of Paris is only marketable within a restricted geographic region. It was determined that the market within the appropriate region could absorb a couple of hundred tons of plaster of Paris per day. This market was expected to grow over time. As the market grew it was reconmended that increasing amounts of phosphogypsum be dedicated to this use.

(e) Setting retarder for cement: Unlike plaster of Paris, setting retarder for cement could be produced more cheaply from natural gypsum than from phosphogypsum. As a consequence phosphogypsum-based retarder would only be marketable if the fertilizer complex enjoyed a locational advantage. The favorable location of the fertilizer complex and its access to rail transportation were decisive in the regard. These were in fact sufficiently powerful assets to establish the fertilizer complex as a competitive marketer of setting retarder for cement.

Setting retarder from natural gypsum cost 12 DL per ton to produce. Production costs for a 500 ton/day plant producing setting retarder from phosphogypsum were estimated at 23.69 DL per ton. Thus the transportation advantage required to render phosphogypsum-based retarder competitive was $23.69 - 12.00$, or 11.69 DL per ton. From the point of view of potential consumers of setting retarder $-$ i.e. cement plants $$ the transportation cost from the fertilizer complex would have to be at least 11.69 DL per toa lower than the transportation costs from producers of natural gypsum bafed retarder in order to render the fertilizer plant's retarder economically attractive.

Within the fertilizer complex's potential marketing region for setting retarder there was only one producer of natural gypsum based retarder. The distances from this producer and the fertilizer complex to seven cement retarder consumers are shown in the table below. The transporation modes available in each case are also indicated. The magnitude of the transportation advantage to the fertilizer complex, if any, is also shown. As can be seen the fertilizer complex enjoyed a sufficient transportation cost advantage, 11.69 DL or more, to enable it to successfully compete at four consumer locations. In all four cases the cost advantage results from the availability of railroad transportation from the fertilizer complex. Rail transportation costs are 7 DL per ton per 100 km in Dalmar, while trucking costs are estimated to be double this amount, or 14 DL per ton per 100 km.

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Table 11. Transportation Summary*

 $*tr = truek$ RR = railroad

Monetary unit = DL

Distances in km

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All four of the consumers which the fertilizer complex could expect to supply would enjoy a transportation cost advantage of at least 12.60 DL. This is .93 DL above the minimum cost advantage (11.69 DL) required to render the fertilizer complex's setting retarder attractive. The fertilizer complex could take advantage of this 0.93 DL difference to make a profit. The fertilizer manufacturer could afford to set its selling price up to .93 DL per ton above its production cost of 23.69 DL per ton.

The setting retarder and the plaster of Paris discussed above were to be produced in the same plant. The four potential setting retarder consumers had a total demand of 600 tons per day when operating at full capacity. It could not however be expected that the cement plants would operate at full capacity year-round. The recommendation was therefore for a plant set to produce 200 tons of plaster of Paris and 400 tons of setting retarder per day. As the market for plaster of Paris expanded the setting retarder production could be phased out.

Total investment requirements for a 600 ton per day plant were estimated at 24,250,000 DL. Preproduction and working capital requirements were estimated at 1,697,000 DL. This gives a total capital requirement of 25,947,000 DL. The plant was to be amortised over a 20-year period. The production of the 600 tons per day of plaster of Paris/setting retarder would consume approximately 660 tons of the roughly 3,000 tons per day of phosphogypsum which would be generated by the phosphoric acid plant.

(f) Sulfuric acid and cement (Huller-Kuhne process); Dalmar was a net importer of sulphur for sulphuric acid production. It was expected that this would continue to be the case in spite of foreseeable increases in domestically available sources. Thus production of sulphuric acid from phosphogypsum would relieve Dalmar of the need to import a corresponding amount of sulphur. From a technical point of view two possible plant sizes were considered feasible: 570 tons per day and 850 tons per day. As discussed below, from an economic point of view only the 850 tons per day plant was viable.

The joint production cost for a ton of cement and a ton of sulphuric acid for a plant with 850 tons per day production capacity was estimated at approximately 360 DL per ton. Cement in Dalmar is produced at 145 DL per ton from standard raw materials. This gives an imputed production cost for the sulphuric acid of 215 DL per ton (360-145). A sulphuric acid plant with a 850 tons per day capacity, producing sulphuric acid from sulphur, would only have production costs this high when the price of sulphur was in the \$150 per ton range. At the time of Dalmar's investigations large amounts of recovered sulphur from sour natural gas wells in Canada were available. Sulphur was selling in the \$70-\$75 per ton range. Given this situation Dalmar could not expect sulphur prices to rise high enough within the short-term future to render sulphuric acid from phosphogypsum competitive.

However the original 360 DL per ton production cost estimate was based on using fuel oil as the heat source in the Müller-Kühne process. Petrocoke is available in Dalmar at prices well below those of fuel oil and can be substituted for it. At the time of the report petrocoke was actually a waste product in Dalmar, and its disposal was presenting environmental problems. The main problem was the release of sulphur dioxide into the atmosphere when the petrocoke was burned. In the Müller-Kühne process the sulphur dioxide would not be released into the atmosphere. The sulphur dioxide would be channeled into the production of the sulphuric acid. Thus use of petrocoke in place of fuel oil would serve two purposes. It would lower the production costs for the cement and sulphuric acid, and it would help dispose of Dalmar's waste petrocoke.

At the time of the study petrocoke was a waste product with no market value. In previous years petrocoke sold for 70 DL per ton. Using these two alternative costs - no price and 70 DL per ton $-$ - the cost of producing cement and sulphuric acid from phosphogypsum would be in the $255 - 285$ DL per ton range. This in turn $-$ again using 145 DL for the cost of cement $-$, gives a cost for sulphuric acid in the $110 - 140$ DL per ton range. A 850 ton per day plant producing sulphuric acid from natural gypsum has costs in this range when the price of sulphur is in the $$65 - 85 per ton range. Thus sulphuric acid from phosphogypsum would have been competitive with sulphuric acid from sulphur at then existing world prices for sulphur if petrocoke was used as the fuel.

A plant size of 570 tons per day would not have been economically viable even using petrocoke as the heat source. Even using a value of U for the

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cost of petrocoke, production costs for a ton of cement and a ton of sulphuric acid would have been 305 DL per ton in a plant of this size. This gives an imputed cost for the sulphuric acid of 160 DL per ton. This would only be competitive with sulphuric acid from natural sulphur when world prices for sulphur reached \$100 per ton.

Investment costs for a plant with a 850 ton capacity were estimated at 325 million DL. Preinvestment and working capital requirements were estimated at 22.750 million DL. Total capital requirements would thus be 347.750 million DL. A Muller-Kuhne unit of this size would consume 1,725 tons of phosphogypsum per day. Thus the plaster of Paris/cement retarder plant plus the Müller-Kühne unit would together use 2,385 of the approximately 3,000 tons per day of phosphogypsum available. The remaining 600 tons were to be used to produce ammonium sulphate.

{g) Anmonium sulfate

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As a fertilizer ammonium sulfate would compete in the market with urea which was also being produced by the fertilizer complex. However several factors contributed to an evaluation that it would be economically advantageous to produce ammonium sulfate. First, ammonium sulfate rather than urea is the preferred fertilizer in irrigated areas. Dalmar has significant amounts of irrigated land and hopes to expand the number of acres under irrigation as part of its effort to increase food production. Second more armnonia would be produced at the fertilizer complex than could be consumed domestically. The excess ammonium could either be used in conjunction with phosphogypsum to produce ammonium sulfate or it could be exported. The exportation of the ammonia would have required construction of special port facilities. On the other hand if the ammonia was used to produce ammonium sulfate, the ammonium sulfate would replace domestic consumption of urea. Some urea might then have to be exported. However, exportation of this urea would not require construction of special port facilities. Thus it was believed that it would be economically more advantageous to use the excess annonia to produce armaonium sulfate and to export the urea rather than to export the ammonia.

The 600 tons per day of phosphogypsum available after production of setting retarder, plaster of Paris, cement and sulphuric acid would yield 400 tons of ammonium sulfate. At this volume the production costs for the aamonium sulfate would be some 8 DL per ton higher than world prices for ammonium sulphate. However about 340 tons per day of calcium carbonate would be produced as a by-product. The calcium carbonate would have a value of at least 25 DL per ton. Thus the returns from sales of calcium carbonate could be used to subsidize the sales price of the ammonium sulphate. Investment costs for the ammonium sulphate plant were estimated at 100,357,250 DL. Preproduction and working capital needs were estimated at 7,025,000 DL, resulting in a total capital requirement of 107,382,250 DL.

D. Input Requirements and Production Costs to Reprocess Phosphogypsum into Five End Products

Tables 12 and 13 present input requirements for each of the three processes selected as economically viable in Dalmar. Input requirements per ton of output are shown for raw materials, utilities, and energy. Where available unit costs, costs per ton of output, and total annual expenditures required are also shown. Following the presentation of input requirements, a summary of the investment, labor, overhead and maintenance requirements for the entire reprocessing operation is presented.

Using a 20 year amortization period and a 9% interest rate for the long term loans, the internal rate of return was calculated to be over 12% for the combined operation of these three plants. This was considered sufficiently attractive to warrant proceding to preparation of detailed feasibility studies for the reprocessing of the phosphogypsum into the stated marketable goods.

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Table 12. Input requirements, setting retarder/plaster of Paris

Note: Monetary unit $= DL$

Steam Fuel Oil

.65 t .0075 t

30/t 288/t

19.50 2.16

7,800 864

Table 13. Capital requirements and annual operating costs

E. Conclusions

Dalmar clearly portrays the kind of economic conditions facing many third-world countries and the array of economic factors which determine the economic viability of reprocessing phosphogypsum. Increased supply of building materials and increased food production are both important for Dalmar's domestic growth and to help solve balance-of-payment problems. This in turn means that the potential for favorable market conditions for the goods which can be produced from phosphogypsum is high. In spite of this, as may often be the case, no one market is sufficiently large to justify reprocessing all available phosphogypsum into one product. In addition the costs of reprocessing phosphogypsum are relatively high. Thus a phosphoric acid facility will often need to enjoy some economic advantages in order to render reprocessing economically viable. In the case of the facility in Dalmar the critical economic advantages enjoyed by the facility are a good location in terms

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of transportation distances and modes, and a source of inexpensive fuel. These two, transportation and fuel costs, will generally be the most important factors in determining the economic viability of reprocessing phosphogypsum.

Dalmar also shows how reprocessing becomes increasingly attractive as disposal options become limited and expenses increase. Dalmar's initial interest in reprocessing stemmed from such problems. Legal requirements can be critical in rendering disposal expenses so high that reprocessing becomes virtually the only viable option. Reprocessing may also enable a country to solve other waste problems. In Dalmar reprocessing helped solve both the excess ammonia and waste petrocoke problems. Finally reprocessing may enable countries such as Dalmar to substitute domestic production for importation of such critical items as sulphuric acid, cement, sodium sulphate, gypsum and fertilizer.

IX. Case study: Naagel - A country with a need for sulphuric acid considers the economic feasibility of using the Muller-Ku'hne process

Naagel is a country whose government plays an active role in the economy. Prices of a wide range of essential goods are kept in line with urban workers' salaries. This is accomplished through taxes, subsidies, and import policy. Naagel's government also undertakes large investment prograames largely through semi-autonomous governmental institutions. During the 1970s Naagel enjoyed a period of strong economic growth. It took advantage of favourable prices for exports to undertake an intensive capital investment prograame. A primary goal of this progranme was to increase the value of exports. The phosphate/phosphoric acid industry was among those chosen to implement this policy.

A. Need for Domestic Source of Sulphuric Acid

Phosphate rock and its derivates form an important part of Naagel's economy. Naagel has mined phosphate rock and produced phosphoric acid for a number of years. As a consequence it has had a supply of phosphogypsum. Naagel became interested in this phosphogypsum resource during its attempt to increase value of exports. Insufficient domestic supplies of sulphur had forced Naagel to import sulphur to obtain the sulphuric acid required in the manufacture of phosphoric acid. This had not been a happy experience. Wide fluctuations in world prices for sulphur had had ill effects on production costs, stability and profitability of Naagel's phosphoric acid production plants. As Naagel looked forward to increasing its production of phosphoric acid and to increased sales of phosphoric acid on world markets it was clear that this dependence on imported sulphur was undesirable.

As Naagel moves into the latter part of the 1980s and 1990s, phosphoric acid production will have an increasingly significant impact on the country's economic well-being. By the end of the 1980s Naagel's production of phosphate rock can be expected to be double what it was at the end of the 1970s. Further increases in phosphate rock production are foreseeable on into the 1990s. Naagel's capacity to process this rock into phosphoric acid and related products will at least keep pace with these phosphate rock production increases.

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During the first half of the 1970s Naagel's earnings from phosphate rock far exceeded its earnings from phosphoric acid. By the late 1970s earnings from phosphoric acid and phosphate rock were running at roughly equal levels. During the 1980s earnings from phosphoric acid can be expected to outstrip those from phosphate rock. These relations are shown in schematic form in Figures l, 3 and 4.

The trends shown in Figures 1, 3 and 4 have important implications. First, Naagel will need increasing amounts of sulphuric acid to process phosphate rock. Second, as Naagel's export earnings come to depend more on phosphate products than on phosphate rock, these earnings will be increasingly sensitive to fluctuations in sulphuric acid prices. It will thus be increasingly important for Naagel to ensure that it has a stable, economically priced supply of this acid. Finally, Naagel will be producing very large amounts of phosphogypsum. This phosphogypsuc must eicher be dumped or reprocessed. Naagel expects to increase annual phosphoric acid production by 0.5 million tons. It will therefore have an additional 2.75 million tons of phosphogypsum to dispose of annually. These circumstances make it attractive to try to use the Muller-Kuhne process to generate sulphuric acid and simultaneously solve the phosphogypsum disposal problem.

B. Need for Increased Building Materials

Naagel's primary interest in reprocessing phosphogypsum is to obtain sulphuric acid. In fact Naagel's government has additional reasons to consider the Müller-Kühne process. Although Naagel's investment programme has paid off in increased exports in selected industries, Naagel is plagued by persistent unemployment problems. In addition Naagel's export earnings cannot be expected to rise in the future as they have in the past decade. Naagel will be required to address its unemployment problem under conditions of restricted funds. As a consequence Naagel must consider altering its investment programmes. Less stress may have to be placed on capital intensive industrial sectors and more on labour intensive sectors. The construction industry is an obvious and likely avenue for such investment. As Naagel considers the desirability and need for undertaking major construction programncs it should be alert to the most likely problem; supply of materials, and a possible solution: phosphogypsum.

Figure 3. Production of phosphate rock and phosphoric acid

Figure 4. Value of exports: Phosphate rock and phosphoric acid

Note: Broken lines represent future estimates.

If Naagel attempts to step up construction activity it will very likely be faced with shortages of building materials. Naagel has, for example, traditionally had to import cement to meet demand. The country is coamitted to becoming self-sufficient in cement. In general, however, increases in production have been insufficient to meet increases in demand. Given present plans to construct cement factories Naagel may be able to meet its demand for cement by the end of the 1980s. A major construction programme, however, could easily overwhelm this new production capacity. Naagel's increasingly abundant phosphogypsum could be used to supplement this capacity in the form of cement, interim plaster-based products or fly-ash blocks.

C. Economics of Reprocessing Phosphogypsum by the Muller-Kuhne Process in Naagel

Raw material costs and product prices are critical to the profitability of a Huller-Kuhne processing plant as shown for Naagel in the paragraphs below.

Naagel sought to increase phosphoric acid production in its effort to expand exports and value of export earnings. In conjunction with this goal Naagel recognized the importance of freeing itself from dependence on imported sulphur. One way to do this would be to exploit its growing domestic supply of phosphogypsum. To achieve this import substitution sulphuric acid from phosphogypsum replacing sulphuric acid from sulphur - Naagel could utilize the Hiiller-Kiihne process (see section IV.B.l). What Naagel needed to know was whether or not it would be economically advantageous to make this switch.

In the mid 1970s Naagel undertook an economic feasibility study to help decide whether use of the Muller-Kuhne process would be a good solution to its problem of dependence on imported sulphur. It was determined that Naagel's phosphoric acid plants could easily be modified to produce the type of phosphogypsum required in the Müller-Kühne process. The modifications could be made at minimal expense both at already operating plants and in those in design and construction stages. However, the Müller-Kühne process requires coke for its operation and produces not only sulphuric acid but also cement as part of the process. Both of

these factors raised problems in assessing whether or not it would be to Naagel's advantage to invest in Huller-Kuhne processing units.

1. Coke for sulphur

The Müller-Kühne process produces sulphuric acid from phosphogypsum but requires coke to do so. Coke is not available in Naagel. Thus Naagel was faced with the question of whether it was to its advantage to free itself from dependence on imported sulphur at the cost of becoming dependent on imported coke.

The feasibility study envisioned a Müller-Kühne unit with the capacity to produce 330,000 tons of sulphuric acid and 330,000 tons of cement annually. At the time of the report, production of 330,000 tons of sulphuric acid from sulphur would require expenditures of 2,4b4,000 Naagel Kronen (NK) for imported sulphur. To produce the same amount of acid from phosphogypsum would have required an expenditure of 1,700,000 NK to import coke. Thus at the time of the report, Naagel's import expenses would have been reduced by switching to the Müller-Kühne process and importing coke rather than sulphur.

Prices of both coke and sulphur had altered significantly in the decade preceding the report. Consequently some consideration had to be given to possible future price changes. At the time of the report sulphur was in the lower third of the price range that had been experienced in the ten year period. The price of coke on the other hand had been escalating rapidly and was higher than ever. If the price of coke continued to rise it was foreseeable that importation of coke could become the more expensive alternative. Naagel believed, however, that it would be possible to obtain a long-term contract for coke at prices below those used to calculate coke's advantage. If so it would be relatively unlikely that sulphur would, in the future, be the less expensive import over any considerable periods of time, since the sulphur price used in the calculation was already on the low side. In addition a long-term contract for coke would at least provide price stability, a major advantage in itself. A more comprehensive analysis of this problem was not necessary primarily because a larger obstacle stood in the way of the profitability of the Müller-Kühne process in Naagel. Naagel's then

existing pricing policy for cement precluded any possibility of realizing a profit from the Müller-Kühne process.

2. Cement pricing policy

The Huller-Kuhne process produces cement in the same process that it produces the sulphuric acid. There was therefore no direct way to compare the cost of producing sulphuric acid from phosphogypsum with the cost of producing sulphuric arid from sulphur. The economic feasibility study did not attempt to attribute part of the investment and production costs to sulphuric acid and the rest ~o cement. Rather it looked at the Huller-Kuhne unit as an investment and tried to answer the question whether the value of the goods produced justified the investment costs.

The economic study calculated that the joint cost to produce a ton of sulphuric acid and a ton of cement would be 27.37 NK. This was calculated for a plant with capacity to produced 1,000 tons of each product daily, and with the plant running at full capacity. This cost included amortization of a loan sufficient to cover initial construction, equipment and set-up expenses. The rate of interest on the loan was 8%. The sulphuric acid was not to be sold and therefore no sales price was available to establish its value. Instead the value of the phosphogypsum derived acid was set at the then current cost of sulphuric acid from sulphur. This was 14 NK per ton. The government price for cement to domestic producers was 7.20 NK per ton. Thus the joint value for a ton of sulphuric acid and a ton of cement was 21.20 NK. This was 6.17 NK below the production costs of 27.37 NK. Under these conditions production of sulphuric acid using the Müller-Kühne process would have to be evaluated as uneconomic. However, the researchers believed that this result might be due to the fact that Naagel's cement prices did not represent true value.

Naagel's price for cement to domestic producers was less than half the price it paid for imported cement. Domestic factories were able to accept this price because all domestic cement, at the time of the study, was produced in fully amortized factories. A Müller-Kühne unit would in essence be a new cement factory. The cement price would have to be sufficient to repay investment' costs. The cement produced by the new

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Müller-Kühne 'cement factory' would be of equal quality to imported cement. It could thus replace imported cement ton for ton. The economic study therefore suggested that new cement producers should be granted a price for cement equal to that of imported cement. At this price, 15 NK per ton, the joint "revenue" from the sulphuric acid and cement would be 29 NK per ton, sufficient to cover the production and investment costs of 27.37 NK per ton. The study was in effect pointing out that the Müller-Kühne process would generate not one but two import substitutions - cement as well as sulphuric acid. Since Naagel was interested in becoming self-sufficient in cement and in fostering domestic industrialization, the study's suggestion of price relief for new cement producers was worth serious consideration.

D. Production Costs for a 1,000 Ton Per Day Capacity Müller-Kühne Unit

Total annual operating costs for a Müller-Kühne unit with an annual production capacity of 330,000 tons of cement and 330,UOO tons of sulphuric acid were estimated at 9,033,000 NK. This sum includes amortization of an initial investment loan of 26,100,100 NK at 8% interest. Costs are calculated for operation at full capacity. Details of the costs are provided in the paragraphs below. A summary table is provided following presentation of the cost breakdowns. Assuming that it would take three years for a unjt to reach full operating capacity, the total capital investment required would be 29,650,000 NK. The additional 3,550,000 NK are required to cover operating deficits which would occur in the first two years.

1. Initial investment

Initial investment costs include costs for civil engineering, construction of buildings, purchase of equipment, payments for technology transfer, and set-up costs. These costs total 26,100,000 NK of which approximately 75% would require expenditure of foreign currencies. A breakdown of these costs is provided in Table 14.

Table 14. Initial investment costs

Item

Construction & civil engineering Equipment Engineering services and fees Initial set-up Initial loan required Resultant annual 3,000,000 17,900,000 l,b00,000 3,b00,000 26,100,000

financial burden 3,748,000

Civil engineering works and buildings were to be amortized over a 20-year period. All other costs were to be amortized over 10 years. In both cases the cost of borrowing money was assumed to be 8% annually. This resulted in total annual interest and amortization payments of 3,748,000 NK.

2. Raw materials and supplies

Total annual costs for raw materials and supplies equal $1,814,000$ NK as shown in the table below.

Table 15. Total requirements for raw materials and supplies

Cost in NK

3. Manpower

It was estimated that manpower requirements for the Muller-Kunne unit would total 150 workers inclusive of all categories required. An average annual salary of 2,000 NK was used to cover all employment categories. This sum is inclusive of charges for employee taxes and benefits. The resultant annual cost for manpower is 330,000 NK.

4. Energy and utilities

Operation of the Müller-Kühne unit would require steam, electricity, cooling water and gas. Gas and electricity were purchased from government utilities. The price per kwh electricity shown in Table 16 includes initial hook-up fees, taxes, and flat charges based on level of services, as well as per kilowatt hour charges. Total annual costs for energy and utilities come to 1,582,000 NK.

Table 16. Energy and utility costs

Annual expenditure for energy and utilities 1,581,560

5. Working capital

Working capital requirements were set at roughly two months' supply of raw materials and miscellaneous equipment; one month's salaries for employees; and 15 days worth of finished products. The value for the finished products (1 ton of cement plus 1 ton of sulphuric acid) was taken to be the cost of production net of financial burdens. Total value

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of the working capital requirement is 600,000 NK. The working capital requirement is assumed to be covered by deficit financing at 8%. This results in an annual financial burden of 48,000 NK. Working capital requirements are shown in Table 17.

Table 17. Working capital requirements

6. Other

Maintenance was set at 5% of initial investment; overhead at 15% of annual salaries*, and insurance at 0.6% of initial investment. These costs are shown along with all other costs in Table 18.

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^{*}The overhead rate (15% of salaries) in this study is significantly lower than that given in the Dalmar study (150% of labour). This reflects widely differing practices in calculating overhead. The Dalmar study was a preliminary rather than true economic feasibility study. Consequently, for example, detailed budgets for administrative and managerial personnel were not worked out. Instead such costs were simply assigned to overhead.

Table 18. Sunaary

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E. Conclusion - Müller-Kühne Processing

The production cost of 27.37 NK per ton of sulphuric acid and cement presented above assumes that the Müller-Kühne unit operates at full capacity in year l. A more realistic assumption is that full operating capacity would not be reached until at least year 3. Under such circumstances the value of a ton of cement and a ton of sulphuric acid would have to be 29.01 NK in order to pay back the required total investment costs of $29,650,000$ NK. With a value for sulphuric acid of 14 NK and a value of 15 NK for cement this might be achievable. However, it leaves no margin for profit, no margin for the eventuality that the unit would have to run at less than full capacity, and no margin for unfavourable changes in costs of inputs or product prices. On the other hand the study does not estimate any value for the savings thac would accrue to the phosphoric acid plant by avoiding dumping and storage costs for phosphogypsum.

Even if Naagel would grant a Hiiller-Kiihne plant a price for its cement equivalent to the price of imported cement the Muller-Kuhne plant had to \cdot be evaluated as at best marginally attractive. Since the study was written, interest rates have increased substantially. It is unlikely that a long-term loan could be secured in today's market at 8% or that 8% represents the opportunity cost for money in Naagel today. Thus it is very unlikely that investment in a Muller-Kiihne plant would be attractive in Naagel today.

The Müller-Kühne process is an energy-intensive process. It is most attractive in areas which have access to cheap energy sources or in which energy is actually being wasted. As was seen, Naagel was not in this position. On the contrary, Naagel would have had to import coke in order to reprocess its phosphogypsum. How access to an inexpensive energy source affects the economic viability of the Müller-Kühne process is illustrated in section VIII.2.f. Here Dalmar, another country seeking to use its phosphogypsum resource, finds that a Müller-Kühne unit is only profitable when a locally available cheap energy source, petrocoke, is substituted for coke. In short, Naagel's search for a domestic source of sulphuric acid foundered, ultimately, on Naagel's lack of a domestic source of inexpensive fuel.

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VIII. Recommend&tions

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1) In the construction of new plants, the tender documents should include specifications for a process that produces phosphogypsum suitable for utilization.

2) In the case of existing plants, a feasibility study should be conducted on possible plant modifications (such as improved stirrers in the reactor) that would allow production of phosphogypsum that could more readily be utilized.

3) A marketing survey should determine existing and potential markets for the phosphogypsum-based products in the surrounding area.

4) Links should be established with institutes for building materials, societies of construction contractors and similar organizations to disseminate information on phosphogypsum-based products.

5) Governments should establish a maximum allowable radioactivity of lb pCi/g in the phosphogypsum and ensure compliance.

6) Industries should routinely measure the radioactivity in their phosphogypsum and take measures to ensure that it does not exceed 16 pCi/g.

7) Industries should seek to use waste heat to process and dry the phosphogypsum-based products.

8) If the phosphoric acid plant is located in a region of abundant and cheap energy, then the phosphogypsum can be processed into chemicals plus cement and/or phosphogypsum building materials. If energy is expensive, phosphogypsum building materials will likely be the preferred route.

9) Developing countries may wish to utilize UNIDO to establish arrangements for the transfer of technology from industries in developed countries.

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Utilization of the Phosphogypsum Produced in the Fertilizer Industry

(please check appropriate box)

subjects *ot* interest.

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- (8) Do you viab to receiye the lateet liet of documents prepared by the Division for Industrial Studies?
- (9) Any other comaentaT

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