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ABSTRACT

The processes used in the production of phosphatic fertilisers are reviewed and those in which uranium can be extracted as a byproduct are described in detail. The current status of the world and Australian phosphate rock and fertiliser industries is described and production figures and marketing information for these industries are also presented.

Techniques for the recovery of byproduct uranium during the processing of phosphate rock to fertilisers are also examined in detail. Recovery from wet-process phosphoric acid by solvent extraction is the most promising approach.

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COST; FERTILIZERS; INDUSTRY; LEACHING; MARKET; ORE PROCESSING; PRODUCTION; ROCKS; SOLVENT EXTRACTION; SUPERPHOSPHATES; URANIUM

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1. INTRODUCTION

Uranium is known to be associated with deposits of phosphate rocks. The proportion of uranium in the rock as mined varies from deposit to deposit, but generally is in the region of 30 to 200 $\mu g\ g^{-1}$. The uranium concentration in the phosphate rock is thus one to two orders of magnitude lower than that in uranium mineralisation (typically 1000 to 5000 $\mu g\ g^{-1}$). The concentration is, however, significantly greater than that in seawater (about 3 $ng\ g^{-1}$), a possible long term source of high cost uranium.

The size of phosphate deposits suggests that they could provide a significant additional medium cost uranium resource. The magnitude and cost range of this potential uranium will depend on the feasibility and economics of uranium extraction. In certain circumstances, the recovery of uranium at a reasonable cost can be achieved if the phosphate in the rock is also recovered. Consequently, the methods for uranium recovery are designed to obtain uranium as a byproduct from existing processes for the production of fertilisers.

The potential of phosphate rock as a possible source of uranium was first investigated in the United States in the late 1940s but the discovery of large reserves of uranium in the early 1950s ended interest in uranium as a by-product from fertiliser processes. In recent years, the fertiliser industry has grown considerably and there has been a revival of interest in the recovery of byproduct uranium.

This report surveys the current methods of processing phosphate rock to produce fertilisers and reviews the merits of uranium recovery processes proposed for integration with the fertiliser industry, including factors which influence the amount of uranium which can be recovered, such as the origin of the rock and the types of fertiliser produced. Detailed information on the world and Australian phosphate rock and fertiliser industries is included; current trends in production rates and usage patterns are presented together with costs of production and selling prices where available.

2. PHOSPHATE ROCK

Approximately 85 per cent of the phosphate rock mined in the world is used to manufacture fertilisers [OECD 1972]. In Australia the percentage is higher, consumption of phosphate rock being almost entirely for the production of phosphatic fertilisers with small quantities for detergents and food preparation [Bureau of Mineral Resources, Geology and Geophysics 1973a]. Phosphate rock is also used in the manufacture of elemental phosphorus and various phosphate chemicals, in feed stocks, in the smelting of iron and the production of steel alloys, and for the corrosion protection of metal surfaces.

In this section the origin and types of natural phosphates are considered, and the relationship between these factors and the composition of the phosphates is discussed. As the production of fertilisers represents by far the greatest use of phosphate rock, all references to the properties and mining of this material are confined to their effects on this industry.

2.1 Phosphate Rock

'Phosphate rock' is a commercial term for rock containing one or more phosphate minerals, usually apatite ($Ca_5(F,Cl,OH)(PO_4)_3$), of sufficient grade and suitable composition to permit its use, either directly or after concentration, in manufacturing commercial products [Dickson 1967]. The term includes phosphatised limestones, sandstones, slates and igneous rocks. The principal generic types of commercial interest are:

(a) Bird guano on coastal islands.

(b) Deposits of apatite.

(c) Primary marine phosphorites and their derivatives.

Guano is a relatively rare deposit of bird excrement found usually on desert islands. It is calcium phosphate derived from guano that is imported to Australia from Nauru, Ocean and Christmas Islands. Apatite veins and segregations in igneous rocks supply only 15 per cent of the world's phosphate requirements [Jaeger *et al.* 1972 - 1973], but extensive deposits have been worked in Russia, Norway and Canada. At present, the largest deposit is at Kirovsk on the Kola Peninsula of the USSR [Liddy 1971].

The phosphorites are marine sedimentary deposits composed largely of phosphate minerals. Many such deposits are upgraded by secondary enrichment and replacement, by mechanical concentration and by leaching to give residual deposits. This type of deposit is extremely important and supplies almost 85 per cent of the world's phosphate requirements; it also contains a higher proportion of uranium than either the guano or apatite deposits.

The composition of phosphorite is complex, some deposits containing as many as 38 phosphate minerals. However, the bulk consists of the carbonate-fluor-hydroxyl apatite series. The phosphate is usually conglomerated into pellets and nodules which are generally elliptical and range in size from 0.05 mm to more than 30 mm. Individual phosphatic layers range in thickness from 1-2 mm through to 2 m. Most are very thin and are interbedded with less phosphatic mudstones and carbonate rocks.

Phosphatic nodules are not limited to phosphate deposits, but are widely scattered in limestones, chalk and glauconitic sands. They also occur on the

present sea bottom. They are typically of irregular shape, black and have a hard, dense, shiny surface.

2.1.1 Composition of phosphate rock

The compositions of a number of phosphate rock samples after beneficiation are listed in Table 1. Phosphates are assessed mainly according to their phosphorus pentoxide (P_2O_5) content, but grade of rock is also commonly expressed as the percentage of tricalcium phosphate (also called bone phosphate of lime). Pure apatite contains about 40% P_2O_5, but phosphate rock can have a wide range of P_2O_5 contents and the average grade of rock produced is 31% P_2O_5 (68% tricalcium phosphate) or higher [Emigh 1972].

The concentrations of other constituents in the rock are also important as they dictate the type of fertiliser process in which the rock can be used and the degree of operating difficulty that will be encountered in using it. In particular, the iron oxide plus alumina content must be low (less than 3%) as these components cause the reversion of phosphates to insoluble forms, and give rise to hygroscopic products which clog seed drills when superphosphate is spread [Dickson 1967]. In Australia, a maximum content of 3 per cent of these combined oxides is acceptable but a content as low as 0.5 per cent may be specified for some applications [Dickson 1967; Liddy 1971]. A high percentage of fluorine may also be objectionable as this element apparently inhibits the solubility of natural and prepared phosphate mixtures. However, this is not always the case as some manufacturers produce up to 4 kg of saleable sodium fluosilicate per ton of superphosphate manufactured. A calcium carbonate content of up to 5 per cent is desirable as the carbon dioxide formed during acidulation of the rock has a beneficial effect in the superphosphate, concentrations greater than 5 per cent consuming large amounts of acid by reaction.

2.1.2 Uranium content of phosphate rock

The radioactivity of phosphate rock was first noted in 1908 by the British physicist R. Strutt (later Lord Rayleigh) who found that samples of phosphorite were many times more radioactive than the average rocks of the Earth's crust. This radioactivity is due almost exclusively to uranium and its decay products [Habashi 1970].

Many phosphate rock deposits have been examined to determine their uranium content. Contents higher than 1000 $\mu g\ g^{-1}$ have been reported, but most phosphate rocks contain between 30 and 200 $\mu g\ g^{-1}$ [Menzel 1968]. Radium is also present as a decay product and is in radioactive equilibrium with the uranium [Menzel 1968; Habashi 1970; Redeker 1971].

The environmental implications of the presence of uranium and daughter products in the phosphatic fertilisers manufactured from phosphate rock were investigated by Menzel [1968]. An evaluation of the most intensive applications of phosphatic fertilisers (from Florida), with relatively high concentrations of uranium, radium and thorium, showed that the addition of uranium and radium over the last 40 years may equal the amounts occurring naturally in the plough layer of soils, but the addition of thorium would be less than that occurring naturally. Menzel [1968] concluded that the radiation hazard which might result from the uptake of radium into food plants must be negligible.

The uranium/phosphate ratio is reasonably constant for any one deposit, and the uranium content has been used to assess the extent and phosphate content of deposits. Texas Gulf Sulphur Co. used the method to gain knowledge of (and control over) the extent of a valuable North Carolina phosphate ore [Redeker 1971]. Under favourable circumstances, aerial radiometric reconnaissance can also be used [Dickson 1967].

Table 2 lists uranium contents of numerous phosphate rocks from a variety of sources. The rocks in the first section of the table are grouped according to their geographic origin. Guano and macrocrystalline apatite contain significantly less uranium than the marine phosphorites. This relationship between the uranium content and origin of the rock is a well known phenomenon [Dickson 1967; Habashi 1970] and has been the subject of a number of investigations [Habashi 1970].

Habashi [1970] proposed the following theory to explain the presence of uranium in phosphate rock. Marine organisms ingest phosphate dissolved initially from apatite by surface waters. After their death, the marine organisms sink to the bottom of the sea, where they decay to form deposits composed mainly of calcium phosphate. During this process, traces of uranium present in the oceans were probably absorbed by the fine grained phosphate and were later incorporated in the apatite structure where they substituted isomorphously for calcium. This action also explains the often observed direct proportionality of uranium content to P_2O_5 content; namely, the more apatite crystals that are available the greater the probability for isomorphous substitution to take place. The suggestion that uranium is built into the apatite structure is also supported by the fact that the uranium-containing phase in phosphate rock cannot be separated or enriched by methods of ore dressing.

2.2 World Production, Trade and Consumption of Phosphate Rock

World production of phosphate rock over the last ten years is listed in

Table 3. The latest [1972] yearly production rate of 94 million tonnes is a 7.8 per cent increase over that for 1971. There are six production areas (USA, USSR, North Africa, Middle East, Togo/Senegal and the Pacific Islands) currently supplying some 95 per cent of the world's production of phosphate rock. The USA, USSR and North Africa together account for approximately 85 per cent of world production and dominate the export trade which amounted to 43.5 million tonnes in 1972 [OECD 1972].

In 1972, the OECD presented data on present and future consumption of phosphates by geographical regions and made estimates of future installed production capacities (Tables 4 and 5), predicting surplus production capacity in 1975 of 30-40 million tonnes of marketable phosphate rock (usually defined as 30.2 to 39.4% P_2O_5 [The British Sulphur Corporation 1973]). However, over the last four years, production of phosphate rock has not kept pace with demand, resulting in the depletion of stockpiles [Rosenzweig 1974]. In 1973, consumption exceeded production by 3 million tonnes, but on the basis of current proposals, production should match consumption in 1975, thereafter providing a growing buffer of capacity. World production of phosphate rock should increase by over 60 per cent (average annual growth rate of more than 10 per cent) from 1973 to 1978; during the same span, exports should jump by 58 per cent. These forecasts were made in mid-May 1974 at a meeting of the International Superphosphate and Compound Manufacturers' Association (ISMA) [Rosenzweig 1974].

The increase in production capacity will be due to enlargement of existing facilities (USA, USSR, North Africa, Togo/Senegal) and the opening of new mines (in the Spanish Sahara, Peru, India and Australia) and will be primarily directed towards export markets [OECD 1972]. Tunisia, Algeria, Morocco, Rio de Oro, Senegal and Togo will increase their yearly output of rock from the 1973 level of 25 million tonnes to 45 million tonnes in 1978. (This increase represents approximately one third of the total world gain in rock output). During this period, exports from these countries will rise from 22 to 37 million tonnes per year. The USA will increase production of rock from 39 million tonnes in 1973 to 64 million in 1978, although exports are expected to fall in 1975 and then rise again to 18 million tonnes per year in 1978 [Rosenzweig 1974].

In the USSR, the production of rock should increase by about one-third to 28 million tonnes per year in 1978, at which time production will be matched by local consumption and exports will cease. In the Middle East, Egypt, Israel, Jordan and Syria plan a threefold expansion in rock production and exports from 1973 to 1978 to reach the respective combined output levels of 7 and 6 million tonnes per year in 1978 [Rosenzweig 1974]. The production of rock in Oceania is confined mainly to Ocean and Nauru Islands, and in the Indian Ocean to Christmas Island. At their present rate of production, deposits on Nauru will be exhausted in 17 to 22 years and those on Ocean Island in 2 years from 1974 [The British Sulphur Corporation 1973; Rosenzweig 1974]. Output from North Queensland (Broken Hill South deposit) is expected to make up the loss of production from Ocean Island by 1977 and provide growth for the region. The total production from Oceania should rise to 8.4 million tonnes and exports to 3.6 million tonnes in 1978 [Rosenzweig 1974].

The OECD has published a detailed examination of trade flows of phosphate rock in 1970 and projected trade flows for 1975 (Tables 6 and 7). Although these figures do not agree in all cases with those more recently estimated (mentioned above), the OECD data reflect the changing patterns in world trade of phosphate rock and allow prediction of possible export markets for Australian phosphate.

2.3 The Phosphate Rock Industry in Australia

Australian production of phosphate rock is confined to South Australia and is negligible compared with domestic requirements (Table 8). Australia's requirements of phosphate rock are imported by the British Phosphate Commissioners from Nauru and the Gilbert and Ellice Islands in the Pacific Ocean and from Christmas Island in the Indian Ocean. Only a minor amount, nearly all from Morocco, is imported from other sources. Tables 9 and 10 indicate the countries supplying phosphate rock and the quantities imported by each state.

Although all phosphate rock currently used in the industry is imported, there are prospects that Australian raw materials will be used in the future and the Department of Secondary Industry [1973] reported the following discoveries that are expected to create this situation.

Extensive deposits of phosphate rock were discovered by Broken Hill South Limited in the Duchess region of N.W. Queensland in 1966. The Company has reported that reserves exceeding 2000 million tonnes of phosphate rock of an average grade of 17 per cent P_2O_5 have now been proved at ten deposits in the northern, central and southern sections of the phosphate region. Approximately two-thirds of the reserves are located almost entirely in the southern Duchess deposit. The combined reserves of the Lady Annie and Lady Jane deposits (central section) are 450 million tonnes which is reported to be sufficient to support long term mining.

Investigations into up-grading the phosphate rock at the mine have shown that flotation is a satisfactory method of beneficiation for present development proposals. Beneficiation tests have produced concentrates with grades up to 36 per cent P_2O_5 and the proportions of deleterious impurities are well within acceptable limits. Additional investigations have shown that the product is suitable for the production of single superphosphate and phosphoric acid [The Australian 1974]. The first commercial production of phosphate concentrates (beneficiated rock) from the Lady Annie deposit is likely to commence in 1977-1978, the production capacity of the field is expected to be 4.0 million tonnes per year with the Australian market absorbing up to 1.5 million tonnes per year [Bureau of Mineral Resources, Geology and Geophysics 1973c, Department of Secondary Industry 1973].

Further details of the Duchess deposit and plans for its development have been reported recently [Byrne 1974a; The Australian 1974]. The Phosphate Hill zone of this deposit contains 315 million tonnes of rock of grade 18.3 per cent P_2O_5 and within this zone and the smaller Ardmore deposit to the west, 40 million tonnes with a grade of 31 per cent can be classified as direct shipping rock. It is reported that the company hopes to bring this zone into production at a rate of one million tonnes per year early in 1976, with production increasing to three million tonnes per year (all to be transported by rail to Townsville) planned for the end of 1977. The substantial increase in the price of phosphate rock late in 1973 has enabled the company to commence utilisation of the Duchess deposits earlier than the Lady Annie and Lady Jane deposits which are still scheduled to come into production in 1977-1978 with the concentrates to be shipped from a port in the Gulf of Carpentaria. Plans to export quantities of rock surplus to Australian requirements to south and east Asian markets have also been announced [The Australian 1974].

2.4 Potential of Phosphate Rock as a Source of Uranium

Table 11 lists approximate quantities of uranium contained in the phosphate rock mined yearly by the world's major producers. These figures should only be regarded as rough estimates as the figures published for uranium contents of phosphate rock may not be representative of the ore which is being mined currently. In addition, the total production of most countries comes from numerous phosphate deposits which could contain vastly different concentrations of uranium.

The extent to which the uranium in phosphate rock is recoverable depends on the subsequent processing of the rock. Factors influencing uranium recovery are discussed in later sections.

3. PROCESSING OF PHOSPHATE ROCK TO PRODUCE FERTILISERS

3.1 General Introduction

The primary phosphate-based fertilisers are produced by a number of relatively simple processes, but the overall industry is complex because of the varying degrees of mixing and blending that are practised. The structure of the world industry is illustrated in Figure 1. Details of the world and Australian consumption of fertilisers are presented in Sections 3.5 and 3.6.

The aim of processing is to convert the phosphate in the rock to a form available to plants. Although only 5 to 10 per cent of the P_2O_5 in the phosphate rock is available from unprocessed rock, finely ground rock of high and low grade is applied directly to the soil in some areas. This method is best suited for pasture and forage crops and for use on acid soils [Slack 1966]; phosphate rock from Tunisia and the Kola Peninsula is used in this manner [Slack 1966; Woodrooffe 1972].

The three basic processes for decomposing phosphate rock to obtain products suitable for use as fertilisers are acid treatment, thermal reduction and thermal treatment without reduction. Acid treatment is the most common method.

The main acid treatment route involves treating beneficiated phosphate rock with sufficient sulphuric acid to give a mixture of monocalcium phosphate ($Ca(H_2PO_4)_2$) and gypsum ($CaSO_4.2H_2O$) known as single superphosphate. The gypsum is not removed from the mixture which seldom contains more than 20% soluble P_2O_5.

If greater quantities of sulphuric acid are added to phosphate rock, phosphoric acid (known as wet-process phosphoric acid) is produced which is filtered from the gypsum. Triple superphosphate, which contains 44 to 47% soluble P_2O_5, is obtained by acidulating phosphate rock with phosphoric acid. Phosphoric acid is also combined with other chemicals to produce highly concentrated fertiliser salts. Nitric and hydrochloric acids are also used to treat phosphate rock; these processes are limited in application and are discussed further in Sections 3.3.5 and 3.3.6.

The thermal reduction method is based on the smelting of phosphate rock mixed with coke and silica in electric or blast furnaces. Elemental phosphorus is produced and is converted to phosphoric acid for use in the fertiliser, detergent and feed grade phosphate industries. Most of the acid utilised in the fertiliser industry goes into the production of liquid mixed fertilisers, the basic operation being the preparation of an ammonium

phosphate solution. The purity of furnace acid is a major advantage for this use as a clear solution is obtained. Wet-process acid can be used but impurities dissolved in the acid, mainly iron and aluminium compounds, form an undesirable precipitate during ammoniation.

Thermal treatment without reduction involves heating phosphate rock to a high temperature in combination with a material to break up the fluorapatite structure to produce defluorinated phosphate rock. Alkali salts, a magnesium silicate (olivine or serpentine) and silica, with a little phosphoric acid in the presence of water, have been used for this purpose. These products contain 19-24% P_2O_5, of which as much as 87 per cent is soluble, and are applied directly to the soil after grinding [Slack 1966].

Detailed descriptions of the above processes used in the fertiliser industry are given in the following sections. The processing of phosphate rock for ammonium phosphate fertilisers and other industries is not discussed because relatively small quantities of rock are involved and most processes would require the manufacture of phosphoric acid as the first step.

3.2 Beneficiation of Phosphate Rock

In order to reduce transportation and subsequent processing costs, nearly all phosphate rock requires upgrading to remove part of the impurities and increase the phosphate content. One exception is rock used directly in furnace processes without beneficiation. The most widely exported phosphate concentrates are within the range 33-35% P_2O_5, followed by material assaying between 31 and 32% P_2O_5 and lesser tonnages of premium grade rock or concentrates whose P_2O_5 content is in excess of 35 per cent [Bureau of Mineral Resources, Geology and Geophysics 1973a].

Phosphate rock from different parts of the world varies widely in grade, in nature of impurities and in degree and type of beneficiation used. Figure 2 shows a number of possible flow diagrams for phosphate treatment. For example, Florida rock is beneficiated by washing, wet screening and flotation to upgrade it from an average concentration in the raw ore of about 15% P_2O_5 to a product containing 31-36% P_2O_5. Apatite ore (18% P_2O_5) mined in the Kola Peninsula is ground and beneficiated by flotation to give a concentrate containing about 40% P_2O_5 [Woodrooffe 1972]. Phosphorite mined in Israel is beneficiated by several processes based on drying, selective grinding, air separating and screening to produce a concentrate containing 28-30% P_2O_5. Wet beneficiation of the same ore achieved a product of between 31 and 32.5% P_2O_5, while thermochemical methods produced a concentrate containing 34.5 to 35.5% P_2O_5. The latter process consisted of calcination, slaking and lime separation and is claimed to produce a high quality phosphate [Sylvester 1971]. Moroccan phosphate is generally beneficiated by a drying and calcining process although some ores are upgraded by washing only to produce a concentrate containing 36.5 to 37.5% P_2O_5 [Argall 1969].

As the Florida phosphate field is one of the largest phosphate producing areas in the world, a detailed description of the beneficiation techniques used there will be given. The basic flowsheet, which is used in the majority of beneficiation plants is shown in Figure 3. Proper desliming is considered essential for optimum performance of the flotation circuits. Slimes are considered to be any material less than 150 mesh Tyler and approximately 80 to 90 per cent is removed by cyclones. Slimes constitute 20 to 25 per cent of the pebble rocks and are composed predominantly of clays, phosphate minerals and quartz. The size distribution of the flotation feed in the Florida deposit ranges from 14 to 150 mesh; this is separated into coarse and fine fractions and each is treated in separate circuits to achieve good recovery at a reasonable unit cost. The point of nominal separation ranges from 28 to 48 mesh with 35 mesh being used by most plants. Flotation plant feed is sized by employing either hydraulic sizing, screen sizing or both.

Most mills use a two-stage flotation process to treat both the coarse and fine phosphate fractions. In the first step (rougher circuit), phosphate particles are coated with an anionic flotation reagent and are floated away from uncoated sand. The coating is then removed and a cationic reagent is used to float residual sand away from the phosphate. The coarse and fine concentrates from the anionic flotation step can be combined for subsequent upgrading or kept apart throughout beneficiation. The same anionic collectors are used for both the coarse and fine circuits to give phosphate recoveries of 70 to 90 per cent. Fatty acid type collectors are used plus a hydrocarbon diluent. Both the coarse and fine rougher concentrates are scrubbed with sulphuric acid in agitated tanks to remove the anionic reagents and diluent.

Cationic amine flotation usually yields from 92 to 98 per cent recovery of phosphate values contained in the rougher concentrate and produces a marketable concentrate containing 2 to 5 per cent acid insoluble material. The final concentrate is dried in a rotary drier before shipment to prospective customers [Aparo 1970].

3.3 Acid Treatment of Phosphate Rock

3.3.1 The production of single superphosphate

Single superphosphate was the first commercial phosphate fertiliser and is still the most popular throughout the world because of its ease of

production although it has been losing ground in recent years (particularly in the United States). Phosphate rock which has been pulverised is mixed with sulphuric acid and the resulting slurry is held in a container until it solidifies. The material is then removed to a storage pile where it cures for approximately three weeks until the reaction between the rock and the acid is complete. The product is used without further treatment other than breaking it up to the desired size or using a granulation process. The main reaction is

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 3H_2O \rightarrow 3CaH_4(PO_4)_2H_2O + 7CaSO_4 + 2HF.$$

Raw materials

In a typical process, 0.6 tonnes of high grade phosphate rock, usually containing not less than 35% P_2O_5, is mixed with 0.5 tonnes of 70% sulphuric acid to produce 1 tonne of single superphosphate which contains approximately 20% soluble P_2O_5.

Process conditions

The main process variables in the manufacture of single superphosphate are acid concentration, acid temperature, acid/rock ratio and particle size of the rock. Typical ranges for these variables in United States plants are given in Table 12. The acid concentration should be as high as possible to give a dry and high grade product but is limited by the necessity for sufficient water to obtain complete reaction and by the tendency to produce undesirable physical conditions (damp and sticky product) if strong acid is used. An excessively low temperature reduces the reaction rate while high temperature has no adverse effects if the evaporated water is replaced.

Acid/rock ratio depends to a considerable extent on the production situation. A ratio close to stoichiometric may be used if a long curing period is feasible or if the physical condition of the product is particularly important, but excess acid is employed if rapid curing is essential or if the product is to be used directly in an ammoniation process. Particle size of the rock usually is as small as the economic balance between cost of grinding and completeness of reaction will allow. Type of rock is important in this respect. Moroccan rock, for example, does not require as fine grinding for good conversion as does Florida rock [Slack 1966].

It is difficult to characterise single superphosphate in terms of its properties because of the possible variations in raw materials and manufacturing conditions. Some typical properties are listed in Table 13.

Manufacturing equipment

Over recent years, there have been gradual changes in the type of equipment used to manufacture single superphosphate. Originally, ground phosphate rock was mixed with sulphuric acid in batches and then dropped into a container (called a den) which, when full, was allowed to stand for some hours until the reaction between the two materials was near completion and the mixture had set. It was then raked out mechanically onto conveyors which took it to storage dumps to cure.

This process was improved by using continuous mixing and the materials were then dropped into the superphosphate den as before. In the latest development, the continuous den, the phosphate rock and acid are mixed and dropped continuously into a den which has a slowly moving conveyor as a floor. The material is finally discharged onto a conveyor belt as before. All three types of operation are used in the Australian industry [Department of Secondary Industry 1973].

Continuous mixers are of three types: horizontal trough-type mixers fitted with a shaft that carries heavy paddles, cone-type mixers using the swirling action of acid and rock streams introduced simultaneously into the cone, and small-volume mixers fitted with a high speed stirrer. The trough-type mixer is used commonly in continuous den plants.

All types of continuous dens receive the rock acid slurry at one point, carry the mix for some distance (linear-horizontal or a circular-horizontal travel) to allow the slurry to set and discharge the product onto a conveyor for transfer to the curing pile. A typical linear-horizontal den consists of a slat-belt conveyor mounted on rollers with a stationary box mounted over it and a revolving cutter at the end. The box must fit closely over the belt to prevent leakages of gases and to allow the sides of the box to retain the slurry until it sets. Variations to this basic design consist of a conveyor made of U-shaped sections that provide their own sidewall, a flexible belt troughed for about half its length to retain the slurry during setting and rotary drum dens which need no cutter because the rolling action imparted during travel keeps the material broken up. A circular-horizontal den consists of a cylindrical vessel that rotates on a vertical axis and contains an inner cylinder to give an annular space. Slurry is introduced just beyond a stationary partition mounted in the annular space; as the den rotates, the superphosphate solidifies, and on completing the circle is removed by a stationary cutter mounted on the side of the partition [Slack 1966].

All dens are designed to allow collection of the gases evolved and subsequent scrubbing of these gases with water. The resulting solution of fluosilicic acid is usually discarded or is recovered in the form of sodium fluosilicate.

Some single superphosphate is granulated but most is used without further treatment after breaking it out of the curing pile. Typical granulation processes are described in Section 3.3.2. Granulation is often combined with ammoniation, although non-granular material is also ammoniated. These processes have been described by Slack [1966].

3.3.2 <u>The production of double and triple superphosphate</u>

Double and triple superphosphate are made by manufacturing processes similar to that for single superphosphate except that sulphuric acid and phosphoric acid are added to phosphate rock to make double superphosphate while phosphoric acid alone is added to make triple superphosphate. The reaction of phosphoric acid and phosphate rock produces impure monocalcium phosphate without dilution from the presence of calcium sulphate. The acid supplies more nutrient phosphate than the phosphate rock to the finished product and a very high nutrient content is obtained. The basic reaction is,

$$Ca_{10}(PO_4)_6F_2 + 14\ H_3PO_4 + 10H_2O \rightarrow 10CaH_4(PO_4)_2\ H_2O + 2HF.$$

Double and triple superphosphate contain typically 40 and 46% P_2O_5 respectively.

Raw materials

The phosphate rock required for the manufacture of triple superphosphate is often of a slightly lower grade than that used for single superphosphate, normally between 32.5 and 33% P_2O_5. The same level of impurities is acceptable.

Wet-process phosphoric acid containing a standard 52 to 54% P_2O_5 is used for the manufacture of double and triple superphosphate. Typical raw material usages for Australian conditions are 0.1 tonnes of sulphuric acid, 0.44 tonnes of phosphoric acid (54% P_2O_5) and 0.57 tonnes of phosphate rock to give one tonne of double superphosphate of analysis 40% P_2O_5. The corresponding quantities are 0.42 tonnes of phosphate rock and 0.58 tonnes of phosphoric acid (54% P_2O_5) to give one tonne of triple superphosphate of analysis 46% P_2O_5 [Department of Secondary Industry 1973].

Process conditions

The basic process conditions for the manufacture of triple superphosphate and typical properties of the product are given in Tables 14 and 15 respectively.

Manufacturing equipment

The equipment used for manufacturing double and triple superphosphate is very similar to that used in the single superphosphate process. Cone mixers or paddle-type mixers are used in most plants in conjunction with a continuous rubber-belt conveyor as the den. Continuous dens of the slat-conveyor type are also used.

The material discharged from the den is cured in piles for several weeks. It is common practice to granulate triple superphosphate after removal from the curing pile. Granulation involves agglomerating finely divided material cut from the curing pile to particles of fairly large size, usually 1.6 to 3.2 mm in diameter. The high soluble phosphorus content of this fertiliser makes a granular product desirable for easier handling in bulk blending or in direct application.

Three granulation processes are in use. The cured product is commonly granulated by treatment with water and steam in a rotary drum, followed by drying and screening. This 'wet and dry' method is also used for single superphosphate. The alternative processes are more complicated but yield improved product properties.

The granulation of triple superphosphate is often combined with ammoniation; the major problem in such processes is the choice of the correct formulation variables to obtain the desired high-analysis fertiliser.

3.3.3 The production of ammonium phosphate

Ammonium phosphates are made by the neutralisation of phosphoric acid with ammonia. The material is formed as a slurry which is then granulated and dried. Curing is not required as the reaction goes to completion rapidly. Both the cation and the anion of ammonium phosphate contain nutrients, in contrast to the superphosphates, and consequently the nutrient content of the fertiliser is very high. This advantage plus high water solubility, good physical characteristics and low production cost have been responsible for the rapid increase in consumption of this fertiliser since 1960. The newest product of the ammonium phosphate type is ammonium polyphosphate which is made by the reaction of ammonia and superphosphoric acid (see below). The product has a high nutrient content, 15 per cent nitrogen and 60% P_2O_5, and a high solubility [Slack 1971].

3.3.4 The production of wet-process phosphoric acid

Production of wet-process phosphoric acid involves four main steps; dissolving the phosphate values in the rock, holding the acidulated slurry until the calcium sulphate crystals grow to an adequate size, separating the acid and calcium sulphate by filtration, and concentrating the acid to the desired level. The reaction for the process used most extensively (the dihydrate process) is:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4.2H_2O + 2HF.$$

Typical material usage is 3.05 tonnes of phosphate rock (75% tricalcium phosphate) and 2.75 tonnes of sulphuric acid (100%), reacting to produce 1.35

tonnes of phosphoric acid (100%) and 5.0 tonnes of gypsum.

Corrosion is a major problem in the production of wet-process phosphoric acid. Pure phosphoric acid is less active than strong acids such as sulphuric and hydrochloric,but its corrosive action is increased significantly by the presence of contaminants introduced from the phosphate rock. Fluorine, chlorine and silicate are particularly undesirable as these chemicals form hydrofluoric, hydrochloric and fluosilicic acids during the dissolution step. The most common materials of construction are rubber-lined mild steel for vessels and large pipes, Carpenter 20 alloy steels for components not suitable for rubber lining, and glass fibre-reinforced cast-epoxy resin for small piping [Pike 1967; Dell 1967].

Process conditions

Several wet processes are in use for the production of phosphoric acid. The main difference in these processes is the degree of hydration of the calcium sulphate byproduct which is determined by the temperature and the concentration of P_2O_5 in the acidulated slurry. In practice, crystallisation is affected by many factors and the desired final product can be difficult to obtain.

Most industrial plants produce phosphoric acid by the dihydrate process (95-96% P_2O_5 recovery) and only aspects of this process are discussed below.

Raw material and product properties

The phosphate rock used in the dihydrate process usually contains between 30 and 35 per cent P_2O_5 with 1.5 to 4.0 per cent combined iron and aluminium oxides. Rock with a high content of organic matter or carbonate causes foaming during the leaching step. This problem is overcome by the addition of approximately 2.3 kg of anti-foaming agent per tonne P_2O_5. Typical agents are tall oil, fatty acids, oleic acids and silicones. The rock is ground to 60 to 70 per cent minus 200 mesh in air-swept ball mills. Strong sulphuric acid (93-98%) is used to allow as much water as possible to be employed in washing the gypsum filter cake.

The phosphoric acid (after filtration) contains 30 to 32 per cent P_2O_5 and is usually concentrated to either a 40 to 42 per cent or 54 per cent solution for the production of ammonium phosphate or triple superphosphate respectively.

Wet-process acid is a very impure product that contains small amounts of a variety of materials. Most of these come from the phosphate rock and consist of organic matter and compounds of iron, aluminium, calcium and fluorine. Some of the impurities are in solid form, and result from imperfect filtration, precipitation during concentration, or post-precipitation that may take place over an extended period. Others remain in solution, mainly as soluble iron and aluminium compounds. Free sulphuric acid is also present. A high content of impurities can be tolerated where the acid is to be used in another process in the same plant. If the acid is transported from the production plant, sufficient solid impurities are removed to reduce problems of precipitation in shipping and handling [Slack 1966].

Manufacturing equipment

The many variations of the dihydrate process are concerned with the design of the digestion equipment and the type of gypsum filter. A typical plant flowsheet is shown in Figure 4.

The most common type of reactor system consists of a single large tank with associated raw material feeding, cooling, fume removal and recycling facilities. Reactor tanks are usually constructed of rubber-lined mild steel with a carbon-brick lining of the rubber to protect it from the slurry [Dell 1967]. The average retention time in all reactor systems is about eight hours and recirculation of slurry is required to reduce the effects of surges and local high concentrations of rock and acid. The recycled slurry also gives the control of supersaturation necessary for good growth of calcium sulphate crystals. In a well-designed and operated plant, undissolved rock should not amount to more than 0.2 to 0.5 per cent of the original P_2O_5.

The slurry in the reaction tank must be cooled to remove the heat generated by the acidulation of the rock. Cooling may be accomplished by blowing air into the slurry, blowing air across the slurry, or flash cooling under vacuum. The latter system, in which a portion of the reactor liquor is withdrawn to a vacuum evaporator-crystalliser, is used in most plants and allows the use of a smaller and more efficient fume scrubbing system.

Filtration of the acid-gypsum slurry is the most difficult step in the production process, the basic requirement for success being proper growth of the gypsum crystals. Continuous production of satisfactory crystals depends on sulphate concentration, slurry recirculation, phosphoric acid concentration and impurities in the rock.

In general, horizontal tilting-pan vacuum filters are used in three of four filter stages. The slurry, containing 30 to 45 per cent solids, is filtered in the first stage to give product acid. Wash water is added to the last stage, (third or fourth) to wash traces of acid from the cake. Filtrate from the third stage is used as the wash liquor in the second stage,

where the intermediate washing gives recycle acid containing about 21% P_2O_5 (recycled to the reactor). Cake thickness varies from 3.8 to 10 cm, and the pressure drop across the filter is between 50 and 66 kPa [Slack 1966]. Filter cloths made of monofilament polypropylene are normally used and the supporting grids are constructed of rubber-coated mild steel. The pans are usually of stainless steel but plastic or rubber-lined mild steel can be used [Dell 1967].

The concentration of product acid is limited to about 32% P_2O_5; at higher concentrations the size of the gypsum crystals decreases rapidly. Concentration to levels higher than 32 per cent is accomplished by the use of single effect vacuum evaporators. Normal practice is to use three stages of concentration, the first two taking the acid to 42 per cent and the last stage to 54 per cent. The upper limit of concentration is set at 54 per cent by the boiling point of the phosphoric acid and the availability of suitable materials of construction. Forced circulation evaporators are generally preferred; the flash chamber is constructed of rubber-lined mild steel and the outside heat exchanger contains tubes constructed of Karbate (impregnated graphite). Forced circulation units are subject to scaling from concentration of calcium sulphates and fluosilicates and must be boiled out with water on a regular schedule. This operation usually requires about 15 per cent of the total operating time [Slack 1966; Pike 1967].

Superphosphoric acid

A process has been developed recently to produce superphosphoric acid containing 70-72% P_2O_5. Superphosphoric acid is a mixture of several species of phosphoric acid (mainly ortho and pyrophosphoric acids) in equilibrium proportions and is manufactured by concentrating wet-process acid in an additional evaporator or by using less water in the furnace process. This acid has the advantages of higher concentration, lower suspended solids content, reduced corrosiveness and certain chemical properties that make it superior as an intermediate in the production of liquid mixed fertilisers [Slack 1966, 1971].

3.3.5 Production of nitric phosphate

The short supply and high price of sulphur has resulted in the development of processes to acidulate phosphate rock with nitric acid instead of sulphuric acid. Nitric phosphates are made by the treatment of phosphate rock with nitric acid (or nitric acid plus sulphuric or phosphoric acid) to give phosphoric acid and calcium nitrate. The resulting slurry is neutralised with ammonia and granulated. The presence of calcium nitrate complicates the process, has a diluting effect on the product and makes it hygroscopic

[Slack 1971].

The basic reaction depends on the amount of nitric acid used [Slack 1966]. The addition of excess acid to yield the required percentage of nitrogen in the product gives the following reaction:

$$Ca_{10}(PO_4)_6F_2 + 20HNO_3 \rightarrow 6H_3PO_4 + 10Ca(NO_3)_2 + 2HF.$$

If excess acid is not required, a nitric acid to calcium oxide mole ratio of 1.8 is sufficient for good process operation:

$$Ca_{10}(PO_4)_6F_2 + 18HNO_3 \rightarrow 4H_3PO_4 + CaH_4(PO_4)_2 + 9Ca(NO_3)_2 + 2HF.$$

The addition of ammonia ideally converts all of the phosphate to dicalcium phosphate ($CaHPO_4$) and produces an acceptable mixture which is too hygroscopic for practical use. The variations in nitric phosphate production are concerned with the removal of calcium nitrate or its conversion to a less hygroscopic compound.

Removal of calcium nitrate

A number of methods have been developed to overcome the calcium nitrate problem. In Europe, the acidulated slurry is cooled and the resulting calcium nitrate crystals are removed by centrifuging and used directly as a fertiliser. In this process, sufficient calcium nitrate is removed by crystallisation for the remaining calcium, when the filtered solution is ammoniated, to precipitate as dicalcium phosphate and the nitrate to be converted to ammonium nitrate.

Alternatively, other compounds are used together with nitric acid to produce insoluble calcium salts. Typical additives are sulphuric acid, phosphoric acid, sulphate compounds (potassium or ammonium sulphate) or carbon dioxide where an ammonia plant is operated in conjunction with a nitric phosphate plant. Phosphoric acid is the most popular additive. In a typical process, phosphate rock is treated with 20 moles of nitric acid and 4 moles of phosphoric acid per mole of calcium phosphate in the rock. The acidulated slurry is then neutralised with ammonia and granulated. The phosphoric acid and ammonia convert the calcium nitrate to dicalcium phosphate and ammonium nitrate which are both acceptable products [Slack 1971].

Production processes

Processing equipment is similar to that used in the production of ammonium phosphate with the addition of extra tanks for the acidulation of the phosphate rock. Two-step ammoniation and granulation is usually practised. Acidulation is carried out in two or three vessels with up to twelve tanks for the ammoniation step. The ammoniated slurry is then granulated in various types of equipment including those mentioned in Section 3.2.3 [Slack 1966].

3.3.6 Acidulation of phosphate rock with hydrochloric acid

In a new process developed recently by the Israel Mining Industries (IMI), phosphate rock is treated with hydrochloric acid to produce phosphoric acid [Ketzinel *et al.* 1972]. In this process, phosphate rock is dissolved in excess hydrochloric acid and the clear liquor is separated from the undissolved residue and fed to a solvent extraction section. Phosphoric and hydrochloric acid are separated in this section and the phosphoric acid is purified by removing the large amounts of calcium and minor quantities of other impurities. The solvents suitable for these operations are primary aliphatic alcohols, usually butanol and iso-amyl alcohol. Phosphoric acid is separated from the hydrochloric acid by distillation.

Further details of this process are given in Section 4.10.4.

3.4 Thermal Treatment of Phosphate Rock

3.4.1 Production of phosphoric acid

Another method of eliminating the sulphur requirements from the production of phosphoric acid is the use of the furnace process. This process also has the advantage that phosphate rock can be used without beneficiation. In the furnace process, phosphate rock mixed with coke and silica is heated to a high temperature in an electric furnace to reduce the phosphate to phosphorus. The phosphorus is burned with air and resulting phosphorus pentoxide is absorbed in water to give phosphoric acid. A blast furnace can be used in a similar manner except that excess coke is needed to provide sufficient heat from its combustion for the smelting reactions. The phosphorus is carried out of the furnace as a vapour in the blast furnace off-gases and is recovered in a manner similar to that outlined above.

3.4.2 Production of defluorinated phosphate rock

An adequate description of this process is given in the introduction to Section 3. The quantities of fertiliser produced are reported to be very low [Slack 1971].

3.5 The World Fertiliser Industry

Table 16 lists the consumption of fertilisers by various countries in terms of tonnes of P_2O_5. Unfortunately, up to date figures detailing the relative usage of the numerous types of phosphatic fertilisers are not available. However, there has been a marked change in favour of the manufacture of high-analysis fertilisers in preference to the traditionally valued single superphosphate. This trend is shown in the decline from 50 per cent in 1960 to 29 per cent in 1969 in the proportion of world phosphate rock consumption used in the manufacture of single superphosphate [The British Sulphur Corporation 1973]. Rosenzweig [1974] has reported that the world consumption of phosphate fertiliser is predicted to rise from 22.4 million tonnes per year in 1971/72 to 30.2 million tonnes per year in 1975/76. North America and Western Europe, which account for almost half the present world consumption, are expected to consume less than 25 per cent of this rise, while Eastern Europe and the USSR, which now account for less than 25 per cent of total consumption, will use nearly 30 per cent of the increase.

ISMA (Section 2.2) have predicted that the production of wet-process phosphoric acid will account for the bulk of the increase in P_2O_5 consumption with more than 90 per cent of the overall growth in phosphates based on wet-process acid for use in the manufacture of NP and NPK compounds and triple superphosphate. The proportionate share of phosphoric acid in overall growth will be smaller in Oceania and socialist Asia*. As a result of this development, phosphoric acid will increase its share of the total world production of phosphate rock to well over 50 per cent by 1976 from less than 33 per cent in 1968. Acid consumption is expected to reach 17.2 million tonnes per year of P_2O_5 in 1975/76, with North America accounting for about one third of this figure, Eastern and Western Europe about 20 per cent each and non-socialist Asia* 13 per cent [Rosenzweig 1974].

In a recent study, the OECD [1972] also concluded that increased usage of certain fertiliser products, which are restricted in use at present, will lead to important structural changes in production and trade of fertilisers. These products are:

- Powdered monoammonium phosphate (12-52-0 or 12-56-0** MAP†) produced from 54 per cent phosphoric acid; MAP forms one of the least costly methods for transporting P_2O_5 over long distances and is easy to granulate (with steam) to make mixed fertilisers (with urea and ammonium nitrates) with which it is very compatible;
- Polyammonium phosphates (15-62-0 or 12-58-0) produced from superphosphoric acid (thermal or wet);

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* Classifications used by Rosenzweig [1974].

** These figures indicate the percentages of nitrogen, phosphorus and potassium in the fertiliser product.

† Higher formulations (12-61-0) may be obtained from superphosphoric acid.

- Triple superphosphate (55 per cent P_2O_5) produced from superphosphoric acid;
- Urea phosphate (18-45-0) produced from urea and concentrated phosphoric acid;
- Monopotassium phosphates (0-52-35)

The OECD predicted that the pattern of world trade in phosphatic fertilisers, which amounted to about 2.8 million tonnes of P_2O_5 in 1968/69 (Table 17), will alter in the 1970s as a result of the following events:

1. A rapid increase in installed phosphoric acid production capacity. Capacity will reach 18.8 million tonnes per year of P_2O_5 in 1975/76, a rise of 7.8 million tonnes per year from 1972. North America will provide more than 30 per cent of this rise, Eastern and Western Europe 20 per cent each and North Africa and the Middle East combined, nearly 17 per cent [Rosenzweig 1974].
2. The 'decaptivation' of phosphoric acid which was previously supplied and consumed internally in integrated plants. This development is indicated by the setting up of phosphoric acid units marketing acid through national outlets (Freeport Sulphur in the US, Société Rupel in Belgium) and the setting up of phosphoric acid units for export from developing countries; *e.g.* Fertilizantes Fosfatados Mexicanos (FFM) in Mexico, Arad Chemical Industries Limited in Israel, Industries Chimiques Maghrebines (ICM) in Tunisia and Bandar Shalpur in Iran. These units are capable of supplying an acid competitive with the acid produced in Western Europe (for example) using imported rock phosphate (see Tables 18 and 19).
3. The increase in the size of phosphoric acid units. Capacities of new units are 600 to 1000 tonnes of P_2O_5 per day with one or two production lines, compared with a large number of units in various parts of the world still producing 100 tonnes per day.
4. The development of international and intercontinental trade in phosphoric acid as a result of technological progress in its transport and storage. International trade in phosphoric acid (Table 20), which increased by approximately 50 per cent in 1970 to 0.2 million tonnes of P_2O_5, is likely to increase rapidly between 1970 and 1975 and will come mainly from units set up in developing countries [OECD 1972]. Estimated figures for the regional distribution of phosphoric acid production capacity in 1975/76 [Rosenzweig 1974] agree with the OECD information

on world trade patterns. North America will have an excess capacity of 2.3 million tonnes of P_2O_5 per year, North Africa and the Middle East nearly 1 million tonnes and Western Europe almost 500,000 tonnes. Lacking in phosphoric acid capacity will be Asia (1.1 million tonnes), Eastern Europe (600,000 tonnes) and Latin America (over 400,000 tonnes). These estimates result in a world surplus of production capacity of more than 1.6 million tonnes per year in 1975/76 and it is predicted that production capacity will not be the major limiting factor on supplies that it is at present.

3.6 The Fertiliser Industry in Australia

3.6.1 Fertiliser types and production rates

The basic products of the fertiliser industry in Australia are single superphosphate, double superphosphate, triple superphosphate and ammonium phosphates. These products are sold either in this form or with the addition of one or more other materials. Table 21 gives an indication of the availability of various types of fertilisers in each State.

Production of phosphatic fertiliser is established in all States and is sufficient for Australia's current requirement. Tables 22 and 23 list the production, sales and consumption of phosphatic fertilisers for the last five years. Production of single superphosphate accounts for about 90 per cent of the total, the balance being high-analysis fertilisers based on phosphoric acid.

Australia is a major world producer and consumer of phosphatic fertiliser The figures presented in Table 16 indicate that Australia ranks as the sixth largest consumer in the world after the United States, Russia, France, China and the Federal Republic of Germany. Based on figures for production in 1969/70, Australia was the largest single producer of single superphosphate in the Western world [Department of Secondary Industry 1973].

3.6.2 Capacity of the industry

The current capacity of the industry to produce single, double and triple superphosphate is significantly greater than current demand and output. The situation also applies to ammonium phosphates in those States where production facilities are located. The existence of a certain amount of surplus capacity for superphosphate manufacture tends to be characteristic of the industry arising from the seasonal pattern of demand. The demand for phosphate fertilisers generally rises sharply in the late summer-autumn period. In these months, sales are at a substantially higher level than capacity.

The present surplus capacity arose from the installation of additional facilities by the industry to meet a high rate of increase in demand averaging some 17 per cent a year between 1962/63 and 1965/66. The fall in demand since 1966/67 has resulted from a number of factors including drought, the cost/price relationship for rural industries and imposition of wheat quotas. The current capacity of the industry is as follows:

single superphosphate	6,350,000 tonnes a year
double and triple superphosphate	254,000 tonnes a year
other high-analysis fertilisers including ammonium phosphates	660,000 tonnes a year.

The capacities of plants manufacturing phosphatic fertilisers range from about 60,000 tonnes/year to 1 million tonnes/year [Department of Secondary Industry 1973]. Economies of scale is not a serious issue for single superphosphate plants. The manufacturing process is relatively simple and the main influence on costs of production is the cost of raw materials rather than capital or overhead costs. Transport costs for the low value product are such that plant size and location are generally influenced much more by the size and location of markets.

The processes for the manufacture of sulphuric and phosphoric acid are more capital intensive and economics of scale are more important for these products.

3.6.3 The structure of the fertiliser industry

There are twelve companies which currently operate the twenty-two plants manufacturing phosphatic fertilisers. The names of these companies and the locations of their plants are given in Table 24. The main factors influencing the location of the plants are proximity to areas of greatest demand, access to a deep water port to receive imported materials, adequate rail facilities, suitable road outlets and availability of seasonal labour.

3.6.4 Trends in the use of phosphatic fertiliser

The absence of detailed statistics makes it difficult to determine trends in the use of high-analysis fertilisers. In 1968/69, sales of high-analysis fertilisers were equivalent to 400,000 tonnes of single superphosphate which represented about 10 per cent of the total sales in that year (Table 25). The growth in sales of high-analysis phosphatic fertilisers is expected to increase slowly.

The trend towards use of high-analysis fertilisers has been much less marked in Australia during the last decade than it has been in many overseas countries. Consumption of single superphosphate has generally fallen overseas, while consumption of high-analysis fertilisers has increased significantly. Probably the most important factor limiting the use of high-analysis fertilisers in Australia is the existence of a general sulphur deficiency in Australian soils. The use of superphosphate (with its sulphate content) has proved to be an effective means of countering this deficiency [Department of Secondary Industry 1973]. In addition, the relative final costs of usage of various types of fertilisers are important. Up to the present, single superphosphate has provided the cheapest method of satisfactory fertilisation in a number of areas of Australian agriculture, including pastures in particular.

High-analysis fertilisers are especially suitable for intensive cropping where greater application of fertiliser is necessary. These fertilisers can be purchased by farmers in the particular mixtures which will suit the individual requirements of each crop. However, in Australia intensive cropping accounts for a relatively small proportion of the total consumption of phosphatic fertilisers (Table 26).

Single superphosphate seems likely to remain the most important single product of the Australian industry. However, the demand for high-analysis fertilisers may continue to increase, particularly in areas of intensive agriculture [Department of Secondary Industry 1973].

3.6.5 <u>The production of phosphoric acid</u>

The production of phosphoric acid in 1968/69 was approximately 95,500 tonnes of acid (100% P_2O_5) [Department of Secondary Industry 1973]. This figure is well below the total capacity of the manufacturing plants (330,000 tonnes/year) and is directly related to the current demand for high-analysis phosphatic fertilisers.

There are five plants in Australia capable of producing wet-process phosphoric acid. The rated design capacities of the plants are shown in Table 27; these figures are only approximate as modifications have been made to some plants. On-stream time in these plants is lower than in many other industries because of significant stoppages for maintenance and servicing [Department of Secondary Industry 1973].

3.6.6 <u>Manufacturing costs and prices</u>

Detailed manufacturing costs of phosphatic fertilisers are not readily available. The Department of Secondary Industry [1973] has published an estimate of an average ex-works cost of single superphosphate (Table 28); although the date is not stated, it appears that these figures apply to the

first half of 1972.

The cost of raw materials, phosphate rock and sulphuric acid is a major component of the cost of bulk single superphosphate. The figures in Table 28 were derived by assuming:

- 0.6 tonnes of rock/tonne of single superphosphate at a cost $17.00 per tonne of phosphate rock.
- 0.37 tonnes of sulphuric acid/tonne of single superphosphate at a cost of $17.08 per tonne (100%). <u>Note</u>: This cost figure is based on factories using sulphur to make their own sulphuric acid.

From these figures, the cost of raw materials in bulk single superphosphate represents approximately 62 per cent of the total cost. Two additional costs which have to be met by the industry are associated with the upsurge of demand in the summer-autumn period. These are the need to finance stocks which are built up and kept until needed and the need to install additional handling and delivery equipment which is used for part of the year only.

The trends in prices and the current retail prices of phosphatic fertilisers in all States are presented in Tables 29 and 30. It should be noted that when comparing prices, the registered phosphorus content of single superphosphate varies between States, ranging from 8.6 per cent in South Australia to 9.6 per cent in Queensland and Western Australia [Department of Secondary Industry 1973].

The figures presented in Tables 29 and 30 indicate a sharp rise in the cost of single superphosphate from $26.50 in 1972 to approximately $45.50 ($34.87 and $11.81 bounty) in July 1974. This increase has been caused mainly by rises in the price of phosphate rock from $17.00 to $33.00 per tonne (private communication) and a tripling in the price of sulphur [Boyce *et al.* 1974]. The former increase added $9.60 per tonne to the cost of single superphosphate and the latter increase probably resulted in a doubling of the factory cost of sulphuric acid and hence an addition of $6.30 per tonne to the cost of the fertiliser product.

4. <u>RECOVERY OF URANIUM FROM PHOSPHATE ROCK</u>

The methods for the recovery of uranium during the manufacture of phosphate fertilisers are reviewed in subsequent sections. It may be economically attractive where:

- An appreciable proportion of the uranium appears in an extractable form.
- Advantage may be taken of operations common to the manufacture of

phosphatic fertiliser, and required for uranium extraction, *e.g.* crushing, grinding and acid treatment of the deposit.

- Sharing of infrastructure and services is possible.

Present technology and economics indicate that uranium can only be recovered at a reasonable cost as a byproduct from the manufacture of wet-process phosphoric acid because the dissolution of essentially all the phosphate values in the rock is necessary to effect the maximum dissolution of uranium. Recovery processes based on solvent extraction from phosphoric acid are reviewed in greater detail than other methods because of their more advanced state of development.

4.1 Concentration of Uranium in Phosphate Rock by Ore-dressing Techniques

Attempts to concentrate uranium in phosphate rock by the ore-dressing techniques of heavy liquid separations, air separation and flotation were unsuccessful because the uranium could not be physically separated [Stephan *et al.* 1950].

4.2 Recovery of Uranium from Phosphate Rock by Pyrometallurgical Techniques

4.2.1 Recovery from the furnace process

Electric-furnace treatment of phosphate rock (Section 3.4) gives very little volatilisation of uranium. Most of the uranium remains in the slag from which it can be recovered by acid leaching [Stephan *et al.* 1950; Lowe 1952; Driessen & de Saint-Charmant 1962]; however complete dissolution of the slag is required and the yield is low.

4.2.2 Recovery of uranium during the thermal processing of phosphate rock

Although the thermal treatment of phosphate rock in the presence of additives destroys the fluorapatite structure and produces a soluble phosphate (Section 3.4), the extraction of uranium is not enhanced. Roasting and sintering tests using salt mixtures and smelting tests with various fluxes were unsuccessful as essentially all the uranium remained in the slags [Stephan *et al.* 1950]. The volatilisation of uranium during heat treatment of phosphate rock was also investigated and proved to be unsuccessful [Habashi 1970].

4.3 Recovery of Uranium from Phosphate Rock by Wet-processes

Initial attempts to extract uranium selectively from phosphate rock were not successful [Stephan *et al.* 1950]. Alkaline leach methods were ineffective

and acid leaching resulted in the dissolution of uranium in approximately the same proportion as the dissolution of the phosphate rock because uranium is uniformly disseminated throughout the structure of the rock. Strong mineral acids were found to be the most effective reagents [Stephan *et al.* 1950]. In general, the most commonly used acids, sulphuric and phosphoric, leached about 80 to 90 per cent of the uranium and over 90 per cent of the P_2O_5 from uncalcined rock [Stephan *et al.* 1950].

Alter *et al.* [1958a] reported that uranium leaching from raw phosphate rock by hydrochloric acid is greatly influenced by the oxidation state of the medium. Under reducing conditions, 25 to 30 per cent of the uranium is dissolved and most remains in the undissolved residue, while under strongly oxidising conditions 75 per cent dissolved. About 75 per cent of the P_2O_5 is leached irrespective of the oxidation state of the uranium. It was also found that uranium is preferentially extracted during dilute acid leaching of calcined rock. Approximately 70 per cent of the uranium and 15 to 20 per cent of the phosphate passed into solution. The selectivity of calcined rock was thought to be due to the oxidation of the uranium in the rock and to the formation of highly soluble sodium uranate salts.

The extraction of uranium from calcined rock by carbonates, dilute mineral acids, ammonium acetate, aqueous sugar solutions and aqueous aluminium chloride was also studied by Shamgar *et al.* [1961] with limited success.

The IMI phosphoric acid process (Section 3.3.6) involves the digestion of raw phosphate rock with hydrochloric acid. A process for the recovery of uranium from the dissolution liquor is described under Other Extraction Processes in Section 4.10.4, however in another process uranium was recovered from the undissolved residue. In the latter case, acidulation of phosphate rock was carried out under reducing conditions (4 kg of iron powder per kg of rock) to give a residue containing 0.16 per cent uranium (82% of the original uranium in the rock). The residue was roasted at 700°C and the uranium was leached from it under oxidising conditions (using manganese dioxide) with hydrochloric acid to yield a solution containing 90 per cent of the uranium originally in the residue. A precipitate containing 1 to 2 per cent uranium (95% recovery) was obtained by prior reduction of the uranium and neutralising the leach liquor to pH 2 with ammonia. A concentrate of 60 to 70 per cent uranium was obtained from this precipitate through carbonate leaching and re-precipitation with sodium hydroxide. Overall uranium recovery was 50 per cent [Ketzinel *et al.* 1971].

Separation and purification of the uranium from the leach liquor was attempted by anion exchange but was abandoned because of unsatisfactory results. The estimated cost of recovery in Israel was $US27.5/kg U_3O_8 (August 1973) for an annual uranium production of 50 tonnes with the consumption of raw materials accounting for half of this cost.

The potential of the IMI phosphoric acid process as a source of uranium is limited as only 50 tonnes of uranium per year can be produced in Israel as a byproduct [Ketzinel 1972]. As a result, further research was carried out on a process to recover uranium by selective leaching from calcined rock with simultaneous upgrading of the phosphate. A process was proposed which would enable 50 tonnes uranium per year to be recovered from calcined rock [Ketzinel 1972]. This selective leaching process involved dissolution of uranium from calcined rock with acetic acid, which simultaneously removed residual calcium oxide while the phosphate remained unaffected. The acetic solution, which contained the uranium as acetate complex, was passed through an anion exchange resin. The uranium was readily absorbed and a hundredfold concentration of the recovered uranium was achieved on elution. The cost of recovering uranium by this method was estimated to be $77/kg U_3O_8 (September 1971).

4.4 Recovery of Uranium from Florida Phosphate Leached Zone

Investigations of the extraction and recovery of uranium from leached zone extracts were carried out by the International Minerals and Chemical Corporation in connection with the development of several processes for the utilisation of Florida leached zone [Heidt *et al.* 1955a]. As the processes developed for the recovery of uranium are not generally applicable to the types of phosphate deposits mined at present, they are not described in detail.

The leached zone deposits of Florida phosphate clay are associated with the phosphate pebble matrix which is mined to recover the phosphate values. Above the matrix is an overburden of leached zone material which derives its name from the loss of its calcium phosphate content by aqueous leaching. The thickness of the leached zone averages about 1.5 m but in places it is as much as 9 m. The uranium concentration (150 $\mu g\ g^{-1}$) of the leached zone material is, on average, higher than that in the pebble matrix. The leached zone overburden is discarded in normal mining operations.

The leached zone is a finely divided material of which about 30 per cent is -200 mesh. Approximately 70 per cent of the total uranium content,

most of the alumina, and a large percentage of the P_2O_5 is contained in the -200 mesh fraction (Table 31). Mineralogically, the leached zone consists of a mixture of aluminium phosphate, calcium aluminium phosphate, aluminium silicate, and smaller quantities of fine sand and finely divided calcium phosphate pebbles. The top part of the phosphate matrix is similar in chemical analysis and physical characteristics to the -200 mesh portion of the leached zone [Clegg & Foley 1958].

Extensive research and pilot plant work by the International Minerals and Chemical Corporation [Clements & McCullough 1953; Clements *et al.* 1953a, 1953b, 1953c; McCullough & Wrege 1953; Heidt *et al.* 1955a] developed three processes for treating the leached zone material.

- Process I — The products were uranium tetrafluoride, metallurgical grade alumina and ammonium phosphate fertiliser.
- Process II — The products were ammonium diuranate and ammonium phosphate fertiliser.
- Process III — The products were uranium tetrafluoride and ammonium phosphatic fertiliser.

Simplified process flowsheets are shown in Figures 5, 6 and 7.

The Tennessee Valley Authority (TVA) also studied the problem of producing uranium from leached zone material. The TVA process was similar to Process III above, except that all leached zone material, crushed to -25 mm, was used in the process. After drying and calcining, the material was reduced in size to -10 mesh and then leached with strong nitric acid and sulphuric acid. The process produced ammonium diuranate and a nitrophosphate solution was treated to produced a 20% nitrogen, 20% P_2O_5 fertiliser product [Clegg & Foley 1958].

4.5 Recovery of Uranium from Single Superphosphate

The recovery of uranium as a byproduct from the manufacture of single superphosphate has been achieved by solvent extraction of the acidulated phosphate rock in the short period before it sets to the final single superphosphate product and by recovery from the cured single superphosphate.

4.5.1 Solvent extraction from acidulated phosphate rock

This process was developed on a laboratory scale and described by Andresen & Bridger [1955]. A solution of 10 vol.% octyl pyrophosphoric acid in kerosene (the solvent) was capable of extracting 50 per cent of the uranium with a contact time of ten minutes and a solvent to rock ratio of 0.03. The addition of an oxidising agent to the rock had a beneficial effect on uranium recovery. Of the two extraction techniques studied, the first used acidulation corresponding to that employed commercially to prepare superphosphate and the solvent was mixed with the acidulated rock slurry and then the phases were separated. In the second, the above procedure was repeated with an initial acidulation commonly used to produce wet-process phosphoric acid. When this process was used, the aqueous phase separated into two layers, a slurry of acidulated rock on the bottom and a clear liquid above. After the solvent was removed, sufficient additional phosphate rock was added to the aqueous phase to produce superphosphate as the final product.

A major problem in this process was the loss of solvent to the freshly acidulated rock in sufficient amounts to make the cost of uranium recovery prohibitive. Another problem was the instability of the octyl pyrophosphoric acid solvent which would make recycling a difficult proposition. Methods of stripping the uranium from the solvent were not investigated.

4.5.2 Recovery from cured superphosphate

A process was developed at the Battelle Memorial Institute in which cured single superphosphate prepared from calcined rock was leached with water to recover 85 to 90 per cent of the uranium [Stephan *et al.* 1950].

The process involved the following steps:

1. Calcination of the phosphate rock at 1000°C for 30 minutes (to improve the extraction of uranium from 30 to 90 per cent).
2. Manufacture of superphosphate.
3. Countercurrent leaching of the superphosphate with water.
4. Addition of metallic iron to the resulting solution to remove uranium in a 2 to 4 per cent precipitate; iron was an effective precipitant at pH 2, but recovery dropped to less than 10 per cent at pH 1.5.
5. Evaporation of the uranium-free solution to obtain monocalcium phosphate, or evaporation of the solution with the residue from the leaching operation to obtain a product similar to the original superphosphate.

The major disadvantage of this process was the dissolution of 89 to 98 per cent of the phosphate during the leaching step which must be recovered by a relatively expensive evaporation step.

A similar process was also developed but not fully investigated in which uranium was recovered from the superphosphate leach solution (monocalcium phosphate solution) by solvent extraction [Heidt *et al.* 1955b].

This process was also applicable to wet-process phosphoric acid.

Attempts were made to recover uranium from superphosphate leach solutions by adsorption on carbon but were not successful [Igelsrud & Stephan 1949].

Long & Valle-Riestra [1953] studied a process on a laboratory scale for the recovery of up to 80 per cent of the uranium in the cured superphosphate product [Long *et al.* 1956]. The process consisted of:

1. Adding 2 to 3 kg of nitric acid per tonne of roasted ore in the original acidulation step.
2. Extracting the uranium from the superphosphate after curing completely and grinding to -50 mesh by percolation with a 1 to 2 vol.% solution of octyl pyrophosphoric acid (OPPA) in hexane at about a 1:1 ratio of organic to ore.
3. Washing the solids with fresh hexane to remove entrained OPPA.
4. Heating the solids to recover hexane, the drying temperature not exceeding 80°C in order to prevent decomposition of the superphosphate.
5. Stripping the uranium from the loaded OPPA.

Although a high ratio of solvent to ore was required, a concentration of 2 vol.% OPPA in the solvent was sufficient and only brief contact times were required. After treatment by this procedure, superphosphate was found to have the same weight and P_2O_5 analysis, however no agronomic tests of the material were made.

The uranium was stripped from the solvent with either hydrofluoric acid (the best reagent), hydrochloric acid or aqueous polyphosphates. Ferrous sulphate was added to the solvent during the precipitation step to reduce the uranium so that insoluble UF_4 was formed. The solvent was then recycled (Figure 8) after the addition of make-up OPPA to compensate for loss of extracting power (due to hydrolysis) during stripping.

This process had a substantial economic disadvantage because of the high loss of organic solvent to the superphosphate. Raw material costs were estimated to account for 25 per cent of the uranium recovery cost. Such losses are difficult to avoid in any method where the solvent has to be contacted with the entire mass of rock.

The leaching or uranium from superphosphate with saturated calcium phosphate solutions was also investigated [Barnard 1950]. Uranium recoveries from 14 to 55 per cent were obtained under ideal conditions but the process was abandoned because of many practical difficulties.

4.6 Recovery of Uranium from Triple Superphosphate

Two methods were developed to recover uranium from triple superphosphate fertiliser which were similar to those described for the treatment of cured single superphosphate (Section 4.5.2), *i.e.* water leaching of the superphosphate and subsequent evaporation to reconstitute the solid fertiliser [Stephan *et al.* 1950] or recovery of uranium from the superphosphate by solvent extraction.

Triple superphosphate was found to be more amenable to solvent leaching than single superphosphate and the addition of nitric acid to the initial acidulation step was not necessary [Long & Valle-Riestra 1953]. However, the disadvantages of these processes were the same as for the single superphosphate processes.

4.7 Recovery of Uranium from Ammonium Phosphates

The recovery of uranium as a byproduct of the manufacture of ammonium phosphate fertilisers has not received a great deal of attention because uranium can be recovered from the wet-process phosphoric acid before ammoniation and secondly, the production of ammonium phosphate fertilisers has only assumed significance since the intense period of investigation of phosphate fertilisers as a source of uranium.

Stedman & Arkless [1957] proposed a method in which uranium, iron and aluminium were precipitated during the first stage of neutralisation of phosphoric acid with ammonia. Neutralisation was carried out in the normal manner initially to precipitate iron and aluminium. After filtration, a reducing agent (sodium hydrosulphite or ammonium formaldesulphoylate) was added, together with a filter aid, resulting in the precipitation of uranium. This method is identical to that used to produce technical grade phosphates (with uranium as byproduct) from wet-process phosphoric acid developed by the Blockson Chemical Company [Metziger *et al.* 1956; Stoltz 1958]. The process developed by the Blockson Chemical Company is described in Section 4.10.2.

4.8 Recovery of Uranium from Monocalcium Phosphate

The monocalcium phosphate process was developed to eliminate the evaporation step needed in the superphosphate process and to make all of the uranium in phosphate rock available for recovery [Igelsrud *et al.* 1949]. In contrast, recovery from phosphoric acid during the manufacture of triple superphosphate is limited to a maximum of approximately 67 per cent of the uranium in all the rock processed.

The process consisted essentially of the following steps:

1. Digest calcined rock with hot (93°C) 40 to 50 per cent phosphoric acid (acid to rock ratio of 4:1) to dissolve the P_2O_5 (94%) and uranium (95%), then filter off the gangue.
2. Reduce the solution with iron filings then precipitate the uranium (90%) from a hot solution with a fluoride compound.
3. Cool the uranium-free solution to crystallise the monocalcium phosphate.
4. Remove the monocalcium phosphate for use as a fertiliser.
5. Acidify the saturated mother liquor with sulphuric acid to convert the remaining monocalcium phosphate to phosphoric acid.

In this process, the fluoride precipitation step was very costly, the precipitate was too low in uranium (0.1 to 0.2%) and the physical form of the precipitate made washing and filtering very difficult. In addition, the yield of crystalline monocalcium phosphate was poor, the fertiliser product was diluted with mother liquor and uranium was removed from solution when the monocalcium phosphate crystallised. The process also had the disadvantage of requiring modifications to existing practice in the fertiliser industry.

A second process was proposed in which 90 per cent of the P_2O_5 and 80 to 90 per cent of the uranium were leached from uncalcined rock by countercurrent contact with 25 to 30 per cent sulphuric acid to produce a solution which was principally monocalcium phosphate [Stephan *et al.* 1950]. The uranium was then removed following the first process steps; however, the process did not offer significant advantages over recovery from wet-process phosphoric acid.

4.9 Recovery of Uranium from Dicalcium Phosphate

Dicalcium phosphate fertiliser is usually manufactured by dissolving phosphate rock in nitric acid and neutralising the resulting slurry with ammonia (Section 3.3.5). Uranium can be recovered from the phosphoric acid solution before the neutralisation step by extraction with tributyl phosphate in kerosene and precipitation with ammonia [Clements *et al.* 1953d]. This basic method was developed during the study of leached zone material (see Section 4.4, Process III).

In Israel, dicalcium phosphate has been produced by the leaching of phosphate rock with a mixture of hydrochloric and sulphuric acids. Monocalcium phosphate solution is formed initially but the addition of lime precipitates dicalcium phosphate and forms calcium chloride. Alter *et al.*

[1958b] reported the development of a process for the recovery of uranium from the monocalcium phosphate solution. The process involved the electrolysis of this solution resulting in the deposition of uranium on the cathode. Cathodes of copper wire mesh were the most effective and 90 to 95 per cent of the uranium was precipitated. Uranium was stripped from the loaded cathode with phosphoric acid, and the time required for total stripping was 150 hours.

A major disadvantage of the process was that the initial acidulation had to be under oxidising conditions to obtain 80 to 90 per cent dissolution of uranium. Approximately 46 kg of chlorine gas was consumed per kg of uranium recovered to achieve these conditions. Apart from the cost of chlorine, the economics of the process was not favourable. In addition, extensive pilot plant work would be required in a full test of some of the process operations.

4.10 Recovery of Uranium from Wet-process Phosphoric Acid

In the USA at present, the processing of wet-process phosphoric acid is the preferred method of recovering uranium as a byproduct of the manufacture of phosphatic fertilisers. The distribution of uranium during the manufacture of wet-process phosphoric acid in two plants was investigated by Nadig & Burnet [1962]. Approximately 75 to 80 per cent of the uranium entering in the phosphate rock was found in a recoverable form in the product acid at both plants. The remainder was found in two waste streams; the gypsum from the filters and the water from the fume scrubbers.

The recovery of uranium from phosphoric acid solutions was found to pose many problems. Precipitation, adsorption and neutralisation techniques, ion exchange and solvent extraction were investigated extensively before solvent extraction emerged as the most successful method.

4.10.1 Precipitation and absorption techniques

The search for a suitable precipitating agent for uranium in phosphoric acid solutions (pH 0.2 to 0.6) involved a large number of inorganic and organic reagents. The most promising were bismuth, antimony, fluoride and oxalate compounds, all of which prepcipitated 90 per cent or more of the uranium from solution. However, the processes were involved, required excessive quantities of reagents, and produced low-grade precipitates. The large amount of phosphate, with its complexing action, and other extraneous components prevented the development of an inexpensive, simple and effective precipitation process. In all precipitation tests, reduction of the solution

was necessary to obtain uranium recovery and iron was suitable for this purpose [Stephan *et al.* 1950]. Comprehensive results of precipitation tests are presented by Bailes [1949a, 1950], George [1950] and Stephan *et al.* [1950].

Dasher *et al.* [1950] showed that finely ground monazite removed 75 to 80 per cent of the uranium from dilute phosphoric acid in one step and if the acid was reduced and re-treated with monazite, 92 to 97 per cent of the uranium was recovered. However fine monazite was unfilterable and coarse monazite was required in prohibitive amounts. As an alternative to physical handling, tests with granular monazite in a column were made but the results were not encouraging.

The adsorption of uranium from wet-process phosphoric acid solutions by activated carbon alone was found by Igelsrud & Stephan [1949] to be completely ineffective.

4.10.2 Neutralisation methods

Neutralisation techniques are not suitable for the extraction of uranium from wet-process phosphoric acid if the neutralising step interferes with the process of producing fertilisers. Hence, neutralisation techniques have been only applied in the manufacture of ammonium phosphates (Section 3.3.3) and technical grade phosphate chemicals. A process was developed on a laboratory scale for the recovery of uranium from wet-process acid by reduction and neutralisation with ammonia. The resulting solution was evaporated to produce monoammonium phosphate [Frohling *et al.* 1948; Clevenger 1950]. The process was later adapted for commercial application by the Blockson Chemical Company.

Although ammonia is usually used in neutralisation processes, potassium or calcium hydroxides also precipitate reduced uranium effectively from phosphoric acid [Woody & Clevenger 1950]. When potassium hydroxide was added to phosphoric acid, the first precipitate formed was mainly silicofluoride containing little uranium. On adding more potassium hydroxide, the uranium precipitated more completely and at a lower pH than when ammonia was used. The fertiliser product was monopotassium phosphate. This process, although metallurgically superior, was not as economically attractive as the ammonium phosphate process. The precipitates obtained using lime were of lower grade than those obtained with the soluble alkali as the lime was not fully utilised.

The first commercial plant to recover uranium as a byproduct from the processing of phosphate rock (1500 tonnes of phosphate daily) was built in

Illinois by the Blockson Chemical Company in 1952. This company produced technical grades of sodium phosphate which were required to meet strict purity specifications. As this process has a restricted field of application, only the essential features will be described. A detailed account of the development of the process is given by Stoltz [1958].

The method employed for uranium recovery began with the partial neutralisation of wet-process phosphoric acid to form monosodium phosphate at a pH of 4-5. The bulk of the impurities, largely calcium, iron and aluminium phosphates and silicates were precipitated at this stage and were filtered off. The addition of a strong oxidising agent, such as chlorine, to the acid prior to the neutralisation step resulted in retention of about 80 to 90 per cent of the uranium in solution. After filtration, the addition of sodium hydrosulphite to the filtrate precipitated 90 to 95 per cent of the uranium in solution as a gelatinous uranous phosphate. This product was filtered off after addition of diatomaceous earth as filter aid and upgraded by a simple procedure to a product containing 40-60% U_3O_8. Evaluation of the process indicated that 60 to 70 per cent of the uranium in the phosphate rock could be recovered at a very reasonable cost.

The phosphate rock was calcined as a pre-treatment to eliminate organic constituents which could not be tolerated in the sodium phosphate. The calcination step reduced the recovery of the uranium from the rock in the acidulation step which was partially improved by calcining under the best possible oxidising conditions. This method gave a recovery of 85 per cent of the uranium content of the rock compared with above 90 per cent without calcination.

Although this method produced a lower uranium recovery than solvent extraction, it has considerable merit in such areas as simplicity of control, cost of installation and reagent requirements and consumption [Kennedy 1967].

The possibility of recovering uranium by ion exchange and solvent extraction techniques was also investigated by the Blockson Chemical Company. Solvent extraction with organic phosphates achieved good uranium removal but complete phase separation could not be obtained. The 1 per cent organic phosphate that remained in the phosphoric acid caused the formation of stable foams during the neutralisation step which would have caused serious processing troubles in the plant. All available ion exchange resins were found not to have the required specificity for uranium ions.

4.10.3 <u>Ion exchange methods</u>

A process for the recovery of uranium by ion exchange methods was developed at the Dow Chemical Company [Bailes 1949b; Hirschkind & Bailes 1950; Garrett & Moore 1952; Garrett 1952]. It was found that uranium may be recovered from phosphoric acid solutions by oxidising the uranium to the uranyl state to form a uranyl phosphate anion and selectively adsorbing this anion on an anionic exchange resin. Resins which have quaternary ammonium re-active groups were found to be the most effective. When the resin was loaded, uranium was eluted with a small volume of a dilute acid. Eluting agents which gave satisfactory recoveries were dilute hydrochloric, nitric and sulphuric acids, mixtures of dilute sulphuric acid with sulphates, chloride solutions, chloride solutions preceded by treatment with sulphur dioxide gas, dilute sulphuric acid solutions containing hydrazine and hydroxylamine salts and hydrogen sulphide gas in conjunction with dilute sulphuric acid [Long *et al.* 1956].

4.10.4 <u>Recovery of uranium by solvent extraction</u>

The selection of the organic solvent is the most critical feature of the solvent extraction process. The alkyl pyrophosphate esters were found to have the most favourable extraction coefficients of the many solvents tested (Table 32) and a high selectivity for uranium over various contaminants. Pyrophosphates with relatively long chain alkyl groups are virtually insoluble in water but completely miscible in hydrocarbon diluents such as kerosene. Compounds made with alcohols ranging from 4 to 17 carbons have been tested. The extracting power per mole of ester increases with increasing chain length up to 12 carbons but, for economic reasons, octyl and decyl esters have been used most extensively.

Octyl pyrophosphoric acid (OPPA) was the solvent initially selected for pilot plant investigation. It was prepared by the reaction of capryl alcohol (2-octanol) and phosphorus pentoxide:

$$2C_8H_{17}OH + P_2O_5 \rightarrow C_8H_{17}O\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}OC_8H_{17}$$

Unfortunately OPPA is chemically unstable and tends to hydrolyse readily to octyl orthophosphoric acid (OPA) which is a less effective extractant by a factor of at least ten. The hydrolysis is accelerated in the presence of strong acids and by increased temperatures. The uranium extraction coefficient of the active solvent also varies with temperature in the range 27 to 55°C, being substantially less at higher temperatures. It was also found that reduction of the acid from an emf of -0.30 to 0.0 V increased the extraction coefficient of OPA solutions over ten times and that of OPPA solutions over twenty times [Ellis 1952]. A mechanism for the extraction of uranium by OPPA was proposed recently by Habashi [1970]. The results of this work, performed under laboratory conditions, do little more than confirm the earlier and more extensive investigations of Ellis [1952].

The basic process developed for the recovery of uranium from phosphoric acid consisted of:

1. Contacting the acid with a 1-2 vol.% solution of an alkylpyrophosphate in kerosene.
2. Separating the phases.
3. Recovering the uranium from the solvent as a fluoride salt by precipitation with hydrogen fluoride.
4. Re-using the solvent on a continuous basis with a required amount of fresh solvent makeup.

The above process was investigated extensively in the laboratory, followed by pilot plant testing and construction of an industrial size plant in Florida by the International Minerals and Chemical Corporation. Detailed descriptions of the laboratory work have been presented by Ellis [1952] and Heidt *et al.* [1955b].

The IMC plant and process

In spite of prior pilot-plant experiences, considerable difficulty was encountered with the operation of the commercial-scale plant of the IMC process which was described in detail by Greek *et al.* [1957].

The flowsheet of the plant is shown in Figure 9. The basic steps were essentially:

1. Phosphoric acid cooling and clarification.
2. Reduction of uranium with scrap iron.
3. Solvent extraction.
4. Uranium re-extraction and precipitation.
5. Reagent preparation.
6. Product drying and packaging.

Acid production

The initial acidulation released about 70 to 90 per cent of the uranium

in the concentrated rock and yielded a uranium concentration in the phosphoric acid which averaged about 0.0165% U_3O_8. The crude phosphoric acid (Table 33) was received at the uranium recovery plant at 54 to 67°C and was cooled by air in cooling towers to a temperature of 43 to 49°C. The acid then went to a settling tank to remove any solids and was percolated through reduction pits containing scrap iron to reduce the uranium to the tetravalent state.

Reduction

The reduction pits had to be taken offline every 2 to 3 weeks for cleaning [Kennedy 1967] because the stationary bed of scrap iron passivated rapidly owing to the formation of an adherent coating of an iron phosphate and gypsum. The pits were replaced by a rotary stainless steel drum operated in the same manner as a ball mill. The attrition provided in the mill kept the iron surfaces clean and effectively reduced the emf of the solution to the desired figure of 0.0 V. Electrolytic methods have been proposed for the reduction of phosphoric acids to eliminate the introduction of iron into solution [Dickert & Kirk 1952; Flaschenberg *et al.* 1958]. Investigation of these methods did not progress beyond the laboratory stage.

Solvent extraction

Several different types of equipment for solvent extraction were tried. Only centrifuges proved satisfactory for separating the organic from the aqueous phase. Pulse columns and mixer-settlers were unsuitable because of severe emulsion problems. The emulsion problem was never completely solved even by the use of centrifuges and, under the best conditions, the kerosene loss was about one per cent of the volume of acid treated. The extraction process was a two-stage countercurrent liquid-liquid extraction with an organic to aqueous phase ratio of about 1:9. After the extraction step, the pregnant liquor was contacted with 25 per cent sulphuric acid to remove calcium from the solution.

Calcium removal was necessary as this and other metal ions are also complexed by the pyrophosphate ester. The minimum circulation of metal ions through the process was essential for maximum uranium recovery and smooth operation of the plant. If too much calcium remained to be complexed by the ester, the extraction coefficient of the ester was reduced. In addition, emulsions tended to be stabilised by increased amounts of suspended solids, much of it gypsum, which collected at the organic-aqueous interface.

The solvent used at the International Minerals plant was produced from 'decyl alcohol'. The alcohol, mixed with about an equal volume of kerosene, was reacted with P_2O_5 in water-cooled jacketed tanks in which the temperature of the exothermic reaction was kept below 68°C. At higher temperatures, serious decomposition of the solvent occurred. The solvent inventory in the plant was recycled about every 24 hours. Under these conditions, the loss of the pyro-ester through degradation and other causes was about one-third of the inventory per cycle. After a period of recycling in which pyro-ester was maintained at a concentration of about 5 vol.%, the concentration of the alkyl orthophosphoric acid was 10 vol.%, and the total phosphate content of the organic phase was about three times the level in fresh solvent. In practice, it was possible to obtain uranium concentrations of about 1 g U_3O_8/litre in loaded solvent from a concentration of 0.15 to 0.22 g/litre in the feed phosphoric acid.

Uranium was removed from the loaded solvent by a single-stage stripping operation using a 12 per cent solution of hydrofluoric acid or a mixed acid containing 25 per cent sulphuric and 12 per cent hydrofluoric acid. The proportions of acid and organic complex were adjusted to maintain an excess concentration of fluoride ion (15 to 30 times the stoichiometric quantity). The rapid and accurate analysis for fluoride ion in a mixture of hydrofluoric, sulphuric and phosphoric acids was essential to the control of the precipitation step.

<u>Precipitation of uranium tetrafluoride</u>

The mixture from the contacting tank passed to a settling and decanting tank. The precipitated uranium tetrafluoride settled to the bottom from where it and some solution were withdrawn and transferred to a solid bowl centrifuge. Under normal conditions, the centrifuge bowl filled with uranium tetrafluoride in ten to twelve hours. The centrifuge was then shut down for half to one hour to allow the cake to be removed.

After drying, the product was sent to a USAEC installation for further processing. The final product composition varied widely because of the many variables in the processing operation. Typically, the product contained 40-60% U_3O_8, 12-15% fluorine, up to 5% calcium, significant amounts of iron, aluminium, magnesium, sodium, potassium, thorium and yttrium, plus silica and phosphates. Because of the high fluoride content, the product was not fed directly to a refinery circuit; instead it was fed into a multiple hearth roaster to be converted to an oxide. The recovery of uranium from the phosphoric acid feed to the plant varied widely. After 18 months of operation, the plant was expected to have a realistic maximum recovery of

75 per cent of the uranium in the feed.

In an appraisal of the IMC process, Kennedy [1967] emphasised the following points that should be considered in the evaluation of future commercial processes. The solvent extraction process for recovery of uranium from wet-process phosphoric acid is difficult to control because of the wide fluctuation in the uranium concentration in the phosphoric acid feed to the plant. Variations of as much as 50 per cent in the uranium concentration of the daily composite samples of the feed acid, *e.g.* 0.15 to 0.23 g U_3O_8/litre, were quite common despite blending of the ore stockpiles. Since the concentration of the uranium in the feed acid was not subject to control, the plant could have been operated for:

1. Maximum solvent loading and thereby achievement of minimum reagent consumption at the risk of losing some recovery if the uranium concentration in the feed rose rapidly and exceeded the uranium capacity of the solvent.
2. Maximum uranium recovery by circulating sufficient solvent to prevent saturation capacity being reached.

The latter mode of operation proved the more economical because the higher recovery achieved actually lowered the average reagent consumption per kilogram recovered and greatly simplified keeping the various flows in balance.

Oak Ridge solvent extraction processes

A program was initiated in 1967 at ORNL to develop an improved solvent extraction process for the recovery of uranium. The disadvantages of the existing IMC process which warranted improvement were considered to be [Hurst *et al.* 1969]:

1. The extracting reagent (an alkyl-pyrophosphate ester) was unstable and could only undergo limited recycle.
2. Phase separation using this solvent was very poor.
3. The uranium must be recovered from the solvent by a hydrofluoric acid stripping step which is expensive and produces a relatively refractory, low-purity product.

<u>Selection of reagent</u>

A large number of reagents were tested for their ability to extract uranium from phosphoric acid. The synergistic extractant combination of di(2-ethylhexyl) phosphoric acid (D2EHPA) plus trioctylphosphine oxide (TOPO) dissolved in an aliphatic diluent showed the most promise. A detailed account of the factors influencing the extraction coefficient of this reagent was presented by Hurst *et al.* [1969]. For this extractant to be effective, the uranium must be in the hexavalent form. It was found that in fresh acid only a small fraction of the total iron is in the reduced state, and about 50 per cent of the uranium is present as U(IV). The conversion of all uranium to the oxidised state was accomplished by the addition to the acid of one-sixth mole of sodium chlorate per mole of ferrous iron.

Extraction

A complete process flowsheet using this extractant was developed and tested successfully on a bench scale [Hurst *et al.* 1972]. The process flowsheet (Process I) consisted of two cycles (Figure 10). In the first cycle the oxidised acid was cooled to 40 to 45°C, and the uranium was extracted with 0.5 *M* D2EHPA - 0.125 *M* TOPO in an aliphatic diluent. Uranium was recovered from the solvent by contacting it with a phosphoric acid solution containing ferrous iron which reduced the uranium to the less extractable tetravalent state and effected its transfer to the aqueous phase. An inert atmosphere was provided in the stripping units to prevent air oxidation of the strip solution. Under the proper conditions, uranium strip solutions containing about 12 g of uranium per litre (about a factor of 70 richer in uranium than the original acid) were readily obtained.

In the second cycle, the uranium in the first-cycle strip solution was oxidised to the hexavalent state and then extracted with 0.3 *M* D2EHPA - 0.075 *M* TOPO. At least half of the acid raffinate was recycled for further stripping and the balance was returned to the first-cycle extractor to recover any uranium remaining in the solution.

The use of the reductive strip in the first cycle to produce a solution concentrated in uranium allowed re-extraction and stripping of the uranium under more favourable conditions. In addition, the low concentration of uranium in the acid feed to the first cycle limited the amount of uranium that could be loaded into the organic phase. However, in the second cycle the solvent was efficiently loaded because of the higher uranium concentration. The two-cycle operation resulted in a 95 per cent recovery of uranium from the acid compared with an average recovery of 82 per cent in the absence of a reductive strip section [Hurst & Crouse 1973].

The two-cycle process was run continuously with wet-process acid (types A and B, Table 34) using mixer-settlers for periods equivalent to about 40 cycles of the solvent through the stripping section without any significant change in performance. Phase separation in all systems of both cycles was satisfactory. Solids accumulated at the aqueous organic interface but did

not interfere with the operation. For commercial operations, provision would be needed for the periodic removal of solids.

Precipitation and Calcination

The organic extract was scrubbed with water to remove extracted phosphoric acid and then stripped with an ammonium carbonate solution under conditions that resulted in direct precipitation of the uranium as rapid filtering ammonium uranyl tricarbonate (AUT). The AUT was calcined to U_3O_8. The AUT precipitate analysed as 12.7% NH_3, 44.9% U, and 34% CO_3 after being washed and then air-dried. Calcination of the air-dried precipitate for two hours at 600°C yielded a product that analysed as 97.5% U_3O_8, 0.5% Fe, 0.06% PO_4, 0.5% CO_3, 25 $\mu g\ g^{-1}$ Ti, 40 $\mu g\ g^{-1}$ V, and 0.7 $\mu g\ g^{-1}$ Mo.

The total reagent costs for the process were estimated to be less than \$2.2/kg U_3O_8. Since the major cost is that of the relatively expensive solvent (over half the total cost), the solvent losses must be kept at a tolerable level. Solvent losses under the laboratory conditions were less than 0.01 per cent of the acid volume.

The high cost and non-availability of TOPO in commercial quantities are serious disadvantages of the ORNL process, and a mixture of octylphenylphosphoric acid and TBP in a kerosene diluent has been suggested as a suitable and much cheaper alternative [Murthy, Pai & Nagle 1971; Dar *et al.* 1972; Murthy 1972]. In a countercurrent process, 90 per cent of the uranium in reduced phosphoric acid was extracted and the solvent was found to be chemically stable after considerable recycling. The process was examined in bench-scale tests using a two-cycle process similar to the ORNL process. A solvent loading of 3 g U_3O_8/litre was obtained in the second stripping stage. The uranium was stripped from the solvent with hydrogen fluoride to obtain a crude fluoride precipitate containing about 30 per cent U_3O_8 [Dar *et al.* 1972].

In view of this development, an alternative first-cycle process that uses a commercial mixture of mono- and dioctylphenylphosphoric acids as the extractant was investigated at ORNL [Hurst & Crouse 1974]. This solvent has a higher extraction coefficient for uranium than D2EHPA-TOPO and extracts uranium(IV), usually the prevailing oxidation state of uranium in fresh wet-process acid, thus eliminating the liquor oxidation step required in process I (Figure 10). The D2EHPA-TOPO solvent was still used in the second step to produce a high grade U_3O_8 concentrate.

The proposed process (process II) is shown in Figure 11. Uranium was recovered from the first-cycle solvent by contacting it with 10 *M* H_3PO_4

containing sodium chlorate to oxidise the uranium to the less-extractable hexavalent state and effect its transfer to the aqueous phase. The strip solution was loaded with up to 15 to 20 g ℓ^{-1} of uranium (a factor of 100 or more richer in uranium than the original acid). After dilution to 6 *M* H_3PO_4, the strip solution was highly amenable to treatment in a second cycle using the D2EHFA-TOPO solvent. Calcination of the precipitated AUT at 600°C yielded a product that contained > 98% U_3O_8, 0.5% Fe, 0.02% PO_4, 1 μg g^{-1} Ti, 3 μg g^{-1} V, 0.8 μg g^{-1} Mo and < 1 μg g^{-1} rare earths.

The first-cycle flowsheet was demonstrated continuously with the solvent subjected to about 80 complete extraction-stripping cycles. 'Green' (made from calcined rock) and 'brown' (typical) wet-process phosphoric acids were used during this test (Table 34). Uranium recoveries were 98 and 90 per cent, respectively, in the extraction stage and 98 per cent or more in the stripping stage. The solvent showed no appreciable loss of extraction power with cycling and was sufficiently stable for process use. During the processing of 'green acid', operation was smooth and there was essentially no buildup of solids at the aqueous-organic interface. With 'brown acid', results were much more variable. When the feed contained dispersed solids, most of the solids accumulated at the interface and the settlers flooded rapidly. However, with filtered feed, operation was satisfactory.

Total chemical reagent costs were estimated to be less than $2.2/kg U_3O_8 for 95 per cent overall uranium recovery when processing 'green acid' containing 0.12 g U_3O_8/litre. The solvent loss was assumed to be 0.03 per cent of the total acid volume. For 'brown acid', it was concluded that more extensive continuous tests were required to determine the degree of acid clarification needed for tolerable solvent losses.

Gulf Research and Development Corporation and Uranium Recovery Corporation processes

The ORNL process was modified and improved by the Gulf Research and Development Corporation who announced in April 1974 the successful operation of a demonstration 'mobile pilot' plant for uranium recovery from wet-process phosphoric acid. It is believed that this new system would be commercially profitable even with a price of yellowcake in the vicinity of $US15.4 - 17.6/kg U_3O_8. The company has estimated that there is a potential in Florida for an annual yellowcake production of 3,000 tonnes for the next 50 years, based on the ability of the Gulf process to recover about 96 per cent of the available uranium [Nucleonics Week 1974a].

The demonstration unit was mounted on two enclosed truck trailers which were to be transferred to a number of Florida phosphate plants to assess the performance of the recovery process under varying conditions. The first commercial recovery plants were to be under design and construction by 1975 and in production by late 1975 or early 1976.

Another article [Byrne 1974b] reports the plans of Uranium Recovery Corporation (URC) who were scheduled to put into operation early in 1975 a commercial plant to recover uranium from a phosphoric acid plant at Bartlow, Florida. The URC extraction method differs from the Gulf technique, although both are to recover the uranium from wet-process acid. The URC process involves establishment of a network of recovery modules at various phosphate plants in central Florida, and trucking uranium bearing material from the modules to a central processing refinery at Mulberry, Florida, where uranium oxide will be recovered from the solvent. The refinery was scheduled for startup early in 1975 at a capacity of 900 tonnes per year of uranium concentrates.

Other extraction processes

The recovery of uranium by solvent extraction using a reagent of 7 vol.% dodecylphosphoric acid in kerosene was investigated by Deleon and Lazarevic [1971]. A process was proposed which involved the removal of fluorides from the acid, reduction of the acid, solvent extraction and stripping the uranium with phosphoric acid and recovery of the uranium by oxidation, neutralisation and precipitation steps. The precipitate contained from 4-12 per cent uranium and the overall uranium recovery from the acid was 83 per cent. The method was designed to become an integral part of the process of tripoly-phosphate production. From the data available, this process has little chance of success.

A solvent extraction process [Ketzinel *et al.* 1972] was developed to operate in conjunction with the IMI phosphoric acid process (Section 3.3.6). The uranium recovery process was based on extracting the uranium from the recycle stream of the purification step (Figures 12 and 13). In the extraction battery, most of the uranium and other impurities were co-extracted with the phosphoric acid. The loaded organic was then scrubbed with a small stream of purified dilute phosphoric acid in order to back-extract impurities. Most of the uranium was also back-extracted. As this recycle stream was small, an effective concentration of uranium in the stream was obtained to about 300 mg ℓ^{-1} compared with 40-50 mg ℓ^{-1} in the original acidulated solution. It was suggested that uranium could be easily extracted from the recycle stream with OPPA.

A preliminary design and feasibility study for a plant to produce 40-50 tonnes/year of uranium showed [Ketzinel 1972] that uranium could be recovered by extraction with OPPA at a cost of \$15.4/kg U_3O_8 (September 1971). The application of this process is obviously limited to the IMI process and some doubt must exist about the economics of using OPPA as an extractant.

4.11 Comparative Recovery Costs

During the early investigations to determine the feasibility of recovering uranium as a byproduct during the manufacture of phosphatic fertilisers, tentative recovery costs were estimated (Table 35). Much of this costing was based on the results of laboratory investigations and involved assumptions which would need to be verified in pilot plant work. Because of these factors and the time that has elapsed since these costs were estimated, no attempt has been made to update these figures or assess their current validity. However, they do serve to indicate the unfavourable economics of recovering uranium by some methods. In some cases, relatively attractive costs were estimated by allowing credit for the upgrading of the fertiliser. The merits of such processes would have to be contrasted with the usual process for producing the upgraded product; for instance, the fertiliser industry may not be willing to accept a more complicated process. In addition, a suitable market would have to be found for the upgraded product.

Table 36 lists the reported uranium recovery costs for processes developed recently in the USA and Israel. Critical comment on these costs is not possible as a breakdown of costs or sufficient information concerning plants and processes is not available. Commercial interest in the recovery of uranium from phosphates is not confined to the above countries. The USSR is reported recently to have offered aid to Morocco for a feasibility study on extracting uranium from newly discovered Moroccan phosphate deposits. As a result of these finds, Morocco is raising its output of phosphates to 27 million tonnes in 1977 and 45 million in 1981 [Nucleonics Week 1974b].

5. APPRAISAL OF URANIUM RECOVERY FROM PHOSPHATE ROCK

The recovery costs for uranium as a byproduct during the manufacture of phosphate fertiliser from phosphate rocks are least when the fertiliser process involves the manufacture of wet-process phosphoric acid, from which the uranium may be extracted. Recovery from a wet-process phosphoric acid stream, when integrated with phosphate fertiliser manufacture, appears

commercially viable even with a market price for uranium as low as \$US15.4 - 17.6 per kg for yellowcake. Significantly greater costs are involved in recovery from the relatively simple (and widely employed in Australia) manufacture of single superphosphate. Processes developed in Israel could offer alternative methods, however these are only applicable to types of re not normally suitable for fertiliser manufacture.

Unless further low cost reserves of uranium are discovered, increases in the world price of yellowcake could lead to either:

(a) a tendency towards a greater proportion of phosphate rock being processed to phosphoric acid to allow uranium recovery, or

(b) a sufficient increase in the cost of uranium to make an alternative process usable (*e.g.* uranium recovery from single superphosphate). The choice of options in integration will require a detailed study.

The figures presented in Table 11 show that a maximum of 7,963 tonnes of uranium was present in the phosphate rock mined in 1972. A reliable estimate of the percentage of this rock which was converted to phosphoric acid is not available. In any case it is probably more useful to consider a maximum amount based on present trends in the industry. The production of high-analysis fertilisers (requiring the production of phosphoric acid) in proportion to the total production of phosphatic fertilisers is greater in the United States than in most other countries. Approximately 60 per cent of the rock used in that country is converted to phosphoric acid at present [Slack 1971].

The results reported by Greek *et al.* [1957], Nardig & Burnet [1962] and Hurst *et al.* [1972] indicate that approximately 85 per cent of the uranium in phosphate rock is found in wet-process phosphoric acid and 95 per cent of this quantity can be recovered by solvent extraction and precipitation. Based on figures of 60 per cent conversion to phosphoric acid and 80 per cent overall recovery from the rock, estimates have been made of the maximum amount of uranium recoverable from phosphate for current world production figures. These results are presented in Table 37 and indicate that approximately 3,820 tonnes of uranium is potentially available per year. By comparison, the total estimated Western World production of uranium by conventional methods was 20,000 tonnes of uranium in 1972. The phosphate deposits in the United States could yield (on the basis of Table 37) 2,419 tonnes per year of uranium. This figure compares favourably with other recently published estimates of:

(a) A potential production of 2,468 tonnes per year of uranium, based on current phosphoric acid production in Florida and the ability of the Gulf process to recover about 96 per cent of the available uranium [Nucleonics Week 1974a].

(b) 2,308 tonnes per year of uranium 'now pour out of US phosphoric acid plants' [Byrne 1974b].

The production of phosphoric acid in Australia for 1969-1970 was reported as 95,500 tonnes of acid (100% P_2O_5). The quantity of beneficiated rock required to produce this acid is approximately 216,000 tonnes. If an average uranium content of 100 μg g^{-1} is assumed for the beneficiated phosphate rock to be produced in Queensland (Broken Hill South deposit), the quantity of uranium recoverable (based on an overall recovery of 80 per cent) from the current manufacture of phosphoric acid is 17.3 tonnes/year. Alternatively, if all the phosphoric acid plants in Australia were operated at their rated capacity (330,000 tonnes/year), the quantity of uranium recoverable would be 59.8 tonnes/year. Even if all the projected exports of beneficiated phosphate rock from the Broken Hill South deposits (2,500,000 tonnes/year) were in the form of wet-process phosphoric acid, the corresponding maximum production rate of uranium would be only 200 tonnes/year. These quantities are insignificant in comparison to the potential output from processing higher grade uranium ores.

The projected Australian consumption of rock from the Broken Hill South deposit is 1,500,000 tonnes/year (Section 2.3) of which approximately 1,300,000 tonnes will be converted to single superphosphate containing 130 tonnes/year of uranium.

6. CONCLUDING REMARKS

Based on an average uranium content in the rock (before beneficiation) of 70 μg g^{-1} and reserves of 2,000 million tonnes, the amount of uranium in the phosphate rock in the Queensland deposit is 140,000 tonnes or slightly less than Australia's reasonably assured resources (June 1975) of low cost uranium (< $22 kg of U_3O_8); the present world price for uranium could justify its recovery in wet-process phosphoric acid manufacturing processes. However, about 90 per cent of Australian phosphate rock is manufactured into single superphosphate, and the cost of recovering uranium from single superphosphate is likely to be several times the present price of uranium on world markets. In addition, the timescale for mining the phosphate deposit

(approximately 6-7.5 million tonnes of ore per year) leads to a uranium recovery period of 270-330 years, well in excess of the period when uranium is expected to be in demand for Light Water Reactors. Alternatively, Broken Hill South would have to expand its fertiliser undertaking by factors of 9-11 to recover the uranium in about 30 years, and the phosphate export market does not appear capable of supporting the appropriate production rate.

At present, the maximum quantity of uranium recoverable in Australia from the production of wet-process phosphoric acid is 60 tonnes/year and this figure is very unlikely to increase in the near future. This annual production rate represents the potential output (240,000 tonnes/year of P_2O_5) of five plants located in four States of Australia. Consequently, the unit cost of uranium recovery would be adversely affected by the small scale operation.

Unless there is a very rapid depletion in the reserves of low-cost uranium in Australia, the quantity of uranium recoverable from the deposits of phosphate rock in Queensland is not significant.

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TABLE 1

COMPOSITIONS OF PHOSPHATE ROCKS *

Constituent	Formula	Morocco(1)	Morocco(1)	Togo(1)	Senegal(1)	Florida(1)	Florida(2)	Jordan(2)	Safi(2)	Israel(2)	Kosseir(2)	Tunisia(2)	Morocco(2)	Kola(2)	Nauru Island(3)	Ocean Island(3)
Phosphorus pentoxide	P_2O_5	30.52	36.14	36.97	[illegible]	35.57	33.42	33.37	33.47	30.37	30.31	30.83	28.90	38.22	35.9	40.3
Tricalcium phosphate	$Ca_3(PO_4)_2$	(66.65)	(78.93)	(80.74)	([illegible])	(76.68)										
Calcium oxide	CaO	46.27	46.96	45.85	41.[illegible]		48.94	52.06	52.36	54.[illegible]	48.73	51.07	48.30	50.68	54.5	54.1
Carbon dioxide	CO_2	5.35	1.95	2.87	2.24		2.95	3.60	4.45	5.25	2.33	5.35	5.60	0.07	2.0	1.1
Calcium carbonate	$CaCO_3$	-	-	-	-	[illegible]										
H_2O + organic substances	-	2.96	2.22	1.94	2.30	0.5	0.16[a]	0.10[a]	0.00[a]	0.04[a]	0.15[a]	0.38[a]	0.19[a]	0.00[a]	2.5[b]	1.1[b]
Quartz	SiO_2	(1.51)	(1.12)	(2.20)	([illegible])	-										
Quartz and silicates	SiO_2	1.57	1.23	2.41	5.70	4.0	5.29	3.39	1.14	0.28	9.02	1.01	2.20	2.17	0.2	0.4
Magnesium oxide	MgO	1.02	0.41	0.31	0.11	2.3	0.55	0.24	0.40	0.31	0.73	0.78	0.62	0.00		
Sesquioxide	$Fe_2O_3 + Al_2O_3$	0.85	0.71	2.04	4.02		2.06	0.51	0.32	0.47	1.19	0.64	0.51	1.89	0.3	0.2
Fluorine	F_2	3.79	3.83	3.83	3.64		3.86	4.03	4.28	3.63	3.34	3.95	3.95	3.22	2.7	3.1
F_2 as CaF_2	CaF_2	(7.79)	(7.87)	(7.87)	(7.46)	(7.97)										
Alkali metals	$Na_2O + K_2O$	1.50	0.76	0.49	0.16		1.22	1.60	1.95	3.00	1.50	1.73	1.86	1.45	0.5[c]	0.5[c]
Chlorine	Cl_2	0.02	0.03	0.13	0.02		0.003	0.078	0.049	0.700	0.430	0.082	0.100	0.014	0.01	0.01
Sulphur trioxide	SO_3	1.64	1.63	0.27	0.16		1.19	1.01	1.50	2.39	1.95	3.05	3.30	0.00		
TOTAL		98.49	95.90	97.11	98.17		99.07	100.04	100.02	100.70	99.74	98.87	95.53	97.79	101.91	101.01

* post-beneficiation

(1) Jaeger et al. (1972-1973)

(2) Habashi (1970)

(3) Slack (1966)

(a) Organic carbon only

(b) Water only

(c) Na_2O only

TABLE 2A

MEDIAN CONTENTS OF URANIUM IN PHOSPHATE ROCKS[a]

(After Menzel 1968)

Origin of Rock	Number of Samples	Median Content of Uranium ($\mu g\ g^{-1}$)
Florida land pebble, 1926-1935	11	208
Florida land pebble, 1939	4	222
Florida land pebble, 1946-1955	14	148
Florida land pebble, 1959-1964	12	127
Florida soft phosphate, 1927-1945	7	102
Florida waste pond and misc. phosphate, 1928-1943	9	76
Tennessee brown rock, 1927-1935	17	11
Tennessee brown rock, 1939	8	13
Tennessee brown rock, 1944-1955	3	10
Tennessee blue rock, 1926-1930	3	16
Tennessee white rock, 1930-1936	4	10
Tennessee phosphatic limestone, 1926-1929	3	8
South Carolina, 1927-1937	11	399
North Carolina, 1957-1964	3	79
Arkansas, 1938	13	30
Oklahoma, 1932-1941	5	25
Montana, 1930-1953	10	114
Idaho, 1928-1955	5	151
Wyoming, 1929-1961	4	183
Utah, 1936-1961	9	128
Misc. US and Canada 1927-1962	10	12
Mexico and Guatemala, 1953-1962	5	27
West Indies, 1944-1951	12	8
Curacao, 1929-1948	9	14
Venezuela, 1953-1960	4	72
Peru, washed phosphate, 1961-1964	7	106

Origin of Rock	Number of Samples	Median Content of Uranium ($\mu g\ g^{-1}$)
Peru, beneficiated phosphate, 1961	7	167
Brazil, Olinda, 1951-1960	4	274
Brazilian apatite, 1949-1951	6	9
Chile and Ecuador island, 1945-1955	9	3
Morocco, 1937-1943	5	141
Algeria, 1927-1936	12	104
Tunis, 1927-1955	6	48
Egypt, 1936-1937	6	122
Senegal and other African phosphates, 1949-1963	6	107
Spain and other Western European phosphates 1927-1936	5	5
Russian and Polish phosphorite 1930-1936	5	50
Russian apatite, 1932-1943	5	6
Jordan and Turkey 1956-1963	6	48
India, China, and Southeast Asia, 1947-1962	5	12
Christmas Island, 1925-1960	5	27
Nauru Island, 1925-1937	4	65
Ocean Island, 1925-1937	5	98
Makatea Island, 1930-1937	3	101
Australia and misc. island phosphates, 1929-1937	6	30
Seychelles guano, 1931-1935	4	20
Total	316	
Median content		59

(a) Materials were mainly ground samples of phosphate rocks, consisting of microcrystalline fluorapatite minerals and impurities. Many of these were beneficiated rocks, ready for fertiliser manufacture. A few samples of guano, macrocrystalline apatite, and other mineral phosphates were also included.

TABLE 2B

URANIUM CONTENT OF PHOSPHATE ROCKS[(b)]

(After Habashi 1970)

Origin of Rock	Uranium Content, $\mu g\ g^{-1}$
Florida	180
Jordan	170
Safi	155
Israel	140
Kosseir	90
Tunisia	80
Morocco	40
Kola	12

(b) *post-beneficiation*

Note: A complete analysis of the constituents in the above seven rocks is given in Table 1.

TABLE 3

WORLD PRODUCTION OF PHOSPHATE ROCK

(thousands of tonnes)

Country	1953	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
WORLD	25,700	46,030	48,980	56,810	63,960	75,240	78,380	84,240	82,670	85,070	87,540	94,380
Algeria	619	390	348	73	86	120	198	361	420	492	491	-
Australia	3	4	5	6	5	6	12	6	19	14	9	3
Belgium	36	12	14	22	22	22	22	20	-	-	-	-
Brazil	-	566	279	246	279	378	575	649	-	-	-	-
Chile	59	29	36	28	32	15	16	23	17	17	13	-
China	148	600	700	800	900	1,000	1,000	1,000	1,100	1,200	1,200	-
Christmas Is.	285	610	840	863	859	953	1,046	1,118	988	989	975	1,050
Egypt	484	602	612	613	594	661	683	1,441	660	699	713	-
France	83	54	44	31	38	24	24	22	26	26	19	18
French Polynesia	276	317	335	388	308	177	-	-	-	-	-	-
Gilbert & Ellice Is.	287	261	362	328	376	380	454	532	564	572	636	511
India	4	29	13	4	7	16	12	7	78	165	243	230
Indonesia	-	6	1	2	4	4	10	10	-	-	-	-
Israel	23	230	300	240	392	664	730	910	1,061	1,000	764	937
Italy			387	346	268	298	485	-	-	-	-	-
Jordan	40	681	614	565	828	1,036	1,082	1,156	1,089	913	651	714
Korea, DPR	-	200	200	200	200	250	250	300	300	300	300	-
Mexico	-	30	34	33	39	56	50	43	33	46	58	63
Morocco	3,814	8,162	8,549	10,098	9,827	9,438	9,922	10,324	11,294	11,424	12,030	15,105

(Continued)

TABLE 3 (Cont'd.)

Country	1953	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Nauru	1,247	1,566	1,635	1,682	1,720	2,042	1,806	2,262	2,198	2,200	1,913	1,906
Netherlands Antilles	96	132	128	120	115	148	118	93	113	109	61	-
Peru	261	206	192	205	170	56	65	77	20	18	22	-
Philippines	1	4	3	4	4	4	1	1	15	3	5	3
Poland	32	54	60	89	93	88	76	72	35	-	-	-
Senegal	46	638	596	798	1,038	1,135	1,276	1,270	1,035	998	1,454	1,250
Seychelles	9	5	7	4	6	4	4	6	8	7	6	9
South Africa	80	307	455	579	610	1,063	1,352	1,565	1,679	1,685	1,729	1,966
Togo	-	197	476	759	973	1,151	1,140	1,375	1,473	1,508	1,715	1,855
Tunisia	1,719	2,097	2,365	2,751	3,040	3,216	2,810	3,361	2,599	3,021	3,162	3,387
Uganda	5	1	-	172	164	158	147	160	368	300	24	23
USSR												
Apatite	1,180	4,330	4,760	6,380	7,550	8,000	8,800	9,700	10,500	10,900	21,650	-
Phosphate rock	1,250	3,300	3,810	4,350	6,050	6,750	7,500	8,000	8,750	9,500		
United States	12,704	19,693	20,174	23,328	26,704	35,420	36,079	37,423	34,224	35,143	35,277	38,465
Viet-Nam, Dem. R.	-	712	975	1,050	1,050	1,050	1,050	1,050	1,230	1,050	1,145	-

Note: *The series relate to the production of natural phosphate rock, (post-beneficiation) apatite and sometimes include guano with a variable phosphate content.*

Source: *United Nations Statistical Yearbook 1973.*

TABLE 4

WORLD CONSUMPTION OF PHOSPHATE ROCK BY MAIN REGIONS

(Millions of tonnes of marketable phosphate)

Consumption Areas	Actual		Projection - Forecast	
	1968	1969	1975	1980
DEVELOPED COUNTRIES	60.2	62.6	87.7	111.0
North America	23.7	24.7	32.0	40.0
Western Europe	15.1	15.5	19.5	22.0
Eastern Europe	5.1	5.5	9.3	12.0
USSR	9.7	10.1	18.0	26.0
Oceania	3.7	3.6	5.0	7.0
Japan	2.9	3.2	3.9	4.0
DEVELOPING COUNTRIES	7.3	7.3	22.5	35.0
Europe[1]	2.6	3.5	7.7	10.0
Africa	1.7	1.5	4.0	6.5
Latin America	1.1	1.3	4.5	8.0
Asia	1.9	1.9	6.3	10.5
OTHERS	3.4	4.0	5.5	8.5
Communist Asia	2.5	3.0	4.0	6.5
South Africa	0.9	1.0	1.5	2.0
TOTAL	70.9	73.9	115.7	154.5
Annual implied rate of growth (%)	4.2	7.7	6.1	

Source *OECD (1972)*

1. *Spain, Greece, Yugoslavia, Turkey and Cyprus.*

TABLE 5

PHOSPHATE ROCK: WORLD PRODUCTION AND INSTALLED PRODUCTION CAPACITY

(Millions of tonnes of marketable phosphate)

	Actual Production	Production Capacity		
			1975	
	1969	1969/70	Likely	Possible
PRESENT PRODUCERS				
USA	34.2	50.0	55.0	60.0
USSR	15.7	18.0	30.0	33.0
Africa (north of Sahara)	14.3	18.3	27.5	31.0
Morocco	10.7	12.0	18.0	20.0
Tunisia	2.6	4.0	6.0	7.9
Algeria	0.4	0.8	1.5	2.0
Egypt	0.6	1.5	2.0	2.0
Africa (south of Sahara)	2.7	3.2	4.5	4.5
Togo	1.5	1.8	2.5	2.5
Senegal	1.2	1.5	2.0	2.0
Middle East	2.2	3.0	4.0	6.0
Israel	1.1	1.5	2.0	3.0
Jordan	1.1	1.5	2.0	3.0
Latin America	0.2	0.6	1.5	2.0
Others	3.7	5.1	5.8	7.5
South Africa	1.3	1.6	2.0	2.5
Communist Asia	1.6	2.0	2.0	3.0
Others	0.8	1.5	1.8	2.0
Oceania	4.1	4.0	4.0	5.0
POTENTIAL PRODUCERS				
Spanish Sahara	-	-	6.0	6.0
Peru	-	-	2.0	3.0
India	neg.	0.5	1.0	2.0
Syria	-	-	0.3	1.5
Australia	neg.	0.3	1.0	3.0
Angola	-	-	0.5	1.0
WORLD TOTAL	77.1	103.3	143.1	166.5
WESTERN WORLD	59.8	83.0	111.1	130.5

Source *OECD (1972)*

TABLE 6

PHOSPHATE ROCK: TRADE MATRIX BY ORIGIN AND DESTINATION - 1970

(Millions of tonnes of marketable phosphate)

Destination	Developed and Communist Countries					Developing Countries			Total Exports
	West Europe	East Europe	Oceania	Japan	Communist Asia	Europe[2]	Latin America	Asia	
USA	3.9	-	neg.	1.9	-	0.1	1.3	1.2	8.5[1]
USSR	2.0	3.9	-	-	-	-	-	-	5.9
Africa (North of Sahara)	7.6	2.3	0.1	0.6	0.9	2.2	0.2	0.4	14.3
Morocco	6.7	1.3	0.1	0.6	0.6	1.8	0.1	0.2	11.3
Tunisia	0.8	0.8	-	-	-	0.4	0.1	-	2.1
Algeria	0.1	0.2	-	-	0.1	neg.	-	-	0.5
Egypt	neg.	neg.	-	-	0.2	neg.	-	0.2	0.4
Africa (South of Sahara)	2.1	neg.	-	0.2	-	0.1	-	neg.	2.5
Togo	1.4	-	-	0.1	-	-	-	-	1.5
Senegal	0.7	neg.	-	0.1	-	0.1	-	neg.	1.0
Middle East	0.5	0.2	-	neg.	0.1	0.3	0.1	0.3	1.5
Israel	0.5	0.2	-	neg.	-	neg.	0.1	-	0.8
Jordan	-	neg.	-	neg.	0.1	0.3	-	0.3	0.7
Oceania	-	-	3.1	0.4	-	-	-	0.1	3.6
WORLD TOTAL	16.1	6.5	3.2	3.1	1.0	2.8	1.5	1.9	36.2

1. *Excluding 1.6 million tonnes exported to Canada and exports by USA Western States.*

2. *Spain, Greece, Yugoslavia, Turkey and Cyprus.*

Source *OECD (1972)*

TABLE 7

PHOSPHATE ROCK: TRADE MATRIX BY ORIGIN AND DESTINATION - 1975

(Millions of tonnes of marketable phosphates)

	West Europe	East Europe	Japan	Communist Asia	Europe[2]	Africa	Latin America	Asia	Total Exports[1]
USA	5.0	-	3.0	-	0.5	-	2.5	1.0	12.0
USSR	3.0	4.0	-	-	-	-	-	-	7.0
Africa (North of Sahara)	9.5	4.5	0.3	0.5	5.4	0.1	-	0.7	21.1
Morocco	7.0	2.4	0.3	0.3	2.0	-	-	0.5	12.5
Tunisia	0.5	1.0	-	0.2	1.2	0.1	-	0.1	3.1
Spanish Sahara	2.0	0.2	-	-	2.2	-	-	0.1	4.5
Africa (South of Sahara)	1.8	0.2	-	-	1.0	0.5	-	0.8	4.3
Middle East	0.2	0.5	-	0.5	0.8	-	-	1.0	3.0
Latin America	-	-	0.6	-	-	-	0.5	1.1	2.2
WORLD TOTAL	19.5	9.3	3.9	1.0	7.7	0.6	3.0	4.6	49.6

1. *Excluding captive exports: USA to Canada (about 4 million tonnes in 1975) and Pacific Islands to Oceania (Australia and New Zealand).*

2. *Spain, Greece, Yugoslavia, Turkey and Cyprus.*

Source *OECD (1972)*

TABLE 8

PRODUCTION OF PHOSPHATE ROCK IN AUSTRALIA

(tonnes)

	1968	1969	1970	1971	1972
South Australia	5,836	18,550	14,482	6,786	1,051
Value, ex-mine ($'000)	23	73	57	18	

Source: Bureau of Mineral Resources, Geology and Geophysics (1973a)
Bureau of Mineral Resources, Geology and Geophysics (1973b)

TABLE 9

IMPORTS OF PHOSPHATE ROCK: AUSTRALIA

(tonnes)[a]

Country of Origin	1969	1970	1971	1972	1973[p]
Christmas Is.	785,380	718,928	535,021	529,590	885,400
Gilbert & Ellice Is.	354,412	262,717	334,949	195,867	429,046
Morocco	48,829	57,683	27,662	40,226	37,657
Nauru	1,455,006	1,334,971	1,055,804	858,848	1,524,540
USA	153,848	-	-	-	-
Other	-	10	10	-0	108
TOTAL	2,797,476	2,374,309	1,953,447	1,624,532	2,876,751
Value ($'000 fob)	28,294	24,941	21,160	16,722	30,408

p preliminary figure
(a) post-beneficiation
Source: Bureau of Mineral Resources, Geology and Geophysics (1974)

TABLE 10

IMPORTS OF PHOSPHATE ROCK BY IMPORTING STATE

(tonnes)[a]

State	1969-70	1970-71[p]
NSW	485,000	356,000
Victoria	894,000	607,000
Queensland	109,000	109,000
South Australia	373,000	244,000
Western Australia	738,000	732,000
Tasmania	94,000	64,000
TOTAL	2,691,000	2,109,000

p preliminary figure
(a) post-beneficiation
Source: Department of Secondary Industry (1973)

TABLE 11

URANIUM MINED PER YEAR IN PHOSPHATE ROCK

Country	Yearly Production of Phosphate Rock[(a)] 1972 (thousands of tonnes)	Estimated Uranium Content[(b)] ($\mu g\ g^{-1}$)	Estimated Quantity of Uranium (tonnes)
Israel	937	110	103
Jordan	714	140	100
Morocco	15,105	110	1,661
Senegal	1,250	90	113
South Africa	1,966	90	176
Togo	1,855	90	167
Tunisia	3,387	60	203
Russia	10,000	40	400
United States	38,465		
Florida	28,000 (70%)	150*	4,800
Other	10,465	80	840
		Total	7,963

* *Typical figure quoted for average uranium content of Florida Phosphates (Kennedy 1967)*

(a) post-beneficiation

(b) of beneficiated rock

TABLE 12

RANGE OF PROCESS CONDITIONS IN THE MANUFACTURE OF SINGLE SUPERPHOSPHATE

(After Slack 1966)

Variable	Range	Average
Acid concentration wt%	68-75	71
Acid temperature, °C	28-85	55
Particle size of rock,		
through 100 mesh	80-95	90
through 200 mesh	50-95	70
Acid/rock ratio[(a)]	55-65	60

(a) kilogram of 100% sulphuric acid/100 kg of rock.

TABLE 13

TYPICAL PROPERTIES OF SINGLE SUPERPHOSPHATE

(After Slack 1966)

Free acid content affects the physical condition adversely if it is high. In well-cured superphosphate, free acid normally is in the range of 1-2% H_2SO_4.

Moisture content also affects the physical condition. Superphosphate normally contains 5-8% moisture after curing, low moisture content helps in reaching the general objective of 20% available P_2O_5 content.

Citrate solubility is quite important because it is the legal basis for sale. Well-cured superphosphate usually runs less than 1% citrate-insoluble and 20-21% citrate-soluble P_2O_5.

Graininess is a desirable property, especially when nongranular superphosphate is used as a direct fertiliser without mixing with other materials. Dustiness is undesirable also in other applications. The type of mixer used influences these properties.

Hygroscopicity is quite low; the critical relative humidity at 30°C is 94%.

Bulk density for nongranular and granular material range from about 0.8 to 1.12 g/cm^3 respectively.

TABLE 14

TYPICAL PROCESS CONDITIONS FOR THE MANUFACTURE OF TRIPLE SUPERPHOSPHATE

Acid concentration wt.%	52-54
temperature	ambient
Particle size of rock through 200 mesh	70%
The P_2O_5/CaO mol ratio (including P_2O_5 from both the acid and the rock)	0.92-0.95

TABLE 15

TYPICAL PROPERTIES OF TRIPLE SUPERPHOSPHATE

Citrate solubility of phosphate	
pile-cured %	98-99
quick-cured %	96
Critical relative humidity	94% at 34°C
Bulk density	
non-granular g/cm^3	0.88
granular g/cm^3	1.12-1.2

TABLE 16

WORLD CONSUMPTION OF PHOSPHATE FERTILISERS

Consumption in terms of P_2O_5 - thousands of tonnes

Country	1967/68	1968/69	1969/70	1970/71	1971/72	1972/73	Percentage of World Consumption 1972/73
WORLD	16,900	18,000	18,600	19,800	21,200	22,600	100
Algeria	20.1	23.9	39.4	52.6	74.2	76.6	0.34
Argentina	20.8	29.5	38.0	38.8	23.9	30.0	0.13
Australia	880.0	900.0	830.0	744.6	775.3	880.0	3.9
Austria	131.4	108.1	134.6	125.7	136.7	126.0	0.56
Bangladesh	20.2	24.4	30.2	34.0	80.3	40.2	0.18
Belgium	158.9	131.3	144.0	148.2	149.1	148.8	0.66
Brazil	166.0	214.1	236.6	375.3	446.9	708.5	3.14
Bulgaria	260.4	346.0	256.0	271.6	266.0	230.1	1.02
Canada	399.2	315.5	284.0	287.0	339.0	445.0	1.97
Chile	90.0	100.7	87.4	102.1	96.6	76.6	0.34
China	363.0	422.0	511.0	574.0	917.0	1,043.5	4.61
Taiwan	38.3	40.2	40.1	42.5			
Colombia	55.0	49.5	55.4	61.0	61.8	70.0	0.31
Costa Rica	7.5	9.0	10.0	10.4	21.9	25.0	0.11
Cuba	99.0	113.0	115.1	92.1	65.0	51.0	0.23
Czechoslovakia*	248.5	295.9	312.4	349.6	357.9	363.3	1.6
Denmark	119.7	124.2	126.8	126.6	133.3	143.5	0.65
Egypt	38.8	38.6	36.2	45.1	46.3	87.7	0.39
Finland	147.5	170.5	172.1	176.0	178.2	177.5	0.79
France	1,505.2	1,587.4	1,683.7	1,819.5	1,932.0	2,058.4	9.1
German, Dem. R.*	344.4	377.8	389.2	410.0	385.6	497.3	2.2
Germany, Fed. Rep.	787.9	801.7	856.5	913.1	934.9	902.6	3.99
Greece	105.1	116.5	114.0	118.5	123.8	125.0	0.55
Hungary	158.0	176.2	182.9	217.0	250.9	266.2	1.18
India	236.5	389.2	419.8	462.0	565.0	584.0	2.58
Indonesia	13.0	65.9	62.6	50.0	23.1	66.8	0.29
Iran	28.0	26.9	30.0	37.0	66.8	65.2	0.29
Ireland	147.7	159.9	169.0	182.5	172.5	202.2	0.89
Israel	11.8	12.3	14.1	14.5	15.9	15.9	0.07
Italy	464.5	467.3	486.2	518.4	574.5	583.2	2.58
Japan	665.3	701.8	696.7	652.9	661.4	717.0	3.17

(Continued)

TABLE 16 (Cont'd.)

Country	1967/68	1968/69	1969/70	1970/71	1971/72	1972/73	Percentage of World Consumption 1972/73
Kenya	21.0	16.0	21.8	28.9	25.5	22.8	0.1
Korea, P.D.	85.0	75.0	80.0	100.0	98.0	105.0	0.47
Korea, Republic of	132.7	121.4	130.7	124.5	158.2	170.9	0.76
Mexico	110.0	120.4	117.4	130.4	143.7	163.4	0.72
Morocco	31.0	39.6	39.3	44.5	39.0	49.8	0.22
Netherlands	105.7	103.9	107.0	109.4	101.3	104.0	0.46
New Zealand	282.1	324.4	335.2	321.1	347.0	350.0	1.55
Norway	52.7	52.9	54.1	52.3	56.5	51.1	0.23
Pakistan	12.2	39.5	36.6	30.5	38.8	48.7	0.22
Philippines	23.8	45.1	64.0	69.0	50.0	39.8	0.18
Poland*	450.8	525.5	595.4	635.8	718.6	781.6	3.46
Portugal	55.9	61.0	78.1	61.9	69.6	73.4	0.32
Romania	135.2	140.5	169.1	203.2	179.7	172.9	0.77
South Africa	247.0	258.9	261.4	272.0	295.4	313.6	1.38
Southern Rhodesia	25.5	24.5	28.2	30.0	34.4	37.9	0.17
Spain	350.5	389.1	400.2	428.6	453.8	466.8	2.06
Sweden	128.8	139.4	139.2	146.2	153.6	150.0	0.66
Switzerland	43.7	44.6	50.3	50.3	48.5	48.5	0.21
Thailand	35.7	38.1	45.3	36.0	43.3	55.9	0.25
Tunisia	14.4	16.5	21.2	28.0	16.5	17.8	0.079
Turkey	132.2	181.7	200.6	175.9	194.7	246.2	1.09
USSR	1,697.0	1,748.0	1,916.0	2,210.0	2,442.0	2,594.0	11.5
United Kingdom	464.3	447.0	460.4	542.6	511.6	469.7	2.08
United States	4,040.0	4,227.0	4,144.7	4,341.2	4,420.7	4,601.2	20.4
Uruguay	18.8	30.0	29.5	31.4	33.8	40.0	0.18
Venezuela	10.6	11.2	10.3	16.0	25.3	25.0	0.11
Viet-Nam, Dem. R.	15.0	20.0	23.0	63.0	96.0	42.0	0.19
Viet-Nam, Rep. of	31.4	17.0	36.8	34.1	37.2	30.0	0.13
Yugoslavia	177.5	159.4	182.7	182.4	174.6	203.0	0.90

(1) The data refer to commercial phosphoric acid (P_2O_5) and cover the P_2O_5 content of superphosphates, ammonium phosphate and basic slag: to avoid duplication, the P_2O_5 content of ground rock phosphate is excluded. Years generally relate to twelve-month periods 1 July-30 June.*

(2) Countries consuming less than 0.1% of the world consumption have been deleted.

* *Includes ground phosphate rock.*

Source: United Nations Statistical Yearbook 1973.

TABLE 17

SUM OF P_2O_5 IMPORTS AND EXPORTS IN THE WORLD[a]

(thousands of tonnes of P_2O_5)

	1965-1966		1966-1967		1968-1969	
	Imports	Exports	Imports	Exports	Imports	Exports
North America	138	493	154	694	185	1,066
West Europe	782	1,061	784	1,155	1,070	1,258
East Europe	157	108	256	80	404	101
Europe[c]	91	47	96	73	203	81
Africa	82	154[b]	92	172[b]	92	286[b]
Latin America	228	7	238	4	431	5
Asia	404	13	540	13	464	48
Total	1,882	1,883	2,160	2,191	2,849	2,845

(a) This table gives world P_2O_5 imports and exports by regions. By definition these totals include intraregional trade and represent real movements of P_2O_5 in the world (about 13 to 15 per cent of world production).

(b) Mainly Tunisia and Morocco.

(c) Spain, Greece, Yugoslavia, Turkey and Cyprus.

Source OECD (1972)

TABLE 18

PRODUCTION COSTS OF 54 PER CENT PHOSPHORIC ACID IN DIFFERENT LOCATIONS

($US)

Location	Europe	Florida	Europe	Florida	Iran	Morocco	Tunisia	Tunisia	India
Annual capacity (90%) (tonnes P_2O_5)	162,000		270,000		270,000	270,000	270,000	110,000	120,000
Investments ($ million)[a]									
- fixed	18.0		24.0		29.0	29.0	30.0	18.5	28.0
- working	4.5		6.5		[illegible]	7.0	7.0	2.0	4.0
Total	22.5		30.5		36.0	36.0	37.0	20.5	32.0
Production costs ($ tonne P_2O_5)									
variable									
- material costs	56.0	44.0	56.0	44.0	53.0	[illegible]	46.0	[illegible]	80.0
- others	9.5	9.5	9.5	9.5	10.0	10.0	10.0	10.0	10.0
- fixed	19.0	19.0	15.0	15.0	18.2	18.2	19.0	29.0	40.0
return on investment	14.0	14.0	11.5	11.5	13.3	13.3	14.0	19.0	27.0
selling price	98.5	86.5	92.0	80.0	94.5	87.0	89.0	104.0	157.0
$/tonne acid 54%	53.0	46.5	49.5	43.5	51.0	47.0	48.0	56.0	85.0
Clarified acid									
$/tonne P_2O_5	101.0	90.5	94.5	84.0	97.0	88.0	91.0	[illegible]	160.0
$/tonne acid 54%	54.5	49.0	51.0	45.5	54.0	47.5	49.0	57.0	86.0

(a) *On the basis of 1969/70 investment costs for battery limits*

Source OECD (1972)

TABLE 19

PRICES IN EUROPE OF 54 PER CENT PHOSPHORIC ACID FROM VARIOUS SOURCES

(in $US per tonne of P_2O_5[a])

f.o.b. ex works price	Europe 95/100	Mexico 80/85[b]	Morocco 85/90	Tunisia 90/100
Freight				
North Europe	4	22	12	15
South Europe	4/6	22	12	8
c.i.f. prices to point of consumption[c]				
North Europe	99/104	102/107	97/102	105/115
South Europe	99/106	102/107	97/102	[illegible]

(a) *On the basis of 1969/70 investment costs*

(b) *Estimated selling price for the Fertilizantes Fosfatados Mexicanos (FFM) unit*

(c) *Not including handling and storage costs at consumption point (assumed to be equal)*

Source OECD (1972)

TABLE 20

INTERNATIONAL TRADE IN PHOSPHORIC ACID[d]

Producers	Start-up	Capacity Tonnes of P_2O_5 (Acid)	Exports in 1975 Tonnes of P_2O_5 (Acid)
Existing			
Fertilizantes Fosfatados Mexicanos (FFM) - Mexico	1969	370,000	300,000[a]
Arad Chemicals Industries - Israel[c]	1971	165,000	165,000[b]
Bandar Shapur - Iran	1971	100,000	100,000[a]
Industries Chimiques Maghrebines - Tunisia	1971-72	120,000	120,000[a]
Planned			
Office Cherifien des Phosphates - Morocco	1974-75	330,000	250,000[a]
Office Cherifien des Phosphates - Algeria	1975	198,000	100,000[a]
TOTAL		1,283,000	1,035,000

Consumers

Europe (France, Italy, Holland)	*- Contracts signed with ICM (80% of production) and with Arad (60% of production).*
India	*- Contracts signed with FFM and Bandar Shapur (about 150 to 200,000 tonnes of P_2O_5/year).*
Philippines	*- Contracts signed with FFM (25,000 tonnes P_2O_5/year).*
Greece, Brazil, Colombia, Thailand, South Korea	*- Contracts under negotiation with different suppliers.*

(a) - 54% acid *(c) - Exports both to Mediterranean regions and Asia.*

(b) - 69% acid *(d) - Excluding trade of acid produced in Europe and in the United States.*

Source OECD (1972)

TABLE 21

AVAILABILITY OF TYPES OF FERTILISERS

Fertiliser Type	States Available					
	NSW	VIC	QLD	SA	WA	TAS
Low Analysis Fertilisers						
Single superphosphate	x	x	x	x	x	x
Superphosphate with nitrogen compounds	x	x	x	x	x	x
Superphosphate with potassium compounds		x		x	x	x
Superphosphate with both nitrogen and potassium compounds	x	x	x	x	x	x
Superphosphate with sulphur	x	x	x	x		x
Superphosphate with lime	x	x				x
Superphosphate with trace elements	x	x	x	x	x	x
Superphosphate with insecticides	x	x	x	x		
High Analysis Fertilisers						
Double superphosphate	x				x	
Triple superphosphate	x	x	x			
Ammonium phosphates	x		x		x	
N-P mixtures	x	x	x		x	
N-P-K mixtures	x	x	x			

Source: Department of Secondary Industry (1973)

TABLE 22

PRODUCTION AND SALES OF SUPERPHOSPHATE: STATES (financial years) (a)

(tonnes)

Period	NSW	VIC	QLD	SA	WA	TAS	AUST.
PRODUCTION							
1968-69	641,977	1,206,963	173,194	571,393	1,267,320	140,340	4,001,187
1969-70	603,525	1,093,450	158,387	537,052	1,126,275	136,653	3,655,340
1970-71	430,770	998,127	155,339	439,765	985,651	105,363	3,115,014
1971-72	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3,696,418
1972-73	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4,917,780
SALES							
1968-69	658,324	1,260,427	174,086	614,140	1,324,911	137,482	4,169,370
1969-70	619,971	1,102,537	174,699	579,029	1,205,453	138,889	3,820,578
1970-71	512,139	1,088,206	139,763	471,562	1,084,249	116,743	3,412,662
1971-72	627,440	1,179,338	229,796	555,814	1,173,876	111,221	3,877,486
1972-73	789,851	1,245,815	237,395	638,876	1,295,532	161,023	4,368,492

(a) Includes all phosphatic fertilisers in terms of single superphosphate, i.e. 22% P_2O_5 equivalent.

Excludes consumption on rural holdings of less than one acre, in municipal parks and gardens and on other non-commercial holdings. No allowances have been made for changes in stocks on rural holdings.

Source *Bureau of Mineral Resources, Geology and Geophysics (1974)*

TABLE 23

CONSUMPTION OF SUPERPHOSPHATE: STATES AND TERRITORIES, 1968-69 to 1972-73(a)

(tonnes)

State	1968-69	1969-70	1970-71	1971-72	1972-73
NSW	794,531	793,660	731,345	652,426	780,040
Vic.	844,860	838,980	802,228	771,228	853,545
Qld	62,274	78,812	89,627	79,926	91,060
SA	564,352	566,141	509,775	505,903	523,184
WA	1,242,178	1,311,127	1,139,282	1,039,731	1,138,446
Tas.	140,966	134,586	114,985	101,059	124,593
NT	2,443	4,375	5,461	8,409	9,133
ACT	2,168	2,789	1,903	1,562	1,783
Total	3,653,772	3,780,470	3,394,606	3,160,244	3,521,784

(a) Includes all phosphatic fertilisers in terms of single superphosphate, i.e. 22% P_2O_5 equivalent.

Excludes consumption on rural holdings of less than one acre, in municipal parks and gardens and on other non-commercial holdings. No allowances have been made for changes in stocks on rural holdings.

Source *Bureau of Mineral Resources, Geology and Geophysics (1974)*

TABLE 24

FERTILISER PLANT LOCATIONS

New South Wales (2 factories)	
Australian Fertilizers Ltd.	Port Kembla
Greenleaf Fertilizers Ltd.	Walsh Point
(Greenleaf also owns a factory at Cockle Creek which has been temporarily closed down)	
Victoria (3 factories)	
Phosphate Co-op. Co. of Australia Ltd.	Yarraville
Phosphate Co-op. Co. of Australia Ltd.	Geelong
Phosphate Co-op. Co. of Australia Ltd.	Portland
Queensland (3 factories)	
ACF & Shirleys Fertilisers Ltd.	Pinkenba
ACF & Shirleys Fertilisers Ltd.	Cairns
Austral Pacific Fertilisers Ltd.	Gibson Island
South Australia (6 factories)	
Adelaide & Wallaroo Fertilisers Ltd.	Birkenhead
Adelaide & Wallaroo Fertilisers Ltd.	Port Adelaide
Adelaide & Wallaroo Fertilisers Ltd.	Wallaroo
Cresco Fertilisers Ltd.	Birkenhead
Cresco Fertilisers Ltd.	Port Lincoln
Cresco Fertilisers Ltd.	Wallaroo
Western Australia (7 factories)	
Albany Superphosphate Co. Pty. Ltd.	Albany
Cresco Fertilisers (W.A.) Pty. Ltd.	Bayswater
CSBP & Farmers Ltd.	Bunbury
CSBP & Farmers Ltd.	Geraldton
CSBP & Farmers Ltd.	Kwinana
CSBP & Farmers Ltd.	North Fremantle
Esperance Fertilisers Pty. Ltd.	Esperance
Tasmania (1 factory)	
Electrolytic Zinc Co. of Australasia Ltd.	Risdon

In addition to sites of actual manufacture, there are a number of other sites of activity where phosphatic fertilisers are processed. These include storage, mixing, granulating, reprocessing and bagging.

Source: Department of Secondary Industry (1973)

TABLE 25

TYPES OF PHOSPHATIC FERTILISERS SOLD 1968-69

Type	Quantity ('000 tonnes)	% of Total
Single superphosphate including trace elements and insecticides.	3,165	76
Superphosphate content of mixtures with other materials (nitrogen and potassium compounds, sulphur, etc.)	600	14
Double and triple superphosphate, ammonium phosphates sold as such, or included in high analysis mixtures (in terms of single superphosphate).	401	10
	4,166	100

Source: Department of Secondary Industry (1973)

TABLE 26

CONSUMPTION OF SUPERPHOSPHATE BY USAGE, AUSTRALIA, 1968-69 to 1972-73 (a)(b)

(tonnes)

Usage	1968-69	1969-70	1970-71	1971-72	1972-73
Crops -					
Wheat	979,651	867,445	599,599	623,299	688,052
Other cereal	397,732	412,880	463,099	455,992	411,340
Vegetable	29,614	30,705	27,855	26,679	25,091
Fruit & vine	22,243	27,179	27,668	26,731	27,073
Sugar cane	14,098	18,089	27,854	18,544	19,830
Other	71,148	71,670	87,442	36.301	37,439
Total crops	1,514,542	1,427,968	1,233,517	1,187,546	1,208,825
Pastures	2,139,226	2,352,502	2,161,089	1,972,698	2,312,959
TOTAL	3,653,772	3,780,470	3,394,606	3,160,244	3,521,784

(a) *Includes all phosphatic fertilisers in terms of single superphosphate.*

(b) *Year ended 31st March.*

(c) *Excludes consumption on rural holdings of less than one acre, in municipal parks and gardens and on other non-commercial holdings. No allowances have been made for changes in stocks on rural holdings.*

Source Bureau of Mineral Resources, Geology and Geophysics (1974)

TABLE 27

WET-PROCESS PHOSPHORIC ACID PLANTS

Location of Plants	Original Rated Capacity (tonnes per day P_2O_5)	Operations Commenced
New South Wales		
*Australian Fertilizers Ltd. Port Kembla	100	Dec. 1963
Greenleaf Fertilizers Ltd. Walsh Point	200	April 1966
Victoria		
ICI Australia Ltd. Yarraville	170	January 1965
Queensland		
ACF & Shirleys Ltd. Pinkenba	100	June 1966
Western Australia		
CSBP & Farmers Ltd. Kwinana	100	Dec. 1967

* *This plant is closed.*

TABLE 28

AVERAGE EX WORKS COST OF SINGLE SUPERPHOSPHATE

	$	$
Direct materials		16.52
Direct labour		1.05
Factory overheads		
Depreciation	1.15	
Other	2.84	3.99
Net factory cost		21.56
Administration costs		1.08
Selling and distribution costs		1.82
Total cost to make and sell		24.46
Net return		2.04
Total Ex Works Cost		26.50 per tonne

Source *Department of Secondary Industry (1973)*

TABLE 29

TRENDS IN THE RETAIL PRICES OF SINGLE SUPERPHOSPHATE

Bulk Ex Works for Tonne Basis Net of Subsidy (a)

	1 Oct. 1968	1 Oct. 1969	1 Oct. 1970	1 Oct. 1971	1 Oct. 1972	1 Oct. 1973
NSW	18.75	14.81	14.81	15.50	18.95	17.88
VIC.	18.01	14.07	13.88	14.17		
QLD.	18.80	14.62	16.48	16.29		
SA	19.83	14.07	14.07	14.07		
WA	17.96	14.02	13.82	14.32		
TAS. (b)	24.95	21.01	19.83	21.06		

(a) Subsidy 1968 $7.87 per tonne, 1969-1973 $11.81 per tonne

(b) Delivery to purchaser's nearest rail siding or port of shipment.

Source *Bureau of Mineral Resources, Geology and Geophysics (1973a) and Process & Chemical Engineering (1973).*

TABLE 30

CURRENT RETAIL PRICES OF PHOSPHATIC FERTILISERS BY STATES

Bulk Ex Works per Tonne Basis Net of Subsidy [a]

	NSW $	VIC $	QLD $	SA $	WA $	TAS $
Single Superphosphate (as at 1/7/74)	34.87	34.05	35.24	33.58	33.41	40.94
Triple Superphosphate	87.40	-	-	-	-	-
Mono Ammonium Phosphate	-	-	98.00 (1/3/74)	-	-	-
Di Ammonium Phosphate	-	-	113.00 (1/3/74)	-	-	-

(a) *Subsidy* *In force until 31st December 1974*
$11.81 per tonne of single superphosphate
$59.05 per tonne of P_2O_5 in other superphosphates and ammonium phosphate.

Source *Private Communication - Department of Primary Industry*

TABLE 31

AVERAGED CHEMICAL ANALYSIS FOR MINEABLE LEACHED ZONE AND UPPER MATRIX MATERIAL.

(After Clegg and Foley 1958)

Screen size	Weight	Weight per cent, dry basis					
		Al_2O_3	CaO	Fe_2O_3	Insol.	P_2O_5	U_3O_8
		Mineable leached zone					
+14 mesh	5.19	12.03	13.64	2.38	49.82	19.35	0.018
-14 +200 mesh	61.68	2.30	3.39	1.86	90.31	4.38	0.004
-200 mesh	33.12	26.98	7.91	2.79	40.39	16.11	0.029
Head	100	10.98	5.42	2.20	71.67	9.04	0.013
		Upper matrix					
+14 mesh	7.4	8.4	21.92	2.59	37.11	20.56	0.018
-14 +200 mesh	62.4	1.47	7.28	2.59	83.28	6.74	0.0045
-200 mesh	29.2	20.22	11.17	2.98	37.39	16.91	0.027
Head	100	7.10	10.05	1.28	70.25	11.29	0.013

TABLE 32

ABILITY OF VARIOUS COMPOUNDS TO EXTRACT URANIUM FROM PHOSPHORIC ACID (30% P_2O_5)

(Ellis 1952)

Extracted no uranium within the error of the experiment:

butyl acetate
butyl ether
butyl oxalate
Freon 113

The following compounds extracted uranium only slightly:

tri-butyl phosphate
tri-cresyl phosphate
butyl citrate
butyl bisulphide
butyl isothiocyanate
octyl chloride
butyl borate

Benzene phosphonic acid and benzene phosphinic acid were prepared but proved to be fairly soluble in phosphoric acid.

TABLE 33

COMPOSITION OF CRUDE PHOSPHORIC ACID FEED TO IMC URANIUM RECOVERY PLANT

(After Greek et al. 1957)

Component	Measured as	Per cent by weight
Phosphoric acid	P_2O_5	24 -27.5
Fluorine	H_2SiF_6	1.5 - 2.2
Iron	Fe_2O_3	0.75 - 1.0
Sulphuric acid	H_2SO_4	0.2 - 1.5
Calcium	CaO	0.2 - 0.75
Aluminium	Al_2O_3	0.75 - 1.0
Magnesium	MgO	Less than 0.1
Potassium	K_2O	Less than 0.1
Sodium	Na_2O	Less than 0.1
Titanium	TiO_2	Less than 0.1
Thorium	ThO_2	Less than 0.1
Uranium	U_3O_8	0.0090 - 0.0200
Rare earths	Oxides	Less than 0.1

TABLE 34

COMPOSITIONS OF PHOSPHORIC ACIDS USED IN ORNL PROCESSES

Acid from company	Source of phosphate rock	Type of acid	Concentration, g ℓ^{-1}								
			U	Fe(II)	Total Fe	PO_4	V	Al	Ca	SO_4	F
A	Florida	Brown	0.14-0.17	0.3-0.8	7-10	5.0-6.0 M	0.1-0.3	3-6	2-4	19-31	21-30
B	Florida	Brown	0.16-0.19	0.3-2.6	10-12	5.4-6.0 M	0.1-0.3	3-4	2-4	27-33	26-29
C	Florida	Green	0.10-0.13	0.2-0.7	6-7	5.2-5.3 M					
D	Florida	Green	0.07-0.09	2.0-3.5	8-9	5.5-5.7 M					
E	N. Carolina	Green	0.06	3.4	6-8	5.5 M					
F	Western	Green	0.06	2.6	4-5	5.9 M					

TABLE 35

RELATIVE COSTS OF URANIUM RECOVERY FOR VARIOUS FERTILISER PROCESSES

(Butler 1949a, 1949b, Stephan et al. 1950, Long and Valle-Reistra 1953)

Process	Size of Plant tonnes of rock/day	Product % U_3O_8	Cost $US (1950) per kg of U_3O_8
Leach rock with 30% sulphuric acid, recover P_2O_5 as triple superphosphate.	1000	4-5	19.8 (calcined rock) 9.7 (uncalcined)
Leach single superphosphate with water, recover P_2O_5 as superphosphate.	1000	4-5	146
Leach single superphosphate, recover P_2O_5 as monocalcium phosphate.	1000	4-5	103
Leach single superphosphate, recover P_2O_5 as triple superphosphate.	1000	4-5	21.7
Leach single superphosphate made from calcined rock, recover P_2O_5 as superphosphate.	1000	4-5	79.5
Leach single superphosphate made from calcined rock, recover P_2O_5 as monocalcium phosphate.	1000	4-5	64.5
Leach single superphosphate made from calcined rock, recover P_2O_5 as triple superphosphate.	1000	4-5	12.3
Leach superphosphate made from roasted rock with organic solvent, recover P_2O_5 as single superphosphate.	500		58.5
Leach superphosphate made from roasted rock with organic solvent, recover P_2O_5 as triple superphosphate.	500		26.2
Dissolve rock with phosphoric acid, recover P_2O_5 as monocalcium phosphate.	1000	65	40.0
Precipitate uranium from wet-process acid with hydrogen fluoride and limestone.	500	10-20	59.5
Ion exchange from phosphoric acid	500	UF_4 of 95% purity	11.4

TABLE 36

COST OF RECOVERING URANIUM AS A BYPRODUCT DURING THE MANUFACTURE OF PHOSPHORIC ACID

Process	Country	Plant Size	Text Reference	Date of Cost Estimation	Cost, $US kg U_3O_8
IMI phosphoric acid process - recovery of uranium from undissolved residue	Israel	50 tonnes uranium per year	Section 4.3	August 1970	27.5
Selective leaching of uranium from calcined rock with simultaneous upgrading of phosphate	Israel	as above	Section 4.3	September 1971	77
Solvent extraction from IMI process phosphoric acid	Israel	40-50 tonnes of uranium per year	Section 4.10.4	September 1971	15.4
Solvent extraction from wet-process phosphoric acid	U.S.A.	-	Section 4.10.4 (Gulf Process)	April 1974	Presumably 15.4 - 17.6
Solvent extraction from wet-process phosphoric acid	U.S.A.	900 tonnes of uranium concentrates per year	Section 4.10.4 (URC Process)	June 1974	15.4 - 17.6

TABLE 37

MAXIMUM QUANTITY OF URANIUM RECOVERABLE FROM PHOSPHATE ROCK

Country	Yearly Production of Phosphate Rock[a], 1972 (thousands of tonnes)	Estimated Quantity of Uranium in Rock (tonnes)	Estimated Quantity of Uranium Recoverable from the Production of Phosphoric Acid (b) (tonnes)
Israel	937	103	49
Jordan	714	100	48
Morocco	15,105	1,661	797
Senegal	1,250	113	54
South Africa	1,966	176	85
Togo	1,855	167	80
Tunisia	3,387	203	97
Russia	10,000	400	192
United States	38,465		
Florida	28,000 (70%)	4,200	2,016
Other	10,465	840	403
		Total 7,963	3,821

(a) *post-beneficiation*

(b) *60% of the rock is assumed to be processed to phosphoric acid.*

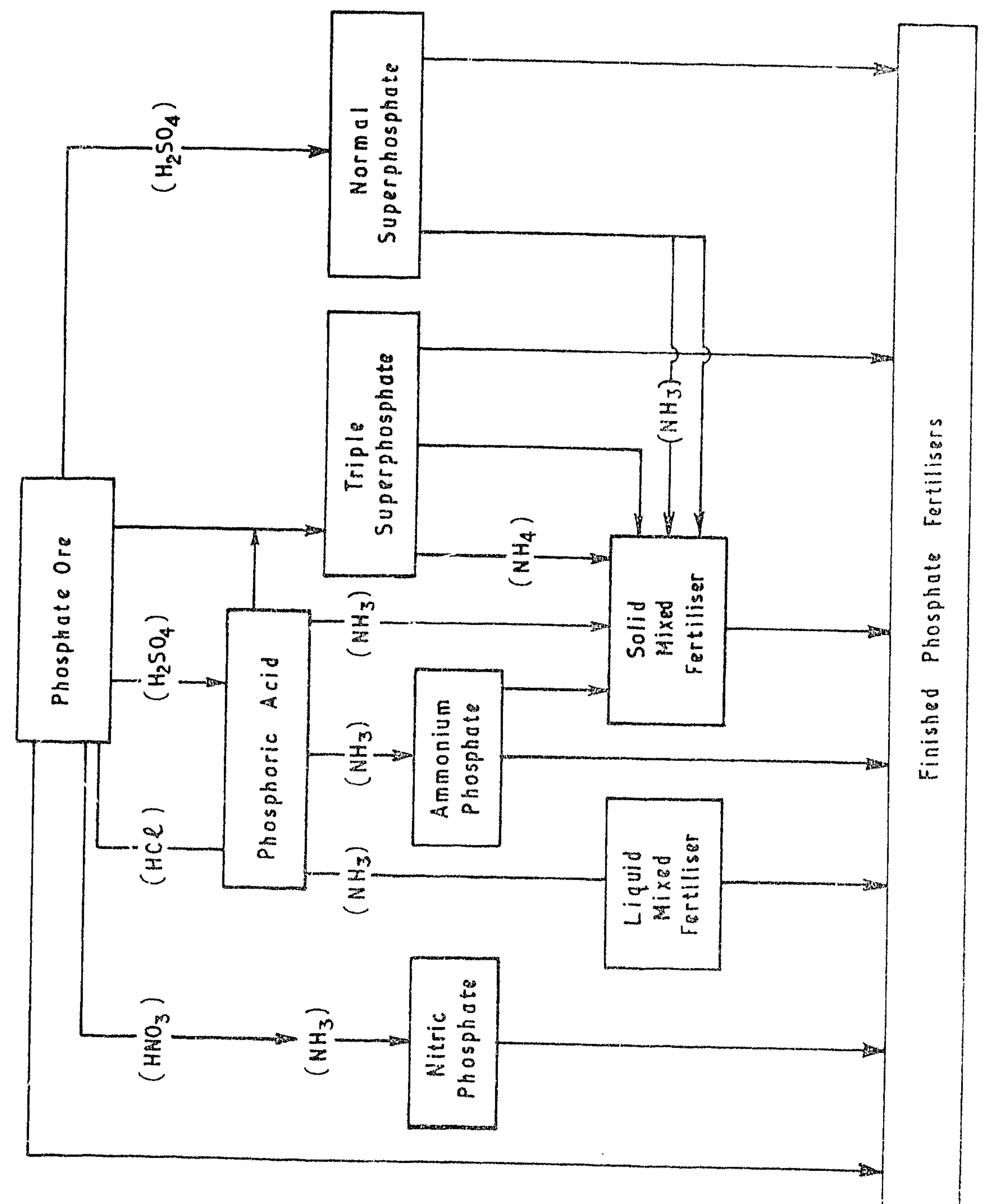


FIGURE 1. THE PHOSPHATIC FERTILISER INDUSTRY

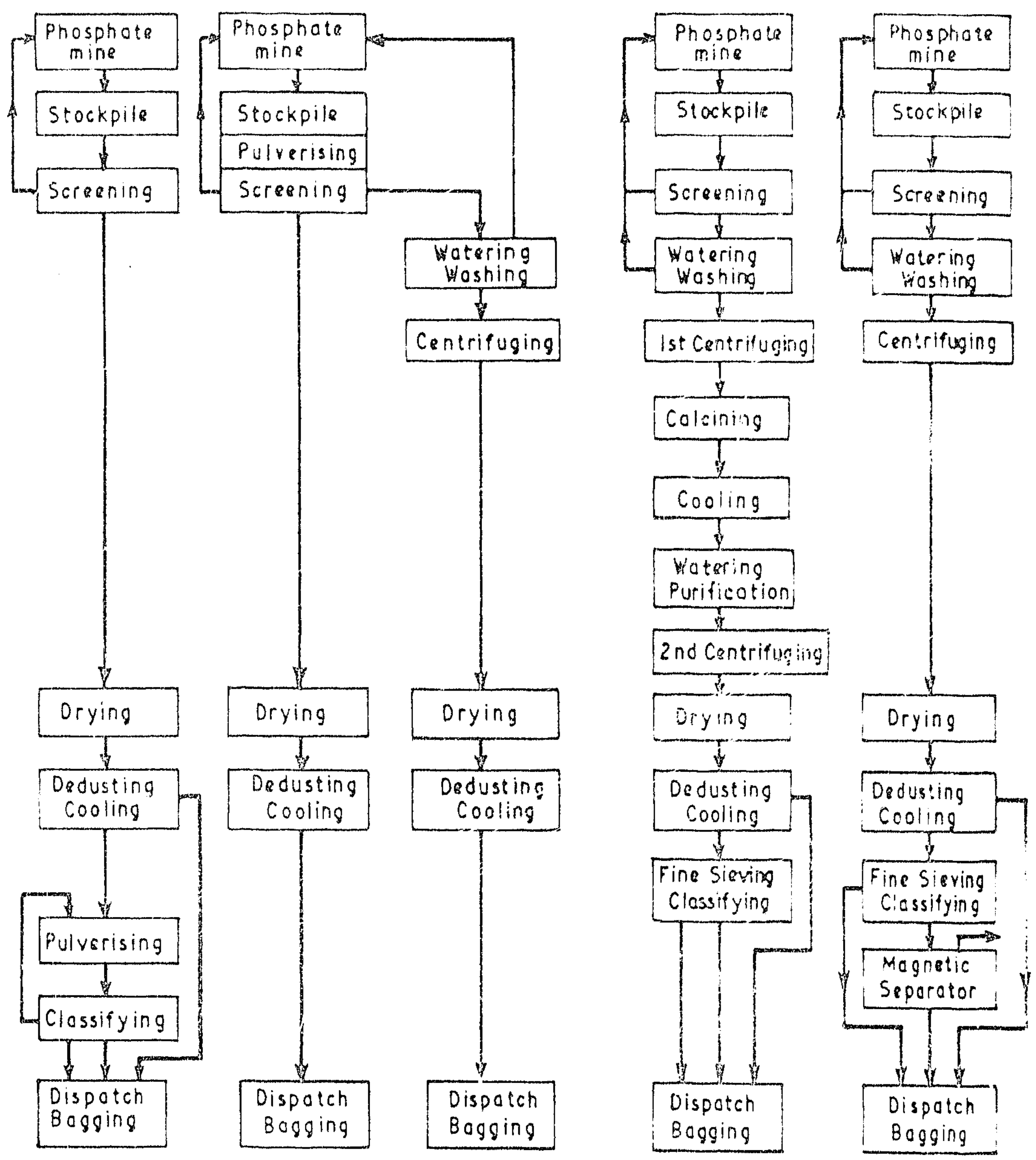


FIGURE 2. POSSSIBLE FLOW DIAGRAMS FOR BENEFICIATION OF CRUDE PHOSPHATE ROCK (After Jaeger et al. 1972-1973)

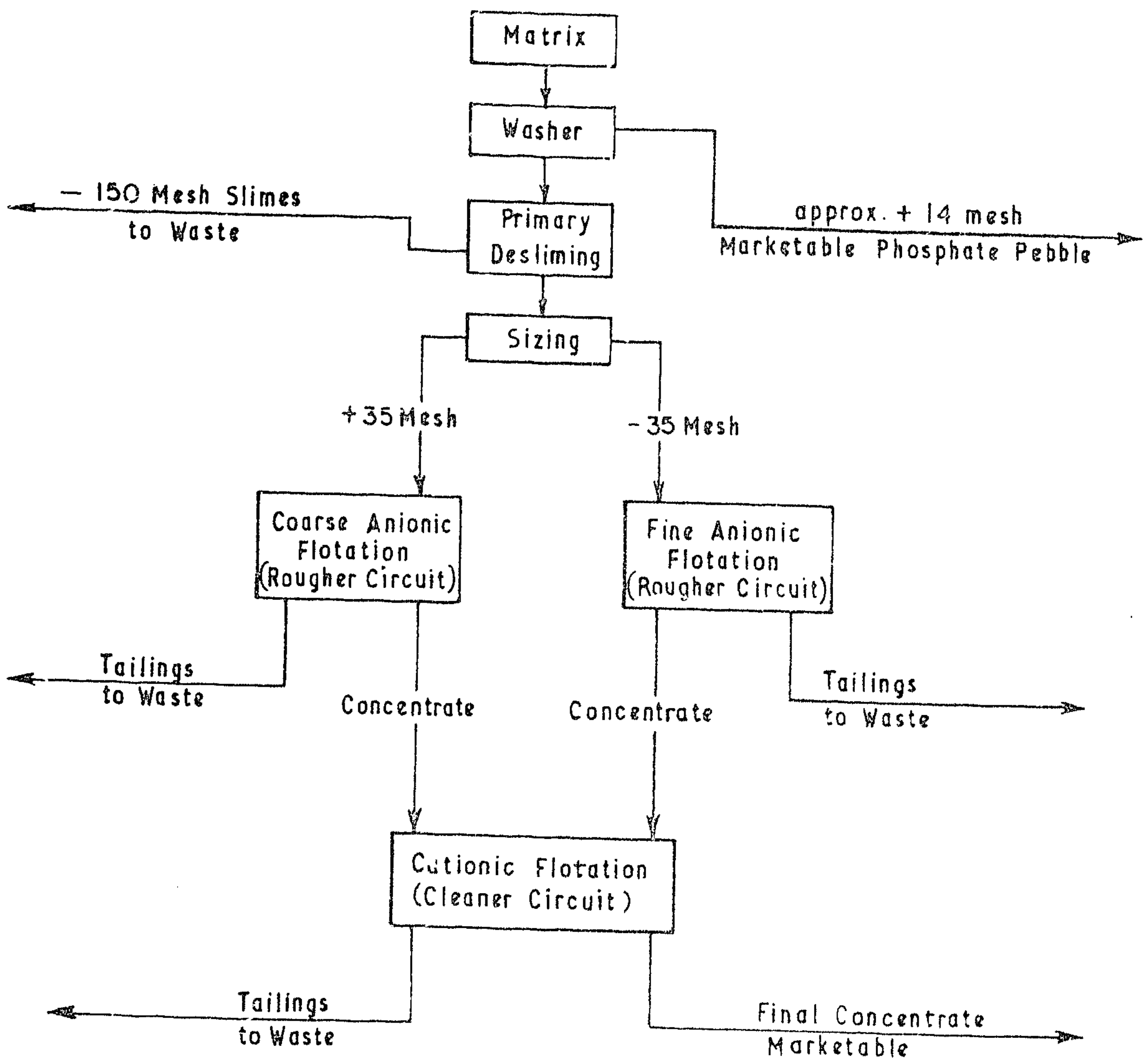


FIGURE 3. BASIC FLOWSHEET FOR BENEFICIATION OF FLORIDA PHOSPHATE (After Aparo 1970)

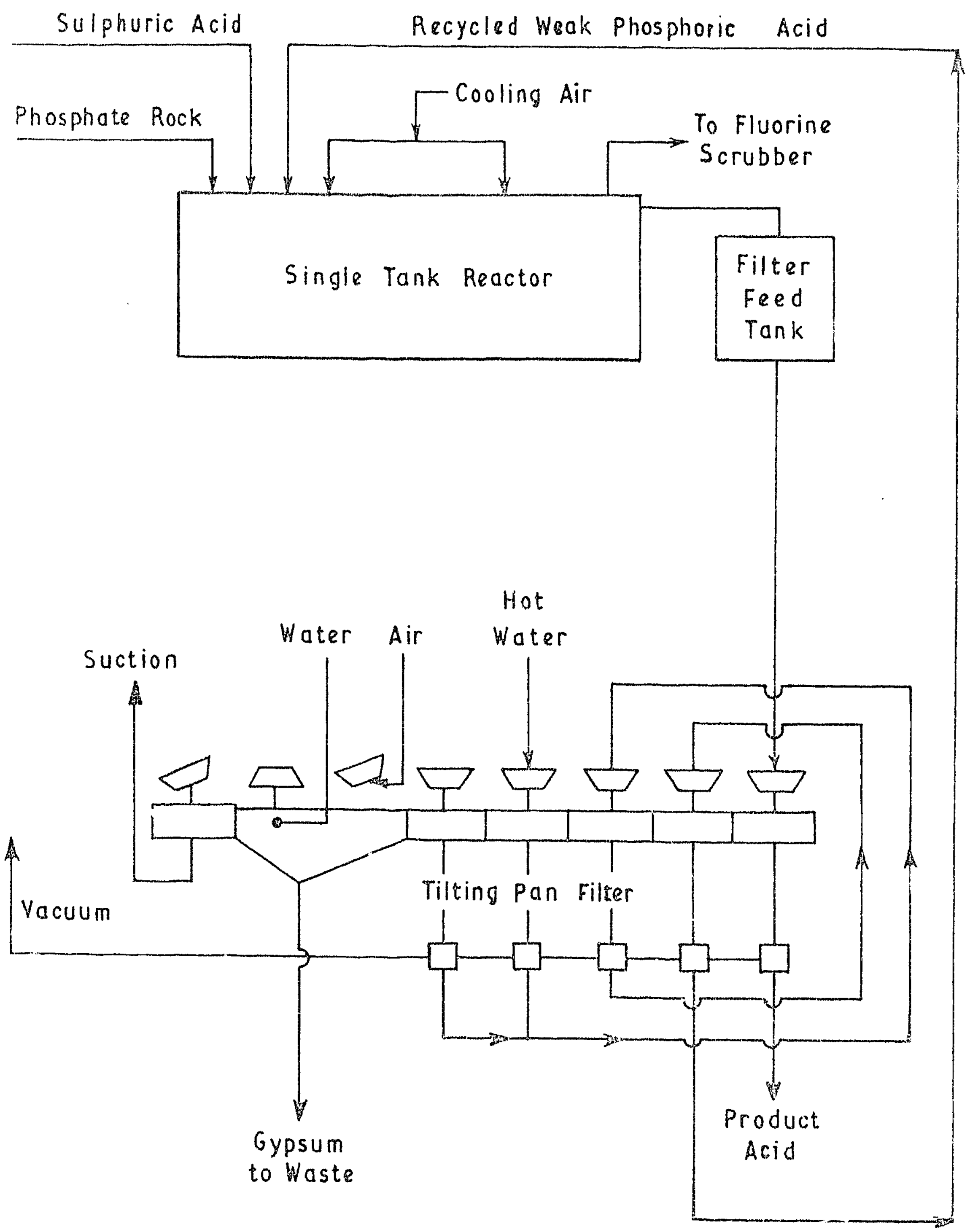


FIGURE 4. FLOWSHEET FOR THE MANUFACTURE OF WET-PROCESS PHOSPHORIC ACID

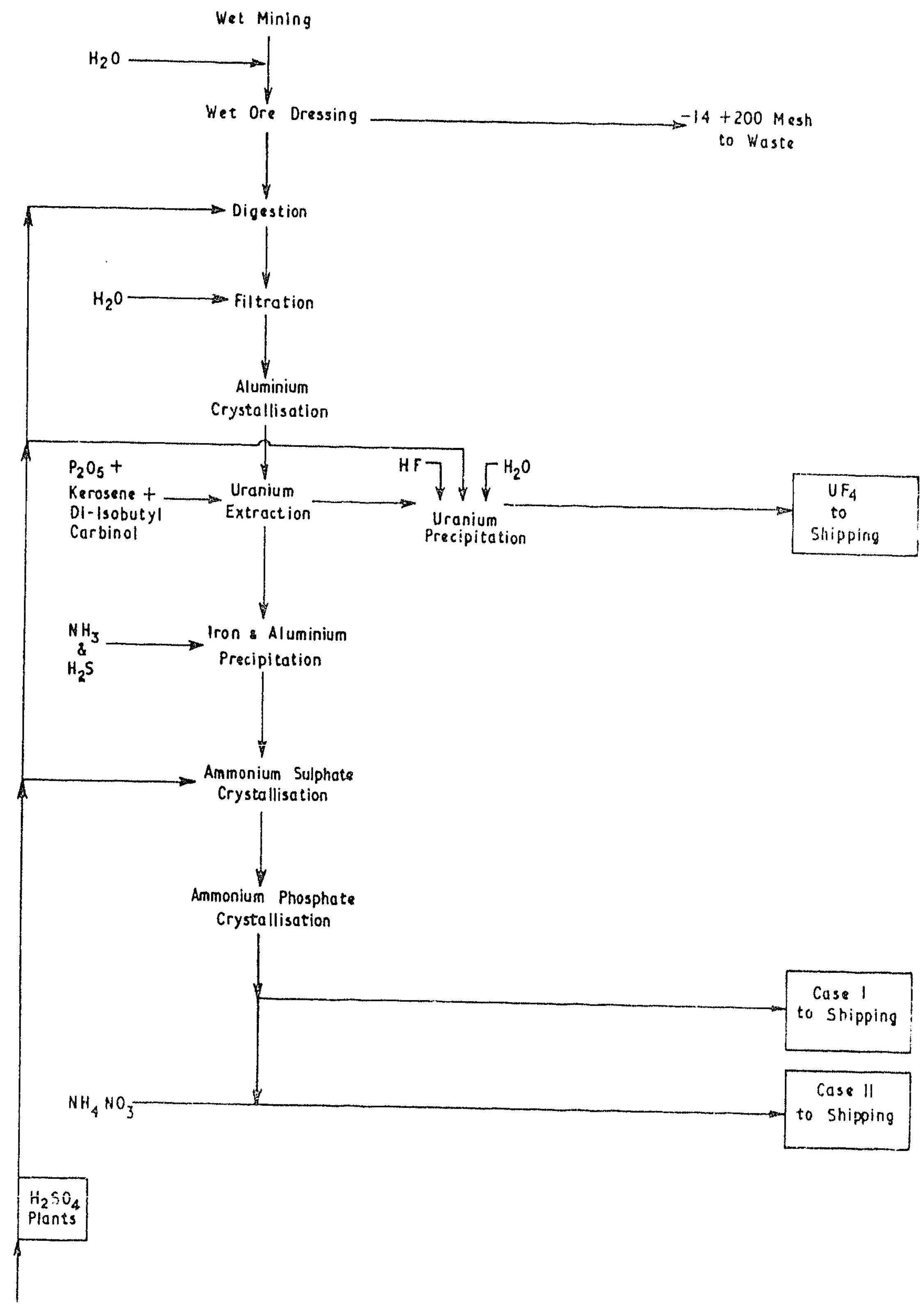


FIGURE 5. RECOVERY OF URANIUM FROM LEACHED ZONE MATERIAL - IMC PROCESS I

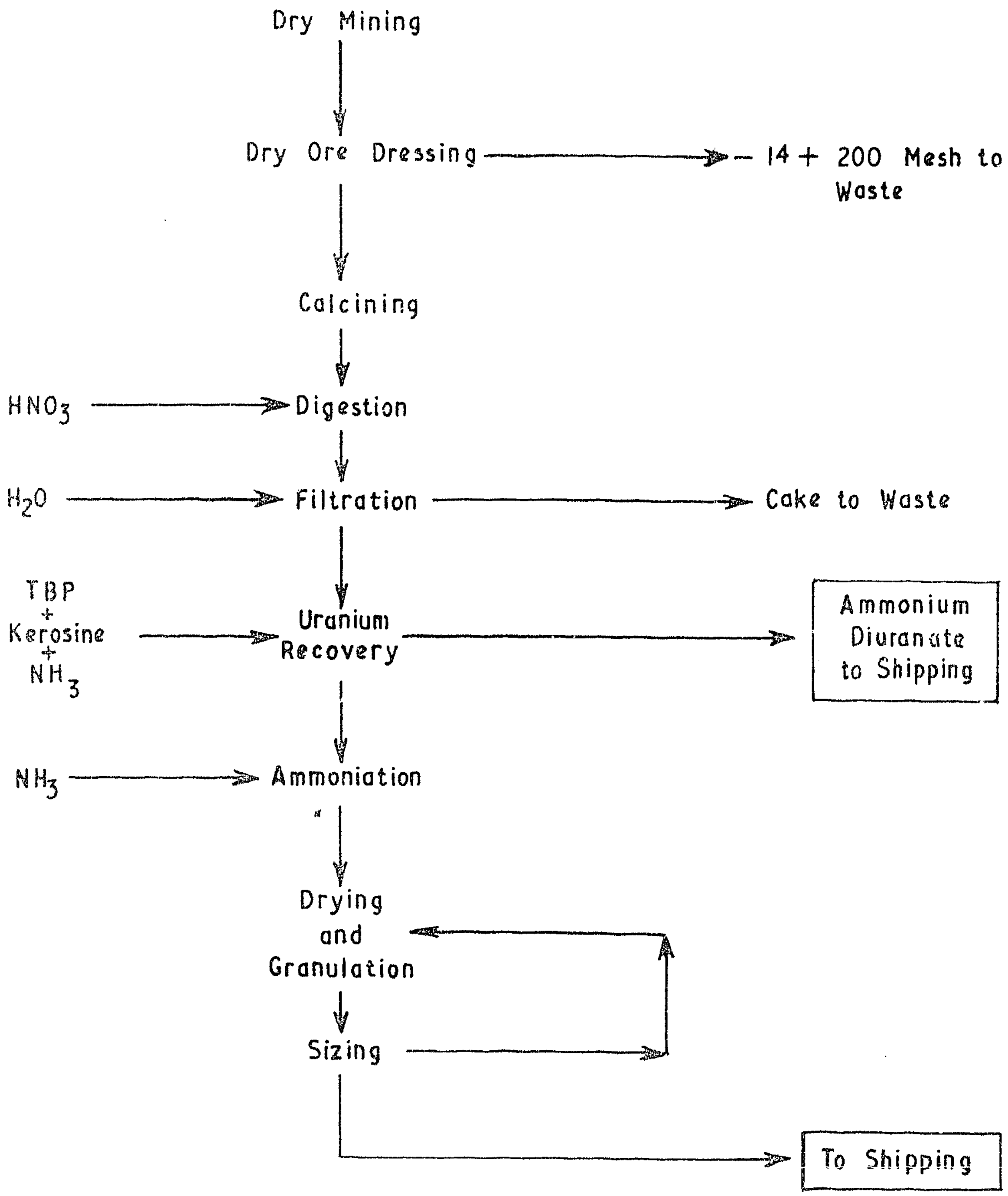


FIGURE 6. RECOVERY OF URANIUM FROM LEACHED ZONE MATERIAL - IMC PROCESS II

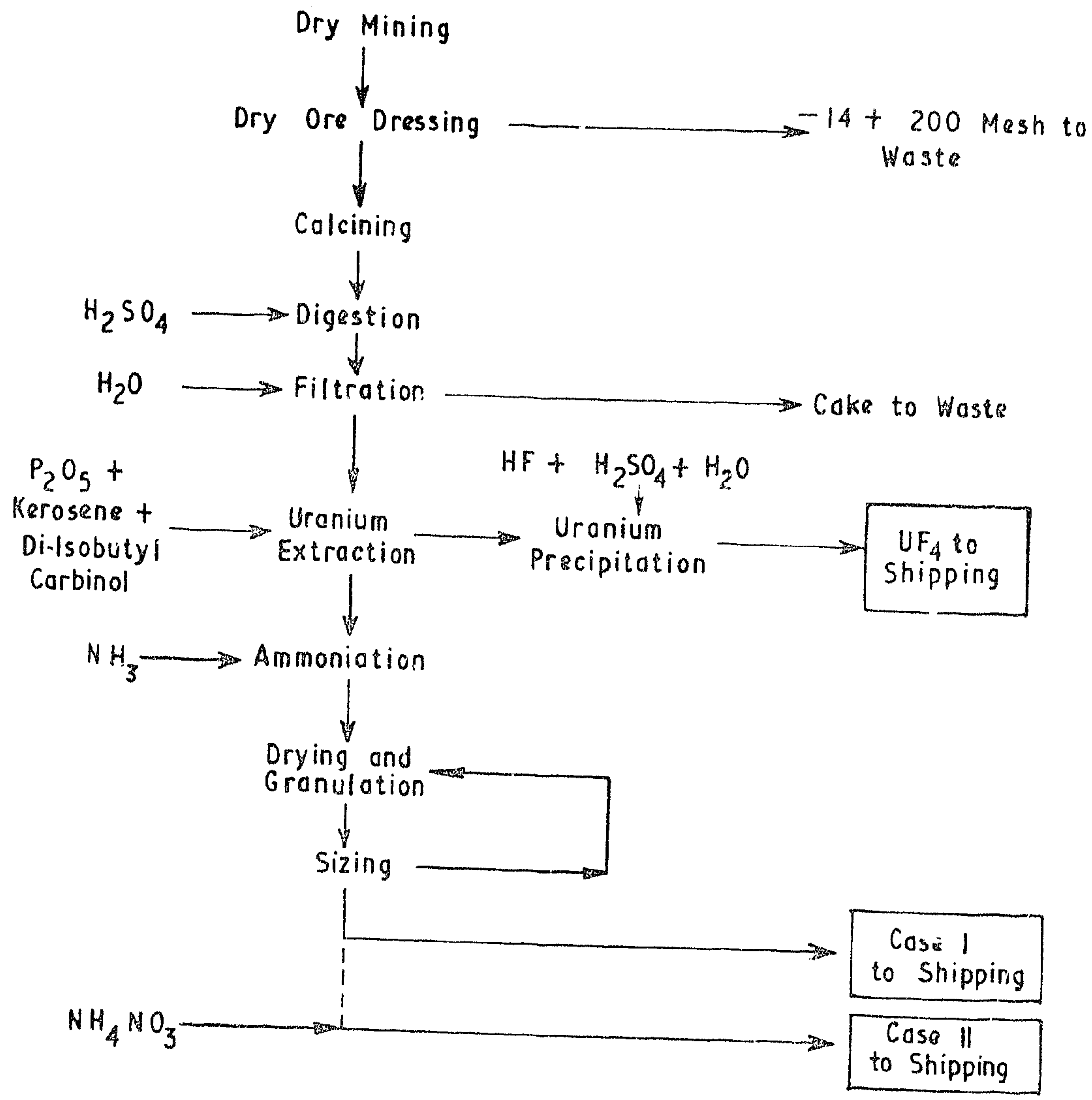


FIGURE 7. RECOVERY OF URANIUM FROM LEACHED ZONE MATERIAL - IMC PROCESS III

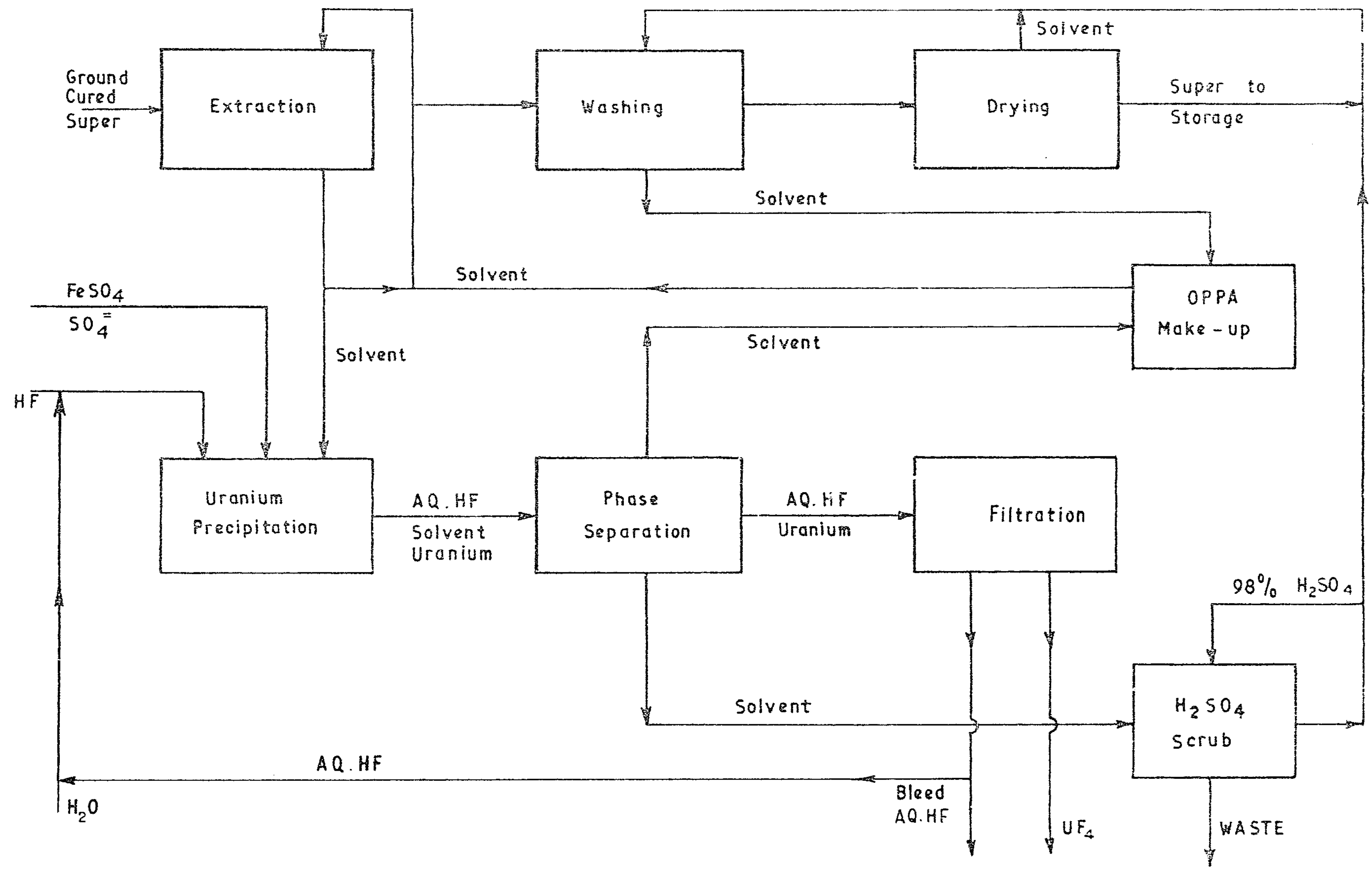


FIGURE 8. DOW PROCESS FOR THE RECOVERY OF URANIUM FROM CURED SINGLE SUPERPHOSPHATE (After Long and Valle-Riestra 1953)

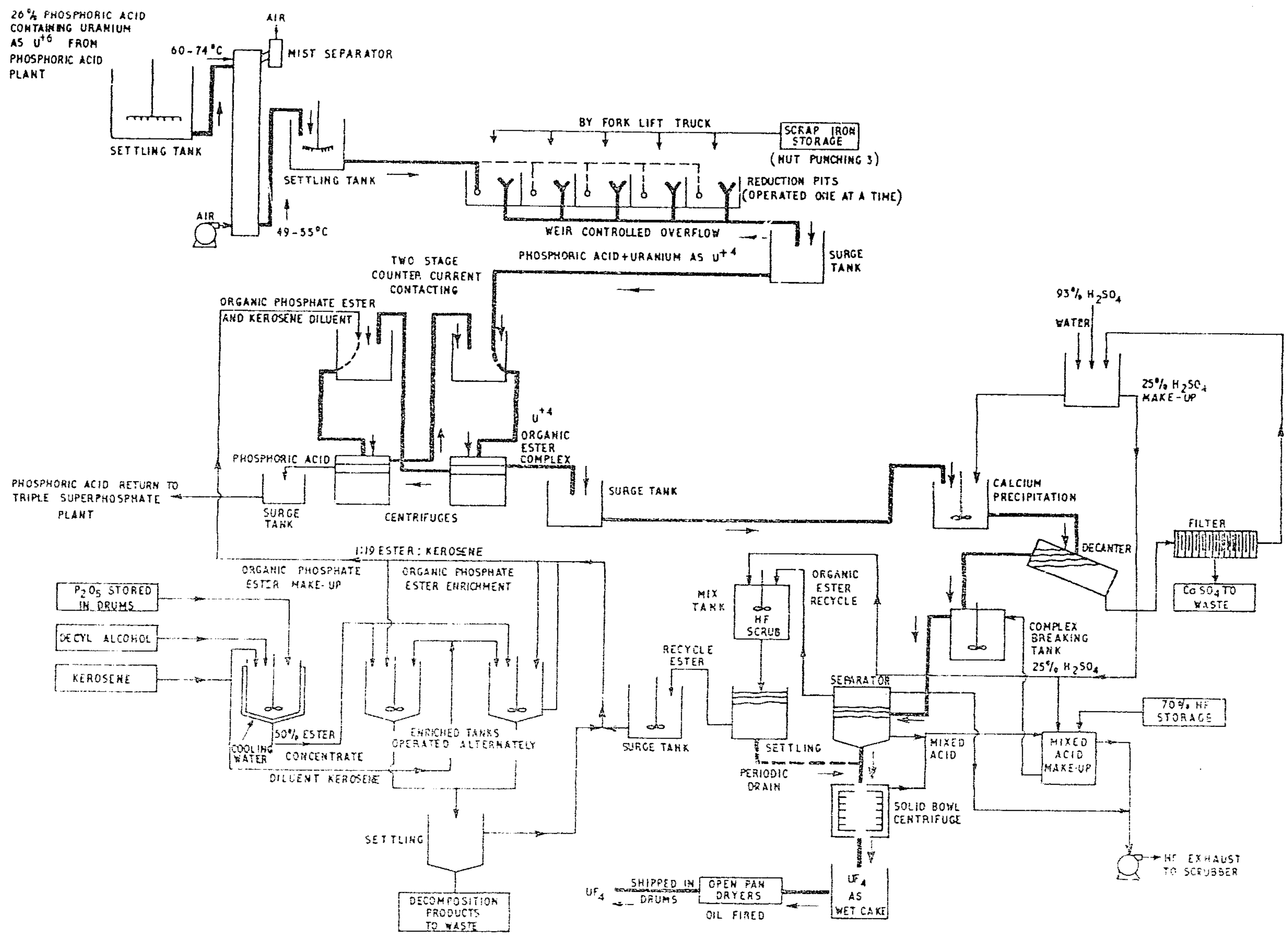
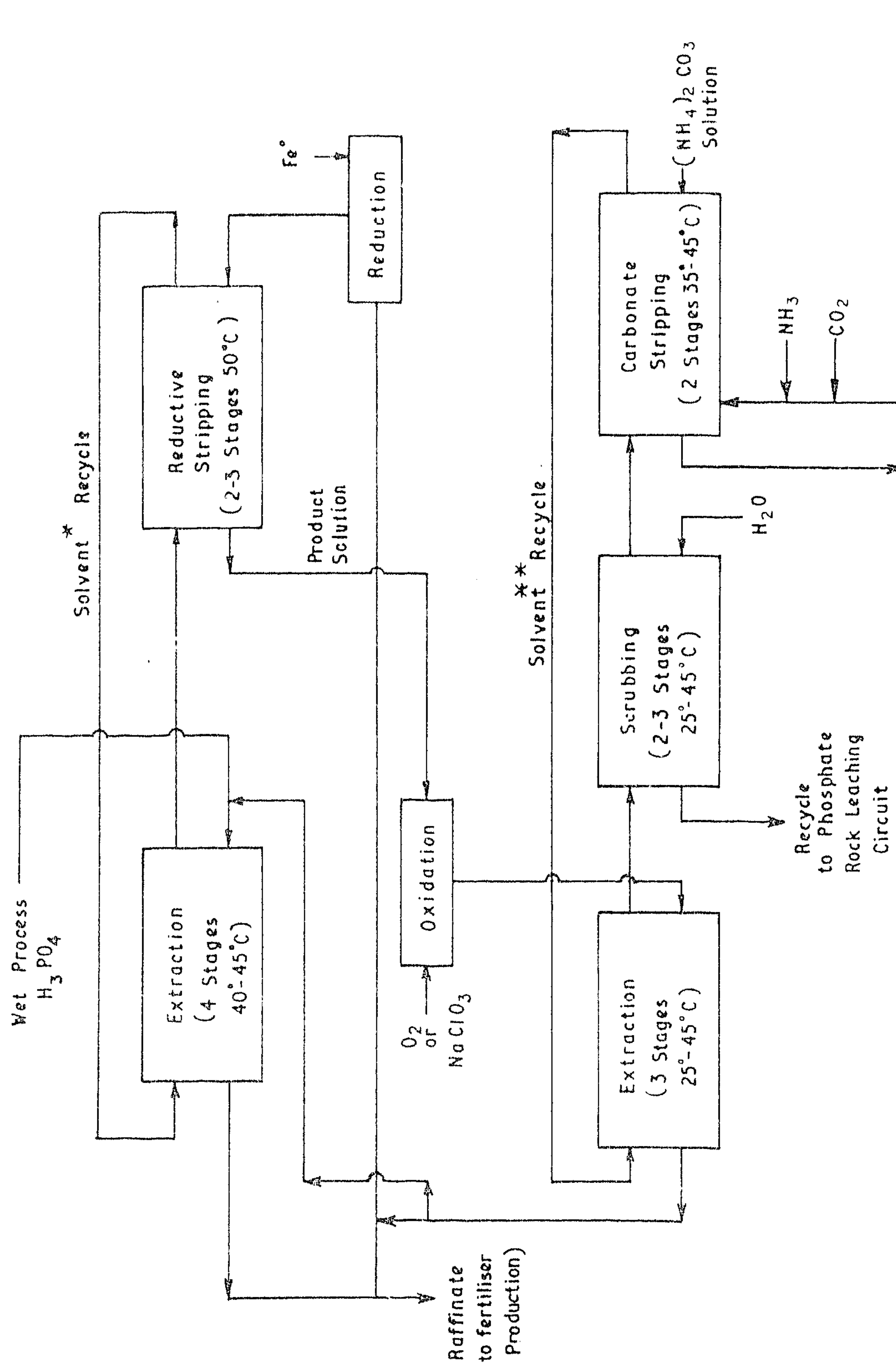
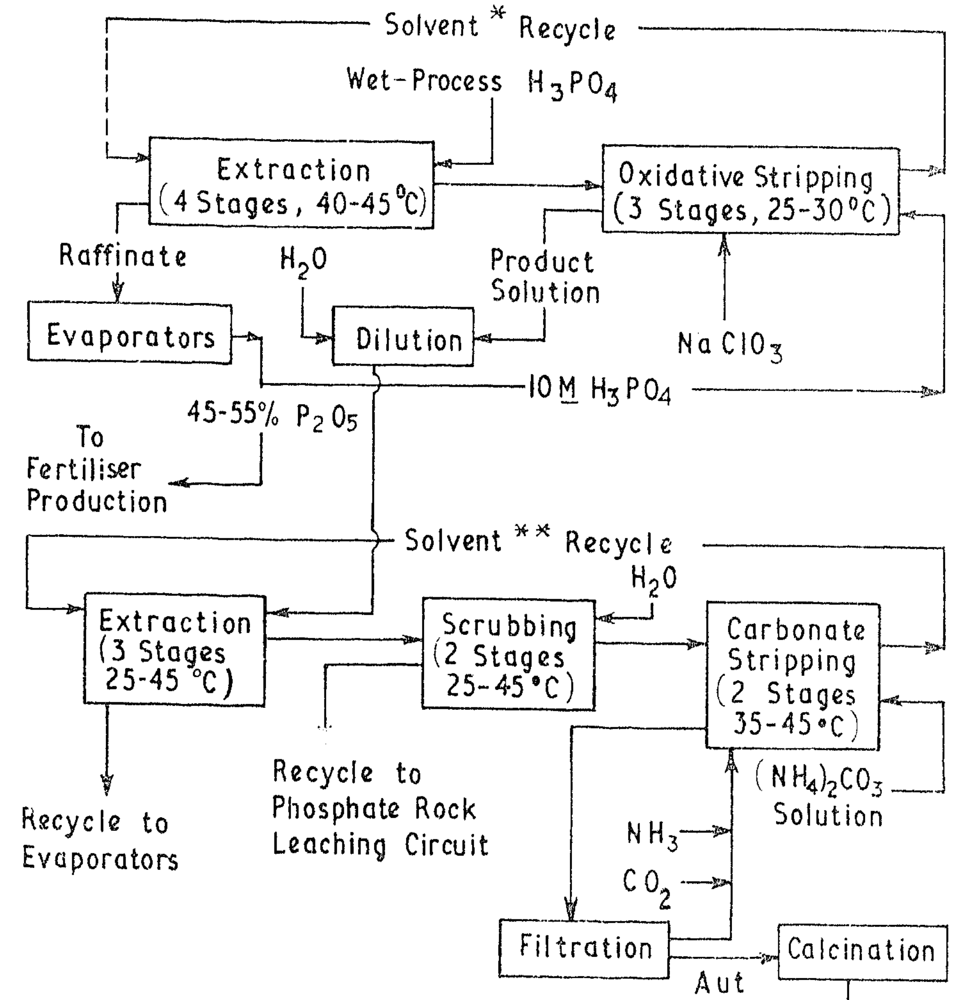


FIGURE 9. FLOWSHEET FOR THE IMC URANIUM RECOVERY PLANT (After Greek et al. 1957)



* 0·5 M D2EHPA – 0·125 M TOPO–AMSCO 450
** 0·3 M D2EHPA – 0·075 M TOPO–AMSCO 450

FIGURE 10. ORNL PROCESS (I) FLOWSHEET FOR THE RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID (After Hurst et al. 1972)



*0·3-0·4 M OPPA–AMSCO 450
** 0·3 M D2EHPA-0.075 M TOPO–AMSCO 450

FIGURE 11. ORNL PROCESS (II) FLOWSHEET FOR THE RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID (After Hurst and Crouse 1974)

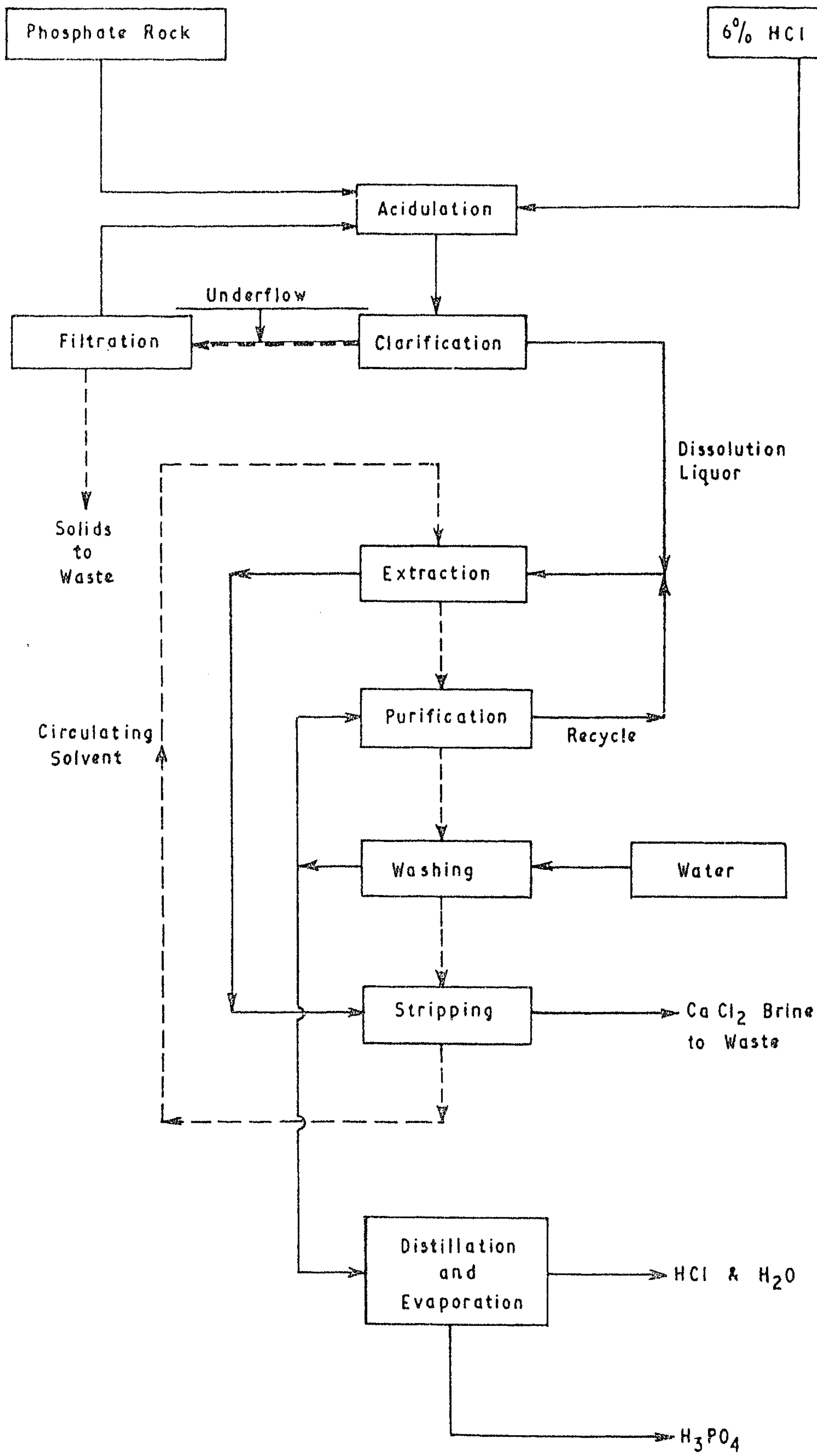


FIGURE 12. THE IMI PROCESS (After Ketzinel 1972)

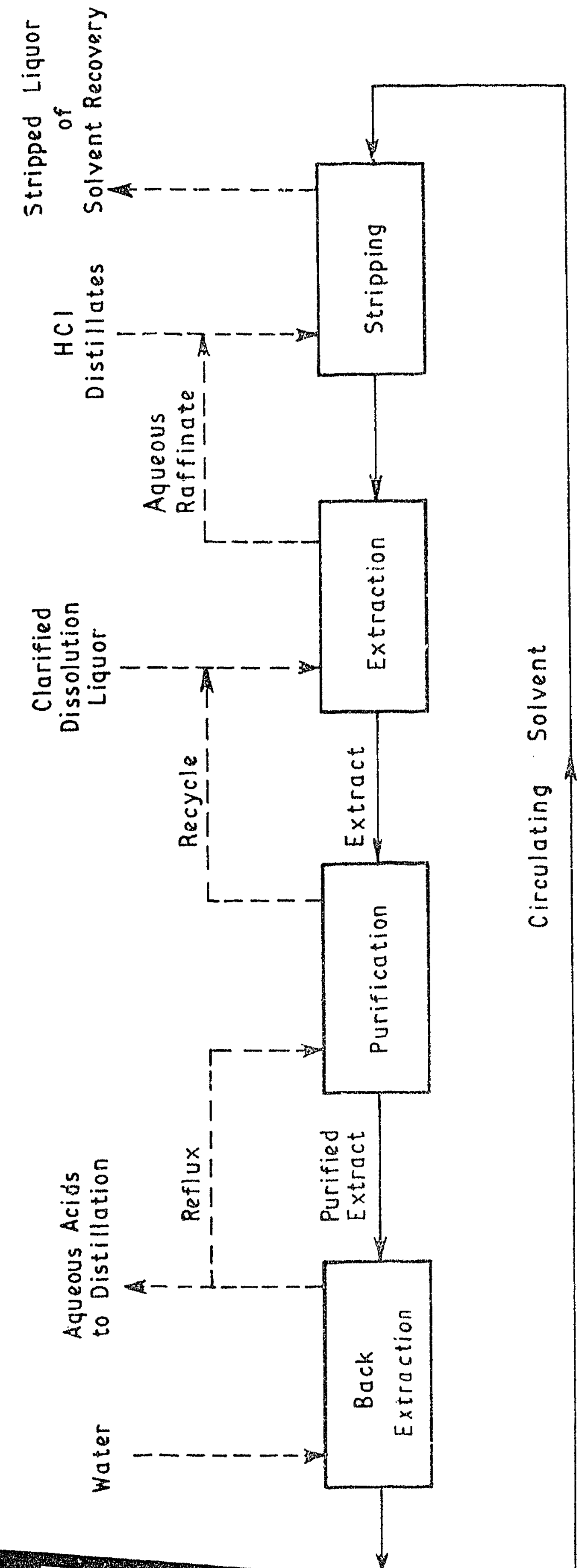


FIGURE 13. SOLVENT EXTRACTION SECTION OF THE IMI PROCESS (After Ketzinel et al. 1972)