PN-ABQ-689
ISN 26202

Preliminary Technical and Economic Assessment of Developing the Toolse Phosphate Deposit, Estonia

Prepared by

International Fertilizer Development Center
P.O. Box 2040
Muscle Shoals, Alabama 35662

for

United States Agency for International Development
Washington, D.C.

Grant No. 180-0249-G-00-2524-00

January 1993

Executive Summary

A United States Agency for International Development (USAID)-sponsored study team composed of a phosphate expert and an environmental expert visited Estonia during November 1992 to gather information for performing a preliminary assessment of the potential for development of the Toolse phosphate deposit. The Toolse deposit is a sedimentary phosphate deposit located in northern Estonia near the town of Kunda.

Valuable information was obtained during this mission, and these data together with data generated after the mission to Estonia were used to develop this report. Although the Estonian contacts were especially helpful in obtaining information, data to perform a preliminary economic assessment were particularly difficult and in some cases impossible to obtain.

The average P_2O_5 content of the ore of the Toolse deposit is 10.6% P_2O_5. Characterization of several Toolse ore and concentrate samples indicates they have several undesirable characteristics for world trade including the following: (1) the P_2O_5 content of concentrates is low (≈28% P_2O_5), (2) the primary gangue mineral is quartz, which is abrasive to processing equipment, (3) the total impurity content is high, (4) some concentrates examined contain undesirable carbonates, and (5) the chlorine contents are above 300 ppm. High chlorine levels promote corrosion in conventional phosphoric acid plants. It is important to note that improved beneficiation techniques could be implemented to raise the grade of Toolse concentrates and lower the quartz contents.

The cadmium content of Toolse concentrates is low (1-5 ppm). These cadmium levels are significantly lower than those in typical sedimentary phosphate concentrates. The low cadmium content may be an incentive to develop the Toolse deposit, particularly because of its proximity to the European market. Cadmium levels in soil, fertilizers, and crops and in livestock grown or raised on cadmium-enriched lands are a major cause of concern in Europe.

Toolse concentrates have been processed in laboratory-scale experiments at the Tallinn Technical University Laboratory of Inorganic Technology to produce high-analysis fertilizers such as triple superphosphate (TSP), monoammonium phosphate (MAP), diammonium phosphate (DAP), and nitrophosphates. Not enough data were available to compare the grades or qualities of these products or potential products with products available on the world market.

By comparing the potential development of the Toolse phosphate deposit with the production from the existing phosphate mine at Kingisepp, Russia, utilizing available data, and making several assumptions, the consultant concluded that a mine at Toolse could support a production rate of 1 million mt of concentrate containing about 28% P_2O_5 per year for a reasonable mine life (over 20 years). Production at levels to support Estonian requirements (250,000 mtpy concentrate) or a hypothetical regional requirement (500,000 mtpy concentrate) could be maintained for over 35 years.

Comparison of the potential mining situation at Toolse with a mining situation in Florida indicates it would be very unlikely that Toolse concentrates could be produced at costs comparable to the current selling prices of phosphate concentrates of a similar grade that are available on the world market (about US $30/mt f.o.b.). Firm estimates of potential costs cannot be given, but the costs of production may approach or exceed reported production costs for concentrates from the Kingisepp mine in Russia for 1992 (about US $38/mt) and estimated for 1993 (about US $56/mt). Production costs for a Central Florida mine used for comparative purposes are about US $22/mt. Capital and production costs to produce concentrates from the Toolse deposit might be about twice as high as the production costs of the Florida mining example.

The Toolse deposit might be developed on an import substitution basis, that is, to supply feedstock for a domestic fertilizer processing industry. Potential delivered costs of phosphate concentrates shipped to Estonia from

several locations in the world might be in the range of $45-$60/mt. It is possible that Toolse concentrates can be produced at a cost comparable to the cost of imported phosphate feedstocks.

Further basic studies of the Toolse deposit are needed in several areas including (1) further delineation of the deposit, (2) beneficiation studies, (3) processing studies, and (4) mining studies. All of these technical studies should be performed to derive reliable data needed to perform a meaningful economic assessment.

The world market situation for phosphate concentrate will probably change after the year 2000 due primarily to the expected contraction of the United States (Florida) phosphate mining industry and anticipated dominance of Morocco in the world market situation. Today, the United States phosphate industry currently accounts for about 15% of the world's phosphate concentrate production while Morocco accounts for about 13% of the total. However, the Morocco reserves are extremely extensive compared with those of the United States. The possible decline in the United States (Florida) international competitive position would most likely result in increased international phosphate prices. After about the year 2000, prices of phosphate concentrate on the world market will probably rise and the quality of concentrates available on the world market may generally decrease. Final development of the Toolse deposit should be designed to coincide with this projected change in world market conditions. A lead time of at least 6 years is estimated to develop the Toolse deposit.

One of the main conclusions reached by this study was that the development of the Toolse deposit is potentially economically viable only if there is a concurrent development of fertilizer processing facilities. Fertilizer production plants must be designed for specific products at capacity levels appropriate to the actual or projected market demand for products. The focus of this study was on developing the Tooise phosphate deposit to produce phosphate rock concentrates; the analyses of fertilizer production

scenarios and a market analysis were beyond the scope of this study. However, an analysis of the potential market and determination of the products required for Estonian or regional use, or perhaps for export, are urgently needed before meaningful mining and fertilizer production scenarios can be developed.

A prefeasibility study of the development of the Toolse deposit is also needed to assess the technical and economic potential of the deposit. While such a study may be largely conceptual in nature, it would provide estimates of potential costs to determine if further investment is warranted. The study results would also help to guide decisions relative to the product mix and the size of the market at different cost profiles. Two basic scenarios should be considered: (1) a mine producing 1 million mt of concentrate strictly for export in the world market and (2) a mine producing concentrate at various production levels to feed an industrial complex designed to produce fertilizer for domestic or regional consumption and perhaps limited export outside the region.

In light of the estimated 6-year minimum lead time required to develop the Toolse deposit and the potential for more favorable world conditions for phosphate marketing after the year 2000, it is imperative that the prefeasibility study be performed immediately.

The recommended prefeasibility study of the Toolse deposit should include (1) a market analysis to establish product requirements, (2) basic studies to determine suitable ore reserves and beneficiation, mining, and processing techniques, (3) conceptual design and cost estimates for an appropriately sized mine and beneficiation plant, (4) conceptual design and cost estimates for an appropriate fertilizer production complex, (5) a plan and cost estimate for infrastructure development associated with the mine and processing complex, (6) an environmental impact assessment, and (7) an economic analysis of the entire project integrating all technical, economic, and social aspects of the development of the Toolse phosphate deposit.

Preliminary Technical and Economic Assessment of Developing the Toolse Phosphate Deposit, Estonia

Introduction

As the result of a request for assistance from the Government of Estonia (GOE) and the Estonian Academy of Sciences, the USAID Director of the Regional Mission for Europe approved the use of funds from the Regional Mission for Europe Project No. 180-0249, Audit, Evaluation and Project Support, for a brief but comprehensive program to evaluate the technical and economic potential and environmental risks, if any, of the commercial development of the phosphate deposit at Toolse, Estonia. Grant number 180-0249-G-00-2524-00 was approved by the Director of the Regional Mission for Europe on October 30, 1992.

The grantee team, hereafter referred to as the team, for the program was composed of an IFDC geologist (Mr. Steven J. Van Kauwenbergh) and an environmental expert (Mr. Richard Zwolak, KBN Engineering and Applied Sciences, Tampa, Florida). The team traveled to Estonia during November 13-21, 1992. Activities in Estonia were primarily coordinated by Dr. Mikhel Veiderma, Vice-President of the Estonian Academy of Sciences. Extensive discussions were held with representatives of the Estonian Academy of Sciences Institute of Geology, the Estonian Geologic Survey, Tallinn Technical University Laboratory of Inorganic Technology, Estonian Research Institute of Agriculture and Land Improvement, the Ministry of the Environment, and Tallinn Technical University Mining Institute. A field trip was conducted to the Maardu phosphate mining and processing complex, the Kunda cement plant and potential phosphate mining area at Toolse, and the Kingisepp phosphate mining and processing complex in Russia. The staff members of the previously mentioned Estonian organizations were particularly helpful in obtaining information to develop this report. In particular, the efforts of Dr. Mikhel Veiderma; Mr. Rein Randsep, Estonian Geologic Survey; and Dr. Vaino Puura of the Institute of Geology should be mentioned. These gentlemen were particularly helpful.

Activities in Estonia were monitored by Mr. Adrian L. De Graffenreid, USAID Representative, U.S. Embassy, Tallinn, Estonia. A brief preliminary report outlining the mission's findings was submitted to Mr. De Graffenreid upon completion of the mission to Estonia.

This report contains only the results of the preliminary technical and economic evaluation of the Toolse phosphate deposit. The results of the environmental expert's investigation are contained in a separate report as defined in the project document. This report contains sections on (1) the general geology of the Estonian phosphate deposits, (2) observations on the previous and present mining of Baltic Basin phosphates, (3) characterization of phosphate samples from the Toolse deposit, (4) world production of phosphate rock, (5) the potential for mining the Toolse deposit, and (6) recommendations for further work.

The only major problem encountered in obtaining information in Estonia concerned determining the availability and affordability of inputs for processing and the absence of basic data and/or preliminary cost estimates. Traditional sources of materials (mainly Russia) are questionable and reported prices are in a constant state of flux. Quite often the response of Estonian contacts to specific questions concerning the costs of certain operations or inputs and the availability of materials was "I would hesitate to even venture a guess."

General Geology

Outcrops of phosphorite in the Baltic Basin extend along the southern margin of the Gulf of Finland along the north coast of Estonia into Russia to the east of St. Petersburg (as far east as Volkhov). The total distance the phosphate beds can be traced is about 400 km. In Estonia the phosphate beds gently dip to the south towards the center of the Baltic Basin.

The phosphorites are upper Cambrian to Ordovician in age, about 500 million years old. The phosphorite beds are found above a sequence of lower Cambrian sandstones, siltstones, and shales. Above the phosphorite is a kerogen-rich clay which is called the Dictyonema Shale. Above the Dictyonema Shale, and also in the lower Ordovician, is another clay bed and a sequence of glauconitic sandstones and limestones.

The middle Ordovician is represented by finely crystalline limestones, dolomitized limestones, and marls. The thickness of this sequence (0-40 m) increases to the south.

Quaternary sediments cover this sequence and generally range in thickness from 2 to 3 m. The Quaternary sediments are composed of tills, sands, clays, and peat deposits. The thickness of quaternary sediments can reach 35-40 m in buried river valleys.

The phosphate particles are composed of whole valves or fragments of valves of inarticulate brachiopods of the genus *Obolus* or more rarely *Schmidtites*. Where the phosphate is composed of unbroken or slightly damaged valves (up to 1 cm), it is termed the Obolus Conglomerate. Where the phosphorite is composed of sand-sized shell fragments, it is termed Obolus Sandstone. The phosphorite beds range in thickness from 1 to 8 m.

Several areas in Estonia have been identified as phosphate deposits including Toolse, Aseri, Tsitre, Maardu, and Rakvere.

Previous and Present Mining of Phosphorites in the Baltic Basin

Two mines have been developed on the Baltic Basin phosphorite deposits. The Maardu deposit and processing complex is located in northern Estonia near the coast on the eastern outskirts of Tallinn. The Kingisepp complex is located in Russia about 20 km east of the Estonia-Russia border. The main road from Tallinn to St. Petersburg (M11) passes through the Kingisepp mining and processing complex.

Maardu

In 1920 a mine was developed and a concentration plant with an annual output of 4,000 mt of concentrate was built at Maardu. Few details are known concerning this venture. With the assistance of German capital and technology a new mine and concentration plant was developed in 1938. Flotation techniques were to be used to produce concentrates with up to 33% P_2O_5 to be used for the production of single superphosphate (SSP).

The advent of World War II and Russian occupation stopped these plans. After the war, mining was resumed. Both of the early mines utilized underground mining methods until the early 1960s when an open pit utilizing large draglines was developed.

Phosphate ore (≈10.5% P_2O_5) was mainly upgraded by a dry screening method to about 20% P_2O_5. The German-built flotation plant apparently has worked intermittently. Russian flotation reagents produced concentrates in the range of 22%-25% P_2O_5. In the early 1980s Swedish flotation reagents were used to produce concentrates at 28% P_2O_5 or higher.

The phosphate mine at Maardu was closed in 1991. At maximum capacity the mine produced 400,000 mtpy of concentrates. This capacity was achieved mainly with dry screening. In the last 2 years of operation the mine produced 200,000 mtpy of concentrate. The mine was closed due to exhaustion of reserves. The final pit cut was examined and about 12-14 m of overburden was stripped to mine only about 1 m of phosphate ore. Large draglines were used to strip overburden and apparently bucket wheel excavators were used to mine the ore.

Almost all the production from Toolse was exported to Russia. A minor amount of the concentrate was used to reduce the free acid content of SSP produced at Maardu based on igneous apatite concentrates from the Kola peninsula. Approximately half the production from Maardu was used in Russia as a direct application fertilizer and half was used to produce triple superphosphate (TSP). This TSP production utilized phosphoric acid derived from Kola apatite concentrates. All Estonian and Russian sources questioned by the team indicated the concentrates from Maardu and Kingisepp were not suitable for direct application.

A new single superphosphate (SSP) plant was installed at Maardu approximately 10 years ago. The capacity of this plant is 250,000 mtpy of run-of-pile SSP (containing about 22% P_2O_5). Granular SSP can also be produced. Kola rock and sulfur are imported from Russia by rail. The Maardu plant used to make its own sulfuric acid but this plant was closed due to environmental concerns. The Maardu plant also presently produces a calcium carbonate filler material and a glauconite-based pigment.

A major problem at Maardu was spontaneous ignition of spoiled Dictyonema Shale. The Dictyonema Shale contains pyrite. This pyrite oxidizes liberating heat causing the kerogen (organic matter) in the shale to self-ignite. Temperatures of over 1000°C were said to have been measured in burning dump piles. After excavation, it apparently takes about 2 months for the shales to develop enough heat to self-ignite. The fires burn back into the dump piles until they extinguish themselves due to lack of

oxygen or are doused by groundwater. If the dump piles are disturbed and allowed to dry out, unburnt shale will reignite.

The shale is said to contain high levels of various heavy metals and uranium loosely bound to the organic matter. These elements are liberated to immediate area of the spoil piles when the shale is exposed and oxidized and/or ignites. No data were available to determine if these pollutants had moved outside the mining area in the atmosphere, surface water, or groundwater.

An experimental program was instituted in the last years of mining to alleviate the problem of spontaneous ignition. Apparently the shale was selectively spoiled and dumped in a water-filled pit. This program was said to have been only partially successful.

The shale fires were said to be very smoky and foul smelling due to the release of sulfur oxides into the atmosphere. The problem apparently was very evident to the Estonian population since the main highway (M-11) to the east from Tallinn crosses the mining area. While the program to alleviate the Dictyonema Shale burning problem was said to only have been partially successful, it was reported that no major oil shale fires had occurred during the last 5 years. The environmental issues associated with mining are more fully developed in the report of the environmental expert.

The newer SSP plant at Maardu is still operating at 50,000 mtpy of SSP. The beneficiation plant is said to be in working order. Two draglines are still onsite; one dragline is partially dismantled.

Kingisepp

The Kingisepp deposit was discovered in the mid-1950s, and the phosphorite beds in the area are essentially a continuation of those occurring along the Estonian coast. The deposit is located in a relatively uninhabited area between the Narva and Ruga Rivers about 20 km inside the Russian-Estonian border. The geologic section is similar to the section at Toolse and Maardu, but the Dictyonema Shale is not present. The phosphate beds dip gently to the south. Thickness of the beds increases to the south and P_2O_5 content increases to the east.

At the initiation of mining in 1963 about 380,000,000 mt of reserves was identified to a maximum depth of 35 m. The potential limit of mining is now said to be about 23 m. In 1992 the remaining reserves were established at 250,000,000 mt. The exact criteria used to establish these reserves was not given. The term "reserves" usually implies the quantity of ore or concentrate that can be mined or produced at a profit.

The Kingisepp deposit averages about 20 m of overburden. The average thickness of the producing bed is 2.4 m with a minimum of 1.0 m and a maximum of 3.0 m. The ore averages 6.6% P_2O_5 with a range of 5.5 to 9.0 wt % P_2O_5. At Kingisepp the upper part of the phosphorite bed is the richest (8.0-9.0 wt % P_2O_5) with decreasing P_2O_5 contents to the bottom of the bed. The phosphorite bed at Kingisepp contains dolomitized intercalations. These intercalations are spoiled in order to keep the MgO contents of the final concentrate at acceptable levels.

Mining began on the north side of the main highway from Tallinn to St. Petersburg near the site of the processing complex. At the present time all mining is conducted on the south side of the highway. Six pits have been developed that are about 2.5 km in width moving to the south. The overburden is mined with large draglines in a single bench. The ore bed is selectively removed and ore is trucked to the beneficiation plants. A substantial amount of water must be pumped from the pits. At the time of the mission they were pumping a total of about 10,000 m^3/hour from three pits.

Production for the last year was 7-8 million mt of ore to produce 1.2 million mt of concentrate at 28% P_2O_5. A single stage of anionic flotation using fatty acids (anionic flotation) is used. About one-half kilogram fatty acid reagent is mixed with 2 kg of kerosene as an extender per metric ton of ore. Recovery of P_2O_5 in flotation is 80%. The grade of the concentrate could be improved but the 80% limit of recovery was set by Russian authorities early in the development of the deposit.

All the production from Kingisepp is shipped to other points in Russia. There is a phosphoric acid plant and a TSP plant that is working on the site. This plant utilizes igneous apatite concentrates from the Kola peninsula. Approximately half of the Kingisepp phosphate concentrate production is used for direct application fertilizer and half is used in small TSP plants in Russia using phosphoric acid produced from Kola phosphate rock. All transportation from the area is by rail. At maximum capacity

the entire Kingisepp complex empioys about 5,000 workers. At the present time about 3,500 workers are employed.

The selling price of Kingisepp concentrate was quoted as 1,400 roubles/mt. This converts to a price of about US $49/mt (28.67 roubles = $1 [12-17-92]). The production cost was quoted as 1,100 roubles or about US $38/mt. The selling price and production costs were said to be increasing in 1993 primarily due to increased costs in raw materials and fuel to perhaps 2,000 roubles/mt (about US $70) and 1,600 roubles/mt (about US $56), respectively. It is not known how these costs were derived or if they have any basis in economic reality.

Exploration in the Rakvere and Toolse Areas

The Government of the Former Soviet Union studied the development of phosphate mines in the Rakvere and Toolse areas in the late 1960s to early 1970s. A report, in Russian, was produced in 1972. This report has not been translated. Excerpts from this report were presented to the team. The report contains volumes on the geology, reserves, economics, and mining of the Rakvere and Toolse deposits. The work was performed mainly by the Russians. It has been 20 years since the study was performed and the Estonian officials indicated it was very difficult to find anyone who had participated in the study.

In the mid-1980s the central Soviet government decided to develop an underground mine in the Kabala district of the Rakvere area producing 12 million mtpy of ore. This announcement was met by strong opposition from the Estonian populace. The Rakvere area is highly populated and is a major Estonian agricultural area. Opposition to the Russian development of the Rakvere phosphate deposit developed into what is informally termed "the phosphorite war." Indeed, it is said that this situation fueled the independence movement from the Former Soviet Union.

Opposition to development of the phosphate mine centered mainly around environmental issues. Studies were performed involving several Estonian institutions, and several prominent Estonian scientists raised concerns about the potential effects of

mining. Paradoxically, some of these same scientists are promoting the development of the Toolse deposit at the present time.

In the Kabala district the phosphorite bed lies at a depth of 60-110 m. The average thickness of the bed is 5.7 m and the average P_2O_5 content is 12.3 wt %. Approximately 188 million mt of reserves (100% P_2O_5 basis, or approximately 1.5 billion mt of ore) has been proved in the Kabala area. Additional reserves are available; 605 million mt (100% P_2O_5 basis) has been estimated in the entire Rakvere district. An oil shale bed lies about 30 m above the phosphorite bed, and this oil shale seam was to be mined in conjunction with the phosphorite.

The Toolse deposit was investigated by the drilling of 750-800 boreholes. Over 20,000 m of core was taken. About 4,500 samples from the phosphorite bed were analyzed. In the northern part of the deposit (to the north of the northern end of the present limestone quarry), boreholes were drilled on 200-m centers. To the south of the limestone quarry boreholes are widely spaced and/or are sporadically located. The Toolse deposit appears to have been investigated primarily to develop an open-cast mine.

A general cross-section of the geologic section in the Toolse area is shown in Figure 1. A map of ore types and thickness of overburden is shown in Figure 2. The average P_2O_5 content of the portion of the phosphorite bed that is minable (>3% P_2O_5) is 10.6% P_2O_5. The upper part of the bed is sandy, and at Toolse the lower part of the bed is the potential ore zone. The phosphorite ore is said to be finer at Toolse than at Maardu and much richer in pyrite. The range of MgO contents in the ore is 0.5-5.9 wt %. Silica contents range from 21.6% to 88.6% and average 70.9%. The Fe_2O_3 contents average 1.5 wt % and range from 0.2 to 5.0 wt %. The CO_2 contents average 6.7 wt % and range from 0.2 to 13.1 wt %. Extensive maps can be found in the Russian report based on major element distributions in the deposit. Maps were also examined listing minor element compositions such as vanadium and molybdenum.

The average thickness of the phosphate bed in the Toolse deposit was given as 2.9 m. In the area of the limestone mine the bed is about 2.5 m thick.

Based on chemical and physical characteristics, the deposit has been subdivided into four ore types (Figure 2): (1) normal silicate ore, (2) high silicate ore,

(3) weathered ore, and (4) a ferruginous (high iron content, possibly pyritic) ore. The exact criteria used to subdivide these ore types was not given. The deposit is cut roughly in half by the buried Toolse River valley. The deposit is roughly bounded on the east by the buried Kunda River valley. To the west the phosphate beds thin and decrease in P_2O_5 content. To the south and southeast the beds continue at depth into the Rakvere area. The thickest and richest phosphate ore is found to the west of the Toolse River.

Overburden thickness at Toolse ranges from 5 to 55 m and averages about 24 m. The Dictyonema Shale is present above the phosphorite zone and is said to be more reactive than at Maardu.

Two aquifers are present in the area. The surficial aquifer is located in the Ordovician limestones and quaternary sediments. The clay zone below the glauconite bed is an aquilude. Below the clay bed the phosphorite beds and Cambrian sediments form another aquifer. The surficial aquifer is used by the local rural population while the lower aquifer is pumped for villages, towns, and large farms. Both aquifers would be disturbed by mining.

Actual proven reserves at Toolse were given as 262,667,000 mt of ore. Passive proven reserves are listed as 106,158,000 mt of ore. A third category, passive probable reserves, is given as 105,704,000 mt. The total mining area was quoted as about 52 km^2. The exact criteria used to differentiate the various types of reserves could not be determined. It is assumed actual proven reserves corresponds to minable reserves.

Characterization of Phosphate Ore and Concentrate Samples From the Toolse Deposit

Introduction

Five phosphate samples were provided to IFDC by the staff of the Tallinn Technical University Laboratory of Inorganic Technology. Four of the samples were concentrate samples. One sample was the ore (Sample No. TK-1) from which one of the concentrates was produced (Sample No. 69P). The concentrate samples were beneficiated in Russia at various facilities. No details of the beneficiation treatments were given other than the use of cationic or anionic flotation. Concentrate samples

No. 73P, No. 74F, and No. 75S were produced by anionic flotation. Concentrate sample No. 69P was produced by cationic flotation.

The samples were selected to give a representative cross-section of the various concentrate types that can be produced from ores of the Toolse deposit. The letter of the alphabet in each sample number represents the type of concentrate.

Sample numbers containing a "P" indicate a concentrate containing significant pyrite (FeS_2). Sample numbers containing an "S" indicate a siliceous concentrate, and sample numbers containing an "F" indicate a ferruginous (high iron) type. The criteria used to separate the concentrates into the various types were developed by the Tallinn Technical University Laboratory of Inorganic Technology. The relationship of this classification to the various geologic ore types (Figure 2) could not be determined. The amounts and types of samples were limited and these samples were said to be the best samples available.

The samples were chemically analyzed at IFDC by a variety of methods. A spectrophotometric vanadomolybdate method was used to determine P_2O_5. Induction-couple plasma spectroscopy (ICP) was used to determine Al_2O_3, Fe_2O_3, Na_2O, K_2O, MgO, MnO, TiO_2, and Cd^{2+}. EDTA titration was used to determine CaO. Fluorine was measured by a specific ion electrode. A gravimetric method was used to analyze the silica content. Total S was determined by ICP and was cross-checked by a gravimetric method ($BaSO_4$ precipitation) after sodium hydroxide fusion. Chloride was analyzed by distillation and a silver titration method. Carbonate and carbon were determined by an acid dissolution and gas evolution method.

Concentrate samples 73P, 74F, and 75S were only analyzed chemically. Concentrate sample 69P and the ore from which it was derived, TK-2, were subjected to a complete characterization process.

The mineralogical components of the samples were determined by a combination of XRD diffraction and optical microscopy. Chemical and mineralogical compositions were equated by an IFDC-developed computer mass balancing program (MINERAL). The MINERAL program utilizes linear programming to solve a matrix equation formed from sample data and chemical data from selected mineral standards. The apatite compositions were estimated by the determination of unit-cell dimensions and

the application of previously established statistical models. Textural analyses could not be performed due to the disaggregated nature of the samples.

Composition of the Apatite

All the samples were subjected to XRD analysis to determine the unit-cell dimensions of the apatite component. In this procedure the 14 most intense peaks of the apatite diffraction pattern are measured, peaks with interferences are removed, and the unit-cell dimensions are calculated by an iterative least-squares procedure. The apatite variety found in sedimentary rocks is the carbonate-apatite called francolite.

The "a" unit-cell dimension of francolite shows the most variability and is used to compare the *francolite* of the Toolse deposit samples to statistical models developed from hundreds of francolite samples from around the world.

Table 1 lists the "a" unit-cell dimensions, empirical formulas, and hypothetical maximum P_2O_5 contents that would be present in 100% pure francolite concentrates of each Toolse sample. Francolites, as a group, exhibit systematically varying chemical compositions and physical properties. The principal substitution in francolites is the substitution of CO_3 for PO_4. This substitution has been shown by statistical models to occur on a one-to-one basis. With increasing CO_3 substitution, increases are also found in the Na^{+1}, Mg^{2+}, and F^{-1} contents. Francolite "a" unit-cell dimensions vary from about 9.320Å for the most highly substituted varieties (≈7 wt % CO_2) to about 9.370Å for varieties with essentially no carbonate substitution. The P_2O_5 contents of the most highly substituted varieties are about 34 wt % P_2O_5, and the P_2O_5 contents of the varieties with essentially no carbonate substitution are similar to igneous fluorapatites at about 42 wt % P_2O_5.

The Toolse samples, as a group, have a rather narrow range of unit-cell "a" dimensions varying from 9.355Å to 9.362Å. The TK-2 ore sample and 69P concentrate sample exhibit the highest "a" unit-cell dimensions of the group and have hypothetically the lowest CO_2 substitution and highest P_2O_5 content (40.7 wt % and 41.1 wt %, respectively). The other three samples have slightly lower "a" unit-cell dimensions (9.355Å to 9.356Å) and slightly lower hypothetical P_2O_5 contents at about 40 wt % P_2O_5. As a group the Toolse samples are considered to contain francolites with a low degree of carbonate substitution.

One other physical property of francolites that systematically varies quite substantially is that of the refractive index. The average refractive index of the most highly substituted francolites is about 1.597, while the refractive index of francolites with essentially no carbonate substitution is about 1.633. It was very difficult to measure the refractive index of the Toolse samples. Most of the phosphate grains are highly stained presumably with organic matter and/or iron oxides and contain inclusions of fine pyrite. There are very few relatively unstained clear phosphate grains in the samples to use to perform suitable refractive index measurements.

The average mean refractive index (N_D^{25}) measured for Toolse sample 69P was 1.607. This measurement corresponds to an apatite with about 5% wt % CO_2 substitution and a maximum P_2O_5 content of about 36 wt %. This hypothetical composition does not agree with the composition predicted by XRD techniques. However, this observation does not indicate that the XRD predicted composition is in error. Quite often there is more than one type of francolite in a given sample. The clear phosphate grains of the sample that are suitable for optical examination are not typical of the sample as a whole. That is, there appears to be more than one variety of francolite in the Toolse samples.

Mineralogical Composition

The TK-2 ore sample was resolved into five mineral components (Figure 3, Table 2). Quartz (SiO_2) and francolite were identified by XRD. Pyrite (FeS_2) and carbonates (dolomite and calcite) were determined optically. The exact nature of the carbonate component was not determined optically. Dolomite [$Ca,Mg(CO_3)_2$] and calcite ($CaCO_3$) were determined by XRD in the 69P concentrate sample and were assumed to be present in sample TK-2.

Quartz (69.3 wt %) is the most abundant mineral species and principal gangue mineral. Francolite (20.5 wt %) is the second most abundant species. Pyrite (4.0 wt %), dolomite (1.9 wt %), and calcite (0.8 wt %) are minor but significant components of sample TK-2.

Unassigned chemical components include 0.76 wt % Al_2O_3. No aluminum-bearing phases were identified; some clays or feldspars may be present. In the calculations all Fe_2O_3 was assigned to pyrite; some Fe_2O_3 is probably present as oxides. The remaining unresolved chemical components are minor and may be present in mineral species or

compounds in too low a concentration to be detected by XRD or optical methods; some of these chemical components may also be substituted in the crystal structures of identified species.

Of the analyzed chemical components, 98.2% have been assigned to the five minerals identified. On this basis it is assumed that no significant mineral components remain undetected.

The 69P concentrate sample was resolved into five mineral components (Figure 4, Table 3). Francolite, quartz, calcite, and dolomite were identified by XRD. Pyrite was identified optically.

Francolite (60.0 wt %) is the most abundant mineral species present in sample 69P. Quartz (27.3 wt %) is the second most abundant mineral species and principal gangue mineral. The carbonates, calcite, and dolomite, collectively constitute about 6.9 wt %. Pyrite (3.4 wt %) is the fifth most abundant mineral component.

Unassigned chemical components include 0.68 wt % CaO. The only CaO-bearing minerals identified are francolite, calcite, and dolomite. The CaO content of the francolite is limited by the calculated composition and the ratios of several other chemical species found in the francolite. The CaO content of dolomite is limited by the amounts of MgO and CO_2 available. The CaO contents of the calcite are limited by the CO_2 available. All available MgO and CO_3 were utilized in the calculations. Minor discrepancies in the chemical analyses may contribute to this apparent imbalance. The actual dolomite composition may be calcium rich rather than the stoichiometric composition assumed. Unidentified CaO-bearing phases may also be present.

The remaining unresolved chemical components are minor and may be present in species or compounds in too low a concentration to be detected by XRD or optical methods; some of these chemical components may also be substituted in the crystal structures of identified species. Of the analyzed chemical components, approximately 97.9% have been assigned to the five minerals identified. On this basis, it is assumed that no mineral components remain undetected.

The objective of beneficiation is to increase the content of desired mineral components and lower the impurity contents at acceptable losses of the desired

mineral component. With beneficiation the francolite component was increased from 20.5 wt % to about 60.0 wt % or a 293% increase. Concurrently, the quartz component was reduced from 69.3 wt % to 27.3 wt %.

With beneficiation the pyrite content decreased a minor amount from 4.0 wt % to 3.43 wt %. This indicates that not all the pyrite is intimately associated with the phosphate particles. Some of the pyrite has been liberated, and the concentration of pyrite is not enhanced by the flotation process.

Significantly, the combined carbonate content of the TK-2 ore, 2.7 wt %, is increased by beneficiation to 6.8 wt % in the 69P concentrate sample or an increase of 251%. Carbonate contents are typically increased with increasing phosphate contents in flotation processes.

Chemical Composition

The chemical compositions of samples TK-7 and 69P are listed in Tables 2 and 3, respectively. The chemical compositions of concentrate samples 73P, 74F, and 75S are listed in Table 4. The chemical characteristics of the Toolse concentrate samples are summarized in Table 5.

The CaO/P_2O_5 ratios of the Toolse concentrate samples range from 1.46 to 1.54 (Table 4). The CaO/P_2O_5 ratios of the concentrates are higher than the range predicted by the apatite compositions (1.35-1.39) due to the presence of carbonates. Carbonates cause foaming during acidulation and consume excess acid. Dissolution of dolomite also releases magnesium into processing systems.

The R_2O_3 (Fe_2O_3 + Al_2O_3) + MgO/P_2O_5 ratios (Table 4) of the samples (0.10-0.15) are near or above the ratio considered the maximum favorable for chemical processing (0.12). Most of the Fe_2O_3 appears to be contained as pyrite. Pyrite is insoluble under sulfuric acid attack. Any Fe_2O_3 present in concentrates as oxides will be solubilized under acid attack. High Fe_2O_3 and MgO contents in concentrates and acids can lead to processing problems and undesirable qualities in products. High Fe_2O_3 and MgO contents can produce products which are difficult to dry or remain sticky. High Fe_2O_3 and MgO contents can lead to the formation of unwanted sludges in phosphoric acid production. When high impurity phosphoric acids are concentrated from filter grade (28% P) to merchant grade (54% P_2O_5) for shipping, oftentimes

water-insoluble phosphate compounds containing Al_2O_3, Fe_2O_3, and MgO form and precipitate. High magnesium levels can contribute to the production of acids with high viscosities which are difficult or impossible to pump effectively.

Silica is the most abundant impurity (16.0 to 27.3 wt %) and its abundance is inversely proportional to the P_2O_5 grades. The silica contents are contained as quartz although some feldspars or clays may be present. While silica is relatively inert in chemical processing, it dilutes the concentrate and is very abrasive causing erosion of processing equipment.

The chlorine contents of the samples are high ranging from 303 ppm to 428 ppm. In an attempt to determine if the chlorine component could be reduced, sample 73P was washed with water and re-analyzed. The washing procedure involved placing 1 g of a sample in a beaker with 100 mL of distilled water and stirring for 1½ hours. The sample was allowed to settle, decanted, and filtered. The sample was washed with approximately 20 mL of distilled water during filtration, dried at 105°C, and Cl^- was determined once again. Using this procedure the Cl^- content of the sample was reduced to 306 ppm. This indicates that about 20% of the chlorine content is water soluble. This procedure was designed merely to prove if a portion of the chlorine compounds in the samples were removable. Further testing would be required to determine if a portion of the Cl^- could be removed from Toolse concentrates in an industrial setting. Corrosion in most phosphoric acid plants becomes a serious problem somewhere between 200 and 300 ppm Cl^-.

The sulfur contents of the samples range from 1.1 to 1.77 wt % and are contained as pyrite. The cadmium contents of the concentrates are low (1-5 ppm).

The neutral ammonium citrate (NAC)-soluble P_2O_5 of the concentrates ranged from 2.9% to 3.6% P_2O_5 (second extraction). The samples were analyzed after a second extraction. The first NAC extraction was used to remove free carbonates. This level of NAC solubility is somewhat above the level predicted by statistical models based on francolite compositions (2.0%-2.9% P_2O_5). This condition may indicate that more than one francolite composition is present. The presence of a more highly carbonate-substituted francolite can enhance solubility measurements. The NAC solubilities of the Toolse concentrates are typical of samples from Paleozoic phosphate deposits or younger deposits that have been highly weathered. The most highly

carbonate-substituted francolites have NAC solubilities of about 7.0% P_2O_5. General IFDC experience has shown that a level of about 4.0% NAC-soluble P_2O_5 is required for a phosphate rock to be used as an effective direct application fertilizer under suitable agroclimatic conditions. Phosphate rocks with lower reactivities can be effective for direct application under tropical conditions with soils that have a very low pH (4-5) and on long-term crops such as rubber trees and oil palm.

Beneficiation

Experimental beneficiation involving the production of Toolse concentrates has examined both anionic and cationic flotation. Data provided by the Tallinn Technical University Laboratory of Inorganic Technology indicate that anionic flotation is the most effective route. However, details of the beneficiation treatments were not provided. Concentrates produced by anionic flotation (17 samples) had an average of 27.1 wt % P_2O_5 and ranged from 27.1 to 29.7 wt % P_2O_5. Concentrates produced by cationic flotation (5 samples) averaged 25.5 wt % P_2O_5 and ranged from 21.9 to 28.0 wt % P_2O_5.

Microscopic examination of concentrate samples 69P (Figures 5 and 6) and 73P (Figures 7 and 8) indicates that the quartz gangue is liberated and clean. Further reduction of the quartz contents should be possible. Often a two-stage flotation process is used to upgrade quartz containing phosphate ores. The first flotation is usually a direct anionic phosphate flotation using fatty acids diluted with fuel oil or kerosene as an extender. A mild acid wash (0.5% sulfuric acid or less) then is used to remove the reagents. The second stage is a cationic flotation of the remaining silica. It may also be possible to reduce the silica content during the first stage of flotation by adjusting the pH and using sodium silicate as a quartz depressant. No evidence was presented to suggest that these approaches were attempted with the Toolse ores.

Further reductions of the calcite and dolomite contents will be difficult. Calcite and dolomite behave similarly to francolite in most flotation processes. Calcite and dolomite are successfully removed from igneous ores in Finland and Brazil through the use of special flotation reagents and depressants. Flotation has not been used successfully anywhere in the world on a commercial basis to remove carbonates from sedimentary ores.

Carbonates can be removed from sedimentary ores by calcination at over 830°C. Calcination is used to remove carbonates and organic matter from phosphate concentrates at the Texasgulf operation in North Carolina, U.S.A., in fluid bed calciners. There are several mines in North Africa and the Middle East where calcination units are in operation. Usually these calcination units employ a water-slaking process to remove fine CaO and MgO produced by the process.

Calcination may also remove a portion of the pyrite. Pyrites are typically roasted to produce sulfuric acid at over 420°C.

Further definitive testwork would be needed to establish the most cost-effective methods of beneficiating Toolse phosphate ores to the highest grades possible with acceptable recovery. It should be mentioned that grade and recovery are usually inversely proportional. That is, higher analysis concentrates are usually produced at lower recoveries in any specific situation.

Utilization and Processing

The Toolse phosphate concentrates possess several chemical and physical characteristics which make them both desirable and undesirable for world trade as concentrates or feedstocks for chemical processing. It is possible that some of the undesirable characteristics could be corrected or minimized by further processing. It is possible that some of the undesirable characteristics could be corrected or minimized by excluding the mining of certain ore types.

The P_2O_5 contents of the Toolse concentrates are low at about 28% P_2O_5. Phosphate rock concentrates traded on the world market are normally in the range of 30-32 wt % P_2O_5 or higher. While higher analysis concentrates cost more per metric ton, the shipping costs per unit volume are the same. In some cases the delivered cost per unit of P_2O_5 for high analysis concentrates may be less than lower analysis concentrates. Higher analysis feedstocks produce higher analysis (and usually higher quality) products, and fewer processing problems are usually encountered with higher analysis and quality concentrates.

The primary dilutant of the Toolse concentrates is silica which is abrasive in processing. Refinements in beneficiation techniques may be possible to further upgrade the P_2O_5 contents of the Toolse phosphate ores and reduce the silica contents.

Any reduction in the silica contents and upgrading of P_2O_5 would make the concentrates more attractive for world market trade.

Phosphate rocks with similar P_2O_5 contents (26-28 wt % P_2O_5) and silica contents are typically utilized in the indigenous Florida phosphate rock processing industry in wet-process phosphoric acid manufacture. One of the constraints to using these low analysis concentrates is low filtration rates when the phosphoric acid is separated from byproduct gypsum. These low to medium grade concentrates also typically have higher impurity contents than phosphate rock used for world trade. Due to these high impurity contents, significant amounts of P_2O_5 containing sludges are produced during the wet phosphoric acid manufacturing process. Sludges produced during phosphoric acid production in Florida are typically reintroduced into the manufacturing processes of ammonium phosphates and TSP and recovered. These added value high analysis products can be more economically transported than low analysis phosphate rock concentrate.

The Toolse concentrates have high total impurity contents. The major impurity is Fe_2O_3. Much of this Fe_2O_3 is contained as pyrite, and this pyrite should not be very vulnerable to sulfur acid attack. However, the very presence of the iron impurities will not be a strong selling point when marketing the concentrates. When the Fe_2O_3, Al_2O_3, and MgO contents are added and ratioed to the total P_2O_5 contents, the concentrates are near or over the maximum ratio considered favorable in commercial ores (0.12). An IFDC analysis of 29 Central Florida concentrates (>28% P_2O_5) indicates a total average R_2O_3 + MgO content of about 3.0 wt % and a R_2O_3 + MgO/P_2O_5 of 0.10. An analysis of 16 Moroccan concentrate samples (>31% P_2O_5) indicates a total R_2O_3 + MgO content of 0.96 wt % and a R_2O_3 + MgO/P_2O_5 of 0.03.

Phosphate rock concentrates, or phosphoric acids, with high total impurity contents produce products with lower water-soluble P_2O_5 contents as a percentage of total P_2O_5 due to the formation of water-insoluble impurity/phosphate compounds. Water solubility is one of the primary criteria used to evaluate fertilizer products on the world market. Minimum water-soluble P_2O_5 requirements have been established by most countries for specific products.

Phosphate rocks with high pyrite contents (Western United States) are known to produce phosphoric acids with corrosive properties. While a portion of the pyrite is removed with beneficiation, a portion is encapsulated within the phosphate particles.

Based on the magnesium and carbonate contents, all the Toolse concentrates appear to have a dolomite component. Calcite is also present. Carbonates cause foaming during acidulation, and excess sulfuric acid must be added to the wet-process phosphoric acid system to dissolve the carbonates. The dissolution of dolomite introduces free magnesium into any processing system. As previously discussed in the beneficiation section, those carbonates will be difficult to remove. It is possible that the deposit could be mined to avoid high carbonate areas. It is impossible to evaluate this option at this time.

Excess sulfuric acid consumption is a cost which must be evaluated with respect to the potential costs of removal and overall production costs. Foaming can be partly compensated for by certain plant design features. The use of antifoam agents can significantly increase the cost of production. Magnesium, and other impurities, can be tolerated if suitable products can be produced; however, the presence of carbonates (and associated magnesium) will not be a favorable factor when attempting to market Toolse concentrates.

Most of the phosphate rocks marketed around the world have chlorine contents below 200 ppm. Chlorine contents of Central Florida concentrates range from about 65 ppm to 175 ppm. Chlorine contents of Moroccan phosphate rocks are generally above 100 ppm and below 200 ppm. Some exceptionally high P_2O_5 sedimentary concentrates such as Togo (≈35% P_2O_5) may contain Cl^- contents as high as 300 ppm.

Phosphoric acid plants around the world are generally designed to handle rocks with chloride contents below 200-300 ppm. If high chlorine rocks are used in plants designed for low chlorine rocks, maintenance costs will increase proportionally to increased corrosion. Phosphoric acid plants can be designed with more corrosion-resistant stainless steels and alternative materials such as plastics and concrete. However, the initial cost of such plants may be higher than "normal" plants.

The high level of chlorine in Toolse phosphate concentrate (from about 300 to 430 ppm) will not be a positive factor in marketing Toolse concentrates. Fertilizer

manufacturers with plants designed for low chlorine concentrates would look elsewhere on the market for suitable concentrates.

The cadmium contents of Toolse concentrates are very low (1-5 ppm as shown in Tables 2, 3, and 4). An IFDC survey of 38 sedimentary phosphate deposits (207 samples) indicates the worldwide average for phosphate rock products from these deposits is 21 ppm Cd^{2+}. The averages for Morocco ph sphate rock and production from Central Florida, the major players in world phosphate rock trade, are about 22 ppm Cd^{2+} and 9 ppm Cd^{2+}, respectively. Production from the Khouribga area in Morocco averages about 15 ppm Cd^{2+}.

Igneous phosphate rock concentrates have much lower Cd^{2+} contents. A survey of 11 igneous phosphate rock deposits in eight countries indicated an average of 1-5 ppm in concentrates.

Cadmium contents of soils and fertilizer products are a major cause of concern mainly in Europe. The contribution of cadmium to European soils is not only from processed fertilizers. A significant amount of the cadmium deposition in European soils is due to airborne fallout presumably from industrial activities and the application of sewage sludges and animal manures as fertilizers. Legislation regarding cadmium limits in raw materials and fertilizer products is in a state of flux or pending in Europe. In the broadest sense, what has been suggested thus far is to restrict the use of certain high cadmium-containing rocks such as Togo phosphate rock (≈60 ppm Cd^{2+}) and Senegal phosphate rock (≈85 ppm Cd^{2+}). While fertilizers are not the only source of Cd^{2+} in soils, they are probably focused on as one source that can be controlled.

Cadmium is concentrated with phosphorus in the production of phosphoric acid. Products with high P_2O_5 contents derived from raw materials with high cadmium contents have cadmium contents that are enriched compared to the source raw materials.

Cadmium can be removed from phosphate rock. The only known practical method is high temperature (≈800°-1100°C) calcination under inert or reducing conditions. High temperature calcination is expensive. The only known production-scale calcination plant in the world designed to remove cadmium from phosphate rock is on Nauru Island. The cost of Nauru concentrate is about $55/mt versus about $90/mt of

calcined rock or a $35/mt cost for calcination. This plant makes limited runs, is remotely located, and fuel (Bunker C fuel oil) is expensive. This cost could probably be reduced with higher capacity and a cheaper energy source. Perhaps the cost of calcination could be as low as $15/mt of rock.

Several methods have been developed to remove cadmium from phosphoric acid. The lowest costs mentioned in the industry for removal of cadmium from phosphoric acid are in the range of $10-$20/metric ton of P_2O_5. If Nauru rock (38 wt % P_2O_5) costs $15/mt to calcine, the cost per metric ton of P_2O_5 would be about $39.50/mt. It is generally perceived among the industry that if cadmium levels of fertilizer products must be lowered the most practical and cost-effective opportunity for removal is in the manufacture of phosphoric acid.

The lowest cost solution to reducing cadmium levels in fertilizers is obviously to use sources of phosphate rock that have low cadmium contents such as igneous phosphate concentrates or sedimentary sources such as Toolse phosphate rock concentrate. The low cadmium content of Toolse phosphate rock concentrate (and potentially low cadmium content of products produced from these concentrates) is probably one of the strongest incentives for the development of the deposit. Another significant factor is that the European market, the market with the most potential for marketing low cadmium concentrates or products, is relatively close.

Tests have been performed in the Laboratory of Inorganic Technology to prove the suitability of Toolse concentrates for the production of phosphoric acid, TSP, MAP, DAP, nitroammonium phosphates, and nitrophosphates. Both calcined and uncalcined concentrates were utilized.

Phosphate concentrates from 23.1% to 29.7% P_2O_5 were used to produce phosphoric acid by the dihydrate process. The filter-grade acids obtained analyzed from 20% to 28% P_2O_5. The product acids contained 0.6-2.0 wt % Fe_2O_3, 0.9-1.6% F, 0.3-2.7% SO_3, and 0.6-2.8% MgO. Filtration rates were quoted as between 0.5 to .3 m^3/m^2h or 4.2 to 19.4 mtpd/m^2.

Phosphoric acids produced from approximately 32 wt % P_2O_5 Central Florida rock typically contain about 1.0 wt % Fe_2O_3 and <0.5 wt % MgO. Typical filtration rates for processing Florida rocks are about 7 mtpd/m^2.

TSP was made using Kola phosphoric acid and acid made from Toolse concentrates. Using a den process the products made using Kola phosphoric acid contained 37.0%-42.2% available P_2O_5. (The parameters for determining "available" P_2O_5 were not defined.) The P_2O_5 conversion rate was 84%-95% in the finished products. Using a den process, Toolse phosphoric acid, and Toolse concentrates resulted in products with 40.5%-43.4% available P_2O_5. The P_2O_5 conversion rate was 67%-82% in the finished product.

Using phosphoric acid produced from various types of acid, MAP was produced containing 48%-54% available P_2O_5 and 9%-13% N. DAP was produced containing 48%-50% available P_2O_5 and 14%-15% N. Typical grades for wet-process acids made with Florida phosphate concentrates of average impurity contents are 18-46-0 (N-P_2O_5-K_2O) for DAP and 11-55-0 for MAP.

Samples of phosphoric acid obtained from Estonian concentrates were evaporated to 54%-55% P_2O_5, mixed with 50% nitric acid, and ammoniated to pH 5 to produce nitroammonium phosphates. The finished products usually contained 49.5%-51.1% total nutrients. The physical properties of the finished products were only fair and one product was sticky and could not be dried.

Nitrophosphate tests revealed several difficulties. There was considerable foam emission during digestion. A considerable amount of nitrogen volatilized. Iron compounds (mainly pyrite) were solubilized. The insoluble residue filtered poorly. The use of calcined concentrates eliminated foaming and nitrogen losses and the solubility of iron compounds decreased significantly.

A mixed nitric-sulfuric acid process was also tested. Effects similar to the use of only nitric acid were observed. Samples of siliceous phosphorite concentrate (25%-27% P_2O_5) were treated with a solution of HNO_3 and $(NH_4)_2SO_4$. The filtrate of this solution was ammoniated to pH 4.5, evaporated and mixed with potassium chloride. Using this process 90% of the P_2O_5 was solubilized and 82% of the Fe_2O_3 was solubilized. A product grade of 19-9-21 was obtained.

A mixed nitric acid, sulfuric acid, and ammonium sulfate process was also tested. A product with a 1-0.8-0.8 grade ratio was obtained with suitable filtration rates and conversions of the phosphate concentrate during digestion.

The Estonian studies concluded that the siliceous and pyritic types of Toolse concentrates are preferable for the manufacture of TSP and phosphoric acid. The higher grade concentrates (28% P_2O_5 and up) are preferred for TSP. Concentrates with 25%-28% P_2O_5 are suitable for wet-process phosphoric acid. Concentrates of other types are recommended for nitrophosphate production.

The Estonian studies are both interesting and exhaustive. However, additional data are needed to compare the potential Toolse deposit products to products available on the world market. Some tests were run in parallel with Kola phosphate concentrates. Any further studies would have to include comparative processing tests to rocks such as Florida or Moroccan concentrates. These tests should also be made with Toolse concentrates produced using improved beneficiation techniques.

World Production of Phosphate Rock

The world's top 12 producing countries account for approximately 95% of the world's total phosphate rock production (over 150 million mt). Approximately 95% of the world's economic phosphate reserves are held by the world's top 10 producers. Sedimentary phosphate deposits currently produce about 81% of the total world production of phosphate rock. When the production of igneous phosphate rock concentrates from the Former Soviet Union is subtracted from recent world production figures, production of sedimentary phosphate rock amounts to approximately 94% of world production.

Phosphate concentrates are recovered from igneous phosphate deposits in the Former Soviet Union, South Africa, Brazil, Finland, and Zimbabwe. Due to limited reserves and other factors, the future production is not foreseen to increase. Additional production and long-term future production will continue to be dominated by production from sedimentary deposits.

Eight countries currently dominate the world phosphate rock trade (Table 6). Morocco is currently the number one rock exporting country while the United States is the number one phosphate product exporting country and total metric tons equivalent of phosphate rock exporting country. One projection to the year 2000 (Table 6) indicates the Moroccans will increase their share of the total market. The United States will maintain its position, and Jordan (the third most prolific producing country) will increase its production. In this projection the total metric tons equivalent of phosphate rock exported from the top eight countries is to grow from 73.5 million mt to 92.0 million mt. Other projections are not so optimistic. World Bank estimates indicate the stagnant phosphate rock market of the 1980s will continue to the end of the century and there may even be a contraction of the industry.

Beyond the year 2000, production from the southeastern United States is predicted to fall sharply (Table 7) to about 24.5 million mt by the year 2015. This decrease in production is primarily due to the mine out of much of the Central Florida phosphate district. Some of the production lost from the Central Florida district will be replaced by mines operating primarily to the south of the central district. However, in this area the overburden is thicker and mining is more costly. Ore grades are lower and beneficiation is more costly. Concentrates produced from this area generally are of lower grade and quality.

If phosphate rock prices increase significantly, areas of Florida that are considered uneconomic to mine at the present time may be reclassified as reserves. The U.S. Bureau of Mines estimated in 1989 that there was 487,000,000 mt of phosphate rock concentrate reserves remaining in the Florida phosphate mining areas that could be produced at <US $30/mt. If the cost is raised to US $40/mt, the reserve estimate increases to 745,000,000 mt. If the production cost is raised to US $60/mt, the estimate of reserves is 1,583,000,000 mt. It is doubtful if phosphate rock prices will reach levels to support such production costs in the foreseeable future.

Additional U.S. production will also be available from the North Carolina phosphate district. The Texasgulf mine at Aurora, North Carolina, currently produces about 5.0-5.5 million mt of phosphate rock concentrate per year. Plans are currently being developed to increase production.

After the year 2000, phosphate rock trade will become increasingly dominated by Morocco. Morocco possesses about one-half of the world's known reserves and hypothetically could produce under current economic conditions at current levels or increased levels for hundreds of years. Morocco is in a particularly advantageous position with respect to the medium- and long-term future. Under these conditions it is foreseen that phosphate rock prices will increase when demand approaches the limits of supply. Substantial opportunities will exist at this time to control the worldwide supply of phosphate rock.

It has been widely suggested for many years that, in general, there has been a continuous decrease in world phosphate rock quality as reserves of high-quality rock are being depleted. Perhaps it would be more appropriate to say that high-grade and quality concentrates from some sources are becoming depleted (principally Florida) and, in general, the quality of phosphate rock that is utilized on a worldwide basis is lower. High-grade phosphate rock is available from many sources (Togo, Senegal, and Morocco, to name a few). However, premium rocks from these sources are not available at costs comparable to those of 20 or 30 years ago. Because of the general decrease in the quality of available phosphate rock, phosphate fertilizer process engineers are modifying their technology and exploring new technologies to cope with lower grade rocks containing higher levels of impurities.

It is impossible to predict what the world "average" phosphate concentrate will assay in perhaps 10 years. However, it might be a safe assumption that the quality of phosphate rock utilized on the world market will continue to decline and concentrates such as the Toolse concentrate will be increasingly utilized as higher grade and quality resources are depleted.

A window of opportunity may exist on a worldwide basis to develop phosphate deposits near the year 2000 to the year 2010 primarily due to the projected contraction of the Florida phosphate rock producing industry and restructuring of world trade. It is impossible to predict when the changes in the world market will occur. In order to take advantage of this "window of opportunity" potential producers must be poised for production.

A prefeasibility study of the Toolse phosphate deposit would probably take about 2-3 years. An intensive full-scale feasibility study based on sound data developed

during the feasibility study and additional data may require 1-2 years. Construction of a mine beneficiation plant, and perhaps downstream processing facilities, would probably take from 3-5 years to attain full capacity. Under this scenario, production at Toolse could occur somewhat after the year 2000.

Potential Mining and Production of the Toolse Phosphate Deposit

The tonnage of ore available at Toolse is given in Figure 1 as 59,400 mt/ha. This estimate appears to have been derived by measuring the area of high silicate, silicate (normal), and ferruginous ore types of Figure 2 at <34 m and dividing the total tonnage of proven reserves (262,667,000 mt) by the area measurement (about 4,500 ha). It is not known if this is the exact area used to derive the proven reserve estimate. The map of Figure 2 may not show all reserves that are available at <34 m. It appears additional ore may be available at <34 m to the southeast of the map area and east of buried Kunda River Valley. If the total tonnage of proven reserves (262,667,000 mt) is divided by the total area given for the mining area (52 km^2), the tonnage available per hectare is somewhat lower at 50,500 mt.

Current data indicate the Toolse ores can be concentrated to about 28% P_2O_5. Data from Estonian studies and Kingisepp indicate 28% P_2O_5 can be obtained at beneficiation recoveries of 80%. Mining losses of phosphate must be added to beneficiation losses. As a best case scenario, 5% mining losses were assumed. As a worst case scenario, 20% mining losses were assumed. A P_2O_5 content of 10.6% P_2O_5 for the original ore was used for all calculations.

Using the above assumptions, 5% mining losses, and an original ore tonnage of 59,400 mt/ha, 16,929 mt of concentrate per hectare can be obtained from the Toolse deposit. This is considered the "best case" scenario. At 20% mining losses and 59,400 mt/ha, an average of 14,256 mt/ha of concentrate is available. At 5% losses and 50,500 mt/ha, 14,392 mt/ha of concentrate is available. At 20% losses and 50,500 mt/ha, 12,120 mt/ha of concentrate is potentially available at Toolse. This is considered the "worst case" scenario.

The original map used to produce Figure 2 was placed on a digitizing board and potential mining areas were measured. The practical limit for mining with large draglines at Kingisepp was given as 23 m. To ease calculations this limit was extended to 25 m and a straight line was drawn between the 20 m and 30 m isopach lines of overburden thickness. It should be noted that in actuality this line is definitely not a straight line.

The normal silicate ore type was considered the only ore type that was definitely known to be feasible to mine and produce suitable concentrates. The ferruginous ore type was considered potentially minable.

Several capacities for the mine were conside ed. A capacity of 1 to 2 million mt of concentrate per year is probably needed to compete on the world market. The Estonian requirement for P_2O_5 before the current socio-politico-economic disruption was 60,000-70,000 mt of P_2O_5/year. A production level of 70,000 mt of P_2O_5/year calculates to 250,000 mtpy of concentrates at 28% P_2O_5. No figures for consumption of P_2O_5 for all the Baltic states were available. A figure of 500,000 mtpy of concentrate, double the Estonia level, was assumed as reasonable for a regional requirement.

From an Estonian viewpoint it would be very desirable to confine any phosphate mine within the present limestone mine for the Kunda cement plant. Approximately 10-12 m of overburden has been removed in this area and the phosphate bed is below about 14-17 m of additional overburden. This limestone mine currently produces about 500,000 mtpy and the current pit area is approximately 2.5 km^2. A proposal has been put forth to build a new cement plant which at the maximum capacity would use 2.5 million mt of limestone per year.

The various areas in the Toolse deposit that were measured and mine lives at various production capacities are presented in Table 8. Assuming all ore types under the present pit can be utilized, a 2.0 million mtpy concentrate-producing mine would outgrow the present pit in 1.5-2.1 years. At 1.0 million mtpy capacity the present pit would be outgrown in 3.1-4.3 years. Assuming limestone production at current levels, a 500,000 mtpy concentrate-producing mine would overtake limestone mining in 10 years (Figure 9). A 250,000 mtpy concentrate producing mine would overtake the present limestone mine in about 20 years. Figure 9 also estimates phosphate/limestone mining scenarios at a limestone production rate of 2.5 million mtpy.

A further complication in this scenario is that the limestone mine is moving to the south while the best phosphate ore with the least overburden and most densely drilled and known area of the deposit is north of the limestone mine. Logic, and the economics of removing overburden, would suggest the best place to open the deposit would be at the northern extremity of the deposit where the overburden is the thinnest. Preferably this would be on the west side of the Toolse River where the phosphate beds are the thickest and richest.

If the Toolse phosphate mine is limited to producing normal silicate ore at <25 m overburden, the mine would be exhausted between about 9 and 13 years at a 2.0 million mtpy capacity. At 1.0 million mtpy capacity the normal silicate ore would be exhausted in about 18 to 25 years. If all ore types are mined with <25 m overburden, with the exception of the weathered ore, the mine could operate from about 12 to 17 years at 2.0 million mtpy of concentrate. On this basis a 1.0 million mtpy concentrate mine would be exhausted between about 24 and 33 years.

Using the assumptions of this analysis, the Toolse deposit is not capable of supporting a 2.0 million mtpy concentrate mining and processing operation for a reasonable mine life. Most mining-processing operations of this nature are designed for a minimum life of 20 years. With proper maintenance and periodic upgrading, such operations can be maintained indefinitely. The deposit could probably support a 1.0 million mtpy concentrate mine. Of course, reserves of suitable ore types for processing would have to be definitely established. Production from the Toolse area could support production of concentrates at 250,000 mtpy and 500,000 mtpy far into the future under the assumptions and scenarios considered.

Preliminary estimates of mining costs were impossible due to a lack of data. The Estonian economy is also in a constant state of flux. Quite often Estonian officials would not even venture guesses at the potential costs of raw materials. There is a 0.5 million mtpy sulfuric acid plant supposedly operating at Kivoli based on sour gas production from Russia. The status of the sulfuric acid plant was unknown; the Maardu SSP production plant was buying sulfuric acid from Russia. Within Tallinn there is an old paper mill. Paper mills are sources of flotation reagents as a byproduct of processing. The status of this plant is unknown. Salaries are currently incredibly low by

western standards. For instance, ranking government officials may have salaries of the equivalent of US $50-$125/month.

One estimate of production costs based on a Finnish geologist's appraisal of the early 1970s Russian study was $3/mt for ore and $12/mt for finished concentrate. Considering the costs given for production at Kingisepp (about $38/mt, 1992), a similar mining scenario with an increased beneficiation requirement, this estimate appears to be grossly low. Of course the costs in Russia may have no basis in economic reality. They could be artificially high. On the other hand, they could be subsidized and therefore artificially low. If the figures for production at Kingisepp are real, it is possible that a more highly efficient mining system at Toolse could reduce the costs of production.

The latest available production costs in Florida for the newest high capacity mine (4-5 million mt of concentrate) are over $22/mt. A breakdown of this production cost is not known. This mine uses high capacity draglines (50-70 m buckets) to mine 5-7 m of soft overburden and remove 2-4 m of ore at about 9% P_2O_5; therefore, the overburden to ore ratio is about 2:1. The same dragline removes the overburden and mines the ore. Production in the pit is divided between several draglines. When some draglines are stripping overburden, others are mining ore and feeding the beneficiation plant. The ore is very friable (easily broken up) and is slurried to the beneficiation plant. This is a very low-cost method of transportation. The ore is then screened and deslimed and the feed size phosphate (minus about 1.0 m to about plus 106 microns) is upgraded by a two-stage flotation process. The phosphate feed is not ground before flotation. Concentrates of similar grade to Estonian concentrates (28% P_2O_5) are currently available for <$30 (f.o.b.) from Florida sources.

If the maximum minable overburden at Toolse is limited to 25 m and the minimum depth of overburden is considered 5 m, the average overburden thickness would be 15 m. The ore zone averages about 2.9 m in thickness. Therefore, the average overburden to ore ratio would be about 5:1. Physically speaking, it would take about 2.5 times the earth moving capacity to mine the Toolse deposit as compared with the Florida deposits.

Mining the Toolse deposit would also be more difficult than mining the Florida deposits. The overburden at Toolse must be blasted. The costs of drilling and blasting

must be added to mine production costs. Mining would undoubtedly have to be a two-stage and possibly three-stage process at Toolse. Overburden stripping would probably have to end at the Dictyonema Shale bed. Although a solution to spontaneous ignition of this bed has not been found, this bed will probably have to be removed and selectively handled. The upper part of the phosphorite bed then must be removed before the lower ore zone can be selectively mined.

The ore at Toolse might be transported from the pit to the beneficiation plant by slurry-pipeline methods. Slurry methods are among the lowest cost methods of transporting bulk materials. Inspections of the ore at Kingisepp indicate numerous lumps (over 5 cm in diameter). The bulk characteristics of Toolse ore are not known but crushing and grinding might be required before transportation by pipeline. Similar to Kingisepp, transportation by large trucks may be required. These trucks (in terms of 100 to 200 mt capacity) require the building of special roads to the beneficiation plant. Truck transportation of ores, while very flexible, is relatively expensive. It is possible that the Toolse ores could be transported by conveyor systems. In any case, ore transportation will probably be considerably more expensive than in Florida.

Beneficiation costs will be higher than costs in Florida. Selectively screening oversize waste and desliming unwanted clays from the ore typically rejects 40%-50% (by weight) of the components of the Florida ores before flotation. Therefore, only about 50%-60% (by weight) of the ore that is mined is selectively submitted to flotation. Based on limited data, it appears all the ore mined at Toolse must be subjected to grinding, preflotation desliming, and flotation. Flotation is one of the most capital intensive and costly facets of phosphate ore processing.

Another problem at Toolse may be ore dilution. Estonian geologists indicated the contact between the upper bed (<3 wt % P_2O_5) and the lower ore zone is gradual. It is said that it is very difficult to distinguish between the upper portion of the bed and ore zone. If portions of the upper bed are mined with the lower ore zone, an increased amount of ore with a lower P_2O_5 content will potentially be processed. This will also throw the beneficiation plant out of equilibrium and result in a lower output of concentrates perhaps at a lower P_2O_5 content. Careful pit control would probably be required at Toolse.

One comparative advantage in the development of the Toolse deposit may be the availability of electrical power. The bulk of the mining equipment (including large draglines) and processing equipment would utilize electrical energy. High voltage transmission lines already exist in the area. Large power plants based on Estonian oil shale production are located within 50 km to the east. The Estonian oil shale mines have produced close to 30 million mt of oil shale per year to feed the power industry. Use of oil shale is presently below 20 million mt. Prior to the current political situation, about 60% of the power generated was exported to Russia and the other Baltic states. At the present time, 60% of the power is utilized in Estonia and 40% is exported.

The oil shale mining and power generation industry is in a state of rationalization. No estimates were obtained of the current or potential future costs of power. A detailed analysis would be required to determine the potential costs associated with electrical power under specified production scenarios. The assumption that there is potential for readily available low cost power to operate a mine at Toolse does seem reasonable at this time. Potentially low labor costs in Estonia could also be a positive factor in developing a mine at Toolse although this situation is probably far from stabilizing. Another positive factor in the development of the Toolse deposit is the existence of a well established railway system in the area.

The potential costs of mining and producing concentrates from the Toolse deposit can only be estimated by exhaustive and relatively detailed studies. Such studies would have to take into account the production needed, mining factors, beneficiation factors, and potential value of the concentrates produced. For instance, the economic limit to overburden stripping can only be determined by back calculating from the value of concentrates, estimated beneficiation costs, and potential mining costs.

Based on the previous discussion comparing potential production from Toolse and production from Florida (a production system operating in a free market under world market conditions), it is very safe to assume that production costs will exceed the $22 production costs for Florida concentrates and exceed the <$30 quoted for the selling cost for Florida concentrates of similar grade. Production costs may approach and exceed the $38 quoted for Kingisepp concentrates and may approach the potential production costs quoted for 1993 (about $56).

Mining at Toolse might be economically justifiable if it is conducted on the basis of import substitution; that is, if mining is conducted to provide materials for a fertilizer industry rather than buying raw materials at world market prices. Concentrates in the range of 30%-32% P_2O_5 would probably be purchased. Such concentrates currently cost between $35 and $45/mt in high volume (shiploads). Shipping and handling costs probably would add between $10-$15/mt. Therefore, costs of concentrates to an Estonian location (probably near Tallinn) might range from $45 to $60/mt. It may be possible to produce Toolse concentrates in this cost range.

Summary, Conclusions, and Recommendations

Characterization of samples from the Toolse deposit and examination of pre-existing data indicate concentrates from the Toolse deposit have several physical and chemical characteristics which make them undesirable for world trade. The P_2O_5 content of the concentrates is generally low at approximately 28% P_2O_5. The primary gangue mineral is quartz which is abrasive in processing. The Toolse concentrates have a high total impurity content. The main impurities are Fe_2O_3 and MgO. Some concentrates have a high carbonate content. Carbonates consume excess acid in processing. One of the carbonates, dolomite, dissolves under any acid attack process method releasing magnesium in processing systems. The chlorine contents are over 300 ppm. The stainless steels typically used in phosphoric acid plants corrode excessively at chlorine contents of 200-300 ppm.

Improved beneficiation techniques can probably be used to further upgrade the ores and lower the quartz content. It would be very difficult to lower the Fe_2O_3 and MgO impurity levels. Limited testwork indicates most of the chlorine cannot be removed by simple water washing.

A capacity of 1.0 to 2.0 million mt of concentrate is probably needed for a mine at Toolse to compete on the world market. A mine-beneficiation plant life of 20 years is considered a minimum under these conditions. Based on potential ore yields, one grade, potential recovery, a maximum depth of overburden of <25 m, and area measurements of specific ore types within the deposit, it is estimated that the Toolse deposit could support a 1.0 million mtpy concentrate production level for 18-33 years. Production at levels to supply Estonian requirements (250,000 mtpy concentrate) or a

potential regional requirement (500,000 mtpy concentrate) could be maintained for over 35 years.

From an Estonian viewpoint it would be advantageous to confine or begin the phosphate mine within the present limestone mine for the Kunda cement plant. At 1.0 million mtpy concentrate capacity the phosphate mine would outgrow the present limestone mine in 3.1-4.3 years. Assuming limestone production at current levels, a 500,000 mtpy concentrate phosphate mine would overtake limestone mining in 10 years. A 250,000 mtpy concentrate mine would overtake the limestone mine in about 20 years. A further complication is the limestone mine is moving to the south while the best phosphate ore and most densely drilled area of the deposit is found to the north. The most logical place to make the first cut for the phosphate mine is near the northern extremity of the deposit where the overburden is the thinnest. The highest grade and thickest phosphate beds are found on the western side of the Toolse River.

A complicating factor in mining the deposit is the handling of the Dictyonema Shale bed above the ore zone which spontaneously ignites causing atmospheric pollution and releases heavy metals to the biosphere. Although no solution has been found to the Dictyonema Shale problem, it is safe to assume any mining plan will have to include a stage to selectively remove and handle this material.

Comparison of the potential mining/production scenario at Toolse to a mine in Florida indicates the costs to produce Toolse concentrates will be high. Production costs at a newer large capacity Florida mine (4-5 million mtpy concentrate) are over $22/mt. A mine at Toolse, on the average, will have 2.5 times as much overburden that must be blasted and removed in comparison to the soft and relatively thin (5-7 m) overburden found in Florida. Pit mining in Florida is accomplished by the use of one dragline in each pit section working with other draglines alternatively stripping overburden or supplying ore to the beneficiation plant by slurry methods. Mining at Toolse would be a two- or three-stage operation probably involving truck transportation to the beneficiation plant.

Beneficiation costs at Toolse would also be higher. All the Toolse ore must be subjected to grinding and flotation processing. Preflotation screening and slimes removal in Florida selectively reject 40% to 50% of the total weight of the ore. The flotation feed does not have to be ground when processing Florida ores.

Concentrates of similar grade to Toolse concentrates (≈28% P_2O_5) are available at costs of <$30/mt (f.o.b.) from Florida sources. Costs to produce Toolse concentrates would be higher than this level and may approach or exceed the levels quoted for Kingisepp concentrates ($38.00/mt, 1992, or an estimated $56.00/mt, 1993).

No definite cost estimate can be placed on the production of Toolse concentrates at this time. However, perhaps the Florida-Toolse comparison can be extended one step further. A mine developed at Toolse would have to physically handle about 2.5 times as much overburden as the Florida mine per unit of ore. Any beneficiation plant at Toolse would have to incorporate a flotation section about twice as large per unit of ore when compared with the Florida mine. Therefore, capital and production costs might be approximately twice as high or possibly higher than the example from Florida. Any mine developed at Toolse would also operate at a much lower capacity than the Florida example used for comparison further increasing costs due to the economics of scale. One factor that might decrease the costs of production at the Toolse deposit is the potential for low cost electrical power and labor.

The Toolse deposit might be developed on an import substitution basis. Toolse concentrates are suitable for the production of phosphoric acid and several high analysis fertilizers although the suitability of these fertilizers for world market trade must be assessed. Potential costs of phosphate concentrates shipped to Estonia may be in the range of $45-$60/mt. It is possible Toolse concentrates can be produced at costs comparable to the potential costs of imported phosphate feedstocks and utilized in an Estonian-based fertilizer industry to produce value-added products. The preliminary evaluation of an Estonian-based fertilizer industry was beyond the scope of this study.

Further studies of the Toolse phosphate deposit are needed in several areas including additional delineation of the deposit, beneficiation studies, processing studies, and mining studies. Before such studies are instituted, the Russian report on the deposit should be re-evaluated (also translated if English-speaking consultants are utilized). All of these studies should be performed to derive data to eventually perform economic studies.

A prefeasibility study of the development of the Toolse phosphate deposit would be required to assess the economic potential of the deposit. While such studies are

largely conceptual in nature, they provide estimates of potential costs to determine if further investment is warranted. Several scenarios might be considered in such a prefeasibility study.

One scenario could be a mine producing 1.0 million mtpy of concentrate for export. This plan would assume all capital, loans, and other raw materials needed would be obtained at world market levels. All new mining equipment would be utilized. The cost to produce phosphate concentrate (at a competitive return on investment) would be compared to the prices of similar concentrates on the world market.

Another scenario which might be investigated is a mine producing concentrate to supply an integrated production complex producing fertilizers at production levels for export and/or Estonian or regional needs. Such a scenario would emphasize the production of value-added products and/or products for import substitution.

It would probably be worthwhile to develop a scenario in which all technically and economically suitable advantages possessed by Estonia are utilized. That is, the operation at Maardu and oil shale mining operations would be surveyed for used mining and processing equipment. The costs of new equipment obtained with loans at world market rates often offset any comparative advantage possessed by development at a specific site.

The world phosphate concentrate market situation will change between the years 2000-2010 due primarily to the projected contraction of the Florida phosphate industry and anticipated dominance of Morocco in the world phosphate rock industry. At this time prices will probably rise and the quality of concentrates available on the world market may decrease. Concentrates such as the Toolse concentrate may be increasingly more attractive as higher analysis and quality concentrates become more difficult to obtain and are increasingly more expensive. A lead time of 2-3 years for a prefeasibility study and 1-2 years for detailed engineering studies based on sound prefeasibility study data might be required before actual construction at Toolse could begin. An additional 3-5 years would be required for mine development and the development of any downstream processing facilities. Instituting further studies within the next few years, if favorable, would place the eventual full stream production of any facility at Toolse within this window of opportunity within the world phosphate market.

The low cadmium levels of Toolse concentrates (2-5 ppm) may be an incentive to develop the deposit. These cadmium levels are significantly lower than typical sedimentary phosphate rock concentrates. Cadmium levels in soil and fertilizers, and in crops and livestock grown or raised on cadmium-enriched farmlands are a major cause of concern in Europe. The present and potential future market for low cadmium phosphate rock concentrates and fertilizer products should be assessed.

Table 1. Unit-Cell Dimensions, Empirical Formulas, and Hypothetical Maximum P_2O_5 Contents in Pure Concentrates of Toolse Phosphate Samples

Sample No.	"a" Unit-Cell Dimension (Å)	Empirical Formulas	Maximum P_2O_5 Pure Concentrate
TK-2	9.360 ± 0.001	$Ca_{9.90}Na_{0.07}Mg_{0.03}PO_{4_{5.74}}CO_{3_{0.26}}F_{2.05}$	40.7
69P	9.362 ± 0.002	$Ca_{9.92}Na_{0.06}Mg_{0.02}PO_{4_{5.79}}CO_{3_{0.21}}F_{2.04}$	41.1
73P	9.355 ± 0.001	$Ca_{9.84}Na_{0.12}Mg_{0.04}PO_{4_{5.59}}CO_{3_{0.41}}F_{2.08}$	39.9
74F	9.356 ± 0.001	$Ca_{9.85}Na_{0.11}Mg_{0.04}PO_{4_{5.62}}CO_{3_{0.38}}F_{2.08}$	40.0
75S	9.356 ± 0.001	$Ca_{9.85}Na_{0.11}Mg_{0.04}PO_{4_{5.62}}CO_{3_{0.38}}F_{2.08}$	40.0

Table 2. Chemical and Approximate Mineralogical Modal Analysis of Toolse Ore Sample No. TK-2

Chemical Analyses		Quartz (SiO_2)	Francolite[a]	Pyrite (FeS_2)	Dolomite [$CaMg(CO_3)_2$]	Calcite $CaCO_3$	Unassigned
	(wt %)						
P_2O_5	8.19		8.19				
CaO	12.3		11.21		0.57	0.46	0.06
F	0.77		0.77				
SiO_2	69.3	69.3					
Al_2O_3	0.76						0.76
Fe_2O_3	2.24			2.2			0.04
Na_2O	0.17		0.04				0.13
K_2O	0.15						0.15
MgO	0.43		0.02		0.41		
MnO	0.04						0.04
TiO_2	0.15						0.15
Total S	1.77			1.77			
Cl (ppm)	125						125
Cd (ppm)	1						
CO_2	1.5		0.25		0.89	0.36	
C (organic)	0.46						0.46
Free H_2O[b,c]	0.1						
LOI[b,d]	4.0						
NAC P_2O_5[b,e]	3.4						
	98.24	69.3	20.48	3.97	1.87	0.82	1.8
-O = F[f]	0.32		0.32				
	97.92	69.3	20.16	3.97	1.87	0.82	1.8

a. See text for composition.
b. Not included in totals.
c. Free H_2O = weight loss, 105°C, 1 hour.
d. Loss-on-Ignition (LOI) = weight loss, 1000°C, 1 hour.
e. AOAC method, second extraction.
f. Fluorine correction, 2 F^- substitute for 1 O^{2-}.

Table 2. Chemical and Approximate Mineralogical Modal Analysis of Toolse Concentrate Sample No. 69P

Chemical Analyses		Francolite[a]	Quartz (SiO_2)	Pyrite (FeS_2)	Calcite $CaCO_3$	Dolomite [$CaMg(CO_3)_2$]	Unassigned
	(wt %)						
P_2O_5	24.2	24.2					
CaO	36.6	32.85			2.14	0.92	0.69
F	2.29	2.29					
SiO_2	27.3		27.3				
Al_2O_3	0.29						0.29
Fe_2O_3	1.9			1.9			
Na_2O	0.49	0.09					0.40
K_2O	0.12						0.12
MgO	0.71	0.05				0.66	
MnO	0.11						0.11
TiO_2	0.13						0.13
Total S	1.56			1.53			0.03
Cl (ppm)	369 (ppm)						369 (ppm)
Cd (ppm)	2 (ppm)						2 (ppm)
CO_2	3.70	0.57			1.68	1.45	
C (organic)	0.28						0.28
Free H_2O[b,c]	0.10						-
LOI[b,d]	5.6						-
NAC P_2O_5[b,e]	3.6						
	99.72	60.05	27.3	3.43	3.82	3.03	2.09
-O = F[f]	0.96	0.96					
	98.76	59.09	27.3	3.43	3.82	3.03	2.09

a. See text for composition.
b. Not included in totals.
c. Free H_2O = weight loss, 105°C, 1 hour.
d. Loss-on-Ignition (LOI) = weight loss, 1000°C, 1 hour.
e. AOAC method, second extraction.
f. Fluorine correction, 2 F^- substitute for 1 O^{2-}.

Table 4. Chemical Analyses of Three Concentrates From the Toolse Deposit

Chemical Analyses	Sample No. 73P[a]	74F[b]	75S[c]
	(wt %)		
P_2O_5	28.8	26.3	24.6
CaO	42.3	40.6	37.4
F	2.67	2.56	2.36
SiO_2	16.0	16.3	26.8
Al_2O_3	0.3	0.81	0.40
Fe_2O_3	1.94	2.37	1.82
Na_2O	0.57	0.56	0.51
K_2O	0.11	0.25	0.10
MgO	0.57	0.68	0.41
MnO	0.12	0.12	0.10
TiO_2	0.14	0.22	0.16
Total S	1.56	1.18	1.10
Cl (ppm)	367	428	303
Cd (ppm)	5	1	2
CO_2	3.9	4.7	3.4
C (organic)	0.42	0.57	0.58
Free H_2O[d,e]	0.2	-	0.3
LOI[d,f]	7.4	-	6.8
NAC P_2O_5[d,g]	3.6	3.4	2.9
Total	99.44	97.26	99.77

a. Pyritic ore, anionic flotation.
b. Ferruginous ore, anionic flotation.
c. Siliceous ore, anionic flotation.
d. Not included in totals.
e. Free H_2O = weight loss, 105°C, 1 hour.
f. Loss-on-Ignition (LOI) = weight loss, 105°C.
g. AOAC method, second extraction.
h. Reduced to 306 ppm after water washing.

Table 5. Summary of Chemical Characteristics of Toolse Concentrate Samples

Sample No.	Grade (% P_2O_5)	SiO_2 Content	CaO/P_2O_5	$R_2O_3 + MgO/P_2O_5$	Cl	Cd
					- (ppm)-	
69P	24.2	27.3	1.51	0.12	369	2
73P	28.8	16.0	1.47	0.10	367	5
74F	26.3	16.3	1.54	0.15	428	1
75S	24.6	26.8	1.46	0.11	303	2

Table 6. Major World Producers – Phosphate Exporters

Country	1990			1995			2000		
	Rock	Products[a]	Total	Rock	Products[a]	Total	Rock	Products[a]	Total
	(million metric tons equivalent phosphate rock)								
Morocco	13.0	10.0	23.0	16.0	15.0	31.0	19.0	19.0	38.0
United States[b]	8.0	17.7	25.7	8.5	18.5	27.0	7.0	18.0	25.0
Jordan	5.5	1.0	6.5	6.0	1.0	7.0	8.0	2.0	10.0
Tunisia	1.2	5.3	6.5	0.7	5.3	6.0	0.7	5.3	6.0
Togo	3.4	0	3.4	3.4	0	3.4	3.0	0	3.0
Israel	3.6	0	3.6	3.5	0	3.5	3.5	0	3.5
South Africa	2.6	0	2.6	2.6	0	2.6	3.0	0	3.0
Senegal	2.2	0	2.2	2.5	0	2.5	3.5	0	3.5

a. Values refer to amount of rock concentrate used for chemically processed products.
b. Domestic use in the United States will be about 22-23 million mt in the 1990s.

Table 7. Projected U.S Phosphate Concentrate Production, 1995-2015

	1995	2000	2005	2010	2015
	(million metric tons)				
Florida and North Carolina	39.2	48.1	31.2	24.5	24.5
Western United States	6.8	5.8	5.8	5.8	5.8
Total United States	46.0	53.9	37.0	30.3	30.3

Table 8. Calculation of Mine Longevities at Various Production Capacities in Various Areas Utilizing Specific Ore Types, Toolse Deposit, Estonia

Mining Area	Area	Capacity	Mine Life[a]
Present pit, all ore types	2.54 km^2	2.0 mt concentrate/year	2.1-1.5
		1.0 mt concentrate/year	4.3-3.1
		500,000 mt concentrate/year	8.6-6.2
		250,000 mt concentrate/year	17.2-12.3
Present pit, normal silicate ore types	1.59 km^2	2.0 mt concentrate/year	1.3-1.0
		1.0 mt concentrate/year	2.7-1.9
		500,000 mt concentrate/year	5.4-3.8
		250,000 mt concentrate/year	10.76-7.7
Normal silicate ore zone, <25 m overburden (including present limestone pit)	15 km^2	2.0 mt concentrate/year	12.7-9.1
		1.0 mt concentrate/year	25.4-18.2
		500,000 mt concentrate/year	50.7-36.4
		250,000 mt concentrate/year	101.5-72.7
All ore types except weathered type with <25 m overburden (including present limestone pit)	19.6 km^2	2.0 mt concentrate/year	16.6-11.9
		1.0 mt concentrate/year	33.2-23.7
		500,000 mt concentrate/year	66.4-47.5
		250,000 mt concentrate/year	131.7-95.0

a. Best and worst case scenarios. Best case = 59,400 mt/ha, 5% mining loss, 80% beneficiation recovery. Worst case = 50,500 mt/ha, 20% mining loss, 80% beneficiation recovery.

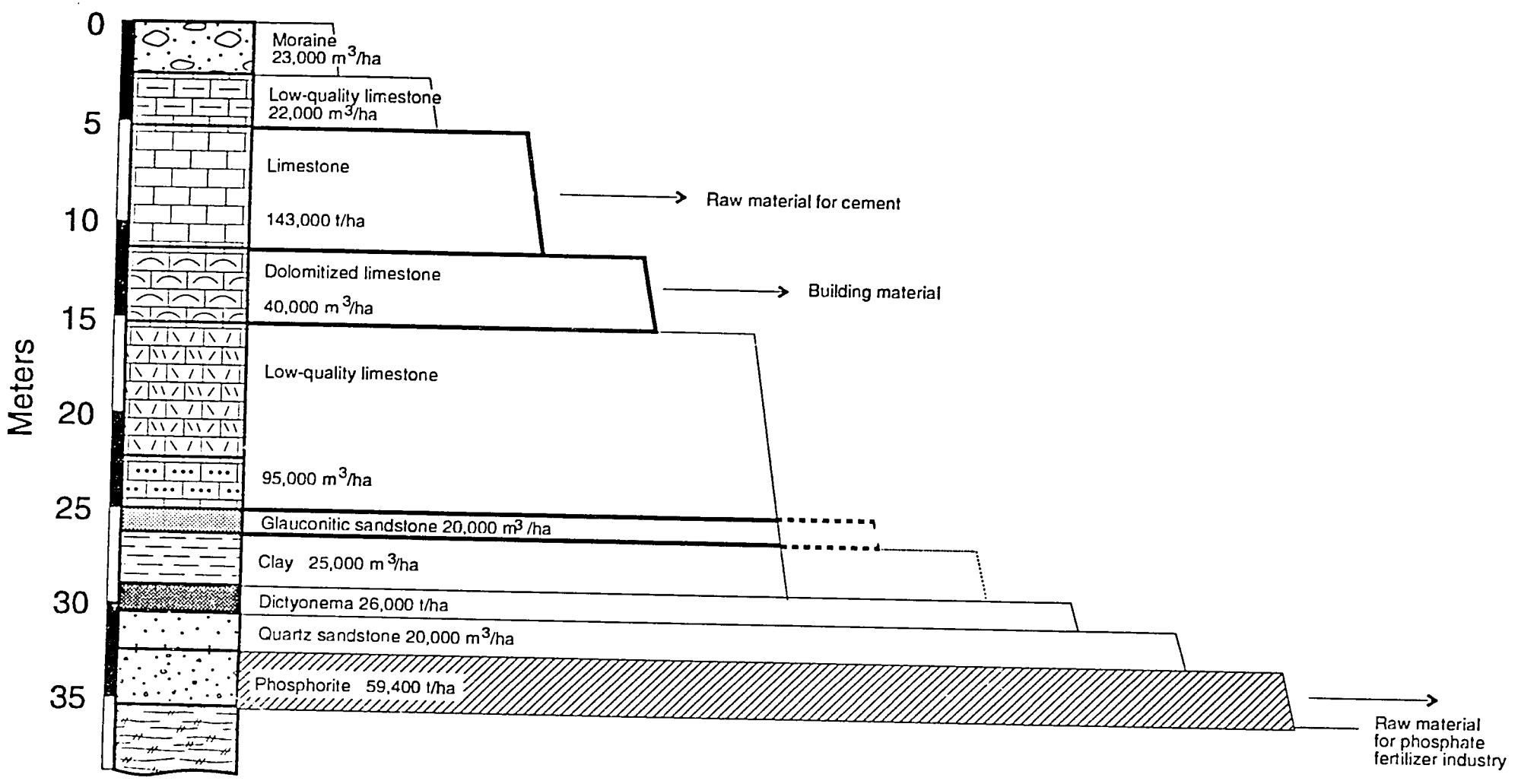
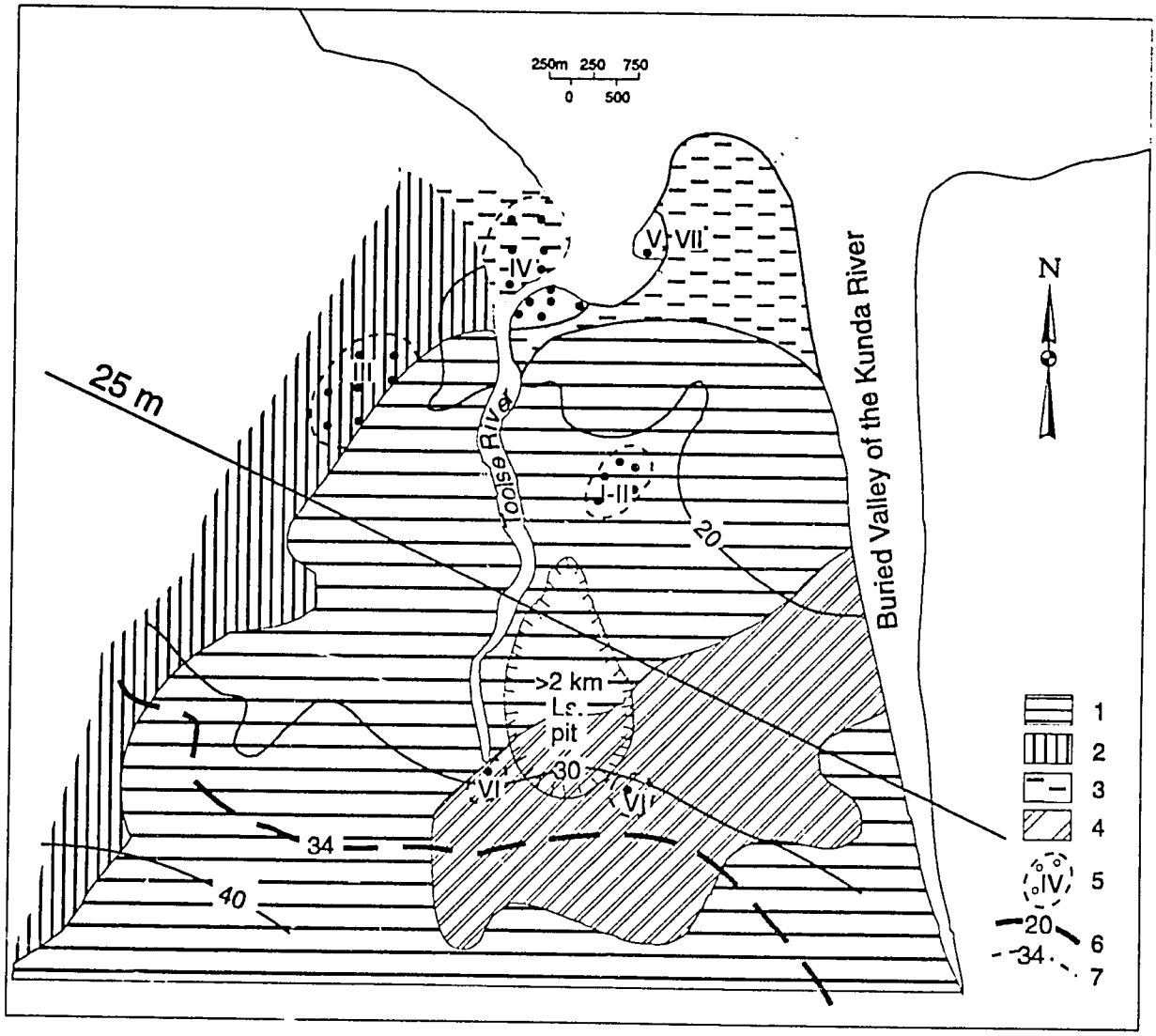


Figure 1. General Cross Section of the Toolse Phosphate Deposit Area.



Toolse Deposit Area.

Figure 2. Distribution of Phosphorite Ore Types in the Toolse Area. The Limits of the Limestone Pit Are a Crude Estimate.

Phosphate Ore Types:

1 - Silicate (normal).
2 - High Silicate.
3 - Weathered.
4 - Ferruginous (pyritic?).
5 - Sample locations.
6 - Overburden thickness
7 - Stripping limit of deposit by open-cast pit as determined by Russian studies

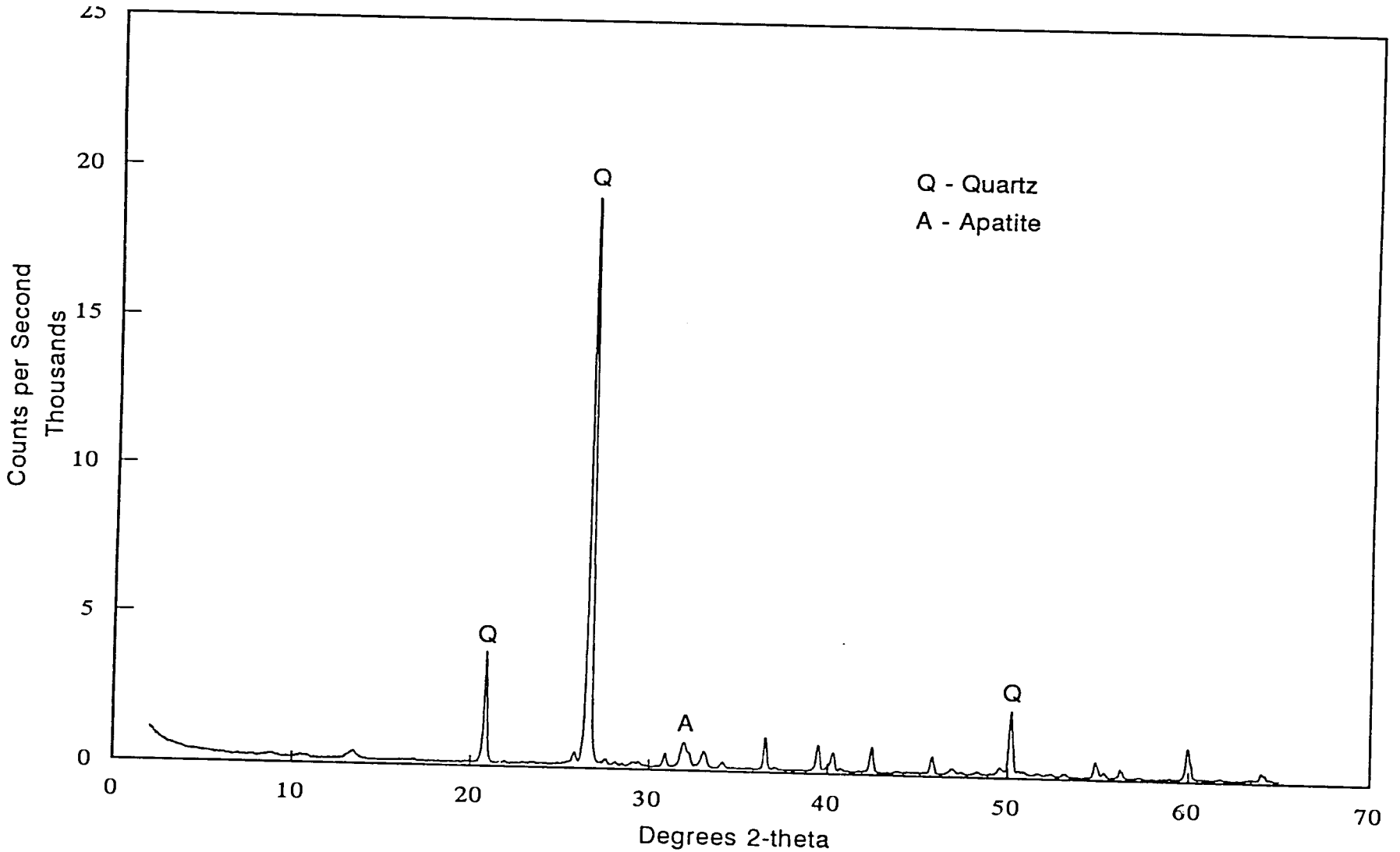


Figure 3. X-ray Diffraction Pattern, Toolse Ore Sample #TK-2.

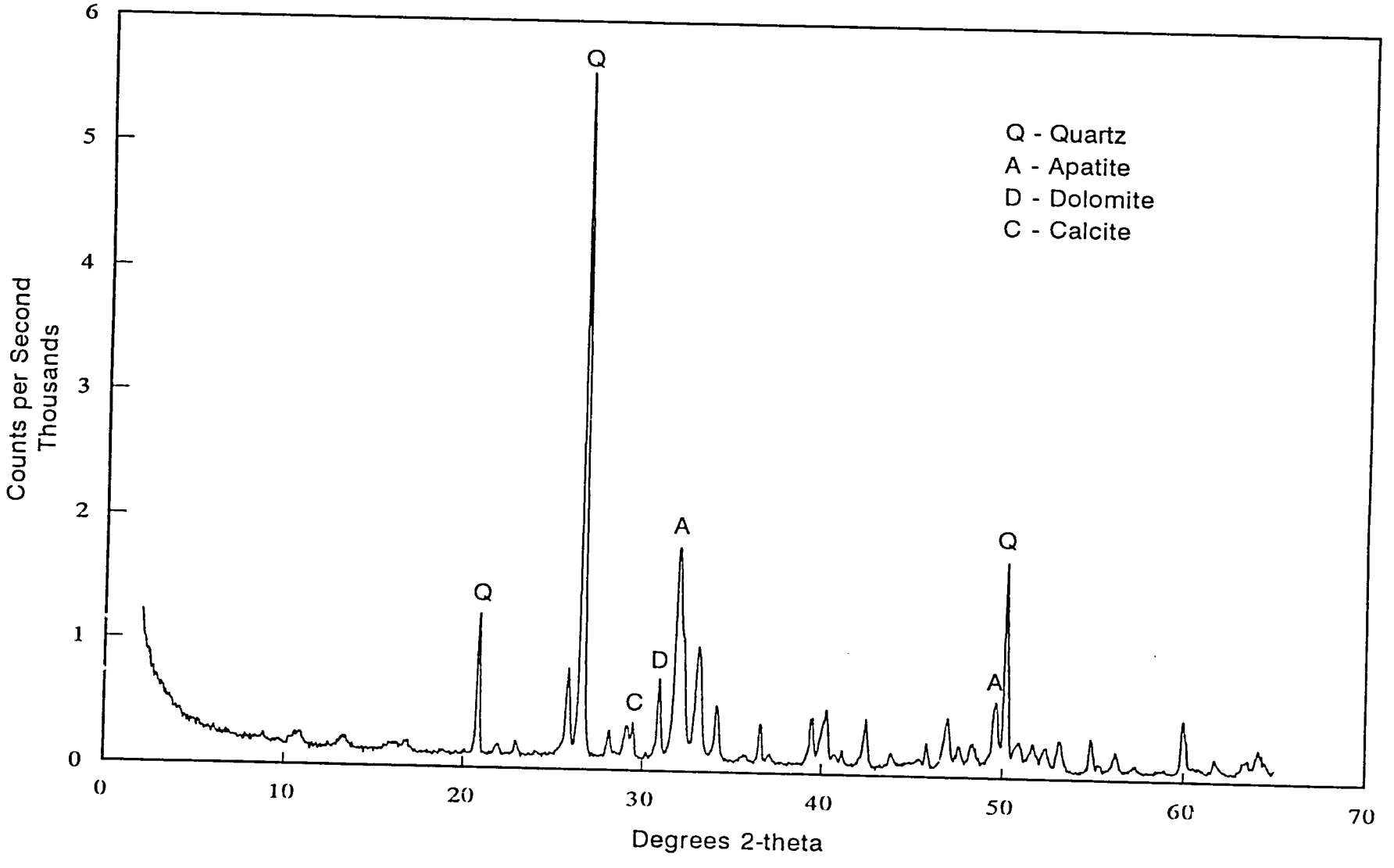


Figure 4. X-ray Diffraction Pattern, Toolse Concentrate Sample #69P.

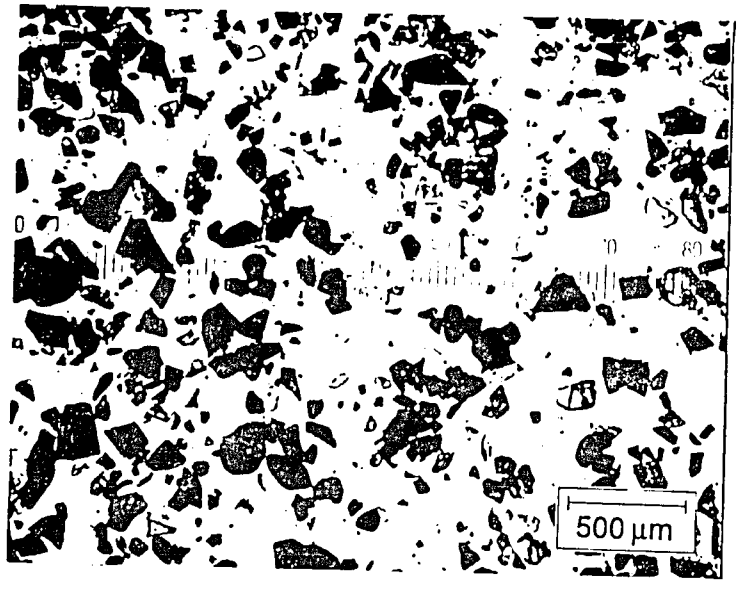


Figure 5. Plane - Polarized Light Photomicrograph, Toolse Concentrate Sample No. 69P.

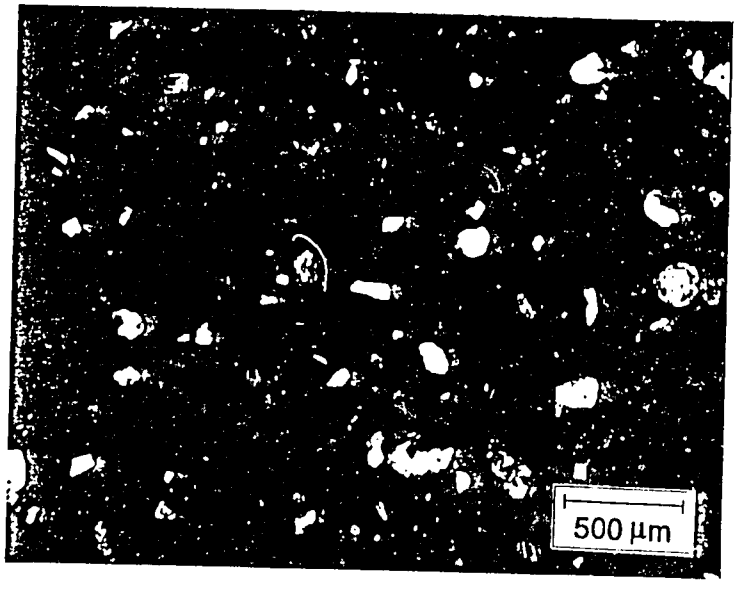


Figure 6. Crossed - Nicols Photomicrograph of Figure 5. Bright Grains Are Mainly Liberated Quartz Particles.

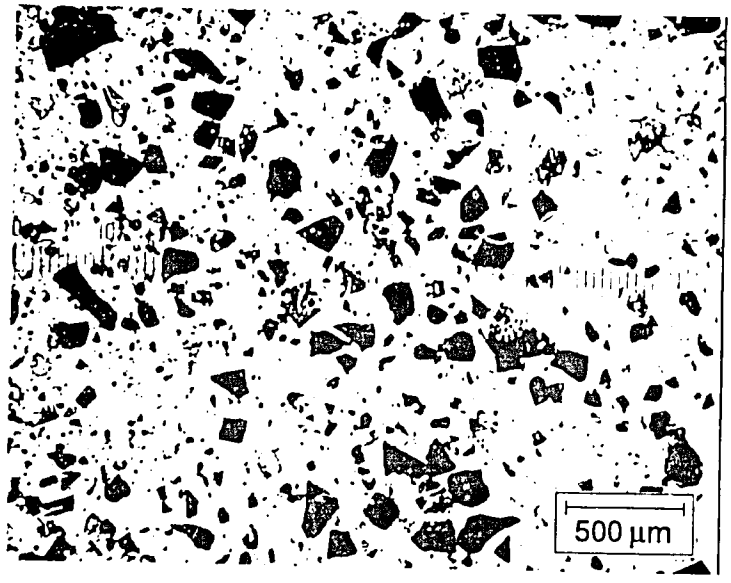


Figure 7. Plane - Polarized Light Photomicrograph, Toolse Concentrate Sample No. 73P.

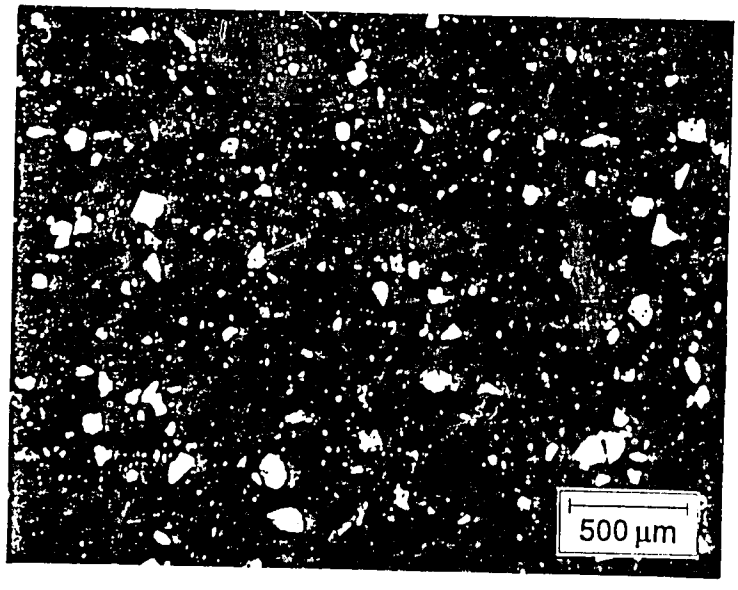


Figure 8. Crossed - Nicols Photomicrograph of Figure 7. Bright Grains Are Mainly Liberated Quartz Particles.

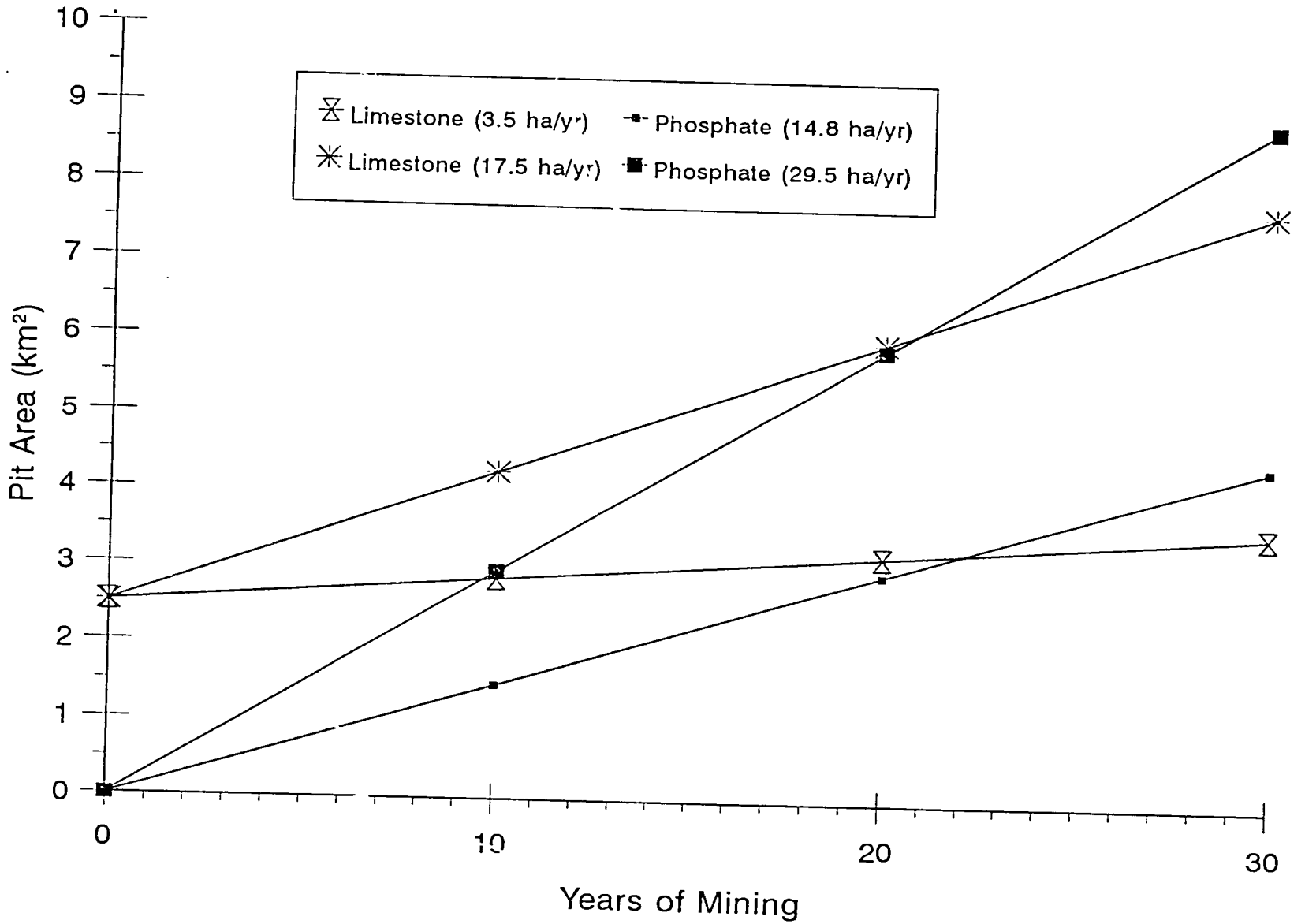


Figure 9. Two Limestone Quarrying Scenarios vs. Two Phosphate Mining Scenarios in the Present Limestone Pit.