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PHOSPHATE DEPOSITS KAPUNDA
Production of Phosphoric Acid

by

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to

SOUTH AUSTRALIAN GOVERNMENT
DEPARTMENT OF MINES

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1. INTRODUCTION

An investigation of methods of producing phosphoric acid from Kapunda phosphate deposits by a "wet process" was requested by the South Australian Government Department of Mines. This process involves the solution of the phosphate by acid attack followed by a solvent extraction of the phosphoric acid into an organic solvent and subsequent recovery of the acid from the solvent.

Owing to the lack of specific information on the process, the work has been confined mainly to investigation of the leaching of the ore and the effect of the major variables on the extraction of the phosphoric acid into the organic phase. A rough estimate of the relative costs of using sulphuric, nitric and hydrochloric acids has been prepared from data found in the literature. As a result of this estimate the subsequent work was confined almost exclusively to the use of sulphuric acid.

2. SUMMARY

The phosphate in the material supplied from Klemm's Quarry was in the form of apatite. The apatite is finely disseminated in the ore and could not be readily concentrated by flotation.

At least 90 per cent of the phosphate was leached from the ore with either nitric,hydrochloric or sulphuric acids.

A crude phosphoric acid was produced from the ore by leaching with a minimum quantity of sulphuric acid. This acid was relatively dilute and contained iron, aluminium and sulphate as impurities.

Phosphoric acid could be produced from the leach liquors by solvent extraction with n butyl alcohol. If sulphuric acid were used in the leaching of the ore the final product would contain some sulphate. The acid produced by solvent extraction would be more concentrated but also more expensive.

Very little work was done on the use of hydrochloric and nitric acids and an economic assessment showed that processes using these acids might be too expensive.

If sulphuric acid were used neither of the products would be suitable for use for the surface preparation of steel. The most promising possible outlet for the phosphoric acid would be in the fertilizer industry for upgrading the P_2O_5 content of super phosphate.

3. MATERIAL EXAMINED

Samples of phosphate rock from an area near Kapunda were obtained by Mr. Willington of the South Australian Government Department of Mines. The samples were crushed, mixed and assayed for P_2O_5 with the results shown in Table 1.

TABLE 1: P_2O_5 CONTENT OF SAMPLES OF PHOSPHATE ROCK

Sample No.	Locality	Description	P_2O_5(b) %
1.	Section 105, Hundred of Moorooroo, Quarry being operated by C.R. Bartsch who is supplying Wooltana Industries Ltd. Known as Klemm's Quarry, Moculta.	Average grade material	21.2
2.	Same locality as above	Low grade material	16.6
3.	- ditto -	High grade material	27.5
4.	"	Specially selected high grade material	34.6
5.	"	Cupriferous " " "	36.6(a)
6.	Section 295, Hundred of Belvidere, Kapunda. Known as Tom's Quarry.	10 lb channel sample from east adit at north end of quarry floor.	18.0
7.	Section 1551, Hundred of Belvidere, Kapunda. Known as St. John's Quarry.	Samples from new open cut	19.5

(a) Copper 0.013 per cent.
(b) Reported on a moisture free basis.

The Department of Mines requested that material from Klemm's Quarry, Moculta should be used in the investigation. Samples of high grade, average grade and low grade material from this source were submitted to a more complete chemical analysis with the results shown in Table 2.

TABLE 2: ANALYSIS OF PHOSPHATE ORE FROM KLEMM'S QUARRY

Sample	Average Grade %	Low Grade %	High Grade %
P_2O_5	20.7	16.0	36.3
Fe_2O_3	21.1	29.5	2.74
Al_2O_3	4.8	2.9	1.25
CaO	28.4	22.2	49.0
MgO	0.04	0.04	0.02
Insoluble matter	16.9	19.5	3.95
CO_2	1.63	1.55	1.35
SO_3	0.02	0.01*	0.02
Cl	0.02	0.02	0.02
F	2.17	1.56	3.64
Water at 100°C	0.98	0.82	0.78
Water above 100°C	4.16	5.06	0.84
	100.92	99.15	99.91
Less oxygen equivalent of fluorine.	0.91	0.66	1.53
	100.0	98.5	98.4

* Less than.

The samples from Klemm's Quarry were subjected to a mineralogical examination. X-ray diffraction studies showed that fluorapatite, goethite and quartz were present in all samples. Iron and aluminium phosphates were not detected. Microscopic examination showed that the rock was highly brecciated and consisted of fragments of limonite, quartz, quartzite, laths of muscovite and quartz crystals cemented by ferruginous and silicious material.

Apatite occured as a secondary mineral replacing other minerals particularly in the matrix. Usually it occured as aggregates of fine grained crystals with fibrous radiating or colloform habit. The aggregates were up to 1 mm or more across made up of crystals a few microns in size.

Samples of phosphate material from Tom's Quarry and St. John's Quarry were also submitted for X-ray diffraction study. The phosphate was present in the sample from Tom's Quarry as a form of apatite but in the sample from St. John's Quarry it was present mainly as crandalite, an aluminium phosphate.

The following samples of material from Klemm's Quarry which were used in the leaching tests were stage ground to the particle sizes shown below:

Sample	Material	Particle Size	P_2O_5 Content %
A	Average grade	Minus 100 mesh	20.7
B	- ditto -	" 18 "	20.7
C	"	" 72 "	20.7
D	Low grade	" 100 "	16.0
E	High grade	" 100 "	36.3

4. EXPERIMENTAL PROCEDURE AND RESULTS

4.1 Literature Survey

A search was made of Chemical Abstracts from 1947 to December 1961. References were found to the use of oxygenated solvents e.g., alcohols, in the extraction of inorganic salts. However, with the exception of some information on the use of alcohols for extracting phosphoric acid from solutions made by dissolving high grade rock phosphate in hydrochloric acid[1,2] very little information was of help in planning the project.

Unfortunately the description of the extraction process was given in vague terms and many aspects of the process were not discussed. Extensive preliminary investigations of the process were therefore required to establish the effect of the major variables on the extraction.

4.2 Economic Assessment of the Process

This assessment was made concurrently with the initial investigations and therefore did not affect the planning of the initial work. The approximate costs of producing phosphoric acid using sulphuric, hydrochloric and nitric acids were determined.

4.2.1 Basis for the Economic Assessment

The economic assessment is based on the following data given by Baniel et al[1].

> " The figures given below can serve as a basis for a first estimate of investment and direct operating costs.

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1. Baniel A., Blumberg R. and Alon A., "Phosphoric Acid by Liquid Liquid Extraction", British Chemical Engineering,P 223, April, 1959.

2. Baniel A., and Blumberg R., "Phosphoric Acid from Phosphate Rock and Hydrochloric Acid", Dechema - Monographien Band 33, Seite 57-68, 1959.

Investment US dollars per metric ton P_2O_5 per year
(in the range of 15 to 30 tons P_2O_5/day) - \$100-80.

HCl (100%)	kg/ton	P_2O_5	1800 - 2,000
Solvent alcohol	"	"	5
Water process	M^3/ton	"	18
Water cooling	"	"	200
Power	kwh/ton	"	150
Steam	kg/ton	"	6,000
Labour	man hr/ton		8
Final product	H_3PO_4 % concentration		80 "

The figures quoted above were for a solvent plant which treated high-grade phosphate ore (33% P_2O_5) using 30 per cent HCl to leach the ore. It is reasonable to assume that allowance was made for the hydrochloric acid which could be recovered and that the estimate of 1800 to 2000 kg per metric ton of P_2O_5 represents the nett consumption of hydrochloric acid.

The following assumptions were made:

(a) Plant Capacity

30 metric tons of P_2O_5 produced per day for 300 days per annum, i.e., 8,860 long tons P_2O_5 per year

(b) Exchange £1.0.0 Australian = 2.2 US dollars
£1.5.0 Australian = £1.0.0 sterling

(c) Hydrochloric Acid Road tanker lots -
5½d per lb of 30.5% HCl (Adelaide Chemical Co.) =
£168.6.0 per long ton 100% HCl

(d) Sulphuric Acid Road tanker lots -
£14.4.0 per ton 98% H_2SO_4 (Adelaide Chemical Co.) =
£14.6.0 per long ton 100% H_2SO_4

(e) Nitric Acid Ton lots - approximately
1/1d to 1/2d per lb 65.5% HNO_3 (Adelaide Chemical Co.) =
£185.4.0 per long ton 100% HNO_3

(f) n-Butyl Alcohol Ton lots - £210.0.0 per long ton

(g) Water 2/6d per 1,000 gallons.

(h) Power 2 pence per kwh.

(i) Steam ¼ pence per lb.

(j) Labour 15/-d. per man hour.

(k) Mining, Crushing and Transport

Costed at - £4. 0. 0 per ton of ore

(1) Phosphoric Acid Ton lots -
£104.0.0 Sterling per ton 85% H_3PO_4
(Chemical Age) = £152.18.0 per long ton 100% H_3PO_4

1 long ton P_2O_5 = 1.38 tons 100% H_3PO_4 = £211
The product was therefore valued at £211 per long ton P_2O_5

4.2.2 Costs Common to Each Process

Investment - Using the figure of 80 US dollars per metric ton of P_2O_5 per annum and writing off the cost of the plant over 10 years -

Cost per year = 72,000 dollars
Interest at 5% = 36,000 "

These costs are equivalent to £5.11.0 per long ton of P_2O_5

Alcohol 5 kg per metric ton P_2O_5 = £1. 1.0 per long ton P_2O_5

Water Total consumption (process plus cooling water) is -
48,750 gal per long ton P_2O_5 = £5. 2.0 per long ton P_2O_5

This is the maximum. Some savings could be made by using sea water for cooling if the plant was conveniently located.

Power 150 kwh per metric ton P_2O_5 = £1. 6.0 per long ton P_2O_5

Steam 6,000 kg per metric ton P_2O_5 = £14. 0.0 per long ton P_2O_5

Labour 8 man hours per metric ton = £6. 0.0 per long ton P_2O_5

Mining, Crushing etc. Assuming an average grade of 20% P_2O_5 and an overall recovery of 85%, 5.9 tons of ore must be treated to recover 1 long ton P_2O_5.
Total cost = £23.12.0 per long ton P_2O_5

Summary of Costs Common to each Process

Capital and Interest	5.11.0
Mining and Crushing etc.	23.12.0
Alcohol	1. 1.0
Water	6. 2.0
Power	1. 6.0
Steam	14. 0.0
Labour	6. 2.0
Total Costs	£57.14.0 per long ton P_2O_5

4.2.3 Sulphuric Acid Process

The amount of HCl required for the Israeli process was quoted as 1800 to 2000 kg per metric ton of P_2O_5. Assuming an average figure of 1900 kg, the equivalent amount of 100 per cent sulphuric acid is 2.55 tons per long ton of P_2O_5. In practice a larger amount of sulphuric acid would be required because it would not be possible to recover sulphuric acid from the final product by distillation as is done with hydrochloric acid. Assuming that a further 20 per cent of the sulphuric acid is needed, about 3 tons of sulphuric acid would be required per ton of P_2O_5. Therefore, the cost of sulphuric acid would be approximately £43.0.0 plus £57.14.0 (costs common to each process) = £100.14.0 say £100 per long ton P_2O_5

Sulphuric acid therefore can be considered to be economically suitable. However, certain disadvantages are associated with its use, namely: -

(a) It would not be possible to produce a high grade phosphoric acid free of sulphuric acid because of the difficulty in separating these acids. The presence of sulphuric acid would probably limit the potential uses of the final product.

(b) Because most of the calcium from the apatite is precipitated during the leaching, the concentration of salts in the leach liquor is relatively low. This would result in a lower concentration of phosphoric acid in the alcohol than would be the case if hydrochloric acid were used. A larger quantity of alcohol would be required and the final concentration of phosphoric acid would probably be lower.

(c) The leaching studies have shown that sulphuric acid is not as effective as hydrochloric or nitric acids in dissolving phosphate.

4.2.4 Hydrochloric Acid Process

Assuming an acid consumption of 1900 kg per metric ton P_2O_5 the cost of hydrochloric acid would be £320 per long ton P_2O_5. The estimated cost of producing phosphoric acid is therefore approximately £378.0.0 per long ton P_2O_5.

The only waste product would be a solution of calcium chloride and it is unlikely that there would be a market for this by-product. It can be assumed therefore, that hydrochloric acid could only be considered if it could be obtained for less than 50 per cent of the price used in these calculations.

The total cost of the reagents necessary to make one ton of 100 per cent hydrochloric acid is much less than the price quoted for the commercial acid. 1 ton 100 per cent HCl requires:

Approx.	2.7 tons H_2SO_4	at	£14.6.0/ton =	£38.2.0
	1.6 tons NaCl	at	£ 5.0.0/ton =	£ 8.0.0
				£46.2.0

It is probable therefore, that hydrochloric acid could be made from sulphuric acid and salt for much less than the quoted market price.

4.2.5 Nitric Acid Process

Assuming that nitric acid behaves in a similar manner to hydrochloric acid, 3.3 tons of 100 per cent HNO_3 would be required per long ton of P_2O_5.

The cost of producing phosphoric acid is therefore equal to:

Acid Costs	=	611. 0. 0
plus Common Costs	=	57.14. 0
		£668.14. 0

Say £670.0.0 per long ton of P_2O_5

Nitric acid could probably be made from ammonia for a lower cost than that used in these calculations. However, it is apparent that a considerable proportion of the nitric acid present in the raffinate as calcium nitrate would have to be recovered to make the process economic. Although it is theoretically possible to recover nitric acid from nitrates a suitable type of reactor would be expensive. In order to achieve high recoveries of nitric acid the salts must be decomposed rapidly and the resultant oxides of nitrogen must be removed from the reaction zone as speedily as possible.

4.3 Leaching Investigations

4.3.1 Experimental Procedure

The leaching tests were made on 100 g samples of ore in glass flasks. The leach pulps were stirred continuously throughout the leaching period. For the higher temperature tests the calculated amount of acid was slowly added to the water-ore mixture. When all of the acid had been added the flasks were heated with electrical heating mantles and the pulps were boiled under reflux for the prescribed leaching period.

For low temperature leaching the calculated amounts of acid and water were mixed and allowed to cool to room temperature prior to the addition of the ore. This was done to limit the attack on the iron and aluminium minerals present in the ore.

All of the leached pulps were filtered on Buchner funnels and the residues were washed with distilled water. The combined filtrates and washings were mixed and made to a definite volume with water.

The residues were dried and weighed and leaching efficiencies were calculated from liquor and residue assays.

In most of the tables of results the amount of acid is expressed in terms of the percentage of the theoretical amount of acid required to leach all of the phosphate from the particular sample, and in terms of pounds of bench acid (i.e., 97% H_2SO_4, 35.4% HCl and 70% HNO_3) per short ton of sample. The pulp compositions shown in the tables were calculated from liquor analysis.

The average grade material was used in most of the tests and only a few leaches were carried out on the low and high grade material.

The effect of particle size on the leaching efficiency was determined by leaching samples of the ore which had been stage ground to pass through the various screen sizes given in the tables.

4.3.2 Preliminary Leaching Tests

These tests were made at elevated temperatures because it was assumed before the mineragraphic examination had been made that the phosphate was probably present as relatively insoluble iron and aluminium phosphates. All three acids namely sulphuric, nitric and hydrochloric acids were investigated. The results of these tests are given in Table 3.

With sulphuric and hydrochloric acids high leaching efficiencies were obtained only when twice the amount of acid theoretically required to dissolve the phosphate had been added. Under these conditions nitric acid extracted only about 19 per cent of the phosphate. With 150 per cent of the theoretical amount of acid a slight increase in leaching efficiency for sulphuric and nitric acids was obtained by decreasing the percentage of solids in the leach pulp.

4.3.3 Room Temperature Leaching

Because of the low leaching efficiencies the original ore was examined mineralogically. X-ray diffraction and microscopic studies of the material from Klemm's Quarry showed that the phosphate was present mainly as apatite (see Section 3). Since the phosphate was not chemically associated with the iron and aluminium the apatite might be concentrated by flotation. The flotation concentrate could then be treated by conventional processes. The results of the flotation tests which were made by the Metallurgical Section are given in AMDL Report No. 206. No appreciable concentration of the apatite was achieved in any of the tests.

Apatite should be readily soluble in acid solutions, therefore, the low leaching efficiencies were probably caused by the precipitation of dissolved phosphate as insoluble iron and aluminium phosphates. Some of the residues were examined by X-ray diffraction and iron and aluminium phosphates were found to be present thus confirming the above conclusion. Milder leaching conditions were therefore used in an endeavour to dissolve the apatite without dissolving large quantities of iron and aluminium.

TABLE 3: PRELIMINARY LEACHING TESTS
Temp - at boiling point
Time - 5 hours

Test No.	Type of Acid	Amount of Acid		Percentage of Solids in Pulp	Leaching Efficiency %
		lb/short ton	Percentage of Theoretical		
A/ 1	Sulphuric	1090	120	30	21
A/ 4	"	1360	150	30	18
A/ 7	"	2180	200	25	97
A/10	"	1360	150	20	31
A/ 2	Hydrochloric	2220	120	30	18
A/ 5	"	2780	150	30	30
A/ 8	"	4440	200	25	97
A/11	"	2780	150	20	29
A/ 3	Nitric	1940	120	30	25
A/ 6	"	2420	150	30	18
A/ 9	"	3880	200	25	19
A/12	"	2420	150	20	33

The results of these tests using sulphuric, hydrochloric and nitric acids are shown in Tables 4, 5 and 6 respectively.

The leaching efficiencies obtained with nitric acid were significantly higher than those obtained with either hydrochloric or sulphuric acids. It is evident that the particle size of the ore had a significant effect on the leaching efficiencies of the sulphuric acid tests but the effect was less evident for hydrochloric acid and not significant with nitric acid.

Leaching for periods in excess of 1 hour and increasing the temperature to 40°C made little difference to the amount of phosphate dissolved. Relatively low concentrations of iron and aluminium were present in the leach liquors. The leaching efficiency obtained with the 18-mesh material was not increased by increasing the acid addition to 150 per cent of the theoretical amount for sulphuric and nitric acids but with hydrochloric acid a significant increase was obtained.

Approximately 90 per cent of the phosphate was leached in 1 hour from 100 per cent minus 100-mesh material with each of the 3 acids investigated. Hydrochloric and nitric acids were also effective on minus 18 and minus 72-mesh material, but sulphuric acid gave much lower leaching efficiencies for the coarse ore. The effect of adding sodium chloride to the sulphuric acid leaches was therefore investigated. The amount of sodium chloride used was stoicheiometrically equivalent to the amount of sulphuric acid. The results are shown in Table 7.

Sulphuric plus sodium chloride was effective in leaching the coarse ore at a pulp composition of 20 per cent solids by weight. The additional salts in the final liquor were shown (Section 4.4.4) to be beneficial to the solvent extraction of the phosphoric acid.

TABLE 4: SULPHURIC ACID
Percentage of solids in

Test No.	Amount of Acid		Particle Size of Ore
	lb/short ton	Percentage of Theoretical	Mesh (Tyler)
A/13	1090	120	100
A/16	1090	120	100
A/19	1090	120	100
B/ 1	1090	120	18
C/ 1	1090	120	72
B/ 7	1360	150	18
C/ 6	1090	120	72
B/10	1090	120	18

* RT - Room temperature.

TABLE 5: HYDROCHLORIC ACID
Percentage of solids in

Test No.	Amount of Acid		Particle Size of Ore
	lb/short ton	Percentage of Theoretical	Mesh (Tyler)
A/14	2220	120	100
A/17	2220	120	100
A/20	2220	120	100
B/ 2	2220	120	18
C/ 2	2220	120	72
B/ 8	2780	150	18
C/ 4	2220	120	72
B/11	2220	120	18

* RT - Room temperature.

LEACHING AT ROOM TEMPERATURE
Pulp - 20

Temp °C	Time hr	Leaching Efficiency %	Composition of Liquor in Pulp, g/l P_2O_5	Ca	Fe	Al	SO_4
RT*	2	91	51.1	1.6	1.4	0.9	23.4
40	2	90	-	-	-	-	-
RT	1	91	-	-	-	-	-
RT	2	57	32.3	1.3	0.5	0.8	66.4
RT	2	85	-	-	-	-	-
RT	2	56	-	-	-	-	-
RT	1	82	43.5	1.3	0.5	0.8	43.5
RT	1	57	-	-	-	-	-

LEACHING AT ROOM TEMPERATURE
Pulp - 20

Temp °C	Time hr	Leaching Efficiency %	Composition of Liquor in Pulp, g/l P_2O_5	Ca	Fe	Al
RT*	2	90	50.2	51.4	1.3	0.8
40	2	92	-	-	-	-
RT	1	88	-	-	-	-
RT	2	88	48.5	49.9	0.6	0.8
RT	2	92	-	-	-	-
RT	2	94	-	-	-	-
RT	1	92	47.4	48.5	0.6	0.8
RT	1	85	-	-	-	-

TABLE 6: NITRIC ACID
Percentage of

Test No.	Amount of Acid lb/short ton	Amount of Acid Percentage of Theoretical	Particle Size of Ore Mesh (Tyler)
A/15	1940	120	100
A/18	1940	120	100
A/21	1940	120	100
B/ 3	1940	120	18
C/ 3	1940	120	72
B/ 9	2420	150	18
C/ 5	1940	120	72
B/12	1940	120	18

* RT - Room temperature.

TABLE 7: SULPHURIC ACID LEACHING
Room Temperature
Leaching time: 2 hr

Test No.	Amount of Acid lb/short ton	Amount of Acid Percentage of Theoretical	Particle Size of Ore Mesh (Tyler)
A/37	910	120	100
B/13	910	120	18
C/ 9	910	120	72
A/38	910	120	100
B/14	910	120	18
C/10	910	120	72

LEACHING AT ROOM TEMPERATURE
Solids in Pulp - 20

Temp °C	Time hr	Leaching Efficiency %	Composition of Liquor in Pulp, g/l			
			P_2O_5	Ca	Fe	Al
RT*	2	95	53.5	55.3	1.6	1.1
40	2	95	-	-	-	-
RT	1	94	-	-	-	-
RT	2	94	54.5	55.3	0.8	1.0
RT	2	95	-	-	-	-
RT	2	95	-	-	-	-
RT	1	94	51.9	50.3	0.6	0.6
RT	1	94	-	-	-	-

EFFECT OF SODIUM CHLORIDE

NaCl lb/ton	Percentage of Solids in Pulp	Leaching Efficiency %	Composition of Liquor in Pulp, g/l	
			P_2O_5	SO_4
1250	20	93	49.3	13.6
1250	20	93	48.3	11.8
1250	20	91	45.8	24.3
1250	40	92	151.5	26.2
1250	40	59	98.2	120.3
1250	40	92	141.5	59.7

4.3.4 Direct Production of Phosphoric Acid by Leaching

As a result of the economic assessment the work was directed to the investigation of processes involving the use of sulphuric acid and/or sodium chloride which are materials readily available in South Australia. Since the leach liquors from the previous tests contained few impurities other than sulphuric acid, the possibility of producing phosphoric acid directly by leaching the ore with sulphuric acid was considered. The percentage of solids in the pulp was increased in these tests in an endeavour to produce a higher concentration of phosphoric acid in the final liquor without increasing the relative concentrations of iron, aluminium and sulphate in the final liquor. The results of these tests are shown in Table 8.

With the addition of 120 per cent of the theoretical amount of acid an increase in the percentage of solids in the pulp from 20 to 40 per cent made little difference to the leaching efficiency but greater quantities of iron and alumina were dissolved at the higher pulp composition. In order to reduce the concentration of sulphate in the liquors tests were made using smaller amounts of acid. With 20 per cent of solids in the pulp the leaching efficiency was not significantly altered when the amount of acid was reduced to 100 per cent of theoretical. At 40 per cent solids the leaching efficiency was only slightly lower but greater amounts of aluminium and iron were taken into solution. No advantage was gained by leaching for longer than 2 hours. When the leaching time was less than 2 hours significantly lower leaching efficiencies were obtained. When the acid addition was reduced to 90 per cent of theoretical, the leaching efficiency was much less than that obtained with the theoretical amount of acid. Tests carried out on low grade and high grade material gave lower leaching efficiencies than those for the average grade material.

With the low grade material a relatively larger proportion of the acid was probably consumed in attacking the gangue material. When an increased amount of acid was added the leaching efficiency was increased to 90 per cent without significantly altering the liquor composition. However, with the high grade material an increased amount of acid gave a lower leaching efficiency.

The low leaching efficiencies obtained with the high grade material were probably due to the higher phosphate concentration in the liquor and the higher initial acidity of the sulphuric acid, causing the precipitation of iron and aluminium phosphates. No attempt was made to add the acid in stages because the heat of dilution of the acid would increase the leaching temperature which would tend to favour the dissolution of the iron and aluminium. It is expected that improved leaching efficiencies would be obtained by leaching with less than 20 per cent of solids in the pulp.

4.3.5 Discussion

Nitric acid was the most effective of the three acids in dissolving the phosphate while hydrochloric acid was better than sulphuric acid. However, when the ore was ground to pass a 100-mesh screen, 90 per cent of the phosphate was dissolved in 2 hours at room temperature by all three acids. Sulphuric acid is the cheapest of the three acids and therefore is to be preferred.

When treating the low grade material it was necessary to increase the amount of acid slightly to achieve a leaching efficiency of 90 per cent. The high grade material gave relatively low leaching efficiencies. This was due to the higher concentration of phosphate in the leach liquor and the greater strength of sulphuric acid used to leach the ore. It is reasonable to assume that by using pulps containing a lower percentage of solids improved extraction of the phosphate could be obtained.

When sodium chloride was added to the sulphuric acid leaches containing 20 per cent solids in the pulp the 18-mesh material was leached as efficiently as the 100-mesh material. Also the increased concentration of salts in the final liquor would be beneficial to the solvent extraction stage.

A crude phosphoric acid was made by direct leaching of the ore with a minimum quantity of sulphuric acid. This was possible with sulphuric acid because the formation of the relatively insoluble calcium sulphate removed most of the sulphate from solution. Such a process would not be feasible with hydrochloric or nitric acids. Although relatively little of the total iron and aluminium present in the ore was dissolved in these tests the liquors contained appreciable amounts of iron and aluminium as well as some excess sulphuric acid. With the average grade material the phosphoric acid concentration expressed as P_2O_5 could not be increased beyond 50 grams per litre without greatly increasing the amounts of iron, aluminium and sulphate in solution. The leach liquors would have to be evaporated to produce a concentrated phosphoric acid. The acid would not be suitable for the production of reagents for the surface treatment of steel because of the presence of the iron, aluminium and sulphate. The acid might be utilized in the fertilizer industry by using it together with strong sulphuric acid in the treatment of phosphate rock. This should result in an increased P_2O_5 content of the superphosphate product.

TABLE 8: SULPHURIC ACID LEACHING - Room Temperature

Test No.	Amount of Acid lb/short ton	Amount of Acid Percentage of Theoretical	Particle Size of Ore Mesh (Tyler)	Time hr
A/22	1090	120	100	2
A/23	1090	120	100	2
C/ 7	1360	150	72	2
A/24	910	100	100	2
A/25	910	100	100	2
A/26	1000	110	100	2
A/27	1000	110	100	2
A/28	910	100	100	4
A/29	910	100	100	4
A/30	1000	110	100	4
A/31	1000	110	100	4
A/32	1090	120	100	4
A/33	1090	120	100	4
A/34	910	100	100	1
A/35	910	100	100	0.5
A/36	820	90	100	4
D/ 1	710	100	100	2
D/ 2	710	100	100	2
D/ 3	780	110	100	2
E/ 1	1560	100	100	2
E/2	1560	100	100	2
E/3	1720	110	100	2

DIRECT PRODUCTION OF H_3PO_4

Percentage of Solids in Pulp	Leaching Efficiency %	Composition of Liquor in Pulp, g/l				
		P_2O_5	Ca	Fe	Al	SO_4
30	88	87.8	1.4	3.0	2.3	43.2
40	89	151.0	2.9	9.8	5.1	62.4
20	80	41.8	0.8	0.6	0.9	81.2
20	89	49.7	3.2	0.9	0.7	4.4
40	88	134.8	5.4	6.0	3.3	6.3
20	91	50.7	1.7	1.2	0.8	10.9
40	88	147.6	1.6	8.0	4.4	35.7
20	89	47.8	3.6	0.9	0.8	3.8
40	89	141.0	8.0	5.4	3.4	5.1
20	92	49.4	2.2	1.0	0.9	7.2
40	88	137.0	1.9	7.5	4.7	32.3
20	94	50.6	0.9	1.1	1.1	16.9
40	89	146.2	1.0	8.9	5.0	63.7
40	86	129.0	6.4	3.9	2.4	6.6
40	83	126.5	13.2	3.4	2.0	10.5
40	82	145.5	13.5	3.6	2.0	3.9
20	84	36.9	3.0	0.7	0.5	4.0
40	83	109.8	8.1	2.9	1.7	3.9
20	90	40.7	2.5	0.8	0.6	5.0
20	85	87.8	1.6	1.8	0.8	15.9
40	87	281.5	13.8	11.7	4.1	5.6
20	79	78.2	1.2	2.0	0.9	46.0

4.4 Solvent Extraction

Most of the tests have been concerned with the determination of the effect of the major variables on the extraction of the phosphoric acid.

Only n-butyl alcohol has been used as the extractant. Literature references suggest that isoamyl alcohol could also be used and that it is a more specific extractant for phosphoric acid but the distribution coefficient is much smaller than that of n-butyl alcohol.

4.4.1 Experimental Procedure

Owing to the appreciable mutual solubilities of water and normal butyl alcohol, considerable volume changes can occur on mixing. This effect was reduced by pre-saturating the aqueous and organic phases with the alcohol and with water respectively, prior to each test. Equal volumes of the pre-saturated solutions were transferred to a separating funnel and stirred for 2 hours. The phases were allowed to separate and were assayed separately. Although the phases had been pre-saturated some change in volume was detected in most tests.

The concentration of the acids in the aqueous and organic phases was determined by titrating an aliquot of the solutions with 0.1N NaOH and 0.1N alcoholic KOH respectively. Ethyl alcohol was added to some of the organic solutions to keep them homogeneous during the titration. In the preliminary work indicators were used to detect the end points but the results were unreliable, and end-points were therefore determined from graphs obtained by plotting pH against the quantity of alkali added.

Colorimetric determinations of the phosphoric acid concentration in some of the liquors gave results which were in close agreement with the titration results.

The equilibrium solutions from tests to which neutral salts had been added were assayed by a different method. Calcium was determined by adding sulphuric acid and then reducing the solubility of the calcium sulphate by adding a large volume of ethyl alcohol. The insoluble calcium sulphate was filtered, washed with alcohol and ignited. Chloride was determined by titration with silver nitrate and phosphate by the molybdenum blue colorimetric method. Sulphate was determined by precipitation with barium chloride. The composition of the equilibrium solutions was calculated from the results of these assays.

High concentrations of either nitric or hydrochloric acids could not be employed because these resulted in complete miscibility with the formation of a single phase.

In all tables the concentrations of the various components in the aqueous and organic phases are given as normalities.

4.4.2 Extraction of Single Acids

The distributions of sulphuric, hydrochloric, nitric and phosphoric acids alone between aqueous and n-butyl alcohol phases are given in Table 9.

TABLE 9: DISTRIBUTION OF SINGLE ACIDS

Equilibrium Aqueous Phase	Equilibrium Organic Phase	Ratio $\frac{\text{Organic}}{\text{Aqueous}}$
Sulphuric Acid		
0.84*	0.08	0.10
2.45	0.38	0.16
2.64	1.24	0.27
Hydrochloric Acid		
0.75	0.20	0.27
2.03	0.90	0.44
2.43	1.22	0.50
Nitric Acid		
0.80	0.36	0.45
1.76	0.96	0.55
1.84	0.98	0.53
Phosphoric Acid		
1.29	0.14	0.11
3.65	0.50	0.14
7.04	1.27	0.18

* Concentrations are expressed as normality.

The acids were extracted into the organic phase in the decreasing order:

nitric acid
hydrochloric acid
sulphuric acid, and
phosphoric acid.

4.4.3 Extraction of Mixed Acids

The effect of the addition of sulphuric, hydrochloric, and nitric acids on the extraction of phosphoric acid was examined. The concentration of phosphoric acid was kept as close as possible to 3.5N in the equilibrium aqueous solution for ease of comparison of results. The results are given given in Table 10.

TABLE 10: DISTRIBUTION OF MIXED ACIDS

Equilibrium Aqueous Phase		Equilibrium Organic Phase		Ratio $\frac{\text{Organic}}{\text{Aqueous}}$	
Second Acid	Phosphoric Acid	Second Acid	Phosphoric Acid	Second Acid	Phosphoric Acid
Sulphuric Acid					
0.88*	3.65	0.08	0.64	0.09	0.18
2.48	3.56	0.46	0.94	0.19	0.26
4.62	3.23	1.83	1.78	0.40	0.55
Hydrochloric Acid					
0.71	3.54	0.24	0.94	0.34	0.27
1.33	3.50	0.60	1.25	0.45	0.36
1.85	3.21	0.89	1.43	0.48	0.45
Nitric Acid					
0.58	3.54	0.34	0.92	0.59	0.26
1.10	3.59	0.76	1.20	0.69	0.33
1.54	3.47	1.03	0.32	0.67	0.38

* Concentrations are expressed as normality.

The extraction of the phosphoric acid into the organic phase was increased considerably by the addition of any of the acids. This effect was greatest with nitric and hydrochloric acids. The presence of the phosphoric acid increased the extraction of the other acid slightly.

The distribution of phosphoric acid at various concentration levels in approximately 2.5N sulphuric acid solution is shown in Table 11.

The distribution coefficient was very dependent on the phosphoric acid concentration in the aqueous phase, hence the difficulty of recovering phosphoric acid would increase as the phosphate level in the aqueous solution decreased.

4.4.4 The Effect of Neutral Salts

The concentration of neutral salts in the sulphuric acid leach liquors is very low because of the insolubility of calcium sulphate. One test was made in which the phosphoric acid-sulphuric acid solution was saturated with chemically prepared calcium sulphate prior to the extraction with n-butyl alcohol. The effect of the concentration of calcium chloride on the extraction of phosphoric acid from chloride solutions was also examined. The results of the tests are given in Tables 12 and 13.

It is evident that insufficient calcium sulphate was introduced into the sulphuric acid solutions to significantly increase the distribution of phosphoric acid beyond that obtained with previous tests (Table 10). In the tests with hydrochloric acid the addition of calcium chloride increased the distribution of both the phosphoric acid and the hydrochloric acid. It is likely that with greater concentrations of calcium chloride further increases in the distribution coefficient could be obtained.

Additional experiments were made with sulphuric acid solutions to which sodium chloride was added to increase the concentration of neutral salts. The results of these tests are shown in Table 14. The addition of sodium chloride increased the distribution ratio of the phosphoric acid in both series of tests. However, the extraction of sulphuric and hydrochloric acids was also considerably increased. The sodium chloride concentration cannot be significantly increased beyond 3N because of its limited solubility. Since it would become very costly to increase the sulphuric acid concentration of the original solution beyond 3N the maximum distribution of the phosphoric acid from a 3N H_3PO_4 solution would be about 0.41. The organic phase would contain a very high proportion of sulphuric and hydrochloric acids.

The effect of phosphoric acid concentration on the distribution is shown in Table 15. The original solutions were 3N with respect to both H_2SO_4 and NaCl. The distribution coefficient decreased as the phosphoric acid concentration in the original aqueous solution was decreased. This is in agreement with the results obtained in the absence of the sodium chloride.

TABLE 11: EFFECT OF PHOSPHORIC ACID CONCENTRATION ON DISTRIBUTION COEFFICIENT

Sulphuric Acid Solutions

Equilibrium Aqueous Phase		Equilibrium Organic Phase		Ratio $\frac{\text{Organic}}{\text{Aqueous}}$	
H_2SO_4	H_3PO_4	H_2SO_4	H_2PO_4	H_2SO_4	H_3PO_4
2.45*	5.41	0.75	1.88	0.31	0.35
2.50	2.81	0.58	0.74	0.23	0.26
2.54	1.41	0.47	0.33	0.19	0.23
2.56	0.68	0.44	0.15	0.17	0.22
2.55	0.37	0.43	0.06	0.17	0.16

* Concentrations are expressed as normality.

TABLE 12: THE EFFECT OF NEUTRAL SALTS ON THE EXTRACTION OF PHOSPHORIC ACID WITH N-BUTYL ALCOHOL

Sulphuric Acid Solutions

Equilibrium Aqueous Phase			Equilibrium Organic Phase			Ratio $\frac{\text{Organic}}{\text{Aqueous}}$		
Ca	H_2SO_4	H_3PO_4	Ca	H_2SO_4	H_3PO_4	Ca	H_2SO_4	H_3PO_4
0.03[*]	0.89	-	0.01	0.08	-	0.33	0.09	-
0.02	0.78	3.84	0.002	0.10	0.78	0.10	0.13	0.20

[*] Concentrations are expressed as normality.

TABLE 13: THE EFFECT OF NEUTRAL SALTS ON THE EXTRACTION OF PHOSPHORIC ACID WITH N-BUTYL ALCOHOL

Hydrochloric Acid Solutions

Equilibrium Aqueous Phase			Equilibrium Organic Phase			Ratio $\frac{\text{Organic}}{\text{Aqueous}}$		
Ca[*]	HCl	H_3PO_4	Ca	HCl	H_3PO_4	Ca	HCl	H_3PO_4
0.91	0.72	-	0.01	0.32	-	0.01	0.45	-
1.79	0.63	-	0.02	0.39	-	0.01	0.62	-
2.63	0.54	-	0.03	0.47	-	0.01	0.87	-
0.86	0.57	3.36	0.02	0.37	1.02	0.02	0.65	0.30
1.48	0.55	3.39	0.04	0.45	1.07	0.03	0.82	0.32
2.54	0.44	3.25	0.06	0.49	1.20	0.02	1.11	0.37

[*] Concentrations are expressed as normality.

TABLE 14: EFFECT OF SODIUM CHLORIDE ON H_3PO_4 DISTRIBUTION FROM H_2SO_4 SOLUTIONS

Equilibrium Aqueous Phase					Equilibrium Organic Phase					Ratio $\frac{\text{Organic}}{\text{Aqueous}}$		
H_3PO_4	Mixed Acids	Neutral Salts	SO_4	Cl	H_3PO_4	Mixed Acids	Neutral Salts	SO_4	Cl	H_3PO_4	Mixed Acids	Neutral Salts
3.80*	0.77	1.07	1.02	0.82	0.82	0.22	0.02	0.053	0.19	0.22	0.29	0.02
3.68	0.65	2.03	1.02	1.66	0.88	0.30	0.03	0.032	0.30	0.24	0.46	0.02
3.56	0.58	2.96	1.01	2.52	1.01	0.39	0.04	0.023	0.41	0.28	0.67	0.01
3.53	2.32	1.07	2.74	0.65	1.09	0.63	0.04	0.35	0.32	0.31	0.27	0.04
3.42	2.23	2.08	2.88	1.43	1.22	0.75	0.04	0.24	0.55	0.36	0.34	0.02
3.23	2.08	3.08	2.97	2.19	1.32	0.84	0.03	0.17	0.70	0.41	0.40	0.01

* Concentrations are expressed as normality.

TABLE 15: EFFECT OF CONCENTRATION ON THE DISTRIBUTION OF PHOSPHORIC ACID

Equilibrium Aqueous Phase					Equilibrium Organic Phase					Ratio $\frac{\text{Organic}}{\text{Aqueous}}$		
H_3PO_4	Mixed Acids	Neutral Salts	SO_4	Cl	H_3PO_4	Mixed Acids	Neutral Salts	SO_4	Cl	H_3PO_4	Mixed Acids	Neutral Salts
4.74*	1.97	3.25	3.00	2.22	1.95	0.91	0.05	0.19	0.77	0.41	0.46	0.02
2.46	2.05	3.14	2.90	2.29	0.92	0.81	0.04	0.16	0.69	0.37	0.40	0.01
1.23	2.11	3.07	2.86	2.32	0.44	0.77	0.03	0.15	0.65	0.36	0.37	0.01
0.66	2.13	3.04	2.83	2.34	0.22	0.74	0.02	0.14	0.62	0.33	0.35	0.01
0.36	2.13	3.05	2.82	2.36	0.10	0.73	0.03	0.14	0.62	0.28	0.34	0.01

* Concentrations are expressed as normality.

4.4.5 Back Extraction of Phosphoric Acid into Water

Previous results on the extraction of phosphoric acid into the alcohol phase indicated that it should be relatively easy to back extract the phosphoric acid into water. The following tests were made to confirm this and to give some indication of the amount of sulphate and chloride which would be present in the final product. A synthetic leach liquor was prepared having the following composition:

H_3PO_4	6N
H_2SO_4	3N
NaCl	3N

This liquor contained the highest concentration of phosphoric acid which could conveniently be obtained by leaching and the highest concentration of sodium chloride which could be dissolved in the liquor. Further it would be expensive to increase the concentration of H_2SO_4 beyond 3N. One litre of this solution was contacted with 400 ml of n-butyl alcohol for 2 hours. The organic phase which was separated had the following composition:

H_3PO_4	2.08N
SO_4	0.21N
Cl	0.89N
Neutral Salts	0.07N

The phosphoric acid concentration of the final aqueous solution was 4.77N, giving a distribution coefficient for phosphoric acid of 0.44. Aliquots of the organic phase were contacted with various amounts of water. The results are shown in Table 16.

Considerable amounts of chloride and sulphate were found in the final aqueous solutions. These are mainly present as the acids, and it may be assumed that nearly all of the chloride could be removed by distillation. However the final product would contain a considerable amount of sulphate and would not meet the specifications for use in the surface preparation of steel.

TABLE 16: BACK EXTRACTION OF PHOSPHORIC ACID INTO WATER

Equilibrium Aqueous Phase					Equilibrium Organic Phase					Ratio $\frac{\text{Organic}}{\text{Aqueous}}$		
H_3PO_4	Mixed Acids	Neutral Salts	SO_4	Cl	H_3PO_4	Mixed Acids	Neutral Salts	SO_4	Cl	H_3PO_4	Mixed Acids	Neutral Salts
1.68*	0.80	0.05	0.18	0.67	0.38	0.22	0.01	0.02	0.21	0.23	0.28	0.20
2.70	1.19	0.08	0.31	0.96	0.80	0.44	0.02	0.05	0.41	0.30	0.37	0.25
3.69	1.60	0.22	0.53	1.29	1.38	0.69	0.05	0.11	0.63	0.37	0.43	0.23
4.48	1.86	0.60	0.88	1.58	1.81	0.89	0.05	0.16	0.78	0.40	0.48	0.08

* Concentrations are expressed as normality.

4.4.6 Discussion

All of the acids were extracted to some extent into the organic phase. The phosphoric acid extraction was increased significantly by the presence of one of the other acids. The presence of neutral salts increased the extraction of the phosphoric acid still further in both chloride and sulphate solutions. However, the distribution coefficients obtained for aqueous 5N phosphoric acid (in the presence of 3N sulphuric acid and 3N sodium chloride,) were less than 0.5. The distribution coefficients were smaller at lower phosphoric acid concentrations. Therefore it would be difficult to obtain both high concentrations in the organic phase and a good recovery of the phosphoric acid.

As was expected the back extraction of the phosphoric acid was more efficient. Higher concentrations of phosphoric acid in the aqueous phase, than those obtained in these tests could be achieved by further increasing the organic to aqueous ratio. Relatively high concentrations of both chloride and sulphate were present in the final aqueous extract. Most of the chloride could be removed by distillation but this would not remove the sulphate. In practice the recovered hydrochloric acid could be returned to the leach circuit and used in place of some of the sulphuric acid. This could reduce the sulphate concentration in the final product but the reduction would not be very significant. This product would not meet the specifications required for use in preparation of reagents for the surface treatment of steel.

5. CONCLUSIONS

The phosphate in the material supplied from Klemm's Quarry is mainly in the form of fluor-apatite. It was not possible to concentrate the phosphate mineral by flotation.

The average grade material when ground to pass a 100-mesh screen was leached satisfactorily with any of the three acids investigated. Sulphuric acid alone was not effective in leaching the minus 72 and minus 18-mesh material, but satisfactory leaching efficiencies were obtained in the presence of sodium chloride equivalent in amount to the sulphuric acid. Because of the relatively lower cost of sulphuric acid, the latter method of treating coarse ore would be preferred to that using hydrochloric or nitric acids. Although the low and high grade material did not leach as satisfactorily as the average grade material, this could probably be overcome by slightly varying the leaching conditions.

A crude phosphoric acid was produced by direct leaching of the ore with sulphuric acid. This product contained iron, aluminium and sulphate as impurities and had a relatively low phosphoric acid content.

Most of the solvent extractions tests were made on sulphate solutions. The presence of excess leaching acid and of neutral salts in solution increased the extraction of phosphoric acid into the organic phase but even with a large excess of both acid and neutral salts the distribution coefficient for phosphoric acid did not exceed 0.5. Appreciable amounts of sulphate were extracted into the organic phase from solutions containing sulphate ions and appeared in the final product solution. If sulphuric acid alone were used to leach the ore, the addition to the leach liquor of a neutral salt e.g., sodium chloride together with a further quantity of sulphuric acid would be required to increase the extraction of the phosphoric acid.

Alternatively, the sodium chloride could be added with the sulphuric acid in the leaching stage. This would have the advantage that the ore would not have to be so finely ground to achieve a satisfactory leaching efficiency. In either case some hydrochloric acid could be recovered by distillation of the product and could be recycled to replace some of the sulphuric acid in the leaching stage. The continued recycling of hydrochloric acid would be unlikely to lower significantly the sulphate content of the final product because the extra chloride ions present in the leaching stage would increase the solubility of the calcium sulphate formed during the dissolving of the ore.

The two major potential outlets for the phosphoric acid may be assumed to be in the surface preparation of steel and in the fertilizer industry. Neither the acid produced by direct leaching nor the acid produced by the solvent extraction of liquors containing sulphate would be suitable for the treatment of steel because the sulphate level would exceed the maximum specified limit of 0.1 per cent SO_4. Both products would probably be suitable for upgrading the P_2O_5 content of superphosphate by replacing some of the sulphuric acid used in treating the rock phosphate. Although a much more concentrated acid could be produced by the solvent process, the direct leaching process would be much cheaper.

It was shown in the economic assessment that hydrochloric acid could not be used economically at the price used in the calculations. If hydrochloric acid were made from sulphuric acid and sodium chloride as a part of the process the acid would have to be distilled to avoid the introduction of sulphate into the leach and hence into the product. Assuming that the chloride concentration in the final product could be reduced by distillation to a sufficiently low level to make it suitable for use in the treatment of steel, it would still be necessary to avoid the presence of iron and aluminium because the specifications require that no visible precipitate be formed by adding excess ammonia to the phosphoric acid. If hydrochloric acid were used to leach the Klemm's Quarry material much greater quantities of iron and aluminium would be dissolved and could contaminate the final product. This problem was not encountered by Baniel, Blumberg and Alon[1] in the treatment of Moroccan phosphate which contained only 0.4 per cent of total iron and aluminium oxides.

The problem of contamination of the product with iron and aluminium would also apply to a process using nitric acid as a leachant.

The extent of the phosphate deposits in the Kapunda area are considered to have a considerable influence on the nature of any further work which might be done. Since the direct leaching process is only practicable if the phosphate is present as some form of apatite, the nature of the phosphate minerals is also very important. It is evident from the X-ray diffraction analysis of material from St. John's Quarry that the phosphate is not present as apatite in all of the deposits in the area.

The most promising possible outlet for the phosphoric acid would appear to be in the fertilizer industry since the specifications for this use would not be so difficult to meet. For this purpose the direct leaching of the ore with sulphuric acid would be the most suitable method of producing the phosphoric acid. The phosphoric acid leach liquor could then be used to dilute strong sulphuric acid to approximately 70 per cent acid for the treatment of the phosphate rock in the normal manner. Superphosphate manufactured from the mixed acids would contain more P_2O_5 than the product made by the normal treatment with sulphuric acid alone.