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COMPLETE SPECIFICATION

A Process for the Production of Phosphoric Acid and Gypsum



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We, NISSAN KAGAKU KOGYO KABUSHIKI KAISHA, a corporation organized under the laws of Japan, of 2 Honcho 1-chome, Nihonbashi, Chou-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the production of phosphoric acid and gypsum from phosphate rock.

15 It is an object of the invention to provide an improved process for producing phosphoric acid in a concentrated form and in good yield, and for recovering the gypsum crystals produced. It is a further object of the invention to provide a process whereby good quality crystalline calcium sulphate dihydrate in the form of a large columnar or laminar shaped crystals having exceptionally good filtration and washing characteristics may be obtained.

20 According to the present invention there is provided a method of producing phosphoric acid and crystalline gypsum, which method comprises leaching phosphate rock in an initial reaction stage with a mixture of sulphuric acid and dilute phosphoric acid, said acids mixture containing from 10 to 22% by weight of P_2O_5 and from 20 to 40% by weight of H_2SO_4 and the maximum acid content of the acids mixture being 52% by weight, at a temperature from 3 to 20°C. above the transition temperature of the dihydrate-semihydrates of calcium sulphate for the prevailing concentration of acids and for a period of time of from 10 to 60 minutes, mixing the resulting reaction slurry with from one to two times the volume of a recycle slurry recycled from a later stage and containing hydrated calcium sulphate crystals having a degree of hydration in the range of from 1.90 to 1.96, maintaining the resulting slurry in a hydration-crystalliza-

tion stage at a temperature in the range of from 40 to 65°C. until the calcium sulphate crystals therein have a degree of hydration of from 1.90 to 1.96, recycling a portion of this hydrated slurry for admixture with the reaction slurry, treating the remainder of said hydrated slurry to separate the crystalline gypsum from the crude phosphoric acid product, and thereafter washing the crystalline gypsum with water to remove adherent phosphoric acid. The preferred temperature for the initial reaction stage is 80 to 100°C.

For a better understanding of the invention and to show how the same may be carried into effect, reference will be made, by way of example, to the accompanying drawings, in which:—

Figure 1 is a flow diagram of a process for the treatment of phosphate rock to produce phosphoric acid and crystalline gypsum;

Figure 2 is a graph showing the transition temperature of the dihydrate-semihydrate of calcium sulphate in phosphoric acid solution at different concentrations;

Figure 3 shows the variation in the degree of hydration of calcium sulphate in phosphoric acid solution with respect to time; and

Figure 4 shows the variation in the degree of decomposition of phosphate rock to produce phosphoric acid with time.

In the known method of producing phosphoric acid by treating phosphate rock with sulphuric acid to produce first $CaSO_4 \cdot \frac{1}{2}H_2O$, and then hydrating this semihydrate and crystallizing to obtain gypsum, it was necessary to obtain the semihydrate of calcium sulphate in a stable state which would easily grow into good crystals of gypsum during the hydration operation. In order to do this it was considered necessary to employ a reaction temperature which was higher than the transition temperature of the dihydrate-semihydrate of $CaSO_4$ in the phosphoric acid solution

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of a particular concentration. Figure 2 of the accompanying drawings shows the well-known Nordengren's equilibrium diagram which illustrates the transition temperatures of dihydrate-semihydrate in phosphoric acid solution at different concentrations. However, the effect of free sulphuric acid which must inevitably be present in the phosphoric acid solution, was previously neglected.

We have now discovered that the actual transition temperature of the dihydrate-semihydrate of CaSO_4 in a solution of phosphoric acid containing sulphuric acid is dependent upon the combined concentration of the P_2O_5 and H_2SO_4 . Consequently, if the effective P_2O_5 concentration of the phosphoric acid solution is considered to be equal to the sum of the actual P_2O_5 concentration plus the H_2SO_4 concentration, the semihydrate of CaSO_4 should be obtained in a stable state during the reaction if the reaction temperature is maintained above the transition temperature of the dihydrate-semihydrate of CaSO_4 for a particular effective concentration of phosphoric acid as shown by Nordengren's equilibrium diagram (Figure 2). However, this condition alone is insufficient to produce the desired stable semihydrate crystals under industrial conditions.

As used herein the term "degree of hydration" when applied to calcium sulphate means the average number of molecules of water of crystallization associated with each calcium sulphate molecule. In other words, the degree of hydration will vary at different stages of the process from 0.5 for the semihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, to 2.00 for the dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. For mixtures of the two forms, the numerical value for the degree of hydration will vary between these extremes, and the value will depend upon the proportion of each hydrated form of calcium sulphate in the mixture. The term "degree of decomposition" as used herein represents the percentage conversion of the P_2O_5 content of the phosphate rock to phosphoric acid.

In general, hydration is faster and better at lower temperatures, but it is necessary that the reaction temperature be higher than the transition temperature of dihydrate-semihydrate in order to obtain the semihydrate of CaSO_4 during the reaction. The transition temperature of these hydrated forms in a phosphoric acid solution containing 30% by weight P_2O_5 and 5% by weight H_2SO_4 (or effectively 35% by weight P_2O_5) is 82°C ., and at this temperature needle crystals or small amorphous crystals will be produced. Consequently, the reaction temperatures employed according to this invention should be at least 3°C . above the transition temperature for the particular phosphoric acid concentration, and not more than 20°C . above the transition temperature.

Portionwise charging of the recycled dilute phosphoric acid is likewise advantageous. Particularly on an industrial scale, it is preferred to charge the recycled acid in two portions, with at least $1/2$ of the recycled acid being charged in the initial portion.

Generally, hydration occurs more slowly when the time which was employed for decomposition (or reaction) becomes longer. If the process were carried out without seed crystals being used in the hydration stage, no practical hydration would be achieved therein following a decomposition time exceeding one hour. With seed crystals added, the rate of hydration is enhanced due to the hydration acceleration effect of the seed crystals but there is no great difference in the size of the crystals of calcium sulphate dihydrate obtained after a hydration-crystallization stage following different reaction stage times. Consequently, long reaction times are not advantageous. Reaction times are in the range of from 10 minutes to 1 hour, and it is preferred to have as short a time within this range as is practicable. However, if the reaction time is too short, the resulting crystals are unstable.

The crystals obtained with the use of seed crystals are of large-size, being in the range of $80\text{--}150\mu$. The use of seed crystals also has the effect of improving the degree of decomposition, being above 98% as compared with the 97% maximum level in all cases if seed crystals were not used. The increased size of crystals and the increased speed of hydration will be obtained, in accordance with the invention by the use of seed crystals, only when good columnar shaped crystals with even thickness, although small, would be obtained by treatment of the reaction stage product in a hydration stage without the use of seed crystals.

Referring now to Figure 3 of the accompanying drawings there is shown the variation of the degree of hydration with time following the addition of acid, the curve shown in a broken line representing the increase in the degree of hydration for a process in which seed crystals were not used, and the curve shown in full line representing the increase in the degree of hydration for a process in which seed crystals were initially added to the reaction slurry from the reaction stage.

Figure 4 of the accompanying drawings shows the variation in the degree of decomposition of phosphate rock with time following the reaction stage when the degree of decomposition was usually about 85%, the curve shown in a broken line being based upon an operation in which seed crystals were not added and the curve shown in full line being based upon a similar operation employing the addition of seed crystals.

If seed crystals were not used, the degree of hydration-passage of time curve (Figure 3) would exhibit a typical S-shape. The slow

hydration period in the initial stage is considered to be the period of accumulation of the new solid phase. When seed crystals are added, however, the new solid phase accumulation period is eliminated, as crystals are present from the beginning of reaction and hydration therefore proceeds rapidly from the initial period. In both cases, whether seed crystals are added or not, hydration, once begun, proceeds fairly rapidly until a degree of hydration of about 1.90 is reached, but after that, hydration is generally considerably slower and will not exceed 1.95 easily. Sometimes, the degree of hydration will reach 2.00 when the reaction slurry is left standing for a very long time, but ordinarily, the maximum degree of hydration is about 1.95 in phosphoric acid solution.

The crystals so produced will become completely hydrated gypsum only after they come in contact with water by filtering and water-washing.

When the cloudy semihydrate of CaSO_4 formed in the initial reaction is hydrated and recrystallized after cooling, without addition of seed crystals, it crumbles as the degree of hydration becomes 0.7—1.0, and part of it precipitates as small columnar crystals. There is no tendency for the numerous, minute columnar crystals to grow larger and uniform. This phenomenon is believed to be due to the enfolding in the semihydrate of CaSO_4 of the minute dihydrate of CaSO_4 nuclei which are thereby prevented from growing in size.

However, regardless of the actual explanation, it has been observed that when the degree of hydration reaches 1.81, the hydration of the crystal surfaces is incomplete and the crystals are not clearly formed. As the degree of hydration reaches 1.90, the crystals are not quite complete and become so only after filtering and water-washing.

The condition is somewhat different in the case of seed crystal addition in which there is a tendency for the seed crystal to grow as well as for newly produced dihydrate of CaSO_4 nuclei to be formed. The seed crystals of gypsum grow rapidly during the initial period of reaction and become comparatively large and at the same time, enfolding of new gypsum nuclei by the semihydrate begins gradually and the cloudy semihydrate gradually disappears. During the latter part of the reaction the degree of hydration advances slowly due chiefly to the production of new nuclei and minute gypsum crystals are still numerous at a degree of hydration of 1.84, but the gradual separating out of new columnar gypsum crystals from these nuclei can be observed. Formation of new nuclei becomes almost complete when the degree of hydration reaches 1.90, and if the slurry is left standing further and the degree of hydra-

tion reaches 1.95, the shape of the crystals will become very distinct.

In the practice of the invention, it is important that the seed crystals, contained in the recycle slurry, should have a degree of hydration of at least 1.90. That is, the recycle slurry should be withdrawn from the reaction only after the latter has been held under hydration conditions sufficiently long enough to ensure that the formation of new gypsum nuclei has been substantially completed.

If the degree of hydration of the seed crystal is below about 1.90, say 1.84, the product crystals gradually become inferior in quality, and this may explain prior teachings that the recycling of crystals causes deterioration thereof.

Contrary to such teachings, however, the dihydrate crystals produced according to the present invention remain consistently of high quality regardless of the duration of the recycling step. It is only necessary that the hydration step be carried substantially to completion as indicated above, with the degree of hydration of the crystals in the recycle slurry at least 1.90. The degree of hydration of the seed crystals may, of course, be in excess of this figure, although 1.96 is the practical upper limit since to exceed this limit the residence time in the hydration stage would be unduly extended and there is no corresponding advantage in using a seed crystal slurry having a degree of hydration in excess of 1.96.

For this reason in the practice of the invention, the hydration reaction is deemed to be complete when the degree of hydration of the crystals reaches the value 1.90.

In carrying out the present invention it is proposed to cause hydration and crystallization by recycling to the reaction slurry from one to two times the volume of slurry, the crystals of which have grown sufficiently for them to be used as seed crystals and which crystals have a sufficiently high degree of hydration, i.e. from 1.90 to 1.96, and passing the resulting mixture through at least two hydration-crystallization tanks, preferably 3 to 6 tanks, in order effectively to control the residence time required to secure the desired degree of hydration and crystallization in the process.

In addition of seed crystal in both the mixed acid and the portion-wise charging methods, phosphate rock is decomposed at a reaction temperature of from 3°C . to 20°C . above the transition temperature of dihydrate $\rightleftharpoons$ semihydrate of CaSO_4 in the phosphoric acid solution produced, preferably to give a slurry containing calcium sulphate semihydrate with a degree of hydration not exceeding 0.75. Next, seed crystal slurry containing crystals with a degree of hydration of from 1.90 to 1.96 is recycled and mixed (in from one to two times the volume) with the reac-



columnar



crystals



crystals

tion slurry and this is hydrated, to a degree of hydration of from 1.90 to 1.96, and crystallized in a controlled manner by passing through at least two and preferably three to six crystallizing tanks.

By comparison, if no seed crystals were added, hydration would become very slow as the hydration temperature became higher and conversely the crystals would become larger. With seed crystals present, hydration is fastest at 50°C. and there is generally no great change throughout the range 35°C. to 65°C.

However, amorphous gypsum is not generally formed at 35°C. at which temperature the crystals formed have distinct columnar or laminar shape, but is very easy for minute crystals to be produced mixed with the product crystals. This tendency is particularly marked at hydration temperatures below 40°C.

If seed crystals were not added, the production of fresh dihydrate salt nuclei would be slow at relatively high temperatures, but in the present case, where seed crystals are added, it is believed that the high temperatures do not affect the speed of hydration since dihydrate gypsum nuclei are already present from the initial period.

The hydration temperatures which can be employed in the present invention are temperatures from 40 to 65°C., and the mixed acid concentration may be P_2O_5 from 10 to 22% by weight and H_2SO_4 from 20 to 40% by weight, the maximum concentration of the acids being 52% by weight. Hydration is very slow above this upper acid concentration limit and disadvantageous industrially since there is a tendency for a small quantity of minute gypsum crystals, which are very difficult to remove, to become mixed with the product crystals and to remain even after filtering and water-washing. The preferred range of mixed acid concentrations for industrial application is from 40 to 52% by weight.

About 30 minutes is an appropriate reaction time for the phosphate rock and sulphuric acid reaction but up to one hour may be appropriate when the distribution of time remaining in the process in the continuous method is taken into consideration. The hydration-crystallization time can be made very short by combining optimum conditions.

Preferably, the mixture of the reaction slurry and the recycle slurry is maintained in the hydration-crystallization stage for from 12 to 36 hours.

Referring now to Figure 1 of the accompanying drawings, which illustrates a flow diagram for a preferred embodiment of the invention, three digestion tanks 1, 2 and 3, connected in series discharge into a tank 4. Phosphate rock, previously crushed to the desired fineness, is supplied to the tank 1 from a storage hopper 12. Concentrated sulphuric acid from a storage container 12a is fed to an acid mixing tank 8, and dilute phosphoric

acid, produced in the process, is recycled through a line 13 to the tank 8. Mixed acid is supplied to tank 1 through a line 13a. The feed mixture of rock, sulphuric acid and dilute phosphoric acid is reacted in the tanks 1, 2 and 3, at the desired temperature for from 10 minutes to one hour and is then mixed in the tank 3 with gypsum slurry recycled from a tank 6 through lines 17 and 14. A portion of the dilute phosphoric acid recycle stream in the line 13 is split off through a line 15 and also passed to the tank 3. From the tank 3 the resulting mixture is cooled and passed through a line 16 to crystallization tanks 4, 5 and 6, which are connected in series. The mixture is maintained in these tanks until the degree of hydration of the calcium sulphate crystals in tank 6 is from 1.90 to 1.96. Preferably, the temperature in each of these tanks is lower than in the previous one. As an alternative to recycling slurry from tank 6 to the tank 3, some or all of the recycled slurry can be recycled through lines 17 and 14 to tank 4.

From tank 6, the slurry of hydrated gypsum crystals and product acids is withdrawn through a line 17 and passed to the separating and recovery system represented diagrammatically by the three-section unit 7. In the first section, the crude phosphoric acid, which contains some unreacted sulphuric acid, is separated, preferably by filtration, and passed through a line 18 to purification and/or storage. The crude gypsum product is washed in the centre section, preferably with the wash liquid from the third or final section in which the gypsum product is washed free of remaining acids and soluble salts by washing with water supplied at 20. The wash liquid from this third section is fed to the centre section through line 19, and the wash liquid from the centre section, comprising a dilute solution of phosphoric acid, is recycled through line 13 to the initial reaction stages. The washed gypsum product is withdrawn from the system at 21 for further treatment.

The following Examples 1 and 2 will serve to further illustrate the invention as practised in accordance with the embodiment described above with reference to Figure 1 of the accompanying drawings, Example 3 being included by way of a comparison. All percentages specified in the Examples are by weight.

EXAMPLE 1.

A Makatea phosphate ore was used containing P_2O_5 37.19% and CaO 51.44%. 2,400 Kg/hr of the phosphate rock and 8,427 Kg/hr of a sulphuric acid-dilute phosphoric acid mixture containing 14.6% P_2O_5 and 28.5% H_2SO_4 were reacted continuously in the decomposition tanks 1 and 2 at 90°C. for a decomposition period of 40 minutes. The reaction mixture was mixed in the mixing tank 3 with recycle slurry (degree of hydra-

tion 1.94) from the crystallization tank 6, in twice the quantity of the charged mixture from tank 2. The speed of hydration was arranged such that the temperatures in the crystallization tanks were 60°C. in tank 4; 55°C. in tank 5 and 50°C. in tank 6.

The degrees of hydration produced in the various tanks were:

10	Decomposition Tank	1, D.H.0.60.
		2, D.H.0.57.
	Crystallization Tank	4, D.H.1.68.
		5, D.H.1.86.
		6, D.H.1.94.

The P_2O_5 decomposition degree was 98.3%, P_2O_5 adhering to gypsum 0.07% and yield of P_2O_5 was 97%. The resultant gypsum was in the form of large, columnar crystals with very good filter-ability as raw material for wall-boards. Phosphoric acid was obtained as a by-product in a concentration of 31%.

EXAMPLE 2.

The phosphate ore used was the same as in Example 1, and the crude phosphoric acid obtained as by-product was P_2O_5 30%, H_2SO_4 5%. 2,400 Kg/hr of the phosphate rock and 6,600 Kg/hr of mixed acid, composed of 2/3 of the entire quantity of recycled dilute phosphoric acid and the entire quantity of sulphuric acid (P_2O_5 12.5%, H_2SO_4 35.4%), were reacted continuously in decomposition tanks 1 and 2 at a temperature of 80°C. for a decomposition period of 50 minutes, after which the reaction mixture was mixed with the balance of 1/3 of the recycle phosphoric acid 1.827 Kg/hr (P_2O_5 22.5%, H_2SO_4 3.5%), and recycle slurry was added from the crystallization tank 6 in twice the quantity of the charged mixture from tank 2. The speed of hydration was arranged such that the temperatures in the successive crystallization tanks 4, 5 and 6 were 60°C., 55°C. and 50°C., respectively.

The degrees of hydration in the different tanks were as follows:

45	Decomposition Tank	1, 0.55.
		2, 0.54.
	Crystallization Tank	4, 1.62.
		5, 1.85.
		6, 1.95.

The resultant gypsum was in the form of large, columnar crystals with good filter-ability, similar to that obtained in Example 1.

EXAMPLE 3.

The phosphate ore used was the same as in Example 1, and the phosphoric acid obtained as by-product was P_2O_5 32%, H_2SO_4 8%. 2,400 Kg/hr of the phosphate rock and 7,075 Kg/hr of mixed dilute phosphoric acid and sulphuric acid (P_2O_5 13.3%, H_2SO_4 35.7%) were reacted continuously in decomposition tanks 1 and 2 at a temperature of 80°C. for a decomposition period of 48 minutes, and

thereafter mixed in the mixing tank with the recycle slurry from crystallization tank 6 in a quantity corresponding to half the quantity of mixture charged from the tank 2. The speed of hydration was arranged such that the temperatures in the successive crystallization tanks 4, 5 and 6, were 60°C., 55°C. and 50°C., respectively.

The degrees of hydration in the different tanks were as follows:

	Decomposition Tank	1, 0.56.
		2, 0.53.
	Crystallization Tank	4, 1.55.
		5, 1.75.
		6, 1.77.

The crystalline condition of the gypsum product was inferior and the product contained numerous minute crystals. There was almost no improvement in crystal condition even when the amount of ore treated was reduced to 1,800 Kg/hr.

WHAT WE CLAIM IS:—

1. A method of producing phosphoric acid and crystalline gypsum, which method comprises leaching phosphate rock in an initial reaction stage with a mixture of sulphuric acid and dilute phosphoric acid, said acids mixture containing from 10 to 22% by weight of P_2O_5 and from 20 to 40% by weight of H_2SO_4 , and the maximum acid content of the acids mixture being 52% by weight, at a temperature from 3 to 20°C. above the transition temperature of the dihydrate-semi-hydrate of calcium sulphate for the prevailing concentration of acids and for a period of time of from 10 to 60 minutes, mixing the resulting reaction slurry with from one to two times the volume of a recycle slurry recycled from a later stage and containing hydrated calcium sulphate crystals having a degree of hydration in the range of from 1.90 to 1.96, maintaining the resulting slurry in a hydration-crystallization stage at a temperature in the range of from 40 to 65°C. until the calcium sulphate crystals therein have a degree of hydration of from 1.90 to 1.96, recycling a portion of this hydrated slurry for admixture with reaction slurry, treating the remainder of said hydrated slurry to separate the crystalline gypsum from the crude phosphoric acid product, and thereafter washing the crystalline gypsum with water to remove adherent phosphoric acid.

2. A method according to Claim 1, in which the dilute phosphoric acid wash liquid produced by washing the gypsum is recycled to the initial reaction stage for the leaching operation.

3. A method according to Claim 2, wherein a portion of the dilute phosphoric acid wash liquid is recycled to the reaction slurry from the leaching operation.

4. A method according to any preceding claim, wherein the degree of hydration of the

tion 1.94) from the crystallization tank 6, in twice the quantity of the charged mixture from tank 2. The speed of hydration was arranged such that the temperatures in the crystallization tanks were 60°C. in tank 4, 55°C. in tank 5 and 50°C. in tank 6.

The degrees of hydration produced in the various tanks were:

10	Decomposition Tank	1, D.H.0.60.
		2, D.H.0.57.
15	Crystallization Tank	4, D.H.1.68.
		5, D.H.1.86.
		6, D.H.1.94.

The P_2O_5 decomposition degree was 98.3%, P_2O_5 adhering to gypsum 0.07% and yield of P_2O_5 was 97%. The resultant gypsum was in the form of large, columnar crystals with very good filter-ability as raw material for wall-boards. Phosphoric acid was obtained as a by-product in a concentration of 31%.

EXAMPLE 2.

The phosphate ore used was the same as in Example 1, and the crude phosphoric acid obtained as by-product was P_2O_5 30%, H_2SO_4 5%. 2,400 Kg/hr of the phosphate rock and 6,600 Kg/hr of mixed acid, composed of 2/3 of the entire quantity of recycled dilute phosphoric acid and the entire quantity of sulphuric acid (P_2O_5 12.5%, H_2SO_4 35.4%), were reacted continuously in decomposition tanks 1 and 2 at a temperature of 80°C. for a decomposition period of 50 minutes, after which the reaction mixture was mixed with the balance of 1/3 of the recycle phosphoric acid 1.827 Kg/hr (P_2O_5 22.5%, H_2SO_4 3.5%), and recycle slurry was added from the crystallization tank 6 in twice the quantity of the charged mixture from tank 2. The speed of hydration was arranged such that the temperatures in the successive crystallization tanks 4, 5 and 6 were 60°C., 55°C. and 50°C., respectively.

The degrees of hydration in the different tanks were as follows:

45	Decomposition Tank	1, 0.55.
		2, 0.54.
50	Crystallization Tank	4, 1.62.
		5, 1.85.
		6, 1.95.

The resultant gypsum was in the form of large, columnar crystals with good filter-ability, similar to that obtained in Example 1.

EXAMPLE 3.

The phosphate ore used was the same as in Example 1, and the phosphoric acid obtained as by-product was P_2O_5 32%, H_2SO_4 8%. 2,400 Kg/hr of the phosphate rock and 7,075 Kg/hr of mixed dilute phosphoric acid and sulphuric acid (P_2O_5 13.3%, H_2SO_4 35.7%) were reacted continuously in decomposition tanks 1 and 2 at a temperature of 80°C. for a decomposition period of 48 minutes, and

thereafter mixed in the mixing tank with the recycle slurry from crystallization tank 6 in a quantity corresponding to half the quantity of mixture charged from the tank 2. The speed of hydration was arranged such that the temperatures in the successive crystallization tanks 4, 5 and 6, were 60°C., 55°C. and 50°C., respectively.

The degrees of hydration in the different tanks were as follows:

75	Decomposition Tank	1, 0.56.
		2, 0.53.
80	Crystallization Tank	4, 1.55.
		5, 1.75.
		6, 1.77.

The crystalline condition of the gypsum product was inferior and the product contained numerous minute crystals. There was almost no improvement in crystal condition even when the amount of ore treated was reduced to 1,800 Kg/hr.

WHAT WE CLAIM IS:—

1. A method of producing phosphoric acid and crystalline gypsum, which method comprises leaching phosphate rock in an initial reaction stage with a mixture of sulphuric acid and dilute phosphoric acid, said acids mixture containing from 10 to 22% by weight of P_2O_5 and from 20 to 40% by weight of H_2SO_4 and the maximum acid content of the acids mixture being 52% by weight, at a temperature from 3 to 20°C. above the transition temperature of the dihydrate-semihydrate of calcium sulphate for the prevailing concentration of acids and for a period of time of from 10 to 60 minutes, mixing the resulting reaction slurry with from one to two times the volume of a recycle slurry recycled from a later stage and containing hydrated calcium sulphate crystals having a degree of hydration in the range of from 1.90 to 1.96, maintaining the resulting slurry in a hydration-crystallization stage at a temperature in the range of from 40 to 65°C. until the calcium sulphate crystals therein have a degree of hydration of from 1.90 to 1.96, recycling a portion of this hydrated slurry for admixture with reaction slurry, treating the remainder of said hydrated slurry to separate the crystalline gypsum from the crude phosphoric acid product, and thereafter washing the crystalline gypsum with water to remove adherent phosphoric acid.

2. A method according to Claim 1, in which the dilute phosphoric acid wash liquid produced by washing the gypsum is recycled to the initial reaction stage for the leaching operation.

3. A method according to Claim 2, wherein a portion of the dilute phosphoric acid wash liquid is recycled to the reaction slurry from the leaching operation.

4. A method according to any preceding claim, wherein the degree of hydration of the



calcium sulphate in the initial reaction stage does not exceed 0.75.

- 5 A method according to any preceding claim, wherein the mixture of reaction slurry and recycled slurry is maintained in the hydration-crystallization stage for from 12 to 36 hours.

- 6 A method according to any preceding claim, wherein the temperature employed in the initial reaction stage is from 80 to 100°C.

- 10 7. A method of producing phosphoric acid and crystals of gypsum, substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

- 15 8. A method of producing phosphoric acid

and crystals of gypsum, substantially as described in Example 1 or 2 of the foregoing Examples.

9. Crystalline gypsum, whenever produced by the method claimed in any preceding claim.

10. Phosphoric acid whenever produced by the method claimed in any one of Claims 1 to 8.

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