

SPECIFICATION

Treatment of Calcium Aluminium Phosphates

The present invention relates to the treatment of an ore substantially comprising a calcium aluminophosphate to extract phosphorus in the form of P_2O_5 .

5 It has long been known to treat natural phosphates with a strong acid, such as sulphuric acid, in order to solubilise the rock and recover the phosphoric acid from the leaching solution. 5

In general, the phosphatic rocks used are calcium phosphates, such as apatites containing a small quantity of other metals such as aluminium or iron. However, calcium aluminophosphate, which is more particularly found in the Thies deposits in Senegal, where aluminium extraction can be carried out in an advantageous manner, is also able to supply phosphoric acid. This ore is generally in the form of 10 two phases having substantially identical compositions and represented by the standard formula: $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$. Numerous processes have already been proposed for the successful utilization of this ore and more particularly calcium aluminophosphates. Examples of (a) thermal reductions, which supply the phosphorus, (b) alkaline leaching, which supplies an alkali metal phosphate and an alkali 15 metal aluminate, which must then be separated to recover a phosphate and metallurgical alumina, and (c) wet acid leaching with sulphuric acid, which supplies a calcium sulphate, which is filtered off, and a phosphoric ammonium sulphate solution, which is precipitated in the form of alum, e.g. by adding ammonium bisulphate. 15

All these processes require numerous complex time-consuming operations, which make difficult the separation of the aluminium and the phosphorus, resulting in low yields and often by-products that 20 it is difficult to utilise. For this reason, they are not used on an industrial scale and the industry is seeking an industrially profitable process for leaching calcium aluminophosphate ores and for separating aluminium and phosphorus recoverable in a workable form. 20

The present invention is based on the discovery that by leaching a calcium aluminophosphate, e.g. 25 one containing iron, by an excess of concentrated sulphuric acid at a given temperature for a given time, a paste is obtained which, by controlled take-up with water in a selected quantity and for a selected period, makes it possible to obtain a good selectivity of the phosphorus and aluminium (and of the iron), the aluminium and iron phosphates in the anhydrous state having a solubilisation rate in water slower than those of hydrated sulphates and of phosphate ions. 25

In accordance with the present invention, a phosphatic rock substantially constituted by calcium 30 aluminophosphate, which may contain iron and other metals in small concentrations, is leached by a process in which the ground rock is calcined in the presence of concentrated sulphuric acid in stoichiometric excess with respect to the aluminium, calcium and any iron ions contained in the starting rock for up to 5 hours at a temperature above $120^\circ C$ to produce a paste containing aluminium 35 sulphate and possibly iron and/or other sulphates in substantially anhydrous form, together with phosphoric acid and sulphuric acid, the paste then undergoing controlled take-up by means of water or a recycled aqueous phosphoric and/or sulphuric acid solution, so that there is produced (a) a solid residue that substantially contains aluminium, calcium and possibly iron from the starting rock, and (b) an aqueous phosphoric and sulphuric acid phase, which is separated. When various preferred features 40 are combined, the stoichiometric excess of the sulphuric acid, with respect to the aluminium, calcium and iron ions contained in the rock, is above 0.2 and preferably approximately 0.5 and the time of treatment is between 3 and 4 hours and the temperature is between 230 and $250^\circ C$. Also in accordance with a combination of preferred embodiments of the present invention, the controlled take-up with water of the resulting calcined paste is carried out at a water: paste weight ratio between 0.2:1 45 and 5:1, preferably between 0.8:1 and 1.2:1, at a temperature below $100^\circ C$, preferably between 0 and $40^\circ C$, for a time between 1 minute and 1 hour, preferably 5 to 15 minutes. 45

	P_2O_5	30%	
	Al_2O_3	30%	
	Fe_2O_3	8.7%	
50	CaO	8.5%	50
	H_2O	16%	
	Miscellaneous	6.8%	

Before being treated with sulphuric acid, the initial phosphatic rock is finely ground in order to increase the exchange between the solid and liquid phases. The grains of the rock are preferably below 55 160 microns in size. 55

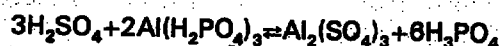
The initial phosphatic rock is preferably dry in order to prevent dilution of the leaching sulphuric acid. However, it is preferably not calcined in order to improve the effect on the P/Al or Fe selectivity and the P_2O_5 solubilisation yield.

The term concentrated sulphuric acid means an acid generally having a concentration above 90% 60 and preferably above 96%. 60

The quantity of concentrated sulphuric acid necessary for treating the calcium aluminophosphate according to the invention must exceed the stoichiometric quantity necessary for converting all the

metallic constituents of the rock into neutral sulphates in order to obtain at least neutral salts which become anhydrous at the calcination temperature used.

In addition, it has been found that once the anhydrous reaction mixture has been made, the P_2O_5 solubilisation yield is linked with the H_2SO_4 residual stoichiometry; the latter significantly decreases and comes close to zero when the excess of sulphuric acid drops. Without wishing to link this with any particular theory; it is thought that these results show that the following equilibrium exists:



During calcination, this reaction is followed by the appearance of insoluble aluminium polyphosphates and consequently it is necessary to displace the equilibrium by an excess of sulphuric acid.

It has also been found that it is not advantageous to partly divide up this excess of sulphuric acid between the leaching of the rock by pasting and sulphuric calcination and the subsequent controlled take-up with water, because in the latter case the overall P_2O_5 solubilisation is not improved: in fact, aluminium and iron solubilise more rapidly on aqueous take-up, which to the same extent reduces the selectivity of the process. Thus, all the sulphuric acid introduced into the process should be introduced at the time of leaching and pasting/calcination of the phosphatic rock. The residual sulphuric acid excess relative to the stoichiometry introduced on etching is a function of the reaction temperature and generally exceeds 0.2, being preferably about 0.5.

The reaction temperature is generally between 120 and 350°C, preferably between 200 and 300°C, more particularly between 230 and 250°C.

During the prior calcination treatment in the presence of sulphuric acid, the phosphatic rock disintegrates, producing phosphoric acid and acid or neutral salts of the different metals, the latter being hydrated to a greater or lesser extent and at the indicated temperature supplying, under the reaction conditions, anhydrous salts and water vapour, which is then eliminated. The water loss of the pasted mass is the fundamental parameter which subsequently controls the solubilising rate of the aluminium and iron sulphates during the control take up by water and consequently the selectivity of the process to the P/Al and P/Fe. When the pasting temperature is below 100°C, it becomes virtually impossible to dehydrate the aluminium and iron sulphates. Between 120 and 200°C, the necessary leaching times for obtaining anhydrous sulphates and consequently the desired selectivity are scarcely compatible with an industrial process (over 5 hours) although a desirable result can be obtained. Beyond 250°C there is a significant sulphuric acid loss and beyond 500°C, although the water losses are very fast and there is a rapid dehydration of the sulphates, there is conversely a reduction in the P_2O_5 solubilisation yield and the selectivity, probably as a result of the increase in the proportion of insoluble aluminium polyphosphate formed.

The reaction time is selected as a function of the temperature, in such a way that there is a weight loss of the mixture substantially equal to the theoretical water loss. For information purposes, the weight loss is 35g of water/100g of Thies phosphate with an H_2SO_4 stoichiometric excess of 0.5.

Conventionally, the reaction time is between a few minutes and 5 hours, preferably between 3 and 4 hours.

The preferred reaction temperature is 230 to 250°C, linked with the preferred reaction time of 3 to 4 hours.

The preceding sulphuric pasting reaction is performed in a known reaction apparatus, such as a static reactor or a reactor with a rotary oven or kiln and scavenging, together with direct or indirect heating. The phosphate/sulphuric acid reaction mixture is preferably prepared by using a continuous screw mixer which delivers the mixture to the intake of the rotary oven where it is calcined. Normally, the components of the mixture are introduced cold. During the initial mixing, whose duration is not critical, reaction may take place and raise the temperature to as hot as 100°C.

Once the calcination in the presence of sulphuric acid is at an end, the reaction mass is cooled. It then undergoes control take-up by means of water or an acid aqueous solution. The determinative parameters of this control take-up stage, in order to obtain a high P_2O_5 solubilisation yield, together with a high P/Al or Fe selectivity, are the temperature, the duration and the weight ratio of the take-up water to the calcined pasted mass.

In the same way, the reaction conditions during pasting can influence the P_2O_5 yield and the P/Al selectivity. Thus, when the pasting - calcination temperature rises, the overall P_2O_5 yield also increases. However, as has been stated hereinbefore in the case of increasing pasting temperatures (above 300°C), the aluminium sulphate solubilisation rate also increases, so that the selectivity is reduced to the same extent. Moreover, in the pasting temperature range of 120 to 500°C, the P_2O_5 solubilisation kinetics vary very little. Moreover, the excess of sulphuric acid excess on pasting influences only the maximum yields and not the solubilisation kinetics.

The controlled water take-up temperature must be as low as possible because it mainly effects the iron and aluminium sulphate solubilisation kinetics. For good P/Al or Fe selectivity, water take-up is generally at a temperature below 100°C and preferably below 50°C, particular preference being given to ambient or an even lower temperature.

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The weight ratio of take-up water to reaction mass resulting from the pasting by sulphuric acid is conventionally between 0.2:1 and 5:1 and preferably between 0.8:1 and 1.2:1. Obviously, this ratio must be as low as possible in order to obtain the most concentrated possible P_2O_5 solution compatible with an optimum P_2O_5 solubilization and an easy technological manipulation of the paste taken up with water.

The water take-up time must be the shortest possible time compatible with the maximum possible P_2O_5 yield in order to obtain a high P/(Al or Fe) selectivity. Thus, all things being equal, the selectivity results from differences in the P_2O_5 dissolution kinetics and the rehydration solubilisation kinetics of the anhydrous aluminium and iron sulphates. The water take-up time is also a function of the temperature at which it is performed. Generally, the water take-up time is between 1 minute and 1 hour, preferably between 1 and 15 minutes. Thus, for water take-up performed at 40°C, the duration is preferably between 1 and 5 minutes, while for water take-up at 0°C it is preferably between 10 and 15 minutes.

Following the controlled water take-up stage, the resulting mass is filtered leading to an aqueous phase of sulphuric acid and phosphoric acid and a solid residue substantially containing aluminium, iron, and other cations present in the initial phosphatic rock. Normally, in a continuous industrial process, the filter cake is washed with water, preferably in counter-flow, in order to extract the final traces of phosphoric acid. Preferably, this washing is performed in a short time, generally less than one minute, in order to obtain, after filtering, an aqueous washing solution that is not excessively enriched by aluminium and iron. The filtrate obtained on washing can be combined with the previously controlled take-up water but, in certain cases, all the water necessary for the controlled take-up can be obtained from the previous washing process as a function of the quantities of water used for the controlled take-up and the washing. The weight ratio of the quantity of water used for washing to the initial pasty reaction mass is conventionally between 0.2:1 and 5:1, preferably between 0.8:1 and 1.2:1.

The filtration flow obtained, which is constituted by sulphuric acid and phosphoric acid in water, contains small quantities of aluminium and iron. The aluminium and iron solubilisation yields, expressed by the weight ratios of the quantities of these metals in the production solution to those present in the starting rock, can be as low as 3% for both aluminium and for iron. However, the weight ratio of the P_2O_5 present in the take-up solution to the P_2O_5 present in the starting rock can be as high as 80%. Its phosphoric acid concentration is a function of the controlled take-up conditions and particularly the weight ratio of H_2O to calcined mass and, if appropriate, the recycling of the filter-cake washing water. Conventionally, the concentration is between 5 and 20% by weight of P_2O_5 . The sulphuric acid concentration of this filtrate is a function of the stoichiometric sulphuric acid excess during the calcination stage, the calcination temperature and time and obviously the control water take-up conditions. Normally, the sulphuric acid concentration is between 10 and 30% by weight of H_2SO_4 .

The sulphuric leaching and water take-up process according to the invention can be used with particular advantage for treating calcium aluminophosphates, which may contain iron, such as Thies phosphate in ore. The P_2O_5 yield compared with the P_2O_5 contained in the starting rock can be as high as 80% with P_2O_5/Al_2O_3 and P_2O_5/Fe_2O_3 selectivities as high as 22 and 75 respectively, expressed by weight, whilst the P_2O_5/Al_2O_3 and P_2O_5/Fe_2O_3 weight ratios are for example approximately 1:1 and 3.5:1 in the case of the calcium aluminophosphate of the Thies deposits.

The cake resulting from the filtering process and, if applicable, the previous washing process, can then be treated to recover metals using processes that do not form part of the present invention.

The aqueous filtering solution can be converted into alkali metal or alkaline-earth metal sulphates and phosphates. It is also possible to recover phosphoric acid by liquid-liquid extractions using water-immiscible solvents. Finally, in a third preferred variant, the process of the invention also incorporates the use as the leaching solution for a calcium phosphate rock that may contain small quantities of aluminium and/or iron, of an aqueous solution of phosphoric and sulphuric acid that constitutes the filtrate after controlled take-up with water of the sulphuric calcination product of the calcium aluminosulphate rock. The result is that a calcium sulphate precipitate and an aqueous solution essentially of crude phosphoric acid are obtained.

According to this variant, the leaching solution of the calcium phosphate rock has sulphuric and phosphoric acid concentrations as described above. If appropriate, prior to its use as a leaching solution, it can be concentrated in known manner and the P_2O_5 weight concentration can be up to 25%, with a H_2SO_4 concentration of 40%. It is also possible to recover the utilisable volatile constituents, such as fluorinated substances, from it.

The calcium phosphate rock used comprises well known ores such as, for example, apatites essentially constituted by tricalcium phosphate, which may contain other metals either in low concentration, such as aluminium and iron, or in traces, such as uranium and rare-earth metals.

The quantity of leaching solution defined above and used for reacting with the calcium phosphate rock defined above is such that there is essentially a stoichiometric equilibrium between the sulphuric acids present in the solution and the cations present in the calcium phosphate rock, the reaction being quantitative. However, in practice and for optimum solubilisation of the calcium phosphate rock, it is

possible to work with a slight excess of stoichiometric sulphuric acid.

The operating conditions for the leaching process are well known with respect to such conditions as temperatures, times and apparatus.

Following the aforementioned reaction, a calcium sulphate suspension is obtained in an aqueous solution substantially constituted by crude phosphoric acid. The suspension is then filtered in known manner, thereby separating the calcium sulphate and an aqueous solution essentially containing crude phosphoric acid, which constitutes the product. This crude phosphoric acid solution then undergoes known treatments, for example, concentration, defluorination, extraction by means of organic solvents to extract the utilisable cations (e.g. uranium and rare-earth metals) or extraction of the purified phosphoric acid. Alternatively, it can be used as such as a starting substance for phosphate fertilisers.

The aforementioned improved variant more particularly applies to a mixed leaching of calcium aluminophosphate and calcium phosphate, utilising the excess of stoichiometric sulphuric acid necessary during the sulphuric calcination of the calcium aluminophosphate rock.

The following examples, in which ratios are by weight unless indicated otherwise, illustrate but do not limit the invention. In Example 3 reference is made to the single figure of the accompanying drawing, which shows an illustrative form of apparatus for use in accordance with the present invention.

Example 1

100g of Thies phosphate, whose composition has been given and whose particle size is below 160μ , is mixed with quantities of 96% H_2SO_4 given in the following table I. Mixing then takes place for 10 minutes during which the temperature rises to $100^\circ C$. The paste obtained is then introduced into a static atmosphere oven at a temperature and for a time given in table I. Following calcination, the mass is cooled to $25^\circ C$ and is take up by water in a water:calcined mass ratio of 1:1 for 15 minutes, followed by filtering. P_2O_5 , Al_2O_3 and Fe_2O_3 are then metered in the filtrate and the solubilisation yields of the components of the ore are calculated. The table also shows the weight losses $\Delta P/100g$ of phosphate during the calcination operations which essentially represent the water loss.

Comparison of tests 1, 2 and 3 shows that inadequate calcination (tests 1 and 3) provides a poor selectivity between P_2O_5 and Al_2O_3 and P_2O_5 and Fe_2O_3 , taking account of the limited dehydration of the aluminium and iron sulphates and consequently their rapid dissolution rate.

Test 4 shows that when the calcination is performed at an increasing temperature, the quantity of P_2O_5 solubilised decreases. In the same way, the comparison of tests 2, 5 and 6 shows that a reduction in the excess of H_2SO_4 reduces to the same extent the yield of solubilised P_2O_5 .

Example 2

This example illustrates the influence of the quantity and temperature of the take-up water and the duration of its application.

The take-up parameters and the results obtained are shown in the following table II.

The calcined mass is obtained by mixing 100g of Thies phosphate with 186g of 96% H_2SO_4 under the same conditions as in example 1. This is followed by calcining the mass at $230^\circ C$ for 5 hours. The pasted mass is cooled at ambient temperature and is taken up and then filtered under the conditions and with the results indicated in the Table. The P_2O_5/Al_2O_3 weight ratio is that of the filtrate. Tests 2 and 7 show that too great a drop of the H_2O /calcined mass weight ratio limits the P_2O_5 yields.

Comparison of test 2 and 8 shows that a rise in the take-up temperature increases the solubilisation of alumina and Fe_2O_3 , whilst comparison of tests 8 and 9 shows that an increase in the take-up time, everything else being equal, increases the solubilisation of alumina and Fe_2O_3 .

Table I

Test No.	g of H_2SO_4 / 100g of Thies phosphate	Calcination temperature in $^\circ C$	Calcination time (h)	Water weight loss (g/100g of phosphate)	P_2O_5 (%)	Al_2O_3 (%)	Fe_2O_3 (%)
1	186	230	1	~15	90	80	80
2	186	230	5	~40	75	5	5
3	186	280	1	~25	80	65	65
4	186	280	5	~90	35	10	10
5	149	230	5	~35	60	6	6
6	124	230	5	~32	15	4	4

Table II

Test No	H_2O /calcined mass, by weight	Take-up temp. ($^\circ C$)	Take-up time (minutes)	P_2O_5 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	P_2O_5 / Al_2O_3
2	1.0	25	15	75	5	5	15
7	0.6	25	15	60	5	5	12
8	1.0	40	15	75	8	8	9.4
9	1.0	40	120	75	20	20	3.7

Example 3

This example illustrates the preferred variant, which also includes the use of the aqueous take-up filtrate as the leaching solution for a calcium phosphate.

The process is described with reference to the attached drawing, which is a diagram of the material flows.

In a pilot installation operating on a continuous basis, 96.3kg/h of 98% sulphuric acid is introduced by line (2) and 53.6kg/h of Thies (Senegal) phosphate ore ground to a grain size of 160μ is introduced by line (3) into a screw mixer (1). The weight composition of the Thies phosphate ore is as follows:

10	P_2O_5	30%	10
	Al_2O_3	30%	
	Fe_2O_3	8.7%	
	CaO	8.5%	
15	H_2O	16%	15
	Miscellaneous	6.8%	

The constituents are introduced at ambient temperature. The mixing time in the screw mixer is 15 minutes, at the end of which the mixture is heated by reaction to $100^\circ C$. The screw mixer delivers directly into a directly heated rotary oven or kiln operating in such a way that the mixture stays there 4 hours at a temperature of $230^\circ C$. During the sulphuric calcination, the mixture loses 22kg/h of water.

20 The paste obtained after calcination is cooled to $25^\circ C$ and introduced into vessel (5) where it undergoes a control take-up at $25^\circ C$ for 5 minutes using an aqueous solution constituted by the combination in (6) of a first washing flow (12) and a second washing flow (19), as will be described hereinafter. In this stage, the take-up water/calcined mass weight ratio is 1. The resulting suspension is transferred by (7) into a filtering means (8) where a solid mass (9) and an aqueous solution (13) are separated. The solid mass is transferred to a high speed filter (10) at $25^\circ C$ where it is washed for 1 minute by means of 60kg/h of water. The suspension is then rapidly filtered leading to a separation of the residue (11) constituted by:

30	$Al_2(SO_4)_3$	51.3kg/h	30
	$Fe_2(SO_4)_3$	11.1kg/h	
	P_2O_5	4.0kg/h	
	H_2O	35.7kg/h	

An aqueous solution (12) is separated which is recycled at (6) to constitute a fraction of the controlled take-up solution.

The flow of the aqueous filtering solution (13) is constituted by:

35	H_2SO_4	31.3kg/h	35
	$Al_2(SO_4)_3$	3.4kg/h	
	$Fe_2(SO_4)_3$	0.7kg/h	
	P_2O_5	18.9kg/h	
	H_2O	81.0kg/h	

40 This solution is introduced as it is into a reactor (14) constituted by a stirred leaching vessel where it is brought into contact at $100^\circ C$ with 35kg/h of ground Taiba (Senegal) phosphate with the following weight composition:

45	P_2O_5	37.6%	45
	CaO	51.4%	
	Miscellaneous	11.0%	

At the end of the reaction, the resulting suspension is filtered in (16) to provide a residue (17) which is washed and then filtered in unit (18) by means of 60kg/h of water to supply a residue (20) comprising:

50	gypsum	54.9kg/h	50
	sterile material	2.8kg/h	
	water	24.6kg/h	

A washing solution (19) is also obtained, which is recycled in the controlled take-up unit (6). An aqueous flow (21) mainly constituted by phosphoric acid is taken from the filtering unit (16). It is concentrated in the evaporation means (22) to supply a flow of 50kg/h of phosphoric acid with 50% P_2O_5 .

The efficiency of the installation expressed by the ratio

P_2O_5 recovered

P_2O_5 of calcium aluminophosphate + P_2O_5 from the calcium phosphate

is 86%.

The above results show that the stoichiometric sulphuric acid excess necessary for the calcination of calcium aluminophosphate for providing a good selectivity of the phosphorus relative to the aluminium is completely reused to stoichiometrically react with a calcium phosphate to provide a further phosphoric acid production.

Claims

1. A process for the treatment of a phosphatic rock essentially constituted by calcium aluminophosphates and optionally containing other cations in small concentrations, comprising calcining the ground rock in the presence of concentrated sulphuric acid in stoichiometric excess with respect to the aluminium, calcium and any iron ions contained in the starting rock for up to 5 hours at a temperature above 120°C to produce a paste containing aluminium sulphate and possibly iron and/or other sulphates in substantially anhydrous form, together with phosphoric acid and sulphuric acid, the paste then undergoing controlled take-up by means of water or a recycled aqueous phosphoric and/or sulphuric acid solution, so that there is produced (a) a solid residue that substantially contains aluminium, calcium and possibly iron from the starting rock, and (b) an aqueous phosphoric and sulphuric acid phase, which is separated.
2. A process as claimed in claim 1, in which the stoichiometric excess of sulphuric acid exceeds 0.2.
3. A process as claimed in claim 2, in which the stoichiometric excess of sulphuric acid is about 0.5.
4. A process as claimed in any preceding claim, in which the calcination time in the presence of concentrated sulphuric acid is between 3 and 4 hours.
5. A process as claimed in any preceding claim, in which the calcination temperature is between 230 and 240°C.
6. A process as claimed in any preceding claim, in which the concentrated sulphuric acid has a concentration above 96%.
7. A process as claimed in any preceding claim, in which the weight ratio of controlled take-up water to calcined mass is between 0.2:1 and 5:1.
8. A process as claimed in claim 7, in which the said ratio is between 0.8:1 and 1.2:1.
9. A process as claimed in any preceding claim, in which the water take-up takes place at a temperature below 100°C.
10. A process as claimed in claim 9, in which the said temperature is between 0 and 40°C.
11. A process as claimed in any preceding claim, in which the controlled take-up is carried out for a time between 1 minute and 1 hour.
12. A process as claimed in claim 11, in which the said time is between 5 and 15 minutes.
13. A process as claimed in any preceding claim, in which the residue is washed with water for a period of less than 1 minute following the controlled take-up and separation of the solid residue and the aqueous phase.
14. A process as claimed in claim 13, in which the washing water is combined with the take-up water of the calcined mass.
15. A process as claimed in any preceding claim, in which, in addition, the aqueous flow containing the phosphoric and sulphuric acids and obtained from the separation following the controlled take-up by means of water, or an aqueous solution of the product of the calcination reaction of the calcium aluminophosphate in the presence of concentrated sulphuric acid, is reacted with a tricalcium phosphate and the reaction product is then separated into a solid that mainly contains gypsum and an aqueous solution that mainly contains phosphoric acid.
16. A process as claimed in claim 15, in which the amount of tricalcium phosphate used in the reaction is such that there is substantially a stoichiometric equilibrium between the calcium of the tricalcium phosphate and the sulphuric acid present in the leaching solution.
17. A process as claimed in claim 15 or 16 in which, after separating the gypsum and the aqueous phosphoric acid solution, the gypsum residue is washed with water and the washing water is recycled in the controlled water take-up stage to constitute a fraction of the control take-up water after sulphuric calcination of the calcium aminophosphate.
18. A process as claimed in claim 17, in which the other fraction of the controlled aqueous take-up solution is constituted by the washing water of the residue of the filtration of the take-up suspension performed with water after sulphuric calcination of the calcium aluminophosphate.
19. A process as claimed in claim 1 carried out in apparatus substantially as hereinbefore described with reference to the accompanying drawing.

The efficiency of the installation expressed by the ratio

P_2O_5 recovered

P_2O_5 of calcium aluminophosphate + P_2O_5 from the calcium phosphate

is 86%.

The above results show that the stoichiometric sulphuric acid excess necessary for the calcination of calcium aluminophosphate for providing a good selectivity of the phosphorus relative to the aluminium is completely reused to stoichiometrically react with a calcium phosphate to provide a further phosphoric acid production.

Claims

1. A process for the treatment of a phosphatic rock essentially constituted by calcium aluminophosphates and optionally containing other cations in small concentrations, comprising calcining the ground rock in the presence of concentrated sulphuric acid in stoichiometric excess with respect to the aluminium, calcium and any iron ions contained in the starting rock for up to 5 hours at a temperature above 120°C to produce a paste containing aluminium sulphate and possibly iron and/or other sulphates in substantially anhydrous form, together with phosphoric acid and sulphuric acid, the paste then undergoing controlled take-up by means of water or a recycled aqueous phosphoric and/or sulphuric acid solution, so that there is produced (a) a solid residue that substantially contains aluminium, calcium and possibly iron from the starting rock, and (b) an aqueous phosphoric and sulphuric acid phase, which is separated.
2. A process as claimed in claim 1, in which the stoichiometric excess of sulphuric acid exceeds 0.2.
3. A process as claimed in claim 2, in which the stoichiometric excess of sulphuric acid is about 0.5.
4. A process as claimed in any preceding claim, in which the calcination time in the presence of concentrated sulphuric acid is between 3 and 4 hours.
5. A process as claimed in any preceding claim, in which the calcination temperature is between 230 and 240°C.
6. A process as claimed in any preceding claim, in which the concentrated sulphuric acid has a concentration above 96%.
7. A process as claimed in any preceding claim, in which the weight ratio of controlled take-up water to calcined mass is between 0.2:1 and 5:1.
8. A process as claimed in claim 7, in which the said ratio is between 0.8:1 and 1.2:1.
9. A process as claimed in any preceding claim, in which the water take-up takes place at a temperature below 100°C.
10. A process as claimed in claim 9, in which the said temperature is between 0 and 40°C.
11. A process as claimed in any preceding claim, in which the controlled take-up is carried out for a time between 1 minute and 1 hour.
12. A process as claimed in claim 11, in which the said time is between 5 and 15 minutes.
13. A process as claimed in any preceding claim, in which the residue is washed with water for a period of less than 1 minute following the controlled take-up and separation of the solid residue and the aqueous phase.
14. A process as claimed in claim 13, in which the washing water is combined with the take-up water of the calcined mass.
15. A process as claimed in any preceding claim, in which, in addition, the aqueous flow containing the phosphoric and sulphuric acids and obtained from the separation following the controlled take-up by means of water, or an aqueous solution of the product of the calcination reaction of the calcium aluminophosphate in the presence of concentrated sulphuric acid, is reacted with a tricalcium phosphate and the reaction product is then separated into a solid that mainly contains gypsum and an aqueous solution that mainly contains phosphoric acid.
16. A process as claimed in claim 15, in which the amount of tricalcium phosphate used in the reaction is such that there is substantially a stoichiometric equilibrium between the calcium of the tricalcium phosphate and the sulphuric acid present in the leaching solution.
17. A process as claimed in claim 15 or 16 in which, after separating the gypsum and the aqueous phosphoric acid solution, the gypsum residue is washed with water and the washing water is recycled in the controlled water take-up stage to constitute a fraction of the control take-up water after sulphuric calcination of the calcium aminophosphate.
18. A process as claimed in claim 17, in which the other fraction of the controlled aqueous take-up solution is constituted by the washing water of the residue of the filtration of the take-up suspension performed with water after sulphuric calcination of the calcium aluminophosphate.
19. A process as claimed in claim 1 carried out in apparatus substantially as hereinbefore described with reference to the accompanying drawing.



(18)

20. A process as claimed in claim 1 substantially as hereinbefore described in any one of the Examples.

21. A process as claimed in any one of claims 1 to 20, in which the calcium aluminophosphate is from the Thies deposits.

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25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained