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3,490,811

IN SITU ACIDULATION OF PHOSPHATE ROCK
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9 Claims

ABSTRACT OF THE DISCLOSURE

Phosphate rock is acidulated in situ by injecting the acidulating acid into an underground phosphate rock deposit through an injection well. The phosphoric acid formed by the acidulation reaction is recovered through a production well. Acidulation may be accomplished with conventional acids, such as sulphuric acid, nitric acid and hydrochloric acid. In the event the permeability of the phosphate deposit becomes seriously diminished due to the deposition of by-product solids, e.g. gypsum, the deposit may be fractured by the imposition of a high well-bore pressure so as to increase the permeability of the phosphate deposit between the injection well and the production well. A group or combination of injection and production wells may be employed, as, for example, a conventional five-spot placement as is commonly employed in oil recovery operations. The phosphoric acid solution recovered at the surface may thereafter be treated in accordance with conventional techniques to produce the phosphoric acid of commerce or phosphatic fertilizer compositions as desired.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to the production of phosphoric acid and phosphatic fertilizer compositions. More particularly, it relates to a novel process for acidulating phosphate rock to produce phosphoric acid solutions.

Description of the prior art

A variety of techniques are well known in the art for the production of phosphoric acid and phosphate fertilizer compositions from phosphate rock. Include among these techniques are those involving the acidulation of phosphate rock with various acids such as sulfuric acid, nitric acid and hydrochloric acid. In this country, sulfuric acid is commonly employed in the production of so-called wet process phosphoric acid. In view of the reoccurring concern as to the availability of adequate supplies of sulfur, however, various nitric acid acidulation techniques have recently been proposed in this country. In other parts of the world, nitric acid acidulation operations are presently being carried out. In addition, hydrochloric acid has been disclosed and employed for the acidulation of phosphate rock.

All of these conventional acidulation techniques relate to the treatment of phosphate rock that has been mined and beneficiated by old and well established mining and beneficiating operations. These operations are described in numerous patents and publications, e.g. U.S. 3,086,654 issued to Hollingsworth et al. and "Washing and Concentrating Florida Pebble Phosphate," by S. J. Swainson, Mining and Metallurgy, October 1944. Since phosphate rock is a relatively low priced commodity, the mining and beneficiating operations employed therewith must generally be carried out under restrictive economic limitations. The separation and recovery of the phosphate material from the accompanying clay and sand particles is not as complete in commercial operations as would be

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technically feasible in the absence of overriding economic considerations.

Conventional mining and beneficiation operations require, nevertheless, a considerable capital investment and entail considerable operating expense. In addition, considerable phosphate deposits exist at depths for which conventional mining techniques are either technically impractical or economically prohibitive.

It is an object of this invention, therefore, to provide a novel process for acidulating phosphate rock.

It is another object of the invention to provide a phosphate rock acidulation process in which the investment and operating costs are minimized.

It is another object of the invention to provide a process for acidulating phosphate rock that is economically feasible with respect to phosphate deposits having a considerable overburden.

With these and other objects in mind, the following is a description of the present invention, the novel features of which are set forth in the appended claims.

SUMMARY OF THE INVENTION

The acidulation of phosphate rock to produce phosphoric acid and phosphatic fertilizer compositions is, in accordance with the present invention, carried out in situ rather than in reaction vessels at the surface as in conventional technology. Acid is pumped into a phosphate-bearing formation through an input well, and the resulting phosphoric acid solution is recovered through a production well. The conventional steps of mining and beneficiating the raw phosphate material are thus avoided. The present invention is of particular advantage with respect to the recovery of the phosphate values from deep formations that are not suitable from an economic viewpoint for conventional open pit mining techniques.

Any of the commonly employed phosphate acidulation reactions may be employed in the novel process of the present invention. Thus, sulfuric acid, which is frequently employed in conventional operations for the production of wet process phosphoric acid, may be injected into the phosphate-bearing formation. Likewise, nitric acid and hydrochloric acid may be employed as the acidulation acid.

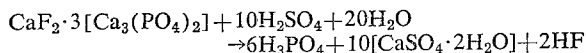
The phosphoric acid solution recovered at the surface may be treated in accordance with conventional techniques to produce the phosphoric acid of commerce or may be treated in accordance with other well known techniques in order to produce various phosphatic fertilizer compositions.

DETAILED DESCRIPTION OF THE INVENTION

The present invention contemplates the acidulation of phosphate rock by means of any of the acids commonly employed in the conventional acidulation operations known in the art. The acids most commonly employed in the acidulation of mined phosphate rock are sulfuric acid, nitric acid and hydrochloric acid. In the acidulation of mined phosphate rock with sulfuric acid in above ground reaction vessels, a weak phosphoric acid solution is obtained, e.g. a 26–32% P_2O_5 acid. This acid is filtered and concentrated typically to a P_2O_5 content of about 52–54%. The fine solids formed in the concentration operation, comprising essentially iron and aluminum phosphates, are removed from the concentrated acid to produce the wet process phosphoric acid of commerce. In addition, the phosphoric acid solution may be treated in a variety of ways, e.g. by ammoniation, to produce mixed phosphatic fertilizer compositions. The phosphoric acid solution formed by the in situ process of the present invention can be treated upon recovery above ground in the same manner as the initial weak phosphoric acid solu-

tion of conventional technology to produce a product grade wet process phosphoric acid or a commercial phosphatic fertilizer composition.

The acidulation with sulfuric acid is generally in accordance with the reaction:



The by-product gypsum will generally tend to stay behind in the formation although a portion of the gypsum formed may be brought to the surface with the product phosphoric acid solution. The by-product gypsum formed in conventional above ground acidulation operations is ordinarily discarded, thus creating a waste problem that is largely eliminated by the practice of the present invention.

In the in situ process of the present invention, the HF formed will tend to react with silicates present in the formation so as to reduce the fluorine content of the product phosphoric acid solution. Since the fluorine content of conventional wet process phosphoric acid must be reduced, as by solvent extraction, in the production of feed grade and food grade acid, the preliminary reduction in fluorine content resulting from the practice of the present invention represents an additional economic advantage in those instances in which a purified wet process phosphoric acid is to be obtained.

The use of nitric acid for phosphate rock acidulation is also well known in the art. In this instance, an acidulation mixture containing product phosphoric acid, unreacted nitric acid and by-product calcium nitrate is obtained. This mixture is recovered from the phosphate-bearing formation through a production well. As with sulfuric acid, conventional technology may thereafter be employed for the separation and purification of the desired phosphoric acid or phosphatic fertilizer composition. For example, the calcium nitrate can be retained in the product solution that may be sold, with or without further treatment such as ammoniation, as a phosphatic fertilizer composition. Alternately, the calcium nitrate may be precipitated from the solution by conventional techniques, typically as calcium nitrate tetrahydrate.

Hydrochloric acid acidulation of phosphate rock, such as disclosed in U.S. 2,880,063 issued in the name of Baniel et al., may also be applied in the in situ process of the present invention. Once again, the conventional treatment of the acidulation mixture obtained by conventional above ground acidulation may also be applied in the treatment of the phosphoric acid solution recovered from the phosphate-bearing formation in the practice of the present invention.

When the by-product of the acidulation reaction is insoluble in the acidulation mixture, e.g. gypsum and calcium chloride, the deposition of the by-product in the formation may be of advantage as indicated above with regard to waste disposal problems. The deposition of the solid by-product in the phosphate-bearing formation may also have some effect on the in situ operation itself. If, for example, the insoluble by-product is deposited in the more permeable regions of the formation, the deposition may have the advantageous effect of diverting the injected acid into the less permeable regions of the phosphate deposit. The overall efficiency of the operation would be enhanced in this instance since the acidulation operation could then be continued economically for a longer period of time before the ratio of injected acid to product acid in the production mixture becomes prohibitive.

If, on the other hand, the deposition of insoluble by-product were to cause an undesirable reduction in the permeability of the deposit, and a consequent reduction in the desired production flow rate, this difficulty may be overcome by increasing the injection pressure to the point at which fracturing of the formation between the injection and production wells results. The fracturing of forma-

tions in this general manner is well known in the art, being applied frequently in the stimulation of oil recovery from subterranean oil-bearing formations. The injection pressure required for the fracturing of a phosphate-bearing formation will depend on various factors such as the nature and size of the phosphate deposit, the nature deposit, the nature and extent of the overburden, the distance between the injection and production wells, and the like.

The horizontal stress necessary to fracture the formation is commonly found to be somewhat more than half, as for example, 60-70% of the vertical stress imposed by the weight of the overburden. In many instances, a vertical stress of about one pound per square inch is found for each foot of overburden. These figures are presented for illustrative purposes only, the required injection pressure being determined by the conditions encountered in the particular formation in question as well known by those skilled in the art of fracturing.

During ordinary in situ acidulation operations, the injection pressure will be maintained at a level so as to establish a pressure gradient across the formation to the production well sufficient to permit a satisfactory flow rate of product phosphoric acid solution from the production well. In some instances, it may be possible to inject the acid into an injection well at the top of an inclining phosphate deposit and to permit the acidulation mixture to gravitate down through the deposit by gravity flow to a production well positioned in the deposit at a lower depth.

One or more injection and production wells may be employed in the practice of the present invention. For example, one injection well may be used in conjunction with a series of production wells spaced apart therefrom in the phosphate-bearing formation. A five-spot placement such as that employed in oil production operations may be employed in a suitable instance, with four production wells positioned about a center injection well.

The present invention may be employed with respect to phosphate deposits having a shallow overburden, e.g. 20-30 feet, in preference to conventional open pit mining techniques and may also be employed in those instances in which the depth of the overburden is such as to render impractical or economically unattractive the use of such open pit mining techniques. With respect to deep deposits, e.g. 150-200 feet, the in situ technique herein disclosed may provide the sole commercially feasible method for recovering the phosphate values from the deposit.

The distance between the injection and production wells is not a critical feature of the invention. While this distance may conveniently be maintained at from about 50 feet to about 200 feet, the wells may be spaced apart at any convenient distance outside this range that the overall circumstances may suggest to those skilled in the art.

When the present invention may be applied to both phosphate-rich sandstone and limestone formation, it is preferably employed in sandstone regions since formations rich in calcium carbonate tend to consume some of the injected acid, thus reducing the overall efficiency of the operation. It is, of course, particularly advantageous when layers of impermeable shale are located above and below the phosphate-rich layer.

In experimental runs in which Florida pebble phosphate was acidulated with 50% sulfuric acid, the in situ recovery of phosphoric acid from a phosphate-containing permeable sandstone was demonstrated. The permeability of the packed sandstone structure did not appear to be diminished by the deposition of the gypsum formed as a by-product of the acidulation reaction.

Therefore, I claim:

1. A process for the production of phosphoric acid comprising:

(a) injecting an acid taken from the group consisting of sulfuric acid, nitric acid and hydrochloric acid

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through an injection well into an underground formation zone containing a deposit of phosphate rock, said acid being employed at sufficient strength to acidulate said phosphate rock to phosphoric acid;

(b) recovering the phosphoric acid produced by the acidulation of said phosphate rock with the injected acid from said underground formation zone through a production well,

whereby the formation of phosphoric acid is accomplished in situ thus avoiding the necessity for employing conventional mining operations and facilitating the recovery of the phosphate values from deep deposits of phosphate rock.

2. The process of claim 1 in which the injected acid is sulfuric acid.

3. The process of claim 1 in which the injected acid is nitric acid.

4. The process of claim 1 in which the injected acid is hydrochloric acid.

5. The process of claim 1 in which the product phosphoric acid is recovered from more than one production well positioned about the injection well.

6. The process of claim 1 in which the distance between said injection well and said production well is from about 50 feet to about 200 feet.

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7. The process of claim 1 in which said acid is continuously injected into the formation until an appreciable quantity of said injected acid is present in the acidulation mixture recovered from said formation zone.

8. The process of claim 1 and including the fracturing of said underground formation zone so as to increase the permeability of said formation zone between said injection and production wells.

9. The process of claim 8 in which said injected acid is sulfuric acid and said fracturing is accomplished in order to relieve blockage due to the deposit of by-product gypsum in said formation zone.

References Cited

UNITED STATES PATENTS

3,437,379	4/1969	Dunseth et al.	299—5
3,278,233	10/1966	Hurd et al.	299—4
3,359,037	12/1967	Every et al.	299—4

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