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A NEW MINERAL PROCESS FOR CLEAN COMMERCIAL PHOSPHORIC ACID PRODUCTION BY SIMULTANEOUS REMOVAL OF SLUDGE ORGANICS, CADMIUM AND OTHER HEAVY METALS AND RECOVERY OF RARE EARTHS

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1. INTRODUCTION

Commercial grade phosphoric acids, depending on their raw material source, present a large varieties of impurity ingredients. These ingredients are commonly classified within 4 groups:

- * Sludge or solids contents
- * Organics
- * Sulfate and fluorine anions
- * A large variety of cationic elements

Depending on the country where the acid will be used and the down-stream product to be manufactured, the acid purchaser will set a number of quality constraints in order to adapt the acid-raw-material to the requirements of his needs.

The present process was developed in order to cope with most of the above listed impurity ingredients. But before we start with the process examination, we shall review briefly the effects of each of the listed impurity group.

- Sludges:

Sludge is the generic name for all kind of solids to be found in phosphoric acid. The solids can originate from filter cloth leaks as well as from so called-post-precipitations. The latter are responsible for the major proportion. Phosphoric acid, after being concentrated by evaporation, is no more thermodynamically equilibrated with most of its dissolved and suspended solid impurities. The equilibrium, however, will re-establish, although very slowly because it occurs within a viscous, generally non agitated medium at temperatures little above ambient. The "post-precipitated" solids appear as very fine particles. This "sludge conversion" takes weeks, even months to achieve.

Sludge, sometimes yielding over 6 weight % with acid out of the 52-54% P_2O_5 acid storage tank, and up to 2% with commercial grade acid, plugs pipes, settles in tanks during transportation in ships and rail-way cars, and causes problems when arriving to final destination. At the least, it calls for dirty periodic cleaning operations.

Sludge removal from acid is tedious and expensive: commercial grade acid is a viscous, high density and corrosive solution, not easy to handle. The solids contained present very small particles, settling slowly. Settling systems usually remove underflow solutions draining only 20% solids by weight. Settling equipment suffers scaling problems and related mechanical breakdowns. Sludge removal by settling has to cope with the drain acid, about 20% of the feed, still carrying the load of the settled solids. Filtration can only be used within limited acid qualities or concentrations.

Eventually, after sludge removal, there may be further precipitations !

- Organics:

Besides calcined phosphate rock, there are more or less organics in all sedimentary ores. After acid production, a part of the organic material stays as a cloudy suspension or floats as a foaming gunk on top of the acid. Organics are responsible for the grey colour of downstream products.

- Sulfates, Fluorides and Chlorides:

Free sulfate in phosphoric acid are the result of process requirements. Wet process phosphoric acid needs excess sulfuric acid to be produced within convenient operating conditions. When originating from dihydrate acid, commercial acid contains more sulfates than with hemihydrate processes: 3-4% instead of 2-3%. Sulfates can be tolerated for most cases; they are removed for specific cases only, like for animal feed grade dicalcium phosphate production.

Fluorides are present in all phosphate ores, usually at about 1% compared to P_2O_5 in sedimentary rock. During phosphoric acid processing and evaporation concentration, up to 70% of the fluorides move into the gas phase and into the calcium sulfate waste stream that leaves the plant; some move into sludge. The remainder however, still represent about 0.3 to 1% F in the 52% P_2O_5 grade acid, (as soluble H_2SiF_6 or HF).

Fluorides in commercial grade acid can be tolerated with downstream fertilizers, they participate with the reactions. They have to be removed when animal feed products are manufactured.

- Cationic Elements:

These Impurities include all metallic components from the phosphatic ore dissolved during the wet process operation: It is the case for the large majority. Most common elements are: Ca, Al, Fe, Mg, Na, K and Si; if they do not exceed normal concentrations, they do not present problems.

A large number of trace elements are present in most ore qualities; their respective concentrations vary considerably from one ore to another:

Sr, Ba;

Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu:

Ti, Th, U,

V, Cr, Mn, Co, Ni, Cu, Zn, Hg, Cd, Tl, Sn, Pb

As, Sb, Bi, Se,

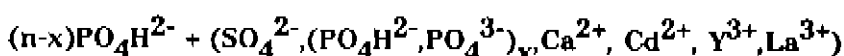
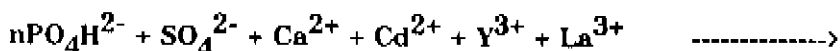
Bold printed elements can be subject to environmental or toxical concern, underlined elements may become subject to recovery considerations.

- Cadmium:

Since World War II, cadmium is considered environmentally undesirable. There are variable cadmium levels in commercial sedimentary phosphate ores: from 5 ppm up to 90 ppm; (above 100 with Western US phosphates). Regulations limiting cadmium with fertilizers are not yet standardized; above 20 ppm in Cd in rock, it is recommended to investigate cadmium removal technologies.

Cadmium removal was developed by organic solvent extraction or precipitation, using for example, cadmium dithiophosphate formation or cadmium amine-chlorhydrate complexation. Ion exchange processes were also selected.

In the process presented here, calcium sulfate co-crystallization technology is used in a 52-54% P_2O_5 phosphoric acid medium. But in fact, the process could be described as a mini-phosphoric acid plant, connected to the tail end of the existing plant.



where x represents about n/4000.

By a special introduction mode for both sulfate and calcium ions into concentrated phosphoric acid, up to 95% of the cadmium can be collected by the precipitated crystals. The crystals also collect a number of other heavy metals like rare earth. They collect PO_4H^- and PO_4^{--} ions, replacing part of the SO_4^{--} ions.

Because of ionic radius similarity for Ca^{++} and Cd^{++} , as well as with rare earth elements, intensive substitution within the calcium-sulfate-phosphate crystal pattern becomes possible. The chemical compound crystallized can be specified as a mixed anhydrite-dicalcium phosphate. The presence of PO_4^{--} ions permits to integrate cations with valences of 3, like Y, Sm, Ce etc...

PROCESS DESCRIPTION

- Objectives

The objectives of the process are: removal of sludge, organics, cadmium and rare earth elements from acid by mineral precipitation; convert the precipitate into pure calcium sulfate dihydrate and collect the other cationic components within a concentrate for storage or recovery of rare earth elements.

- Process description

The process is subject to French patent FR 9879, 04/07/89 Ref. 334 908, and is also subject to international registration since January 10, 1991.

The diagram on the following page depicts process-flow and outcoming products. The process operates on commercial-grade acid, 52-56% P_2O_5 , as it leaves the concentration plant. The additional phosphoric acid produced, represents an increment of 2% P_2O_5 as compared with the purified acid.

At this stage, the acid is still at about 80°C temperature and the suspended solids have not yet started conversion. The acid is heated further up to some 110-120° C and sulfuric acid plus phosphate rock are added within special precipitation reactor. At this temperature, organics are carbonized. The added reactants, sulfuric acid and rock, will result as 2% additional phosphoric production.

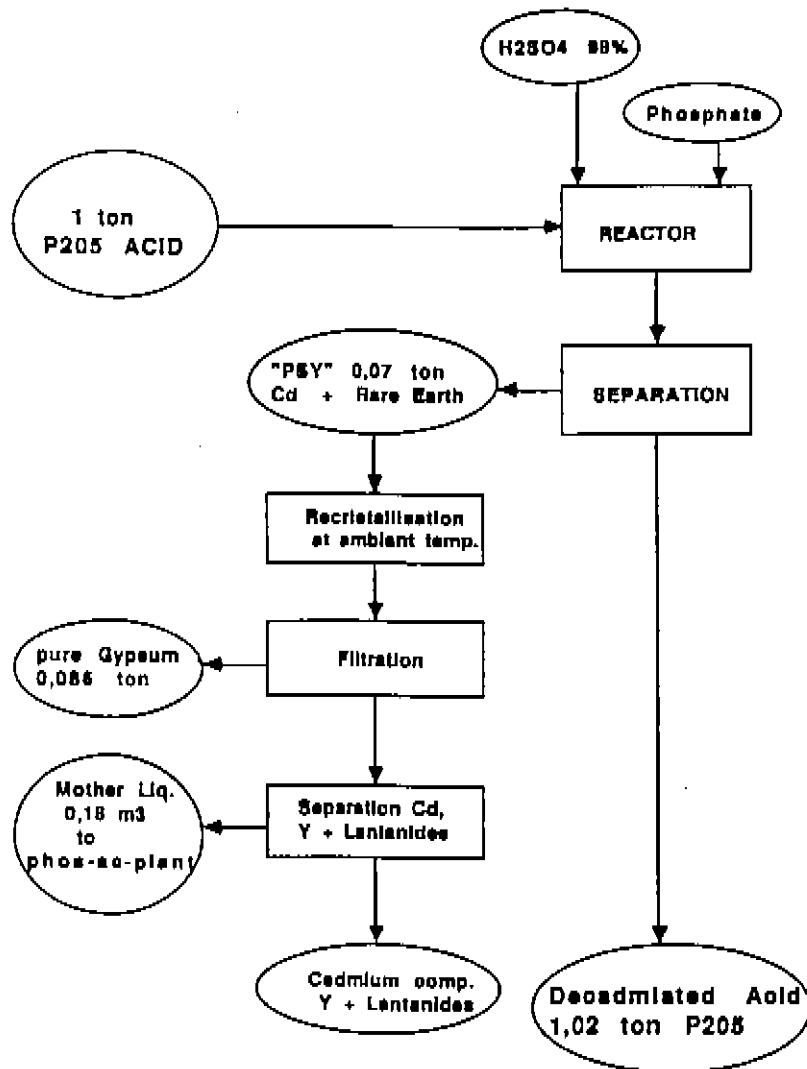
The precipitated solids, some 70 kg per ton of processed P_2O_5 , will collect 95% of cadmium and rare earth from the phosphoric acid. The precipitated solids show well shaped crystals, large enough to be subject to normal vacuum or other type of filtration operation. The composition of the crystals appear to be intermediate between calcium sulfate and dicalcium phosphate, where calcium is widely substituted with most of the elements listed in section 2.4. Elements with widely differing ionic radii, like uranium, mercury, arsenic, are not collected. The rather large participation of PO_4H^- and PO_4^{--} ions permits to collect 3-valency elements, like many of the rare earth lanthanides. We called this precipitate P-S-Y, standing for Phosphate-Sulfate of Yttrium.

Sludge components present within the acid when entering the decadmiation reactor will, to some extent, participate with the reactions and be subject to crystal growth or recrystallized by the high temperature effect.

Anyhow, after filtration, the resulting acid presents no more post-precipitations: from the acids we produced so far, we only collected some 80 ppm postprecipitations after 12 months storage.

For phosphoric acid plants who only want to remove cadmium from acid, the operation can be considered finished; PSY is then stored in special waste deposit area.

DECADMIATION PROCESS by MINERAL PRECIPITATION



However, conversion of PSY being a simple operation, (although anhydrite conversions are, to date, not very common), it is worthwhile to operate PSY through dihydrate conversion. The conversion is operated at ambient temperature in low acidic aqueous solution. Conversion takes, depending on rock and sludge composition between 6 and 20 hours. Pure gypsum will be removed, the mother liquor then containing all the impurities: cadmium, rare earth and cocrystallized PO_4^{--} . There will be 0.18 m^3 mother liquor per mt P_2O_5 purified acid.

Cadmium and rare earth can be easily separated from the mother liquor by precipitation. The cadmium-free mother liquor will then be recycled to the phosphoric acid plant.

Considering a plant to produce $500 \text{ t P}_2\text{O}_5$ of clean, commercial grade acid, sludge organics and fluorides free, with 95% removal of the cadmium, the reactor would be dimensioned 45 m^3 , the PSY recrystallization vessels would have a volume of 75 m^3 , recycled mother liquor would make up $3.75 \text{ m}^3/\text{hour}$, (to be recycled into the phosphoric acid filter-wash water).

PRESENT STATUS OF PROGRESS

In 1989, process was first operated on a bench scale unit (1 liter/day) with Minemet Recherches at Trappes, near Paris. In 1990, a pilot plant unit (10 liter/hour) was set up at Vlaardingen, Holland, where it operated 6 months during 1990. To date, a second pilot plant operates at Rouen, in France. Originally, operated as a batch type unit, it is now, for the purpose of cheaper investment and more simple monitoring, realized as a continuous system.

ECONOMICS

(2) Operating costs can be maintained on the low side because the reactants, (SO_4H_2 and Phosphate ore) are available at any place where phosphoric acid is produced and they will bear no costs since they will eventually result as commercial grade acid. Since decadmiation operation is concomitantly realized with sludge removal and rare earth recoveries, it is obvious that the overall economics will be subject to wide variations from case to case.

The following data will however give some indications permitting to make preliminary investigations.

INVESTMENT COSTS:

500 t P_2O_5 as commercial grade acid, to be decadmiated:
US \$ 4 Million

Operating Costs: (500 t P_2O_5 /day plant)

COST ITEM	US\$/t P_2O_5
Steam, 0.085 t	1.10
El. Energy, 8 KW/t	0.40
Labor, 2 operators/shift	1.20
Maintenance	1.50
Depreciation & Financial Charges	3.80

BENEFITS

Sludge removal	2.00-4.00
Rare earth Recovery	1.00-2.00

BALANCE 2 to 5

CONCLUSIONS

Quality improvements and environmental concerns are currently considered cost consuming factors. In fact, we only can confirm this common statement. However, quality improvements and the environmental action we may take, will also enable us to face near future requirements with better products against the ever strengthening world competition and the increasing burden of quality regulations. Combining operations, investigating new developments, as demonstrated here, can help to carry increasing financial burdens.