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# INFLUENCE OF THE ROCK IMPURITIES ON THE PHOSPHORIC ACID PROCESS, PRODUCTS AND SOME DOWNSTREAM USES

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## Summary

Production of phosphoric acid and phosphatic fertiliser is influenced by soluble impurities contained in the phosphate rock. They will influence the process, the quality of the acid and the gypsum produced as well as the downstream units using this phosphoric acid. This article, through a review of existing publications, summarises their impact on the corrosion, filtration, scaling, phosphoric acid, gypsum, and fertiliser qualities.

## Introduction

Phosphate quality has always been a subject of concern and numerous articles have been written treating the impact of some foreign ions on the production of phosphoric acid and fertilisers.

Considering the production of phosphoric acid, all the elements that are not  $\text{PO}_4^{3-}$  or  $\text{Ca}^{2+}$  are considered as “impurities”. If not soluble, these impurities have a very limited impact on the process; erosion of stainless steel equipment and an impact on the filtration of gypsum as these are the only phenomena that can be detected.

Once the ions are in solution in the acid, other problems such scaling, corrosion, production of sludge, increase of acid viscosity and process instability can occur. Such phenomena can be produced by the presence of one single ion but also by the combination of several of them. For example, if the conditions are favourable, a small increase of the potassium, aluminium or iron content of an acid can produce a large quantity of sludge made of so-called X compound.

These effects are not always detrimental to the process. Silica and aluminium, for example, are often added to the reactor to improve filterability. With such addition, filterability will not be the only improved factor; corrosion speed will be reduced due to the reduction of free fluorine in the reactor.

When the production of phosphoric acid was in its early days, rock quality was an issue in order to find the raw materials giving the best performances. Nowadays, the task of the production staff is to use the phosphate rock they have in their warehouse, to understand its impact on the process and to choose the blend of rock or the appropriate additive that should possibly be added to compensate for any deficiency.

The impact of impurities on the process will be considered through the following aspects:

- process chosen to produce phosphoric acid;
- corrosion;
- filtration;
- phosphoric acid quality;
- gypsum quality;
- scaling;



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- fertiliser production

At the end of the article, charts will summarise the different observations.

## **Process Choice**

Choosing a phosphoric acid process has always been a difficult task. It is based on the overall investment cost, the energy requirement, the calcium sulphate produced, the intended use of the acid ... and the raw materials. Impurity content of the phosphate rock can in some case disqualify a process from the initial selection. It is the case, for example, of the lanthanide content of the rock (La, Ce, Y) which, even in very limited quantities, slow down the conversion of Hemihydrate to Dihydrate (Witkamp, 1989). Rocks containing this element thus disqualify Hemihydrate – Dihydrate processes.

Phosphate containing a high Al content can also cause problems with Hemihydrate – Dihydrate processes as it slows down the re-crystallisation of Hemihydrate to Dihydrate. Indeed, aluminium fluoride ( $AlF_5^{2-}$ ) increases the HH solubility by up to 40% close to the DH solubility (Martynowicz et al, 1996). To temper this problem silica is sometimes added to the rock (Anonymous, 1993).

CO<sub>2</sub> content can also be a limitation with a process having a vacuum flash chamber as the reactor. Indeed, the high CO<sub>2</sub> content in the rock produces a very large quantity of foam inducing a slurry carry over that can hardly be controlled by the use of high quantity of defoamer. Note that a limited amount of carbonate is often seen as a positive feature as it “chemically” grinds the rock during the reaction increasing the speed of reaction and preventing coating (Smith and Bourgot, 1991). A content of 3 to 5% of CO<sub>2</sub> is often appreciated in the rock even though it would result in higher sulphuric acid consumption.

## **Corrosion-Erosion**

Impurities contained in the phosphate rock have positive or negative impact on the corrosion of the stainless steel parts used in the process. Those increasing the corrosion or erosion are: F, Cl, S or S<sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, insoluble SiO<sub>2</sub> (erosion) and in some case ions (salts or complex) capable of oxidation - reduction reactions as Fe<sup>3+</sup>.

### **Impurities increasing the speed of corrosion-erosion**

In the reactor, the presence of chlorides can cause severe increase in corrosion rates, especially in the case of the high strength-high temperature processes. The chloride being increased “pro rata” to the P<sub>2</sub>O<sub>5</sub>, if this is linked with a higher operating temperature, the corrosion rate is greatly increased. PRAYON's PH range of processes have different operating parameters from the other High Strength processes, operating at a lower temperature in the second zone of the Hemihydrate Attack section, and as such are much less sensitive to the chloride level in the phosphate (Smith, 1991).

In the case of under vacuum concentration unit %P<sub>2</sub>O<sub>5</sub> and Cl content are not anymore linked. Independently of the Cl content in the weak acid the chlorine content in a 54% P<sub>2</sub>O<sub>5</sub> acid leaving the concentration is always between 150 and 300 ppm.

The corrosive effect of chloride is greatly reinforced by the sulphate and fluor content in the acid. F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions have a synergical effect on the corrosion and, for a given chlorine content, greatly increase the speed of corrosion of stainless steel alloys (Becker, 1997 and Becker, 1980)

Considering corrosion, three groups of phosphates, according to their chlorine content, can be defined: low, <300 ppm; medium, 300 to 700 ppm and high, > 700ppm (Schorr, 1993).

Stainless steel alloy withstand corrosion once they are passivated. The usual explanation of Passivity is that a thin protective film – either metal oxide or chemisorbed oxygen- forms on the surface of the metal, preventing further contact with the electrolyte (i.e. the phosphoric acid) (Anonymous, 1965). This layer can be destroyed in the presence of reducing substance.

Certain rocks contain pyrite which is converted to H<sub>2</sub>S, HS<sup>-</sup>, S<sub>2</sub><sup>-</sup> during the reaction. Some calcined rocks contain organics matter not fully oxidised during calcination. These reducing substances impair the corrosion resistance of the passive alloys utilised in phosphoric acid service. In some cases MnO is added to maintain the passive condition (Schorr, 1993). When Simplot went to calcined rock,( Bierman and Long, 1981) they had serious corrosion problems (due to the change of redox potential of the acid) which were initially resolved by the addition of MnO<sub>2</sub> and permanently by the aeration of the reactor generated by the foam breaker blades on the agitators.

If the SiO<sub>2</sub> source is from a solid insoluble in phosphoric acid, erosion can be observed. It is mostly observed once the insoluble silica level is high (Halaseh and Naber, 1996).

F<sup>-</sup> is also a very corrosive anion. Its corrosiveness is considered similar to the chlorine. Often it is “passivated” by reacting with silica or aluminium (either contain within the phosphate or add as an additive) and others forming much less aggressive complex ions.

### **Impurities decreasing the speed of corrosion-erosion**

All forms of SiO<sub>2</sub> are not equally soluble in the phosphoric acid (and thus able to react with F<sup>-</sup>): it depends on the mineralogical characterisation of the ore. Diatomite and kaolin are very soluble while olivine, or muscovite are almost insoluble in phosphoric acid (Smith, 1991).

Soluble SiO<sub>2</sub> has a very positive impact on the corrosion as it complexes free fluorine. The reaction products H<sub>2</sub>SiF<sub>6</sub>, a strong acid with medium corrosive capability (Smith, 1991; Halaseh and Naber, 1996). Besides silica, other elements such as Al, Mg can also form complexes with fluorine reducing its corrosive capacity. The fluorinated complexes produced are (AlF<sub>x</sub>) where x = 1 to 6 and MgF<sub>2</sub>.

Schorr (1993) has demonstrated the impact of the free fluorine on corrosiveness. He defined a fluorine complexing ratio :  $F / (SiO_2 + Al_2O_3 + MgO)$  and showed that the higher this ratio, the higher the corrosion speed.

### **Filtration**

The main impurities having an impact of filtration are silica, aluminium and fluorine. Depending upon its content and under which form it is found in the filtration section silica can have a positive or negative impact on the filtration. If the silica source is made of quartz or other insoluble salts in the phosphoric acid and if its particle size is quite small (less than 50 µm), it can impede the filtration requiring larger surface of filtration (Halaseh and Naber, 1996). If soluble, by reacting with the free fluorine it will impede the production of gypsum needles and promote formation of gypsum crystals, which are easy to filter (ratio length on width of the crystals close to 1, cluster).

Combined with F<sup>-</sup>, Na or K, silica can form fluosilicate salts scaling on filter cloth, pans and piping reducing the filtration rate. Chukrovite is a precipitate also commonly found that has similar scaling properties. Process parameters, mostly temperature can emphasis these scaling.

If it is linked with fluorine, aluminium improves filtration. It seems to form  $AlF_5^{2-}$  salts that are incorporated in the calcium sulphate crystal. This incorporation retards the growth of the crystal along the fast growing direction promoting the formation of crystal having a square or cluster shape, easier to filter (Martynowicz et al, 1996).

High aluminium containing rocks offer the best filtration rate. This filtration effect however depletes somewhere beyond 1.4%  $Al_2O_3$  content in rock (Becker, 1997). Considering several sedimentary phosphate, Becker (2001) shows that the increase of filtration rate due to the presence of Al is about 1 t  $P_2O_5/m^2/day$ .

Magnesium in phosphoric acid has a dual effect on the crystallisation, initially combining with the fluorine it improves crystallisation but above a certain threshold its effect in increasing the viscosity of the acid phase causes a rapid deterioration of the filtration rate. This value depends on the presence of other impurities but is of the order of 2-3% (Smith, 1991). With Florida rock, the presence of 1.2% MgO already decrease the filtration rate and the recovery. Once the content reach 1.83%, the reduction is very important (Leyshon, 2000).

Halaseh (1997 and 1998) defines a Fluorine Complexing Ratio as:

$$FCR = \frac{\frac{\%F}{19}}{\frac{\%Al_2O_3}{17} + \frac{\%SiO_2}{15}}$$

He has tested several phosphates of different FCR ratios. He observed that for FCR values between 1.378 and 0.42: as the ratio decreases filterability of the slurry increases, % $P_2O_5$  of the acid increases and corrosion decreases. For ratio lower than 0.42 filterability decrease due to the presence of un-dissolved silica salts and poor crystallisation.

Similar work was performed on Zin and Oron phosphates showing the positive impact of clay addition (Schorr, 1996).

Kruger and Fowles (1998) showed that Na and K has an effect on the supersaturation curve of calcium sulphate promoting the production of smaller crystals. On the other hand, they observe that if aluminium initially promotes crystals growth and thus filtration rate, brings also some disadvantages. At high aluminium to fluoride ratios, Al increases the acid viscosity and density and therefore has a detrimental effect on filtration at those levels. Concerning Mg, they observe that this element has little effect on the crystal morphology itself.

Organic matters present in the phosphate ore, those used for the beneficiation of the phosphate, those added to the reaction section as defoamers or crystal habit modifier, can also affect the gypsum crystallisation (Smith 1991, Theys and Roblin, 2002).

Rare earths in the slurry liquid phase above 0.18%, impair and also eliminate the advantageous effect of aluminium fluoride complex on crystallisation of calcium sulphate and consequently, deteriorate slurry filtration when using Kola rock (Halaseh and Naber, 1996).

In the case of igneous phosphate rock, potassium and iron seems to have a positive effect on the filtration of gypsum within a narrow range of concentrations (Kruger et al, 2000). This effect is not observed with Brazilian rock (Sinden, 2003).

## Phosphoric Acid Quality

Once the soluble impurities contained in the phosphate are found in the acid they will have an impact on the physico-chemical characteristics of the acid but also will influence the down stream production.

Main soluble impurities as MgO, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, CaO, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, SiF<sub>6</sub><sup>2-</sup> have an impact on the density and the viscosity of the acid. This effect can be forecast from analysis of the acid (Becker, 1997).

MgO is often found in the sedimentary rock as dolomite (Astley 2001). It increases the viscosity of the acid produced. Acids with a higher MgO content have often a lower P<sub>2</sub>O<sub>5</sub> in order to ensure the filterability of the slurry. The amount of gypsum solid present in the slurry is also lower to overcome this problem. For example if the high MgO Karatau phosphate is used, to ensure the production of phosphoric acid, reactor must run at 20-23%P<sub>2</sub>O<sub>5</sub> and at 90-95°C in order to reduce the viscosity (Halaseh and Naber, 1996).

If the rock contains a high quantity of carbonate and some organic matters, the acid produced can form foam (Halaseh and Naber, 1996). If these foams which appear in the flash cooling section they can be carried over to the condenser causing a pollution of the cooling water. This phenomenon can be reduced or avoided by the injection of a defoamer. Hemihydrate processes are more susceptible to foaming as they have a more viscous acid and thus need a higher defoamer addition rate.

If acid is being produced for animal feeds, such as dicalcium phosphate, low levels of fluorine must be obtained by defluorination. It is usually done by an addition of Silica to the acid in order to promote the stripping of SiF<sub>4</sub>. Nevertheless, if Al and Mg are present in the acid, they form stable complexes with the fluorine, SiF<sub>4</sub> formation will be reduced and defluorination will be more difficult or even impossible. It explains why when feed grade acid is produced an organic crystal habit modifier is preferred to clay.

Cadmium and other heavy metals can be an issue on the acid quality (Van Kauwenbergh 2002) when downstream production is considered. The main impact is the level of heavy metals in the fertiliser. Acid produced by the Hemihydrate route contains less Cd than by the Dihydrate route. The Cd cocrystallise in the calcium sulphate. This uptake of Cd by co-precipitation is even higher if anhydrite is considered.

Cd removal is possible by calcination of the phosphate, co-precipitation or ion exchange extraction. Davister (1992) did an evaluation of these routes and their respective cost.

Depending upon the P<sub>2</sub>O<sub>5</sub> content of the acid, several other salts beside calcium sulphate can precipitate in the acid. In the case of 27-30% P<sub>2</sub>O<sub>5</sub>, major co-precipitation examples are: fluosilicate of Na or K, fluo-aluminate (Ralstonite) [AlF<sub>6</sub>MgNa], Chukrovite [(SO<sub>4</sub>Ca)<sub>x</sub>(SiF<sub>6</sub>Ca)<sub>y</sub>(AlF<sub>6</sub>CaX)<sub>z</sub>12H<sub>2</sub>O]. During / after concentration the major precipitate are: X-compound [(Fe,Al)KH<sub>14</sub>(PO<sub>4</sub>)<sub>8</sub> 4H<sub>2</sub>O]; Mg<sub>3</sub>Al (SO<sub>4</sub>)<sub>2</sub>F nH<sub>2</sub>O, fluosilicate of Mg, Ca, Al and others (Becker, 1997).

Where acid must be shipped for international consumption, the acid must normally meet MGA (Merchant Grade Acid) specifications. The suspended solids content should be less than 1% on arrival. Florida acid, with its high Al<sub>2</sub>O<sub>3</sub> content, suffers post-precipitation during several weeks after concentration. A low Al<sub>2</sub>O<sub>3</sub> content in the acid simplifies the clarification process and reduces the inventory, as shorter retention times are required for ageing (Smith, 1991). Some igneous rocks suffer of the same post-precipitation problems. In the case of the expansion of Foskor plant in Richards Bay, large desupersaturation and settling tanks were installed for the merchant grade acid (Kirsten et al, 2002).

Acid can have a dark colour due to organic matters. Depending on the use of the acid, this colour has to be removed in some case. This removal can be done by the addition of c to adsorb the carbonaceous impurities followed by filtration (Schorr, 1993). Another option is to use active carbon or oxidising agents such as nitric acid,  $H_2O_2$ ...

$H_2S$  can cause health hazard if present in the acid. PCS Phos acid units operating on the calcined N.Carolina rock monitor the presence of  $H_2S$  on the filter (Sinden, 2003).

## Calcium Sulphate

Phosphogypsum can in some cases be used in the construction industry. The four main uses are:

- as a retarder in the production of cement
- for the production of wallboard/plasterboard
- for the production of gypsum blocks
- for the production of Stucco plaster

Depending each of the usage gypsum quality requirement varies. The main impurities that are considered are:  $P_2O_5$ , F, Cd (ppm),  $Na_2O$ , pH, organic matters, radioactive elements (Smith and Theys, 2000).

Even if the produced calcium sulphate is not used for other applications, its impurities content can have an impact on the Phosphoric acid production.  $Al_2O_3$  and  $Fe_2O_3$  form salts that contain  $P_2O_5$  (Halaseh and Naber, 1996). They thus increase the  $P_2O_5$  co-crystallised loss. In the case of aluminium this effect can mainly be observed with Hemihydrate process.

For Becker (1997), the major ions entering the calcium sulphate by co-precipitation are:  $HPO_4^-$ ,  $AlF_5^{2-}$ ,  $Cd^{++}$ , Rare earths and  $Y^{+++}$ . In the case of Cd, the portion of this ion that precipitates is a function of the calcium sulphate form. In the case of Dihydrate, about 20% of the Cd of the phosphate co-precipitates. This value increases to about 50% for Hemihydrate and 95% for Anhydrite. The Prayon phosphoric acid plant of Engis is a Central-Prayon Process (Dihydrate – Hemihydrate process) using mainly igneous rock. They observe that about 85% of the rock Cd is contained in the Hemihydrate leaving the filter.

In the case of Dihydrate processes, aluminium has a stabilising effect on the dihydrate phase. High Al containing rock (1-1.5%  $Al_2O_3$ ) can still operate within Dihydrate precipitation phase at temperature over 90°C and with a phosphoric acid concentration around 29%  $P_2O_5$  (Becker, 1997).

Considering the radioactive elements, about 80% of the Ra-226 follows the phosphogypsum, while about 86% of the U-238 and about 70% of the Th-232 are found in the phosphoric acid (figures vary with the process). Due to the chemical separation the radioactivity of phosphoric acid is significantly lower than that of the phosphogypsum (Anonymous, 2000). Radioactivity level of gypsum can be an issue especially if the gypsum is used undiluted for down stream application according to the radioactivity level of its phosphate source.

## Scaling

Silica in the acid is considered as a positive feature as it combines with fluorine reducing the corrosion potential of the acid, improving the slurry filterability and enhancing defluorination. Nevertheless, if in too high content (or the amount of fluorine too low) it can cause scaling problems in degassing ducts or cooling water systems (Anonymous, 2001). Indeed, silica reacts with fluorine to form  $\text{H}_2\text{SiF}_6$  that can evolve from the acid in the form of  $\text{SiF}_4$ . Once this product enters into and contacts with water it is solubilised and forms  $\text{H}_2\text{SiF}_6$  and  $\text{SiO}_2$  precipitates. In degassing ducts these silica solids can form very hard scaling especially if the condensation occur in a place where the temperature is above  $60^\circ\text{C}$ . Hemihydrate plants are especially susceptible to this phenomenon.

When this absorption is done by the condenser cooling water, depending on the quality of water, several types of scaling can be observed. If the water contains a high amount of Na or K (like in the case of sea water) fluosilicate scale will be form. They are essentially formed at the inlet of the condenser where the flow of water is high enough to bring the sodium and potassium ions and small enough to be under the solubility constant of fluosilicate salts. If process water is used silicate salts ( $\text{CaF}_2$  or fluosilicate) can be formed that can accumulate in the cooling towers. This point emphasises the interest in using Fluorine recovery tower in concentrations units to avoid the fluosilicate precipitation solids in the cooling system.

Some plants that use pond water containing Na or K to stack the gypsum face fluosilicate scaling in their return water piping system. These scaling are remove by swapping the slurry pipe and the return water pipe on a regular basis, the erosive effect of gypsum allows the removal of the scaling.

Fluosilicate salts of sodium and potassium can also lead to the formation of scaling in the filtration circuit. This is mainly due to the sudden cooling of the slurry during the filtration (Halaseh and Naber, 1996).

To slow down this problem table filters are fitted with hot and high pressure cloth wash and, sometime, a direct injection of steam on the filter cloth. In Prayon filter, the scaling are reduced by a fast separation of the gas and the liquids and the possibility to inject steam in the central valve to maintain the temperature in the filtration circuit. Moreover, the Prayon "Digestion" section design ensures that the slurry fed to the filter is fully de-supersaturated (Smith, 1991).

If the soluble SrO content exceeds 0.5% it can cause serious problems of scaling in concentration heat exchanger section (Halaseh and Naber, 1996). These scalings can hardly be removed by washing and needs mechanical cleaning to be removed. Prayon's plant in Engis had been confronted with that problem in the past. It was solved by using stainless steel pipe submerged in an acid bath, that scale from the outside of the tube and thus could easily be washed with high pressure water.

All the Brazilian igneous rocks contain significant levels of SrO, 0.5-1.1% but it is present in the form of the mineral celestite (the natural  $\text{SrSO}_4$ ). As this form is a highly insoluble mineral they do not face scaling problems.

One of the most surprising scales is chukrovite:  $(\text{SO}_4\text{Ca})_x(\text{SiF}_6\text{Ca})_y(\text{AlF}_6\text{CaX})_z \cdot 12\text{H}_2\text{O}$ . These crystal have the shape of a small double size pyramids (two pyramids on an common basis), which precipitates from filter grade acid while cooling but essentially clogging filter cloths (Becker, 1997).

Another crystal having a similar form is a solid having the composition:  $\text{Ca}_3\text{Al}_3(\text{RE})\text{SO}_4\text{F}_{13}$ . Where RE can be formed from rare earths or Yttrium. In some case  $\text{Al}^{+++}$  can be replaced by other cations as  $\text{Ca}^{2+}$  or  $\text{Si}^{4+}$  and  $\text{F}^-$  by  $\text{OH}^-$  (Robinson, 1978).



## Fertiliser Production

Depending upon the type of fertiliser produced, impurities can directly influence the quality of the product or the production itself. Hallsworth and Enriquez (1980) show the impact of the main impurities on the DAP quality.

MgO, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>, also called MER, affect (Palm 1986, Astley, 2001) the DAP grade by taking the place of H<sup>+</sup> ions thus reducing the room available for nitrogen or phosphate (if they are linked with other anions than PO<sub>4</sub><sup>3-</sup>). Moreover, MgO by its impact on the viscosity can increase the scaling speed of pipe reactor.

Although both R<sub>2</sub>O<sub>3</sub> and MER are used frequently they have little scientific value as they do not fully express the different effects of Al, Fe and MgO.

MER (minor element ratio) is defined by the formula :

$$\frac{\text{Iron + Aluminium + Magnesium}}{\text{P}_2\text{O}_5 \text{ in phosphate.}}$$

The higher the ratio, the higher the risk problems during the production of DAP. Astley (2001) considers that this ratio should be corrected depending upon the type of acid used. If 54%P<sub>2</sub>O<sub>5</sub> acid with low solids content is used to produce DAP, part of the iron is removed with the sludge, then the formula should be corrected.

The new formula becomes:

$$\frac{0.5 \text{ Iron+ Aluminium+ } 1.5 \text{ Magnesium}}{\text{P}_2\text{O}_5}$$

The higher ratio on the MgO showing its higher impact on the production of DAP is due to its total solubility and its low tendency to produce post-precipitate.

Iron produces phosphate salts that are citrate insoluble during the production of DAP (Lloyd, 1988). The iron salts can have the form of the X compound or a pseudomorphs of FeNH<sub>4</sub>(HPO<sub>4</sub>)<sub>2</sub>. Another compound that could be formed due to presence of impurities is MgAl(NH<sub>4</sub>)<sub>2</sub>H(PO<sub>4</sub>)<sub>2</sub>F<sub>2</sub>.

The iron phosphates are only citrate insoluble if they are kept at low Mole Ratios for significant time 10-20minutes at elevated temperatures. It has been possible to produce MAP/DAP and ASP with very low CI's using very contaminate acids (Sinden, 2003)

MAP, due to its lower ammoniation requirement, is less influenced by the presence of impurities in the acid. Al and Fe are considered as positive impurities in this production as it improve the mechanical resistance of granules (Brownlie, 1978). Sinden (2003), does not consider that iron has this positive effect. For him aluminium (with at least 0.2%) and MgO are the impurities improving the mechanical resistance.

Impurities content in the phosphoric acid used for the production of TSP can be an issue as they take the place of protons and reduce the water-soluble content of the phosphoric acid. Indeed, this lack of H<sup>+</sup> reduces the ability of the phosphoric acid to react with the phosphate rock (Sinden 1993). In some cases this problem can be overcome by adding some Sulphuric acid.

Phosphoric acid analysis is thus essential for the production of TSP. Sinden (1993) considers that a good TSP can be done with a "poor" phosphate provided that the purity of the acid is good enough. Beside iron and aluminium, MgO is also considered as a major impurity. These elements have an impact on the physical properties of the TSP.

A less known impurity known to have a negative impact on the production of TSP is Titanium. Some Brazilian rocks contain a high level of this element. It reacts with the phosphate to form a calcium-titanium phosphate salt lowering the water soluble  $P_2O_5$  content of the TSP (Sinden, 1993).

Cd and other heavy metals are becoming a quality concern in the fertiliser production. SSP only contains the Cd inherited from the phosphate, in DAP the Cd is included in the acid and in some case the sludge (containing a high content of Cd due to coprecipitation), MAP as it is often produced from sludge contains also a relatively high content of heavy metal, even higher than that in the DAP produced from the same acid. TSP has the Cd content of the acid and of the phosphate (Van Kauwenbergh, 1992).

Legal limitations on Cd in fertiliser start to appear. These limitations vary wildly from one country to the other and are subject to regular changes. European Community has not yet define a legal limit. Belgium and Luxembourg voluntarily limit the Cd content in fertiliser to 90 mg Cd/kg  $P_2O_5$ . In California (Anonymous, 2001), the limit will be reduced to 400 mg / kg  $P_2O_5$  on Jan.1, 2004 ! Indeed, a recent report (Anonymous, 1999) on fertiliser risk assessment shows that Cd is not an health issue in fertiliser.

Besides Cd, almost all the impurities contained in the fertiliser have greater or less impact on the health and / or the environment. Dylevskaya (2002) as well as Kiiski and Milbone (2003) lists the main one as well as their potential negative impacts.

Depending upon the content of radioactive elements in the fertiliser, radioactive element as Rd,  $U_3O_8$ ,  $K_4O$ , Th could be regulated in the future (van der Westhuizen 2002). In 2000, under the EU legislation, none of the phosphoric acid or phosphate in the world will see their commercialisation restricted by their radioactivity (Anonymous, 2000).

Organic matters contain in the acid or the phosphate can cause odour problems during the production of fertilisers. These odours are mainly due to the Mercaptan (MSH where M is an organic molecule) evolving. They can be strongly reduced by an addition of an oxidising (as NaClO) in the scrubbing system.

## **Conclusion**

Considering their impact on the process, the product qualities, their interaction between them, impurities contained in the phosphate can be considered either as positive or negative factors.

It is thus always a difficult task to evaluate a phosphate rock and to define its implication on the process. One can then understand why phosphoric acid and fertilizer productions have always been considered more as an art than a science.

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Overview charts

Impurities	Process choice	Corrosion	Filtration	Acid quality	Gypsum quality	Scaling	Fertiliser production
CO <sub>2</sub>	Produces slurry carry over if phosphate reacts with sulphuric acid in a vacuum chamber.						
Lanthanide	Impedes the conversion of Hemihydrate to dihydrate.		Decreases filterability.		Rehydration of Hemihydrate to Dihydrate is longer.	Causes scaling	
MgO		Reduces corrosion (complex with F)	Low content: improves filterability by complexing with F. High content decreases filterability (viscosity increase).	Increases viscosity and density of the acid. Keeps F in the acid. Can cause post precipitation.			Impact on DAP and TSP capacity and quality.
Cd	Anhydrite or Hemihydrate crystallisation to remove Cd from acid.			Quality issue in some countries	Quality issue in some countries if gypsum is sold.		Quality issue in some countries.
Al <sub>2</sub> O <sub>3</sub>	Impedes Hemihydrate to Dihydrate conversion.	Reduces corrosion (complex with F).	Low content: improves filterability. Very high content: decreases filterability (viscosity increases).	Increases viscosity and density of the acid. Retains F in the acid. Can cause post precipitation	Stabilises Dihydrate. Form Phosphate salt that co-precipitate in the calcium sulphate.	Causes scaling (Chukrovite and others).	Content should be limited if DAP and TSP are produced. Positive impact on MAP production.

Impurities	Process choice	Corrosion	Filtration	Acid quality	Gypsum quality	Scaling	Fertiliser production
Fe <sub>2</sub> O <sub>3</sub>		Neutral or negative (depending oxydation stage).	Can improve filterability	Increases viscosity and density of the acid. Can cause post precipitation.			Content should be limited if DAP or TSP is produced. Positive impact on MAP production.
Na <sub>2</sub> O			Fluosilicate scaling reduces filterability and promote small crystal (negative impac.t on filtration)	Increases viscosity and density of the acid. Cause post precipitation.	Quality issue if gypsum is sold for plaster.	Causes fluosilicate scaling.	
K <sub>2</sub> O			Can improve filterability but considered having a negative impact due to Fluosilicate scaling and promotion of small crystals	Increases viscosity and density of the acid Can cause post precipitation		Causes fluosilicate scaling.	
SrO	Impede conversion of HH to DH					Hard scaling on heating elements.	
F		Increases corrosion speed.	Free F decreases filterability because elongated gypsum crystal.	H <sub>2</sub> SiF <sub>6</sub> increases viscosity and density of the acid. Can cause post precipitation.	Quality issue if gypsum is sold	Causes fluosilicate and chucrovite scaling.	
Cl		Increases corrosion speed.					
SO <sub>4</sub> <sup>2-</sup>		Increases corrosion speed – synergy with Cl.		Increases viscosity and density of the acid		Form calcium sulphate and Chucrovite scalings.	
S <sup>2-</sup>		Increases corrosion speed.		Health hazard (H <sub>2</sub> S)			

<b>Impurities</b>	<b>Process choice</b>	<b>Corrosion</b>	<b>Filtration</b>	<b>Acid quality</b>	<b>Gypsum quality</b>	<b>Scaling</b>	<b>Fertiliser production</b>
SiO <sub>2</sub>		If insoluble: increases erosion speed. If soluble: reduces corrosion (complex with F).	If insoluble: decreases filterability. If soluble: improves filterability.			Cause fluosilicate scaling.	
Organic matters			Depending their composition, filterability can be increased or decreased.	Produce foam. Colour the acid.	Quality issue if gypsum is sold.		Odour
Radioactive elements				Potential environmental and health problems.	Potential environmental and health problems. Quality issue if gypsum is sold.	Potential environmental and health problems.	Potential environmental and health problems.
TiO <sub>2</sub>							Impact on DAP quality.

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