# Chapter 3 Background on the aspects of treatment of phosphogypsum

## 3.1 Impurities in phosphogypsum

The amounts of impurities in phosphogypsum depend upon the purity of the raw materials used, the operating conditions of the phosphoric acid process, and the age of the stockpile (Salyak, 1988). Classification of phosphogypsums from plant to plant is difficult due to variation in raw material, the fluctuation in the climatic conditions under which they are stored, and the operating conditions of the process ($H_2SO_4$ concentration, acidulation temperature, oxidation conditions, amount of $H_2SO_4$) (Gadalla *et al*, 1987).

To be able to use phosphogypsum for the control of cement hydration, it must first be purified of harmful impurities. These impurities can be classified into two groups, which are (1) free phosphoric acid, phosphates, sodium hexafluorosilicate, sodium sulphate, fluorosilicic acid and organic compounds that adhere to the surface of the gypsum crystals, and (2) dicalcium phosphate, monosodium phosphate and fluorophosphates that substitute in the crystal lattice of gypsum (Ölmez and Erdem, 1989; Wirsching, 1982). Unless neutralized, the impurities contained in phosphogypsum exist in acidic form (Mehta and Brady, 1977).

## 3.2 The influence of phosphogypsum impurities on the mechanical strength and hydration of Portland cement

Tabikh and Miller (1971) stated that the chemical process employed in the production of phosphogypsum yields a product of widely varying impurity concentrations. Presence of large amounts of impurities interfere in an unpredictable way with the hydration of Portland cement.

Saltgitter Industriebau GmbH (1979) reported that the soluble impurities contained in phosphogypsum react with the free CaO in the cement, and form an insoluble precipitate which settles on the cement particles. This coating process then restricts the hydration of the cement, with a resulting delay of the setting time.

Murakami (1968) found that the impurities in phosphogypsum increased the setting time of Portland cement, but not the mechanical strength at any stage. Singh *et al.* (1993) have shown that the mechanical strength of cement is considerably reduced at all ages on using unprocessed phosphogypsum in place of natural gypsum. They both argued that the impurities in phosphogypsum delayed the hydration of tricalcium silicate, which is the main compound in Portland cement. Water-soluble impurities of phosphogypsum gradually enter the aqueous phase of the cement paste, and deposition of a protective coating occurs on the surface of the cement particle. This deposition leads to subsequent suppression of cement hydration. When processed phosphogypsum was used, the compressive strength was improved as a result of the removal of impurities.

Murakami (1968), Singh (1987), as well as Tabikh and Miller (1971) proposed the following mechanisms for the action of some impurities in the hydrating phase:

1. The region of the paste in the immediate vicinity of hydrating particles is very alkaline. Neutralization of phosphatic and fluoride species results in the deposition of basic insoluble tricalcium phosphate and calcium fluoride on the surface of cement grains which provides a protective layer against the attack of water. The formation of this protective layer ($Ca_3(PO_4)_2$ and $CaF_2$) can be shown by the following reaction equations:

$$H_2P_2O_7^{2-} + 4OH^- \rightarrow 2PO_4^{3-} + 3H_2O$$
$$2PO_4^{3-} + 3Ca^{2+} \rightarrow Ca_3(PO_4)_2 \text{ (tricalcium phosphate)}$$

and

$$SiF_6^{2-} + 6OH^- \rightarrow SiO_3^{2-} + 6F^- + 3H_2O$$
$$2F^- + 3Ca^{2+} \rightarrow 3CaF_2 \text{ (calcium fluoride)}$$

2. The action of species such as $Na_2SiF_6$ or $CaH_2P_2O_7$ takes place through two different retarding mechanisms, namely
   (a) simple depositional covering of the hydrating cement particles, or
   (b) the ability of these species to serve as "bridges" or "cross-linking agents" between hydrating cement grains, involving chemical bonding through *Si-O-Si* or *Si-O-P-O-Si* linkages. These structures form more rigid and ordered protective coatings than a simple deposition.

3. The action of lattice-substituted impurities is believed to be due to the slow release of these impurities during dissolution of gypsum, resulting in a more efficient dispersion of the protective material throughout the system.

Bensted (1995) found that when natural gypsum is replaced with by-product gypsums in Portland cement, the amount of ettringite that forms at the beginning of hydration is increased. The alite ($C_3S$) hydration is retarded at first, giving less C-S-H development initially, allowing extra space for the aluminate ($C_3A$) and ferrite ($C_4AF$) to hydrate in and hence apparently to accelerate the initial formation of ettringite. Water-soluble phosphate and fluoride play a significant role in retarding the onset of setting.

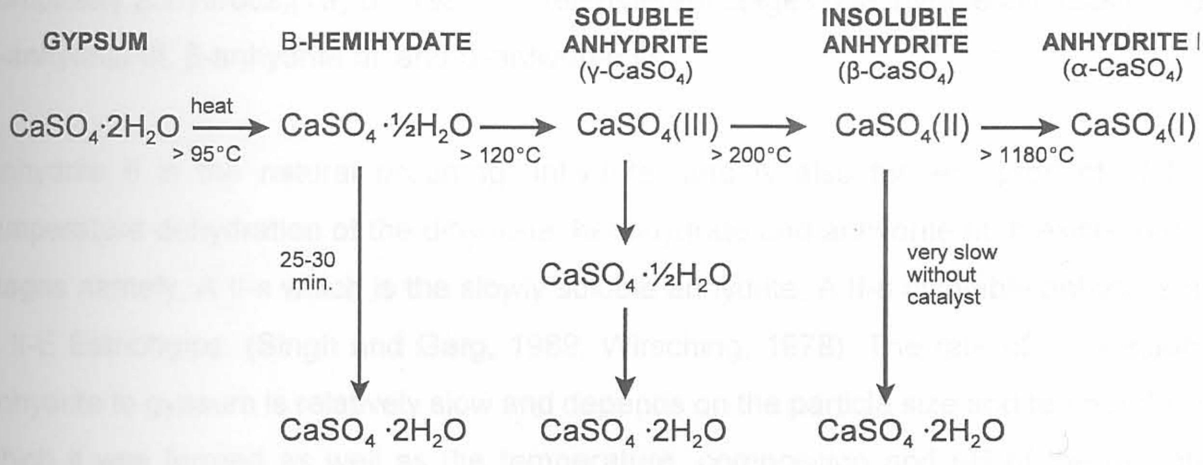
A possible solution was offered by Mehta and Brady (1977), who reported that when phosphogypsum was added to the cement plant raw mix in the range of 2% $SO_3$, the clinkering temperature was reduced, the retarding effect was reduced and there was an increase in the early strengths. When added in this way, the phosphogypsum acted as both a mineralizer for clinker and a set retarder for cement made from this clinker.

## 3.3 Phases of the calcium sulphate/water system

### 3.3.1 Description of the different phases

The $CaSO_4/H_2O$ system consists of five phases, of which four can exist under normal conditions. These phases are calcium sulphate dihydrate ($CaSO_4.2H_2O$), calcium sulphate hemihydrate ($CaSO_4.½H_2O$), anhydrite III (γ-$CaSO_4$), anhydrite II (β-$CaSO_4$) and anhydrite I (α-$CaSO_4$). Anhydrite I only exists at temperatures above 1180 °C. An overview of these phases is presented in Figure 3.1.

**Figure 3.1 The different phases of the calcium sulphate/water system (Bensted, 1995; Luckevich, 2000)**



Calcium sulphate dihydrate is both the starting material for dehydration and the end product of rehydration. It occurs naturally as the mineral gypsum, and is the most common sulphate mineral (Hand, 1997).

Calcium sulphate hemihydrate exists in two forms, termed α and β. These two forms of hemihydrate are the two limiting states of this phase, and are distinguished from each other by their properties, energy relationships and methods of preparation. The α-hemihydrate is produced under pressure in a humid atmosphere and consists of compact, well-formed, mostly transparent, large primary particles (Wirsching, 1978). When the hemihydrate is produced at atmospheric pressure, the water of crystallization is driven off as steam, which causes a disruption in the crystal structure to form the fragmentary crystals of β-hemihydrate (Coburn *et al.*, 1989). β-Hemihydrate forms flaky, irregular secondary particles which consist of extremely small individual crystals.

The α-hemihydrate has a lower water demand on hydration, and this then leads to a stronger hydrated product than the β-hemihydrate. The only reliable method for determining which of these hemihydrates are present is by differential scanning calorimetry, as the two hemihydrates produce qualitatively different traces on heating (Hand, 1997).

The anhydrite III form is also called soluble anhydrite (Wirsching, 1978). Soluble anhydrite has essentially the same crystal structure as hemi-hydrate and readily absorbs water to rehydrate to the hemihydrate form. This form of calcium sulphate is probably never completely anhydrous (Taylor, 1997). Three different stages of anhydrite III exists namely, β-anhydrite III, β-anhydrite III' and α-anhydrite III.

Anhydrite II is the natural occurring anhydrite, and is also the end-product of high-temperature dehydration of the dihydrate, hemihydrate and anhydrite III. It exists in three stages namely, A II-s which is the slowly soluble anhydrite, A II-u insoluble anhydrite and A II-E Estrichgips. (Singh and Garg, 1989; Wirsching, 1978). The rate of conversion of anhydrite to gypsum is relatively slow and depends on the particle size and temperature at which it was formed as well as the temperature, composition and pH of the hydration solution. Table 3.1 describes some of the physical properties of the phases of the $CaSO_4/H_2O$ system.

**Table 3.1** Physical properties of the phases of the $CaSO_4/H_2O$ system (Wirsching, 1978)

| Phase | $CaSO_4.2H_2O$ | $CaSO_4.\frac{1}{2}H_2O$ | | $CaSO_4$ III | $CaSO_4$ II | $CaSO_4$ I |
|---|---|---|---|---|---|---|
| 1. Features | | 2 Forms:<br>α-Form | β-Form | 3 stages:<br>β-Anhydrite III<br>β-Anhydrite III'<br>α-Anhydrite III | 3 stages of reaction of calcined anhydrite II:<br>A II-s :slowly soluble<br>A II-u :insoluble<br>A II-E :Estrichgips | |
| 2. Water of crystallization (% weight) | 20.92 | 6.21 | 6.21 | 0.00 | 0.00 | 0.00 |
| 3. Density (g/cm$^3$) | 2.31 | 2.619 - 2.637 | 2.757 | 2.580 | 2.93 - 2.97 | |
| 4. Lattice structure | Monoclinic | rhombohedral | | hexagonal | rhombic | cubic |
| 5. Solubility in water at 20°C (g/100 g solution) | 0.21 | 0.88 | 0.67 | 0.67-0.88 | 0.27 | insoluble |
| 6. Thermodynamic stability (°C) | <40 | metastable | | metastable | 40 - 1180 | >1180 |
| 7. Production temperature in laboratory (°C) | <40 | 45 - 200<br>in dry air | >45<br>aqueous medium | 50 Vacuum: α- and β-A III<br>100 Air: α- and β-A III<br>100 dry: β-A III' | 200 - 1180 | >1180<br>not stable below |
| 8. Production temperature in industry (°C) | <40 | 120 - 180<br>(dry) | 80 - 180<br>(wet) | 290 (dry) β-A III<br>290 (dry) β-A III'<br>110 (wet) α-A III | between 300 - 900:<br><500: A II-s<br>500 - 700: A II-u<br>>700: A II-E | - |

### 3.3.2 Dehydration, rehydration and crystal structure contributions

Calcium sulphate dihydrate forms a layered lattice, with the water of crystallization arranged between the layers. It may therefore be split easily along the water layers. During its conversion to the hemihydrate, the lattice volume shrinks, and broad channels parallel to the $CaSO_4$ chains are formed in which the water of crystallization of the hemihydrate is loosely bound at definite points. The water can enter and leave relatively easily, which is demonstrated by the ready conversion into anhydrite III in which these channels are free of water. Anhydrite II exhibits a more dense packing of ions and only reacts slowly with water, which explains why it has the highest solubility of the calcium sulphates (Wirsching, 1978).

## 3.4 Influence of the different phases of the calcium sulphate/water system on the properties of Portland cement

During the early and middle periods of reaction in a cement paste, calcium sulphate dissolves and reacts at the surfaces of the cement grains. The factor most directly influencing the course of these reactions is not so much the amount of calcium sulphate available, but the rates at which the relevant ionic species are made available at the surface of the cement grains. The rates at which $Ca^{2+}$ and $SO_4^{2-}$ ions are supplied by the calcium sulphate thus depend on both the amount of calcium sulphate and on its physical and chemical nature. Hemihydrate supplies ions more quickly than gypsum, which in turn supplies them more quickly than insoluble anhydrite (Taylor, 1997). Therefore, the calcium sulphate phases present in the Portland cement mixture will affect the setting time of the cement considerably due to its difference in solubility.

The heat produced on grinding can cause partial conversion of the gypsum into hemihydrate ($CaSO_4.½H_2O$) or γ-$CaSO_4$. The extent to which calcium sulphate dihydrate is dehydrated in a cement mill depends on the temperature and relative humidity existing in it. The conversions affect the rate at which the calcium sulphate dissolves on hydration. Partial conversion to hemihydrate may be desirable, as the water present in gypsum can cause the particles of cement to adhere during storage, with subsequent formation of lumps (Bye, 1999; Taylor, 1997).

The calcium sulphate hemihydrate formed does not have the precise composition implied by its name because compositions covering the range $CaSO_4.0.01 - 0.63H_2O$ are obtained. The name soluble anhydrite is sometimes used for the lower end of the range. These compositions can be interconverted simply by a change in relative humidity or temperature since water molecules can enter or leave the porous structure. In contrast, conversion to calcium sulphate dihydrate involves its dissolution in water from which the dihydrate crystallises as the stable phase at temperatures below approximately 43°C (Bye, 1999).

Hewlett (1998b) reported that at grinding temperatures between 115°C and 130°C, the dihydrate form can dehydrate to the hemihydrate form and to a lesser extend to calcium sulphate anhydrite. These calcium sulphate forms produce a supersaturated solution with regard to the dihydrate form upon mixing with water. This leads to gypsum precipitation and stiffening of the cement or mortar, making it necessary to add more water for workability, which results in a lowering of strength properties. This process is referred to as "False set". The ratios between the different calcium sulphate forms are thus crucial for the cement industry.

The percentages of the dihydrate, hemihydrate and anhydrite forms of calcium sulphate in the gypsum samples can vary significantly among different gypsum types, especially for phosphogypsum originating from different process routes, plants and operating conditions. These percentages can influence the dehydration behaviour of the gypsums. It is necessary to study the dehydration behaviour of each material used in industry separately to obtain an indication of the dihydrate composition of a gypsum in a milled cement sample, as it would have a major effect on the setting behaviour of cement (Strydom and Potgieter, 1999).

## 3.5 Existing treatment methods of phosphogypsum

Several methods have been proposed or adopted for minimizing the effects of impurities in phosphogypsum. Many of these methods have in common a step of rendering soluble, acidic materials insoluble and alkaline.

Suitable and technically applied methods of processing phosphogypsum had been developed in Japan in 1940 and in Germany in 1960. All other processes designed for the use of phosphogypsum failed technically and resulted in their plants having to close down after a short operation period (Wirsching, 1982).

The wet purification units for by-product gypsum consist mostly of slurry containers, flotation machines, hydrocyclones, and filter or centrifuge installations. Investment and expenditure on purification can vary according to the resulting utilisation of the product (Wirsching, 1978).

### 3.5.1 Thermal and washing treatments

Treatment of phosphogypsum with lime water or aqueous cement extracts, converts phosphates into $Ca_3(PO_4)_2$ and complex fluoranions into $CaF_2$ and insoluble silicates and aluminates. These insoluble impurities have smaller effects on the setting behaviour of cement. Another method, which also involves reduction of acidity, involves heating of the unprocessed phosphogypsum with limestone, lime, or cement at 700 - 800 °C. The gypsum is then converted to anhydrite, and the impurities are simultaneously converted to insoluble compounds. Simple washing with water can be effective in dissolving surface absorbed water-soluble impurities, but still leaves the lattice-substituted impurities behind (Tabikh and Miller, 1971).

Ölmez and Erdem (1989) as well as Erdogan *et al.* (1994) investigated the effect of washing of phosphogypsum with water and milk of lime, with and without preceding thermal treatment. They both reported that the untreated phosphogypsum retarded the setting times of Portland cement and also reduced strength, but can be used to control the hydration of Portland cement if washed with milk of lime.

Smadi *et al.* (1999) obtained a better quality of phosphogypsum by calcining washed and unwashed phosphogypsum at temperatures between 170 and 950°C. The treated phosphogypsum samples were used in replacing cement in mortar mixes, and have shown an improvement in mechanical properties compared to the mortars containing untreated phosphogypsum.

### 3.5.2 Acid treatment

Impurities incorporated isomorphically into the gypsum crystal lattice, mainly phosphates, cause lime sensitivity in calcined cement products, with a considerable effect on the setting time. They are not removed by flotation and washing but can be precipitated and rendered harmless by dehydration and recrystallization. They may go into solution during hydrothermal recrystallization if their affinity for the hemihydrate is less than for the dihydrate (Wirsching, 1978).

Jarosiński (1994) treated phosphogypsum in sulphuric acid solutions to purify and convert it into anhydrite II. By applying this method, they could reduce the impurities in phosphogypsum to the level below the requirements for use in anhydrite cement.

### 3.5.3 Treatment with ammonium hydroxide solutions

When phosphatic and fluoride compounds are dissolved in an ammonium hydroxide solution, the solubilities of these compounds increase with an increase in the ammonium hydroxide concentration (Singh *et al.*, 1993). This led to the conclusion that the phosphorous impurities present in phosphogypsum, will combine with the ammonium hydroxide to form water-soluble mono-ammonium phosphate and di-ammonium phosphatic compounds:

$$Ca(H_2PO_4)_2.2H_2O\ (s) + NH_4OH\ (aq) \rightarrow CaHPO_4.2H_2O\ (s) + \underset{\text{mono-ammonium phosphate}}{NH_4H_2PO_4\ (aq)} + H_2O\ (\ell)$$

$3\,CaHPO_4.2H_2O\,(s) + 2\,NH_4OH\,(aq) \rightarrow Ca_3(PO_4)_2.2H_2O\,(s) + (NH_4)_2HPO_4\,(aq) + 6\,H_2O\,(\ell)$

di-ammonium phosphate

$Ca_3(PO_4)_2.2H_2O\,(s) + 2NH_4OH\,(aq) \rightarrow 3Ca(OH)_2\,(s) + NH_4H_2PO_4\,(aq)$

mono-ammonium phosphate

Similarly, fluorides present in phosphogypsum will form water-soluble ammoniated compounds .

This method was found to be successful in reducing the impurities contained in Indian phosphogypsum, by treating the phosphogypsum with 10-20% aqueous ammonium hydroxide and subsequent washing of water. This purified gypsum was suitable for use in cement manufacture, and the cement produced had properties similar to cement containing natural gypsum.

### 3.5.4 Wet sieving

Singh *et al.* (1996) adopted a method which consists of wet sieving the sample through a 300 µm sieve. The results have shown that the amount impurities were significantly reduced in the finer fraction that passed through the sieve, as against to the coarser fraction (10-15% of the sample) that retained over the sieve. The amount of phosphorous impurities contained in the phosphogypsum sample was reduced from 1.28% before sieving, to 0.41% in the finer fraction after sieving.

Al-Jabbari *et al.* (1988) washed the phosphogypsum with water using a 100 µm sieve. They then burned the phosphogypsum and added accelerators (for example calcium hydroxide) to the calcined phosphogypsum in order to improve the setting time and compressive strength of the produced material. The purified phosphogypsum was chemically analysed, and the results indicated that the best and cheapest method of purification was through washing with water using a 100 µm sieve followed by neutralization with calcium hydroxide.