Calcium Sulfate Transitions in Superphosphate

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Thermodynamic equilibrium curves are given for the system calcium sulfate–phosphoric acid–water. Applicability to the liquid phase in superphosphate is discussed. Based on this the calcium sulfate transitions in superphosphate are explained in agreement with several observations.

THE OLD LITERATURE on calcium sulfate and its crystal forms is highly confusing. To explain existing data, several varieties of dihydrate, semihydrate, and anhydrite were postulated. The excellent work by Kelley, Southard, and Anderson (3) has, however, made things clear. Obscurities in nomenclature are elucidated by using the system suggested by Kruis and Späth (4).

In the calcium sulfate–phosphoric acid–water system, only three crystal forms of calcium sulfate can exist: dihydrate, α-semihydrate,* and anhydrite II. The asterisk indicates an over-stoichiometric crystal water content. Kelley, Southard, and Anderson (3) have given equations for the temperature dependence of the free energy for all real and hypothetical reactions in the calcium sulfate–water system. When the activity of water differs from unity, as in electrolyte solutions, an additional term, $nRT \times \ln a$, must be inserted, where:

n = moles of water in the reaction formula

R = general gas constant

T = temperature, °K.

a = activity of water in the solution

For zero free energy, equilibrium conditions between the two modifications of calcium sulfate in the reaction formula are obtained, the transition temperature being a function of water activity. By combining this finding with water vapor pressure data of phosphoric acid solutions (7), the thermodynamic equilibrium curves for the transitions dihydrate–anhydrite II and dihydrate–α-semihydrate* as a function of acid concentration have been obtained (Figure 1). For the metastable equilibrium dihydrate–α-semihydrate,* curves are also obtained from solubility measurements by Taperova and Shul'gina (7, 8) and from direct observations in wet process phosphoric acid by Hultbom and Lehrecke (5). Agreement is good except for low concentrations, where Hultbom and Lehrecke extrapolated their curve to a transition temperature of 107°C. in pure water, and which today is known to be incorrect. The other thermodynamic curve shows the stable equilibrium dihydrate–anhydrite II.

The transitions of calcium sulfate that

Figure 1. The transitions dihydrate-α-semihydrate and dihydrate-anhydrite II in phosphoric acid solutions
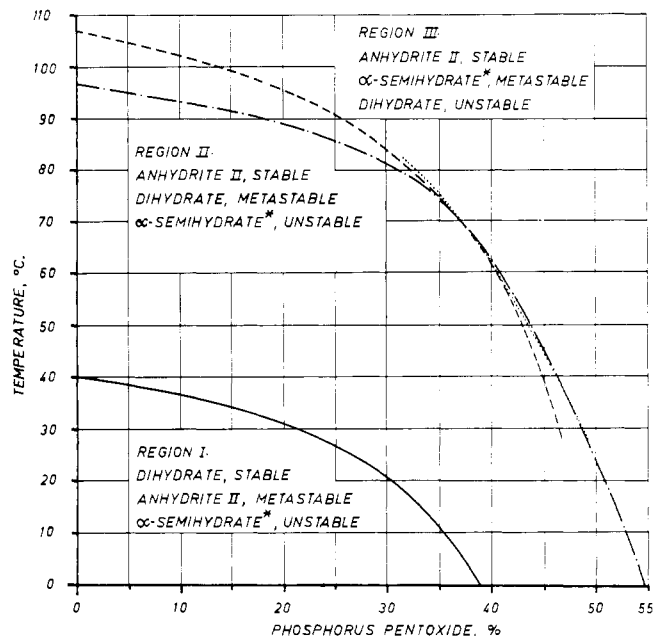
occur in superphosphate are of particular interest, as they explain several observation data and, partly, the caking of granulated material during storage. A superphosphate consists mainly of monocalcium phosphate and calcium sulfate as solid phases and a rather high concentration of phosphoric acid as the liquid phase.

When calculating their thermodynamic relations, Kelley, Southard, and Anderson (3) neglected the influence of dissolved calcium sulfate on water vapor pressure because of its low solubility. The solubility measurements by Taperova and Shul'gina (7, 8) show that the solubility of calcium sulfates increases up to about 15 to 20% phosphorus pentoxide and then decreases. At 40 to 45% phosphorus pentoxide it will be about the same as in pure water. The influence of dissolved calcium sulfate on the water vapor pressure at phosphorus pentoxide concentrations in the liquid phase of a normal superphosphate might be neglected. The solubility diagram of the calcium oxide–water–phosphorus pentoxide system (9) shows that for a normal concentration of phosphorus pentoxide in the liquid phase of superphosphate and at the corresponding temperature range

for the equilibrium dihydrate–α-semihydrate,* the liquid phase may not contain more than 4% calcium oxide. A comparison between vapor pressure data of the previously mentioned system (2) at 25°C. and of the pure phosphoric acid solution (7) with the same phosphorus pentoxide content gives a corresponding decrease in water activity of about 0.015 to 0.020. Information at higher temperatures is not available. Furthermore, the presence of sulfate will be influential. However, the decrease in the equilibrium temperature caused by monocalcium phosphate is estimated to be 4° to 5°C., within the actual range.

In the liquid phase of a superphosphate other ions from impurities are to be considered. There is no information on their influence on water vapor pressure. However, the equilibrium diagram given here is applicable to a qualitative discussion of the transitions in superphosphate. It will be applicable more quantitatively to wet process acids, where impurities have less influence.

The first part of the acidulation of a phosphate rock takes place within region III, Figure 1. Some formation of α-semihydrate* simultaneously as anhydrite II is therefore possible during the re-

action in the den and the first part of the maturing period. Later, during maturing in the piles the temperature decreases, and the system is moving into region II, where the semihydrate can convert into dihydrate, if the supersaturation is high enough for dihydrate nucleation. Within those two regions there is a trend of semihydrate and dihydrate conversion into anhydrite II, but without high temperatures, as in the first part of the reaction in the den, this is known as an extremely slow process.

A matured and bagged superphosphate with a normal moisture content has a temperature and acid concentration in the liquid phase that correspond to region I, where anhydrite may go into solution and crystallize as dihydrate. This can proceed until so much water has been removed from the liquid phase that,

because of the corresponding increase in acid concentration, the equilibrium curve is reached.

With extra hard drying all semihydrate probably converts into anhydrite II. Therefore in region II nothing can happen and the acid concentration in the liquid phase of the superphosphate will be so high that region I may not be reached. The above is in good agreement with several observations reported by Scheel (6) and the remedies recommended to prevent caking of the superphosphate.

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FERTILIZER QUALITY CONTROL

Fertilizer Sampling to Protect Consumers and Producers

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Methods are given for devising fertilizer sampling plans which manufacturers can use for assessing the quality of their products with confidence, or on which government regulations can be based. The sampling plans use defined consumer's and producer's risks to avoid the false information that single snap samples usually give. The methods can be applied to other chemicals which require costly chemical analyses.

THE SOUTH AFRICAN Department of Agricultural Technical Services is revising its regulations which control the qualities of fertilizers and fertilizer mixtures that may be sold to consumers. The regulations will be based on an acceptance sampling plan which recognizes that fertilizers cannot be produced without some unavoidable variation in quality. Hence, whenever a fertilizer is sampled by a government inspector, a number of samples instead of one snap sample will be taken. By this means the true quality of the material sampled will be realistically estimated. However, there remains the possibility that a bad estimate may be obtained by chance. Thus producers run a risk of being penalized although their fertilizers are of good quality and consumers run a risk of accepting poor quality material. The sampling plan envisaged in South Africa is based on defined small producer's and consumer's risks.

This paper discusses not the particular plan adopted in South Africa, but general sampling plans for fertilizers. With the formulas provided it is possible

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to devise plans to suit particular needs and purposes.

The first part of the discussion introduces the concept of defined risks. This may be tediously obvious to many, but it has been included because a sampling plan cannot efficiently be used without fully understanding its principles and operation. The second part shows how to devise a sampling plan for accepting or rejecting a particular batch of fertilizer. The third part shows how to devise a sampling plant to judge the performances of fertilizer producers over a period of time.

The Concept of Defined Risks

Variation in Fertilizer Quality. Consider the chemical analyses of single samples taken from consecutive batches of superphosphate produced by a hypothetical manufacturer. If the phosphate content is plotted against the order in which the batches were made, a diagram such as Figure 1 will be obtained.

Figure 1 shows that variation has occurred, and it must be admitted that a certain amount of variation is unavoidable. In fact, to produce absolutely

uniform material would require absolute control of all variables, including the quality of the raw materials used. Such perfect control is impossible.

In the absence of perfect control, some variation must be accepted. The degree of variation can be reduced with better quality control of manufacture, but an irreducible amount of variation remains.

Representation of Variation by Distribution Curves. Figure 1 helps to view as a whole the variation in quality of the superphosphate. It shows that although the average phosphate content is 19.0% P_2O_5, about half the points fall below this value.

The data can be summarized in a more useful way. If the graph in Figure 1 is turned on end, the % P_2O_5 scale can be divided into classes, or intervals, and the number of points falling into each class can be counted. The percentage frequency with which the points fall into each class can be calculated and the histogram shown in Figure 2 can be constructed.

This histogram is only an approximate representation of the true variation in the superphosphate, because only single samples were taken from each batch.