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Kinetics and thermodynamics of the attack of a phosphate ore by acid solutions at different temperatures

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ABSTRACT

A calorimetric study of the kinetics and thermodynamics of the attack of a phosphate ore from Gafsa region (Tunisia) by phosphoric acid and by a mixture of phosphoric acid and sulfuric acids is undertaken at different temperatures. Two samples of the same ore having different grain size have been used. At 25 °C, the dissolution enthalpy in phosphoric acid solution equals -233.6 ± 2.2 J/g for both of the samples. Attack by the mixture of acids is strongly dependent on the solid granulometry. Interpretation of the calorimetric results by Avrami model shows the existence of three domains attributed to phosphate ore dissolution/$H_2PO_4^-$ neutralisation, hemihydrate (HH) precipitation and hemihydrate/dihydrate (DH) transformation. The attack by the acid mixture was performed at higher temperatures and showed in addition the transitional formation of the anhydrous sulfate (AH) at $T \geq 55$ °C, which transforms into dihydrate after the HH/DH transformation.

1. Introduction

Phosphate fertilizers are produced from phosphate ore. Attack of natural phosphate ores by sulfuric and/or phosphoric acid solution is the basic process for producing phosphoric acid and inorganic phosphorus fertilizers, such as superphosphate. In the wet production process, the raw phosphate ore is converted into phosphoric acid and calcium sulfate by adding solutions of sulfuric and phosphoric acid in the reactor [1]. These acids are introduced simultaneously or successively [2]. In the latter case two processes occur which are dissolution of the ore and precipitation of calcium sulfate [3].

Several kinetic and thermodynamic studies have proposed mechanisms for the digestion of phosphates in either phosphoric or sulfuric acid [3–16]. But only Dorozhkin [11] has studied the dissolution of a natural fluorapatite in a mixture of these acids. Recently Abdel-Aal et al. [17] have studied the crystallization of calcium sulfate dihydrate in solutions having different supersaturation ratios and free sulfate concentrations. These authors added various amount of a solution containing calcium dibasic orthophosphate ($CaHPO_4$) in phosphoric acid (20%) to sulfuric acid solution.

In a series of works [13–15], we have conducted kinetic and thermodynamic studies of the attack of synthetic fluorapatite (Fap), $Ca_{10}(PO_4)_6F_2$, by a mixture of sulfuric and phosphoric acids at different temperatures. The aim of the present work was to study the kinetics and thermodynamics of the attack of a phosphate ore (PN) from Gafsa region (Tunisia) by phosphoric acid solution and by a mixture of phosphoric and sulfuric acids at different temperatures.

2. Experimental

A SETARAM C-80 calorimeter operating in isothermal mode was used. The reversal cells of the calorimeter have been previously provided with electrical resistors in order to perform calibrations in the reaction cell, so time constants have been determined in the same conditions as for the chemical process.

Experiments have been carried out by mixing various amounts (17.07–511.42 mg) of solid with 4.5 mL of acid solution, and the recorded thermograms were integrated to give the corresponding enthalpy. For kinetic investigation, the recorded signals were processed according to the procedure developed in previous papers [9–10], to give the deconvoluted curves.

The ore was supplied by the “Groupe Chimique Tunisien” (GCT) after aqueous enrichment and sifting.

Two samples of the ore have been used. The first one (PN1) has a grain size <500 μm, and the second (PN2) is obtained by grinding

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PN1 in an agate mortar to get a fine particle powder (grain size less than about 120 μm).

X-ray diffraction reveals that the ore contains mainly apatite, calcite and silica (Fig. S1 in Supplementary data). Table S1 in Supplementary data gives the crystal parameters of the apatitic phase. The "a" parameter is close to that of a carbonate fluorapatite containing 8.2% weight of carbonate [18].

Two solutions were used for the attack. The first one having 20% weight P_2O_5 and the second was prepared by mixing 80% volume of a phosphoric acid solution having 20% weight P_2O_5, with 20 vol.% of sulfuric acid (90% weight H_2SO_4).

Phosphorus and calcium amounts in the ore were analyzed by spectrophotometry and EDTA, respectively, according to standard methods. The results are converted into P_2O_5 and CaO (Table S2 in Supplementary data). Calcite amount is determined by an increment method which consists in recording the X-ray diffractograms of mixtures of the ore with known amounts of calcite. The intensity of the most intense peak of calcite ($2\theta = 29°$) as a function of the $CaCO_3$ added is represented by a straight line, and the intercept on the mass axis gives the amount of calcite in the original ore. The result is reported in Table S2 in Supplementary data.

Assuming the apatitic phase is pure Fap, and contains the whole amount of phosphorus, the percentage of Fap in the ore is 55.81. This value leads to the amount of calcium in the apatitic phase. Taking into account the calcite, the total amount of calcium in the ore as CaO is 38.43%, slightly lower than the experimental 39.62% (Table S2 in Supplementary data). The discrepancy results from the existence of small amounts of other phases containing calcium, such as dolomite.

3. Thermodynamics of the ore attack by phosphoric acid solution at 25 °C

Fig. S2 in Supplementary data gives the variation of measured enthalpy deduced by integrating the calorimetric signal as a function of PN dissolved masses (PN1 sample). The slope of the straight line gives a global enthalpy: $\Delta H = -233.6 \pm 2.2$ J/g (PN1). This value corresponds to the total dissolution of the PN in the phosphoric acid solution, since the X-ray diffraction diagram of the residue isolated at the end of the attack, Fig. S3 in Supplementary data, shows only a halo corresponding to silica. Moreover, the attack of the grinded sample PN2 by the same solution leads to the same dissolution enthalpy $\Delta H = -233.7 \pm 2.0$ J/g. The intercept 1.0832 ± 1.0602 has an interval definition round zero value.

Fap and calcium carbonate are the major components of the mineral ore, so their contribution to the dissolution enthalpy can be calculated. Dissolution enthalpy of synthetic Fap in phosphoric acid solution (20% P_2O_5) was measured in previous works [9,12] (−178.6 J/Fap g). We have measured the dissolution enthalpy of $CaCO_3$ in the same experimental conditions by dissolving various amounts of calcite ($CaCO_3$ Normapur, purity >99%) in 4.5 mL of phosphoric acid solution (20% P_2O_5). Fig. S4 in Supplementary data shows the variation of measured enthalpy, as a function of calcium carbonate mass. The enthalpy resulting from the slope equals -303.6 ± 3.1 J/g.

Taking into account the percentage of Fap and calcite, 55.81% and 15.07%, respectively, the calculated enthalpy is -145.5 ± 3.3 J/PN1 g. It differs widely from the measured -233.6 ± 2.2 J/g. Discrepancy between these values results probably from the presence of silica, organic substances and possible other carbonates in the ore sample.

4. Kinetics and thermodynamics of the attack by the acid mixture at 25 °C

4.1. Thermodynamic study

Fig. S5 in Supplementary data shows the variation of the enthalpy measured for 8 h reaction as a function of the PN1 mass attacked by S1 solution. The enthalpy deduced -161.5 ± 1.2 J/g, is clearly more positive than that obtained with phosphoric acid (-233.6 ± 2.2 J/g). The line intercept 1.9629 ± 1.9888 can be considered as null. X-ray diffraction of the solid isolated after the attack, Fig. S6 in Supplementary data, shows the presence of apatite, calcium sulfate dihydrate (DH), calcium sulfate hemihydrate (HH) and silica. The PN1 attack is incomplete even after 8 h.

Similar experiments have been carried out on the PN2 sample and led to an enthalpy of -350.3 ± 2.7 J/g, which is much more negative than the one obtained with PN1. The transformation rate by the mixture of acids seems to be strongly dependent on the solid granulometry.

Fig. S7 in Supplementary data shows examples of deconvoluted thermograms obtained for different masses of PN1. The curves have two overlapped peaks having the same shape as the ones previously obtained by the attack of synthetic Fap by acid mixture at temperatures between 35 and 55 °C [15]. As the X-ray diffraction of the solid isolated after the first peak ($t = 1200$ s) shows the presence of HH and apatite, we can ascribe, as with pure Fap [13], the first peak to the PN dissolution and HH precipitation, whereas the second one corresponds to the HH into DH transformation. However, in the case of PN1, the latter transformation is not completely achieved and the thermograms did not reach the horizontal line after 8 h.

The transitional formation of hemihydrate at 25 °C, which was not previously observed with pure Fap, shows that HH is less soluble in the acid solution resulting from dissolution of PN (industrial conditions) than in the one obtained from synthetic Fap [13]. Fig. S7 in Supplementary data shows that as PN1 mass decreases a better separation between the peaks is observed and the second peak starts later. It seems that when the PN1 mass increases, the dihydrate solubility product is reached earlier and so the transformation of hemihydrate into dihydrate occurs at a shorter time than with smaller amounts of the ore.

4.2. Determination of the enthalpy of the complete PN attack by the acid mixture at 25 °C

As with synthetic Fap [14], the enthalpy corresponding to the total attack of the PN by the acid mixture at 25 °C can be calculated by adding the enthalpy dissolution of PN in phosphoric acid solution, previously determined (-233.6 ± 2.2 J/g), to the precipitation-neutralisation enthalpy. In order to determine the latter, two experimental series were carried out. The first one consists in dissolving various amounts of a PN/H_3PO_4 solution in 1.5 mL of acid mixture at 25 °C. The PN/H_3PO_4 solution was prepared by dissolving 548.53 mg of PN in 11.4508 g of a phosphoric acid solution (20% P_2O_5). These quantities have been chosen in order to get in the final solution an $H_2PO_4^-$ concentration in the same order of magnitude as that obtained by dissolving PN in the acid mixture. However, the PN dissolution in phosphoric acid leads to a mixture containing dispersed colloidal particles, consequently the PN/H_3PO_4 solution was energetically shaken before sampling. The measured enthalpy (Fig. S8a in Supplementary data) can be expressed by a parabolic equation:

$$\Delta H_1 = 8\,10^{-6}\,\mathrm{m}^2 - 0.0298\,\mathrm{m} + 0.3430$$

where *m* (mg) is the calculated H_3PO_4 mass solution in the PN/H_3PO_4 solution samples.

ΔH_1 corresponds not only to $H_2PO_4^-$ neutralisation and dihydrate precipitation but also to dilution of H_3PO_4 in the mixture of sulfuric and phosphoric acids. The enthalpy of that dilution, ΔH_2, has been determined in a previous work [14] by mixing variable amounts of phosphoric acid solution (20% P_2O_5), *m* (mg), to acid mixture (1.5 mL). The measured enthalpy (Fig. S8b in Supplementary data) can be expressed as:

$$\Delta H_2 = 7\,10^{-6}\,\mathrm{m}^2 - 0.0238\,\mathrm{m} + 1.0062$$

The precipitation/neutralisation enthalpy can be deduced from the difference between the heat quantities determined on curves (a) and (b) for a given phosphoric acid mass, and so for a given PN1 amount. The plot of this difference (in J) as a function of the PN mass (mg) in the PN/H_3PO_4 solution, calculated in the latter solution, is represented by a straight line, Fig. S9 in Supplementary data, having 0.144 J/mg as a slope, from which the precipitation-neutralisation enthalpy can be deduced as −144.0 ± 3.3 J/PN1 g. Adding this quantity to the ΔH corresponding to PN dissolution in the phosphoric acid solution (−233.6 ± 2.2 J/g) leads to −377.6 ± 4.0 J/PN g. This latter value corresponds to the total PN attack by acid mixture solution leading to DH precipitation. X-ray diffraction pattern, Fig. S10 in Supplementary data, of the isolated solid at the end of these experiments shows only dihydrate and silica. This value differs from the one corresponding to PN2 (350.3 ± 2.7) by about 7% and is far from that determined for the attack of PN1 (−161.5 ± 1.2 J/g). The advancement of reaction is significantly dependent on the grain size of the solid particles.

Enthalpies of neutralisation of $H_2PO_4^-$ and precipitation of DH from Ca^{2+} and SO_4^{2-} ions were determined, at 55 °C, in a previous work [13] and the values are +55.15 ± 1.30 and −239.88 ± 2.61 J/Fap g, respectively. Neglecting their variation with temperature, we can calculate the enthalpy of neutralisation/precipitation taking into account the amount of phosphorus and calcium in PN. The value obtained, −159.3 ± 2.9 J/PN g, differs from the one determined experimentally (−144.0 ± 3.3 J/g) by 9.5%. The difference is probably due to the above approximation and mainly to the dispersion of the experimental values around the least square line, Fig. S9 in Supplementary data ($R^2 = 0.98$) resulting from a lack of homogeneity of the PN/H_3PO_4 samples.

4.3. Kinetics of the PN dissolution in the acid mixture solution at 25 °C

Due to the presence of various components in PN, it was not possible to derive a kinetic model from deconvoluted thermograms, as with pure Fap [13,14]. However, applying the Avrami model [19–21] shows the succession of processes leading at the end to precipitation of gypsum. According to this model the fraction reacted *x* is related to time through the following relationship: $-\ln(1-x) = kt^n$, with *n* and *k* as constants. At the beginning this model has been developed for phase transitions, then it was applied to chemical processes, and the shift of the curve representing $\ln[-\ln(1-x)]$ over $\ln(t)$ has been assigned to a change in the crystallization [22–24] or reaction process [25–29]. In the case of PN the transformed fraction equals the quotient of the heat quantity (*q*) released from the beginning of the peak until time *t*, over the total heat (*Q*) corresponding to the transformation of total mass of PN. These quantities are calculated by integrating the corresponding surface under the peak. Fig. S11 in Supplementary data shows Avrami curves for various amounts of PN1. The curves exhibit three domains I, II and III, which can be assigned to PN dissolution/$H_2PO_4^-$ neutralisation, hemihydrate precipitation and hemihydrate/dihydrate transformation, respectively. Fig. S11 in Supplementary data allows calculation of the times τ_1 and τ_2 corresponding to the end of the first and second domain, respectively, for various amounts of PN1 (Table S3 in Supplementary data). τ_1 remains constant when the PN1 amount increases slightly but decreases when the PN mass becomes 2 or 3 times higher. This time, at which the hemihydrate precipitation starts, corresponds to the end of dissolution-induction period. It seems to be affected only by a great increase of the supersaturation. However τ_2, which corresponds to the beginning of HH into DH transformation, decreases while the PN1 mass increases. This diminution is in agreement with the observation made previously on thermogenesis: the greater the amount of PN1 the more the two peaks overlap. When the PN1 mass increases the solution reaches more rapidly the dihydrate supersaturation, and so the hemihydrate/dihydrate transformation begins earlier.

Table S3 in Supplementary data gathers Avrami parameters (*k* and *n*) deduced from the Avrami representation for different PN1 masses. This table shows that *k* and *n* parameters keep the same values in every domain for various amounts of PN1. This observation corroborates the predominance of one process in each time domain. The Avrami parameter “*n*” for dissolution, first domain, cannot be explained because for $n > 3$ the mechanism is not easily interpretable [24]. However, for two other domains “*n*” is close to 0.7 and 1. These values indicate that the corresponding phenomena seem to be controlled by diffusion [30].

5. Attack of the PN by acid mixture at different temperatures

In the wet process the acid solution has a composition close to the mixed acid solution and the exothermic effect resulting from the mixing of acids and the attack maintains the reactor around 80 °C. Fig. S12 in Supplementary data shows deconvoluted thermograms obtained at different temperatures with masses of PN1 close to 40 mg. As the temperature increases, the second peak, corresponding to hemihydrate/dihydrate transformation, departs from the first one, and the thermogram contains only two peaks up to 55 °C; when a third peak appears. The same phenomenon has been observed with PN2.

Application of the Avrami model to the thermogenesis curve at 55 °C, Fig. S13 in Supplementary data, shows the appearance of three domains separated by the shifts of the curve at about 230 and 60 000 s. X-Ray patterns obtained from the solids isolated at these times as well as at the end of the attack, Fig. S14(a–c) in Supplementary data show the apatite (Ap) rays in all the recordings, together with that of one or two of the sulfates. The attack leads successively to a mixture of (Ap + AH + HH), (Ap + AH + DH) and (Ap + DH). So the first domain corresponds to PN dissolution and simultaneous precipitation of hemihydrate and anhydrite (AH). The second domain corresponds to the HH into DH transformation and the third one to the AH into DH transformation. The last seems to begin after about 19 h from the beginning at 55 °C and the attack is not finished even after 45 h maturation time under shaking.

Remark. Errors on the slopes and intercepts were calculated according to the standard least square processing method, and error on the sum was determined by applying the formula resulting from the statistical treatment developed by Guedens et al. [31].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.05.006.

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