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Hydration of anhydrite of gypsum ($CaSO_4$.II) in a ball mill

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Abstract

The hydration of an anhydrite of gypsum ($CaSO_4$.II) in a ball mill was studied as a function of time and temperature. The amount of gypsum formed at different intervals of time was determined by weight loss method and powder X-ray diffraction technique. Specific surface area at different time intervals was determined by LASER granulometric method. The results showed that the maximum rate of formation of gypsum was at a longer time than the time for the development of maximum specific surface area. In the presence of activators, the time for maximum rate of gypsum formation and maximum specific surface area shifted towards lower hydration time. Morphological changes during the course of hydration have been studied by the scanning electron microscopic (SEM) technique. A mechanism of hydration has been proposed.

Keywords: Anhydrite; Hydration; Kinetics; Sulfate, Modeling

1. Introduction

Various forms of calcium sulphate hydrate have been reviewed by Hand [1]. Depending on the temperature, calcium sulphate exists as anhydrite ($CaSO_4$), subhydrate ([2]; $CaSO_4.xH_2O$, $0 < x \leq 0.8$) and dihydrate ($CaSO_4.2H_2O$). The $CaSO_4$.II phase of anhydrite is the one that is thermodynamically stable up to 1180 °C and occurs naturally as the mineral anhydrite. It may also be produced by high-temperature (≈ 600 °C) calcinations of natural or by-product gypsum. Under ambient conditions, CaSO4.II reacts very slowly with water, and, hence, the name dead burnt gypsum is also given to this mineral.

The ability of anhydrite to react with water, converting itself into gypsum, is the basis of its use as a construction material. However, this process, known as setting, is very slow. The reactivity can be enhanced considerably by grinding the anhydrite to fine powders and also adding certain activators.

Murat et al. [3] found that the hydration kinetics of pure synthetic orthorhombic anhydrite depends on the temperature of preparation, mechanical activation by grinding and the nature of foreign cations in the solution used as chemical activators. They considered the hydration as dissolution–nucleation–growth process, in which nucleation was the more concerned step.

According to Ottemann [4], the strength development in the anhydrite binder depends on the degree of drying and hydration. Riedel et al. [5] are also of the opinion that strength depends on the degree of hydration. On the other hand, El Hajjouji and Murat [6] disagree with the findings of Ottemann [4] and consider that the pore size, which is influenced by the size of the resulting gypsum crystals, is responsible for the strength of the hardened material. According to them, the size of the resulting gypsum crystals is dependent on the type of activator cation used.

Israel [7] found that there is a direct relationship between the amount of gypsum and flexural tensile strength of the hydrating anhydrite. Depending on the activators, the morphologies are changed. This changes the strength in a different way.

Singh [8] found that in the presence of an activator K_2SO_4, the hydration of anhydrite to gypsum is enhanced considerably, and the morphology of the crystallizing gypsum is changed. This was explained in terms of the formation of a double salt at the surface of anhydrite.

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It appears that controversies exist regarding the mechanism of hydration and requires further investigations. In addition, most of the studies have been made in pastes only. In the present investigation, the hydration of anhydrite of gypsum has been studied in a ball mill, and a mechanism of hydration has been proposed.

2. Experimental

2.1. Materials

Natural anhydrite was obtained from the south Hercynian region of Germany. It consists of 93.7% anhydrite, 4.4% gypsum and 1.9% $CaCO_3$. The particle size was less than 90 μm. The density of the material was 2.31 g/cm^3. H_2SO_4 (pH 1), 5% $MgSO_4.7H_2O$ and a dilute solution of calcium hydroxide were used as activators. To prepare the calcium hydroxide solution, a saturated solution was made at 20 °C and then diluted to 50%.

2.2. Methods

The hydration of anhydrite was studied at room temperature in a laboratory ball mill with a water–solid ratio of 1.32. Hydrations were stopped at different intervals of time, with isopropyl alcohol. The amount of gypsum formed was determined by the powder X-ray diffraction technique, as well as by weight loss method, at 40 and then 350 °C [9]. It is found that the results obtained by the two methods are in good agreement [10].

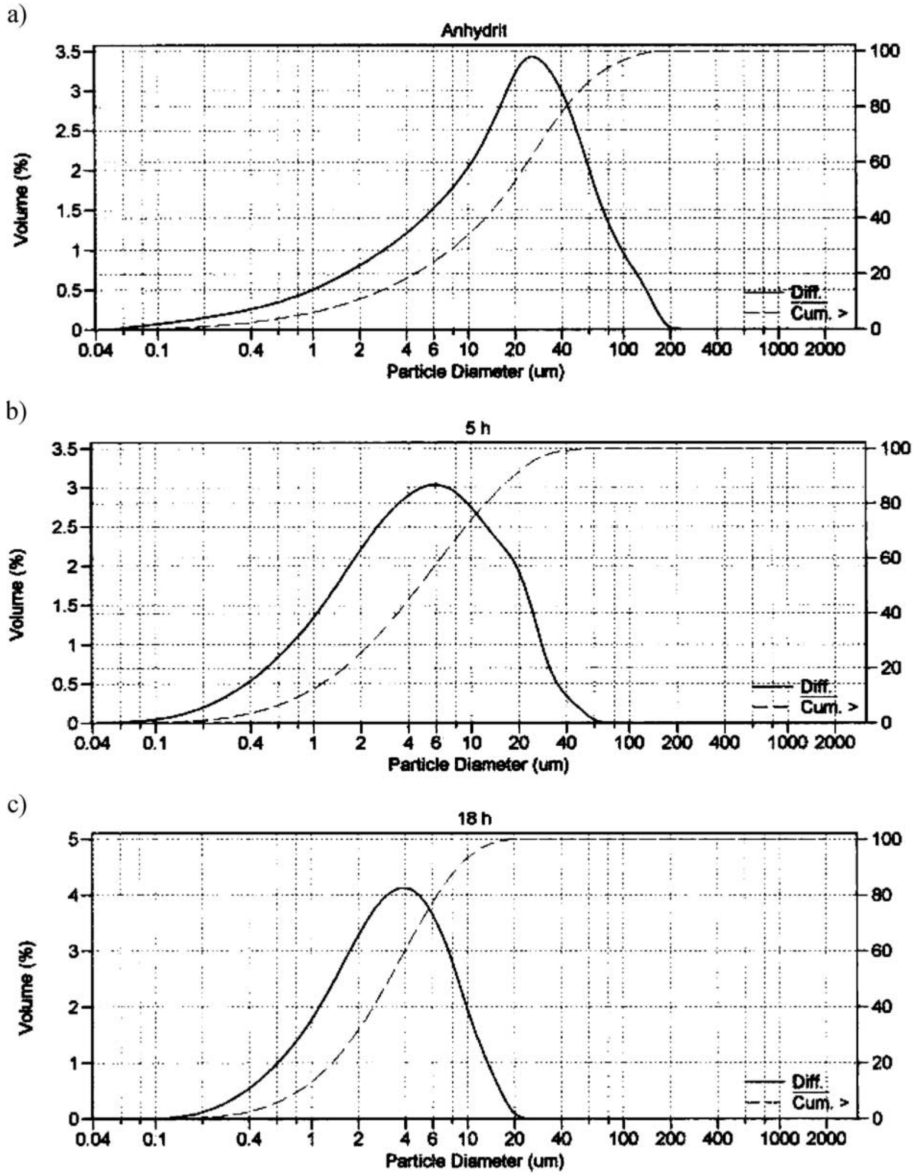

Fig. 1. Variation of percent cumulative and differential volume with particle size.

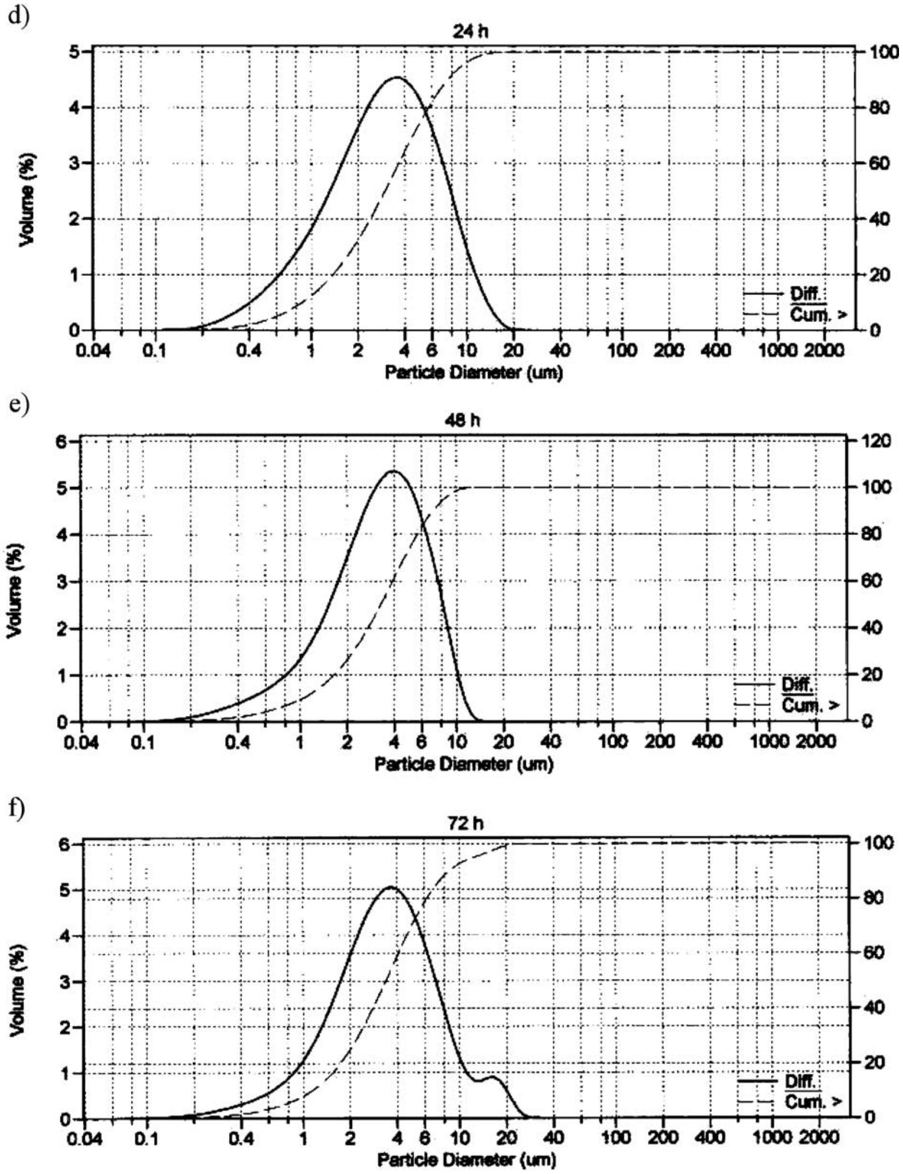

Fig. 1 (*continued*).

Particle size distribution and specific surface areas at different intervals of time were determined by LASER granulometric method [10] by using the Coulter LS-230 instrument.

The experiments were also performed at different temperatures (10, 20 and 40 °C) and in presence of activators.

Scanning electron microscopic (SEM) pictures of some hydrated anhydrites were also recorded.

3. Results and discussion

The particle size distributions in the hydrating anhydrite, at different intervals of time, are shown in Fig. 1. The percent cumulative volume and differential volume are plotted as a function of particle size (log scale). As the time progressed, the particle size decreased due to constant hit by the balls, and the curves for the differential volume became sharp, with a peak at lower particle sizes. At 72 h of hydration, a second small peak also appears, which may be due to the agglomeration of smaller particles or the recrystallization of gypsum. From the particle size distribution, the specific surface areas were calculated and are given in Figs. 2–5.

The variation of the amount of gypsum formed and the specific surface area developed during the hydration of anhydrite with hydration time are given in Fig. 2. The amount of gypsum first increases slowly and then appears at a faster rate (Fig. 2a). The rate of formation of gypsum with hydration time is shown in Fig. 2b. The curve shows that the rate first increases slowly and then

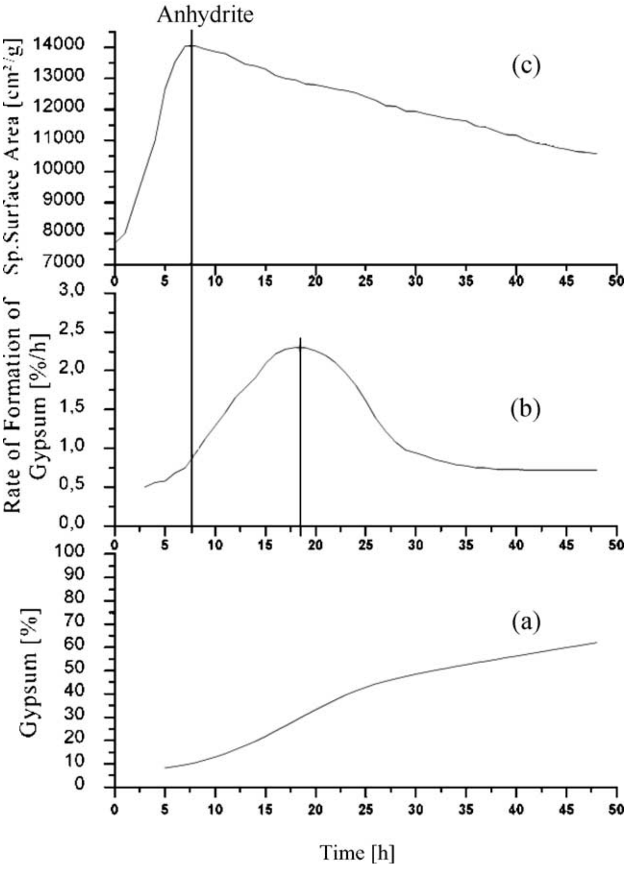

Fig. 2. Variation of (a) percent gypsum formed, (b) rate of formation of gypsum and (c) specific surface area with time in the hydrating anhydrite.

rapidly, with a maximum at about 18 h of hydration. After the maximum, the rate of formation of gypsum decreases and ultimately becomes constant. The variation of specific surface area with hydration time is given in Fig. 2c. The surface area increases continuously with time, reaches a maximum value at about 7.5 h of hydration and then decreases. The figures indicate that the time for the maximum rate of gypsum formation does not coincide with the time for maximum specific surface area. The maximum specific surface area is obtained at a shorter time, whereas the rate of formation of maximum gypsum is obtained at a longer time of hydration with anhydrite.

The hydration studies were also carried out in the presence of different activators such as H_2SO_4 (pH 1), 5% $MgSO_4.7H_2O$ and calcium hydroxide solution (50% dilution of the saturated solution of calcium hydroxide), and the results are presented in Figs. 3–5. Similar results are obtained without activator. The maximum rate of gypsum formation and the maximum value of specific surface area shifted to lower hydration times as compared with that without activator (Fig. 2).

The effect of temperature (10, 20 and 40 °C) on the formation of gypsum and the development of specific surface area in the hydrating anhydrite were also studied. The gypsum formed increased with time at all the temperatures, but the values are always lower at 40 °C (Fig. 6). The amounts of gypsum formed at 10 and 20 °C are almost similar. The solubilities of gypsum and anhydrite in water, at 40 °C, are the same and, hence, at this temperature, they exist in equilibrium. This may be one of the reasons for the lower values of gypsum in hydrating anhydrite at 40 °C. On the other hand, the variation of specific surface area at different temperatures follow the reverse sequence (Fig. 7); that is, the values are highest at 40 °C. The results show that the lower the amount of gypsum formed, the higher the specific surface area.

SEM pictures of anhydrite hydrated for 5 and 18 h in the absence and presence of H_2SO_4 (pH 1) are given in Fig. 8. The figures show that there is very little morphological change with hydration time and in the presence of H_2SO_4. This suggests that the hydration properties of anhydrite are not controlled by the morphology of hydration products.

From the results, the following mechanism can be proposed for the conversion of anhydrite into gypsum during hydration in a ball mill. As soon as anhydrite comes into contact with water, a part of it is dissolved, making the solution saturated with respect to Ca^{2+} and SO_4^{2-} ions.

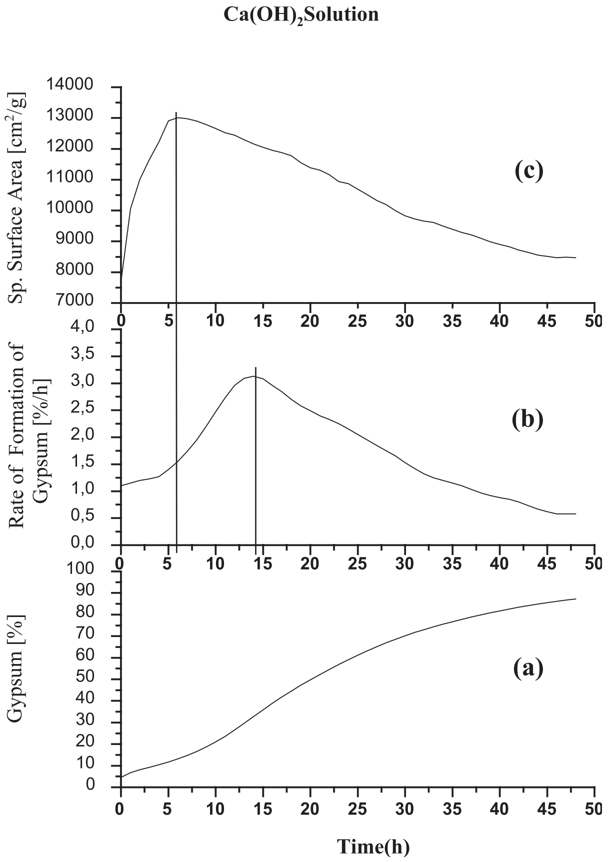

Fig. 3. Variation of (a) percent gypsum formed, (b) rate of formation of gypsum and (c) specific surface area with time in the hydrating anhydrite, in presence of calcium hydroxide solution.

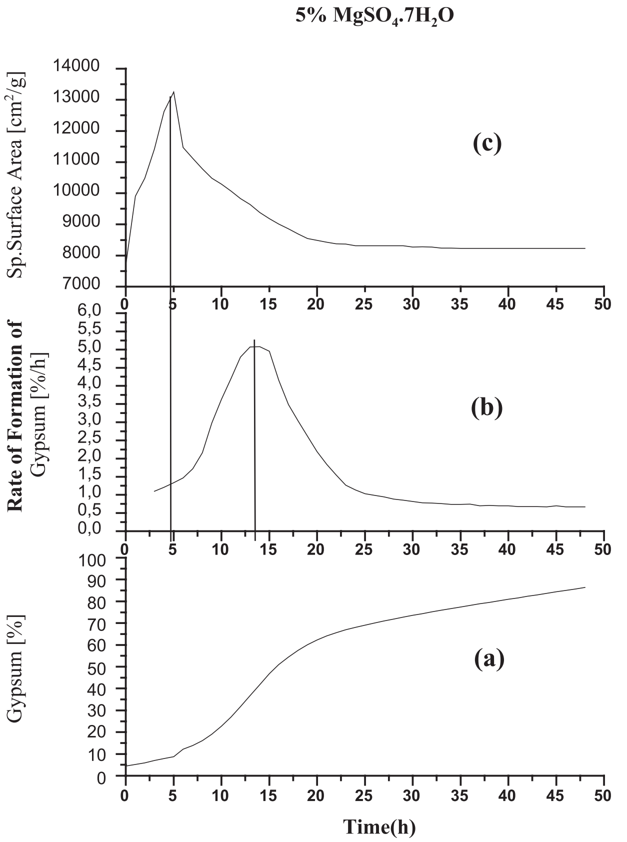

Fig. 4. Variation of (a) percent gypsum formed, (b) rate of formation of gypsum and (c) specific surface area with time in the hydrating anhydrite, in presence of 5% $MgSO_4.7H_2O$ solution.

These ions, which are hydrated in the solution, rapidly get adsorbed at the surface of anhydrite, giving a higher surface area. The thickness of the adsorbed layer increases with time. The Ca^{2+} and SO_4^{2-} ions of anhydrite have a tendency to go into solution, whereas water molecules have a tendency to interact with a fresh surface of anhydrite. The two processes are hindered because of the adsorbed layer. When the thickness of the adsorbed layer increases beyond a certain limit, cracks are formed. However, this is a very slow process; however, in the ball mill, the crack formation in the adsorbed layer is accelerated considerably. Water molecules enter through the cracks and come in contact with a fresh surface of anhydrite. When there are sufficient numbers of Ca^{2+} and SO_4^{2-} ions and water molecules at the surface, nuclei of gypsum are formed. A small amount of gypsum is already present in the anhydrite but, because it is an aged one, may not act as an effective nucleus. If the radius of the nucleus is higher than the critical size, crystallization of gypsum starts and will occur at a faster rate. Once a large amount of gypsum is formed, the remaining anhydrite, if any, is covered with that, and further hydration becomes very difficult. But in the ball mill, the possibility of completion of the hydration is much more than in the paste. The overall mechanism is shown in Fig. 9.

From the above discussions it is clear that there is a time lag between the adsorption and the formation of gypsum crystals. As a result, the time for maximum surface area does not coincide with the maximum rate of gypsum formation.

In the presence of activators, the solution compositions are changed, and activators may also retard the evaporation of water due to reduction in vapour pressure, and, therefore, gauge water is available for a longer period to facilitate the hydration for a prolonged time. As a result, the process of adsorption, breaking of adsorbed layer, nucleation and crystal growth are changed. This simply causes change in the time for the appearance of maximum surface area and maximum rate of gypsum formation in the hydrating anhydrite.

4. Conclusions

From the results, following conclusions can be drawn:

1. During the hydration of natural anhydrite in a ball mill, the time for the rate of formation of the maximum

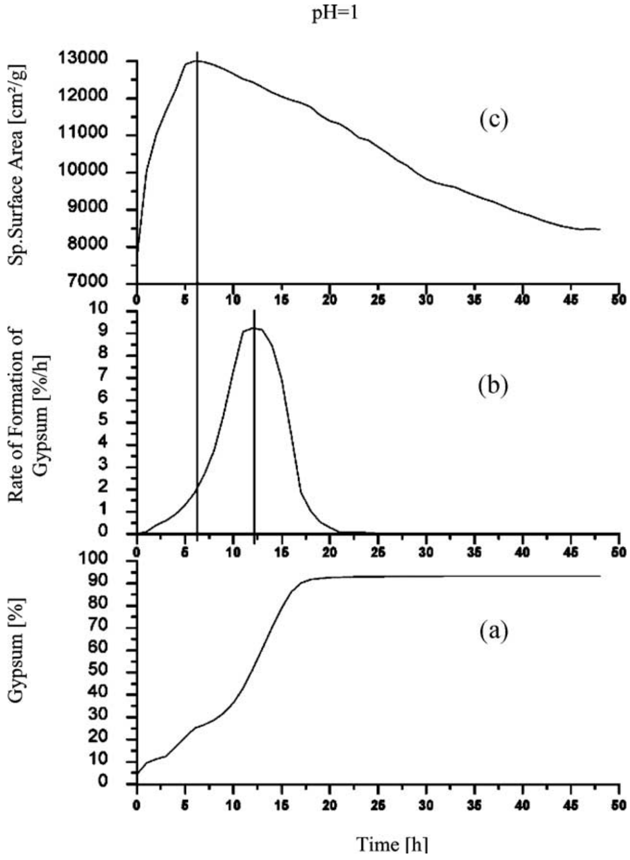

Fig. 5. Variation of (a) percent gypsum formed, (b) rate of formation of gypsum and (c) specific surface area with time in the hydrating anhydrite, in presence of H_2SO_4 (pH 1).

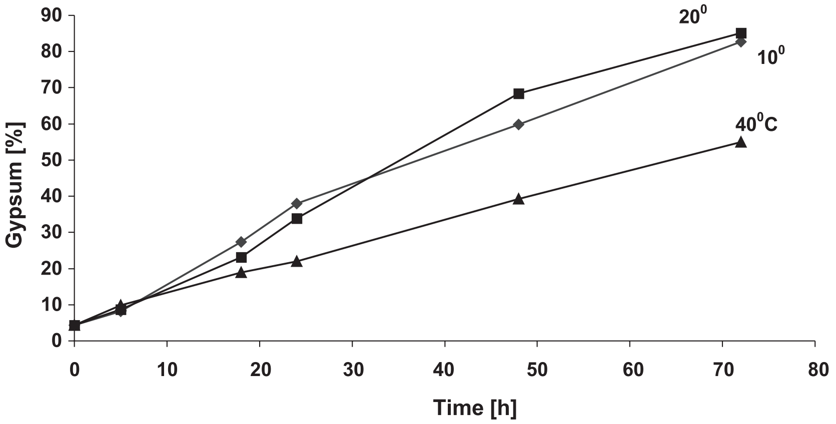

Fig. 6. Variation of amount of gypsum in the hydrating anhydrite, with time, at different temperatures.

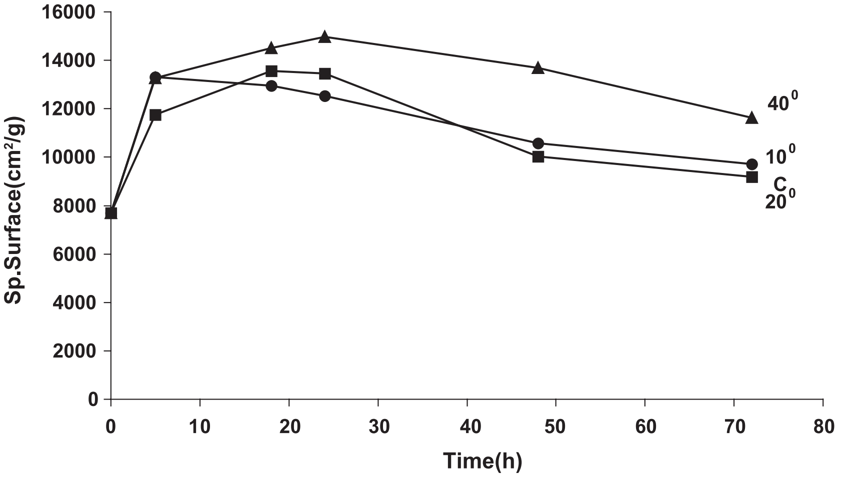

Fig. 7. Variation of specific surface area in the hydrating anhydrite, with time, at different temperatures.

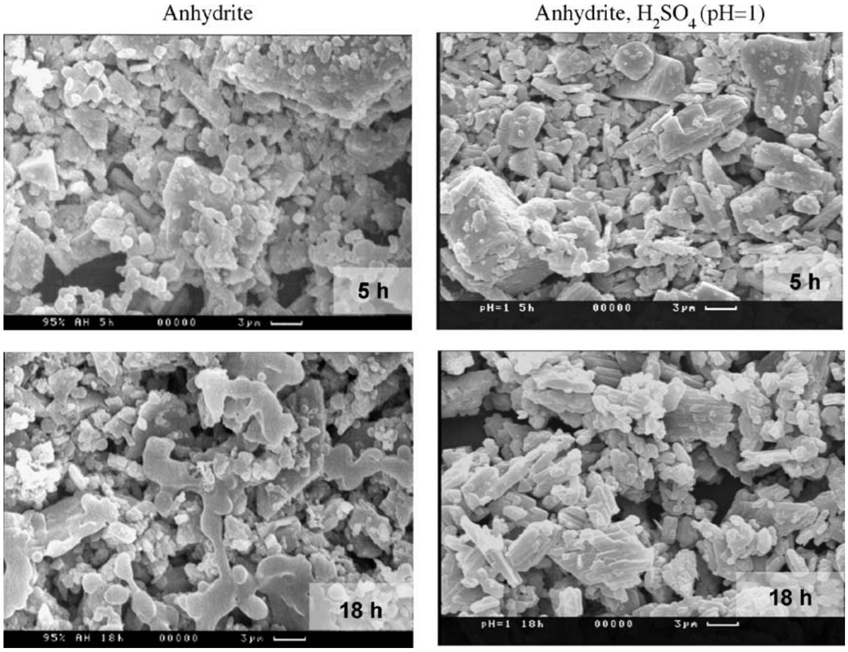

Fig. 8. SEM pictures of anhydrite hydrated for 5 and 18 h in the absence and presence of H_2SO_4 (pH 1).

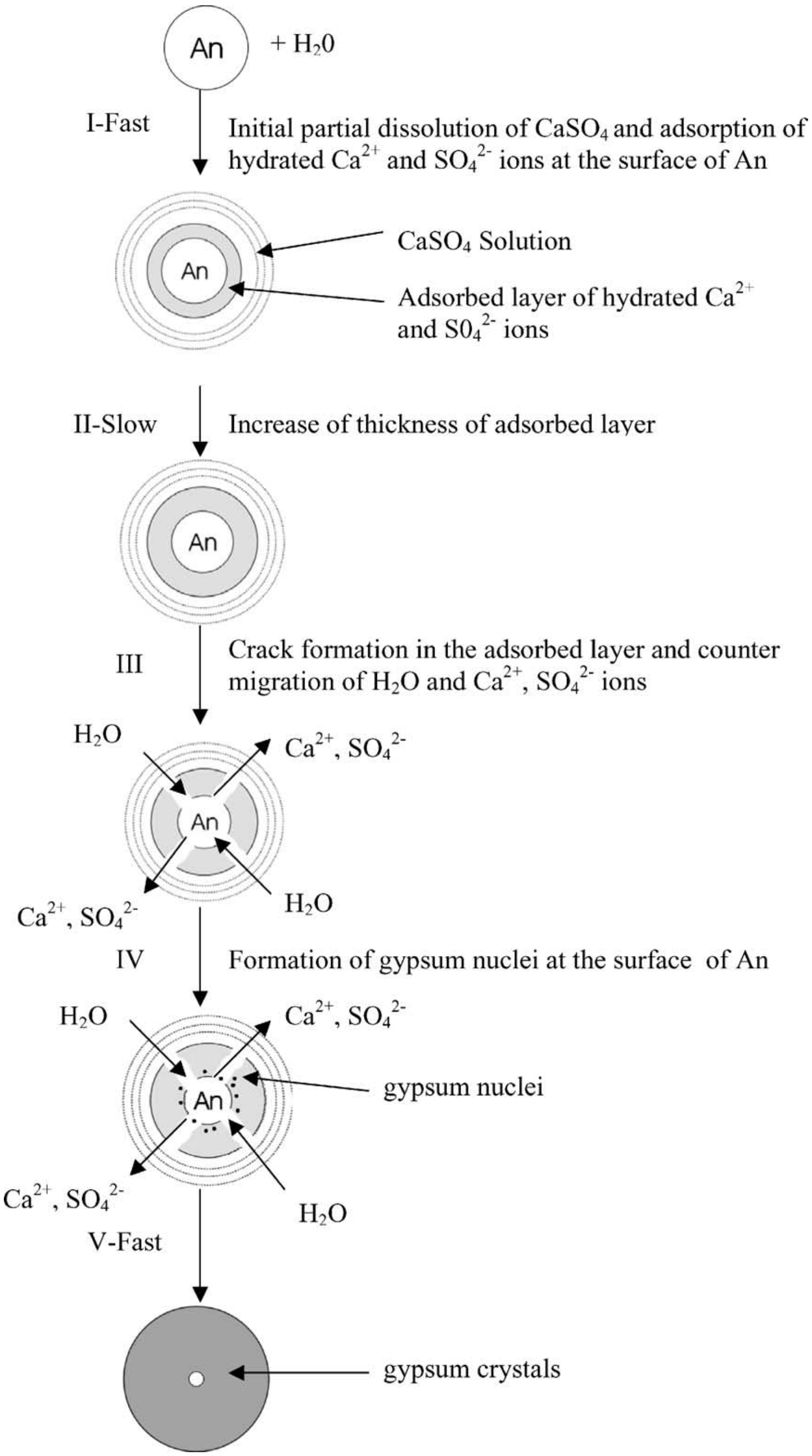

Fig. 9. Mechanism of hydration of anhydrite (An).

amount of gypsum (longer time) does not coincide with the time for the development of maximum specific surface area (shorter time). There is a time lag between the adsorption of ions on the surface of anhydrite increasing the specific surface area and the formation of gypsum.

2. At 40 °C, the amount of gypsum formed was always lower as compared with that formed at 10 and 20 °C, whereas the variation of specific surface area followed the reverse sequence. This simply indicates that the lower the amount of gypsum, the higher the surface area.

3. Activators simply lower the time for the appearance of maximum specific surface area and the rate of formation of maximum gypsum.
4. SEM pictures showed that very little morphological changes occur during the hydration of anhydrite.
5. A plausible mechanism of hydration has been proposed.

Acknowledgements

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