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ACTIVATION OF SOLIDS BY MECHANICAL GRINDING. CONSEQUENCIES FOR CALORIMETRIC INVESTIGATION ON THE HYDRATION RATE OF ORTHORHOMBIC ANHYDRITE.

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ABSTRACT

An increase of the hydration rate of orthorhombic anhydrite has been obtained by mechanical activation (grinding) of the solid : that allows a direct calorimetric investigation on the reaction kinetics. However, experimental conditions for both grinding and storage of the samples before calorimetric test must be accurately defined to obtain reproducible heat flow diagrams.

INTRODUCTION

Although not very quick, the hydration rate of mineral binders such as anhydrous phases of portland or high alumina cements can be investigated by isothermal calorimetry because the hydration enthalpy is sufficiently high (in the range of 120-150 $\mathrm{kcal.gram^{-1}}$ for both tricalcium silicate and monocalcium aluminate, Ref.1). The obtention of a large thermal flow is also possible during hydration of calcium sulfate β hemihydrate because the low value of enthalpy (32 $\mathrm{kcal.gram^{-1}}$, Ref.2) is compensated by the quick setting properties of the material. The hydration of orthorhombic anhydrite $CaSO_4$ even in the presence of a chemical activator such as potassium sulfate (Ref. 3 and 4), is a slow-rate phenomenon and the low value of ΔH (30 $\mathrm{kcal.gram^{-1}}$, Ref. 2) does not allow a direct investigation by calorimetry : the heat flow is weak and stretches for several tens of hours.

In order to obtain short-time heat flow diagrams, the mechanical activation of anhydrite before hydration has been investigated by the Authors. Effectively, the comminution of a solid not only promotes a decrease in the grain-size and an increase in specific surface, but enhances the reactivity of the new surfaces by local amorphization or formation of strains and defects which act as preferen-

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tial chemical sites during a reaction (Ref.5).

EXPERIMENTALS

Synthetic orthorhombic anhydrite $CaSO_4$ is obtained by calcination of pure Merck gypsum powder for 5 hours at 750°C, a temperature which corresponds to the obtention of the anhydrous phase with a high content of superficial defects (Ref.6). After cooling, anhydrite is mechanically ground in a Fritsch centrifugal mill for different times from 4 to 120 min. Then, the grain-size is determined with a laser granulometer and the modification of the crystal structure is analysed by X-ray diffraction.

Samples for hydration investigation are tested at 25°C by calorimetry with a laboratory fluxmeter device developped for studies on calcium sulfates (Ref.7) and monocalcium aluminate (Ref.8).The liquid used for hydration is a 5.0 % K_2SO_4 aqueous solution and the "Liquid/Solid" ratio is equal to 0.5. Calorimetric investigations are made on samples either just after grinding or after storage at 25°C in different conditions before test.

The content of gypsum formed in hydrated samples is obtained by the value of the product $h\frac{L}{2}$ where h and $\frac{L}{2}$ are the height and the width at half height, respectively, of the first DTA peak of gypsum dehydration (test on 600mg ; heating rate : $5K.min^{-1}$ in air).The standardization curve is drawn from DTA investigation on synthetic anhydrite-gypsum mixes.

RESULTS AND DISCUSSION

When mixed with potassium sulfate solution, not-ground anhydrite does not present any hydration peak in calorimetry. With freshly ground samples, the calorimetric test leads to a two parts thermal flow : a first peak which corresponds to the wetting of the solid (W), and a second one (H) related to the hydration reaction. When the grinding time raises, the H peak becomes closer and closer to the wetting peak and the intensity of the latter increases(Fig.1)

The variation of gypsum content in the samples during hydration also depends on the grinding time (Fig.2) and the shorter the time at the maximum of the calorimetric hydration peak, the higher the rate of gypsum formation during the six first hours of hydration.

So the grinding of anhydrite greatly increases the hydration rate, what allows to use calorimetry to make comparative kinetical investigations on the reaction.

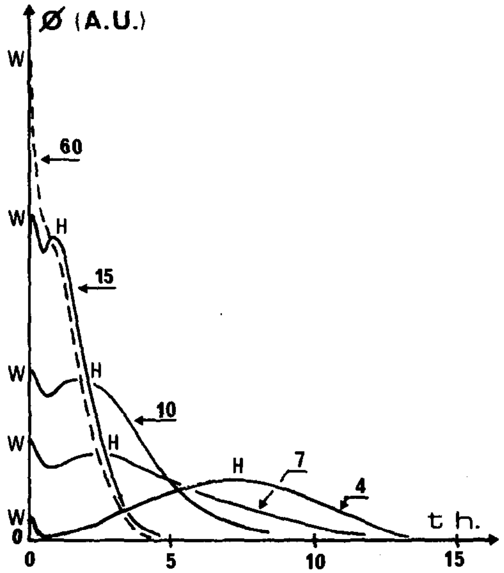

Fig. 1.

Variation of heat flow diagrams during hydration of orthorhombic anhydrite ground for different times (4, 7, 10, 15 and 60 min.)

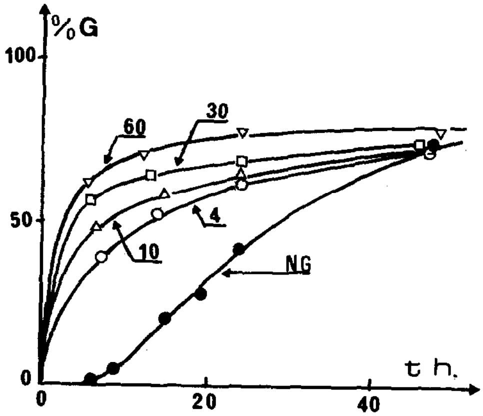

Fig. 2.

Variation of gypsum content in samples, versus hydration time, for not-ground (NG) anhydrite or samples ground for 4, 10, 30 and 60 min.

On the other hand, the intensity of the wetting peak and the position of the H peak versus storage time greatly evolve when ground samples are stored in closed bottles before calorimetric test (Fig. 3A). This points out the important role of defects and superficial sites created by grinding, on the hydration process, and the high sensitivity of the new surfaces to atmospheric water vapour. The same evolution is observed when samples are stored in a closed vessel at constant relative humidity (50% R.H.)(Fig.3B). A less sensitive variation in calorimetric results is obtained when samples are stored in a dessicator containing silicagel and the reproducibility of the heat flow diagram is observed after some days, but the storage must be limited in time because an "ageing" of the dessica-

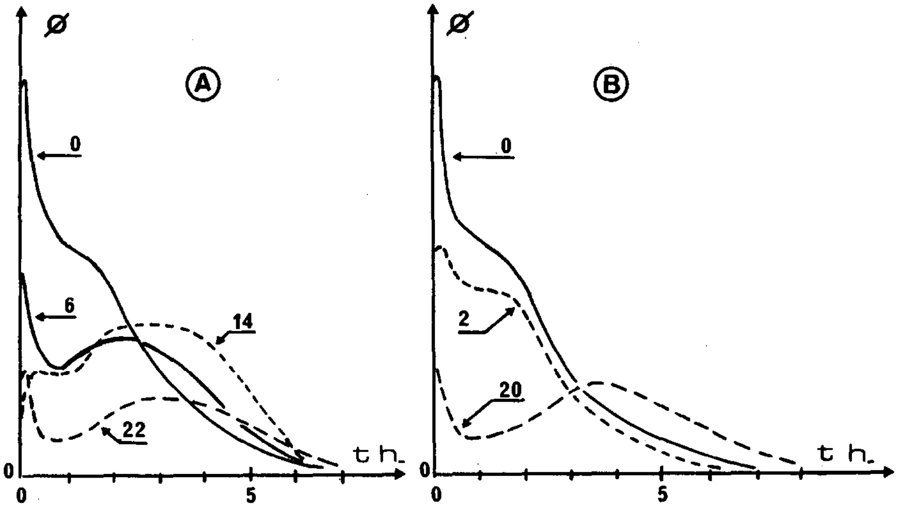

Fig. 3. Thermal flow (in arbitrary unit) versus the time of storage (0, 2, 6, 14, 20, and 22 days) either in closed bottle (A) or at 50% R.H.(B) before calorimetric test.

ting reagent may happen in a period of several weeks.

The grinding conditions also play an important role on the reproducibility of results. Many investigations in this field have led us to diminish the rotation rate of the mill and to increase both the quantity of solid in the jar and the grinding time. In such conditions, the comminuted solid is homogeneous and gives reproducible calorimetric results.

The determination of both the nature of defects created by mechanical grinding and the comparative role played by different chemical activators in hydration mechanism (K_2SO_4 and transition metal sulfates) are in progress and will be presented later.

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