Pergamon

Cement and Concrete Research, Vol. 26, No. 12, pp. 1843-1857, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00173-1

MECHANOCHEMICAL CAPILLARY REACTIONS IN PARTLY DEHYDRATED GYPSUM AND ALUMINIUM HYDROXIDE INTERGROUND POWDER MIXTURES

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(Refereed)
(Received April 26, 1996; Accepted September 23, 1996)

ABSTRACT

Authors activate gypsum and alumina (or gypsum-hemihydrate + alumina) mixtures by intensive grinding in a water-cooled planetary mill and measure water vapour adsorption, heat of solution, phase composition (by XRD) and activation energy of eliminated water (by thermal methods) of activated and non-activated samples. Thermal treatment of mechanically activated samples results in a much more intensive formation of crystalline products, thus e.g. the amount of calcium sulfoaluminate after a 2 hr/1200°C heat treatment of the gypsum + $Al(OH)_3$ sample is much higher in activated samples. Based on these model experiments, authors conclude that gels are formed during mechanical activation, due to chemisorption and mechanochemical capillary reactions, which, in turn, act as crystallization nuclei, greatly affecting thermal reactions. *Copyright © 1996 Elsevier Science Ltd*

Introduction

After Peters' definition [1], mechanochemical reactions are those chemical interactions which occur e.g. during intergrinding between solids of various chemical composition. The mechanical energy introduced into the system covers either directly the reaction energy or the activation energy of the reaction [2, 3]

There are several types of mechanochemical reaction known [4, 5] of which especially important are those, which come about by the mediation of the liquid accommodating the submicron cavities between particles of reacting solids. The liquid (e.g. water) from the solid material can enter into the cavities either by being pressed out of the crystal lattice under mechanical stress prior to accumulation in the cavities or by condensation from adjacent vapour phases.

Interactions between solid particles performed under mechanical stress and simultaneous capillary condensation are denoted as *mechanochemical capillary reactions* [6]. Present work addresses a special system: mechanochemical capillary reactions in partially dehydrated gypsum + aluminium hydroxide mixtures. The $CaSO_4$:Al_2O_3 molar ratio was kept constant in the selected mixture compositions, but the amount and binding energy of the third component i.e. water (crystal water or structural water in the form of OH-groups) varied, hence the used gypsum and aluminium hydroxide were previously dehydrated to various extents. Powder mixtures were then interground. Elimination of crystal and structural water due to particle deformations during grinding and subsequent interaction in mechanochemical capillary reactions were expected. The role of binding energy and of the amount of bonded water in the processes were investigated. Additionally, interest focused on the effect of subsequent vapour adsorption on capillary reactions in the activated systems.

As the quality of commercial plaster of Paris is significantly affected by contamination and also because grinding has an important role in the production of plaster of Paris, investigations were extended by model experiments to assess possible applications of mechanochemical reactions in industrial scale production.

Experimental

Starting materials for the model experiments were prepared of natural gypsum (Alsótelekes occurrence, Hungary) and of synthetic hydrargillite by thermal dehydration to various extents. Gypsum contained 82% $CaSO_4.2H_2O$ with small amounts of anhydrite, dolomite, calcite and magnesite as contaminants. From this raw material, hemihydrate was produced by heat treatment at 84°C for 8 hours and subsequent storage in an air-tight container for 10 hours. Aluminium hydroxide was transformed to a dehydroxilated product (i.e. alumina) by heat treatment at 600°C for 2 hours. Solid mixtures were made from materials pre-ground to particle sizes less than 60 μm whose $CaSO_4:Al_2O_3$ molar ratio was always 1:1. These powder mixtures were homogenised for several hours by ball milling using few balls and then half of the powder mixture was used in its "original" (i.e. non-activated) form, whereas the other half was investigated after "activation" for 1 hour in an air-tight and water cooled drum of an "AGO I" type planetary mill.

Water content of non-activated and activated products was increased by additional vapour adsorption (by storage in saturated water vapour at 23°C for 28 days). The purpose of these treatments was to complete capillary reactions by subsequent saturation of capillaries.

Investigation of the obtained products was performed on the basis of water vapour adsorption isotherms following the potential band theory [6], X-ray diffraction and derivatography as well as by measuring the heat of dissolution in HNO_3-HF solution [7]. Activation energy of the eliminated water was calculated from thermogravimetric curves [8].

Denotations in the figures showing the experimental results and their brief explanation are given in Tables 1 and 2

Results

Water vapour adsorption potential curves [6] of $Al(OH)_3$ and $CaSO_4 \cdot 2H_2O$ powders used as starting materials for the experiments are shown in the top of Fig. 1. where the water content distribution of the different zones are demonstrated: section "a" refers to the zone of physiosorption, section "c" to that of capillary condensation water and section "s" to bonded water. At the same time, the potential bands in section îcî also represent pore sizes (r_K). Distribution of number of pores as a function of pore sizes are given using histograms.

Water uptake of both samples is small; their specific surface is similar to that of usual coarse-disperse systems: their intergranular cavity system is rather coarse with only few submicroscopic pores (somewhat more in the dihydrate than in the aluminium-hydroxide). For further explanation of section "s" in the centre of the figure (water being present not as

TABLE 1

Codes of Samples

Symbol	Denotation
AH	Al-hydroxide, $Al(OH)_3$
A	Al-oxide Al_2O_3
GH_2	gypsum, $CaSO_4 \cdot 2H_2O$
$GH_{0.5}$	gypsum hemihydrate, $CaSO_4 \cdot 0.5H_2O$ (plaster of Paris)
$AHGH_2$	Al-hydroxide + gypsum mixture
AGH	Al-oxide + gypsum mixture
$AHG_{0.5}$	Al-hydroxide + gypsum hemihydrate mixture
*	state after mechanical activation
1-index	state after saturation in water vapour for 40 days
o-index	starting condition

adsorption water, as but crystal water or structural water in the form of OH-groups), results of the thermoanalysis are given below:

- **DTG**-curves,
- Squares are used to demonstrate the temperature range of the water elimination steps (vertical side of the quadrilaterals) and also the quantity of water eliminated in that step: m (horizontal side of quadrilaterals),
- activation energy of water elimination (**ΔG^***) is proportional to the length of horizontal lines in the figure.

The thermoanalytical data referring to section "s" of heat treated samples are given in the bottom of Fig. 1.

TABLE 2

Codes of Samples

Symbol	Dimension	Denotation
w	kg_{water} / kg_{solid}	equilibrium adsorption humidity
g	J / kg	adsorption potential
r_K	nm	radius of Kelvin-capillary
n_w	%	number of Kelvin-capillaries between $r_K + \Delta r_K$
ΔG^*	kJ / kg	activation energy of water elimination
m, Δm	kg / kg	mass and difference mass of water eliminating at T temperature
T	°C	temperature
t	hour, minute	time
Q	kJ / kg	heat of dissolution
Q_0	kJ / kg	heat of dissolution for starting conditions
Q_1	kJ / kg	heat of dissolution after water vapour adsorption
Q_0^*	kJ / kg	heat of dissolution after mechanical activation
Q_1^*	kJ / kg	heat of dissolution after activation and water vapour adsorption
Ω_w	m^2 / kg	specific surface
ΔI	%	change of intensity of XRD peaks

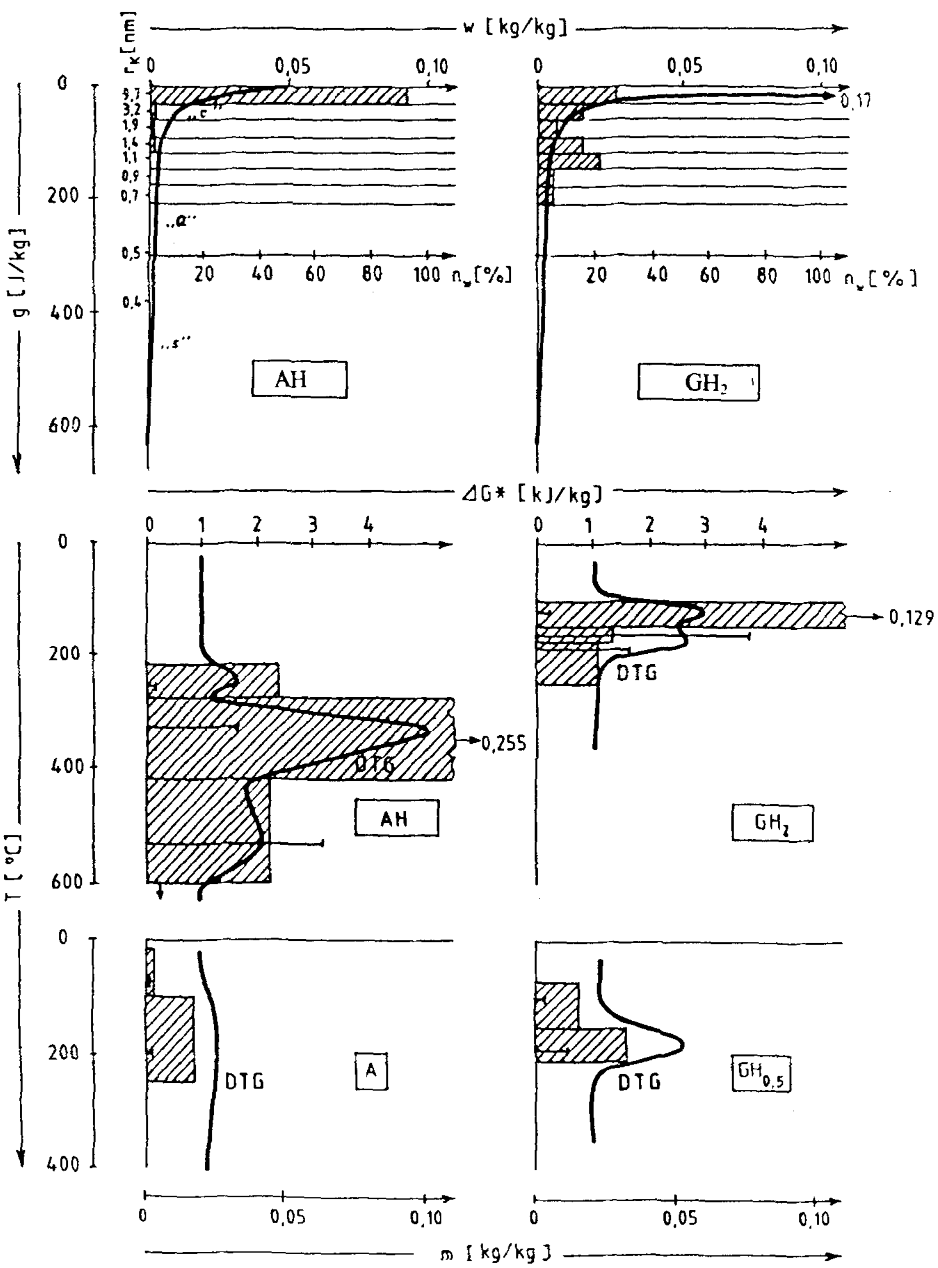

FIG. 1.

Adsorption and thermal curves of $Al(OH)_3$, $CaSO_4.2H_2O$ and of their thermally treated products.

It is clear from the figure that the four samples, as starting materials for experiments, contained different amounts of water with different binding energies within one sample and also from sample to sample.

a.) On continuous heating water is eliminated from aluminium-hydroxide (**AH**) in three stages. There are several explanations of the processes in the literature. Here we follow the Kacsalova-Migály theory [9], which reports transformation of part of hydrargillite to boehmite (AlOOH) with simultaneous formation of amorphous Al_2O_3 (-hydrate?). Then, at elevated temperature (200 - 400°C range) boehmite is formed, which transforms to γ-Al_2O_3 at 600°C by water elimination reaction. Effect of mechanochemical activation is described by Gout et al. [10] as hydrargillite, boehmite and diaspore dehydrate (to produce amorphous Al_2O_3) when milled at room temperature. After prolonged grinding transitional (κ–Al_2O_3) and crystalline alumina (corundum) born. Kacsalova [11] claims that intensive grinding of bayerite results in dehydroxylation and morphological changes as well as destruction of the crystalline order to give amorphous material. At the first stage amorphous aluminium hydroxide and oxide come about, then boehmite and κ-Al_2O_3 are produced. After mechanical activation of aluminium-hydroxide the three distinguishable thermal water elimination peaks disappear and merge to form a single broad signal [10].

The heat treated (denoted by **A**) sample contained a small amount of low energy water. It is probable that this water content is only result of secondary uptake during experimental work.

b.) On heating gypsum (**GH$_2$**), hemihydrate is produced first in the well-known reaction. It is clearly observed in the figure that elimination of one and a half molecules of water requires low activation energy. After completion of the reaction on further heating in dry air β-hemihydrate comes about. However, if hemihydrate is autoclaved, α-hemihydrate is the first product, which transforms to α-$CaSO_4$ III. at 151°C and then to the β modification at 194°C which are both water reactive anhydrites [12]. It is interesting that these two last transformations cannot be observed in the derivatograms, nevertheless we could prove by kinetic calculations that the hemihydrate also decomposes in two closely situated steps.

In heat treated samples (**GH$_{0.5}$**) the half molecule water is bonded with smaller energy than was in the gypsum. Part of the water can be removed by extremely small activation energy. This phenomenon can be derived from the loose crystal structure left behind after elimination of water by heat treatment.

The totally dehydrated gypsum (anhydrite) adsorbs various amounts of water from atmospheres of different relative vapour pressure (φ) [13]. The relationship between the equilibrium water content and the adsorption potential (g) calculated from the relative water vapour pressure is shown in Fig. 2.

Binding energy of water is assessed by the differential thermogravimetric curves in the centre of the figure. It is easy to observe incorporation of water into the lattice of gypsum by adsorption. The water is bonded by two different energies i.e. liable to be removed at two different temperatures; (the thermal valley becomes deeper on the increase of water uptake at both temperatures).

The transformation of anhydrite to hemihydrate in contact with air saturated in water vapour as a function of time starts with *chemisorption*, followed by solid state reaction. Similar transformation (formation of hemihydrate) is characteristic of water adsorption at low vapour pressures (i.e. at high adsorption potential). The transformation of hemihydrate to dihydrate, however, comes about by *capillary reaction*, because it involves a condensed water phase in the intergranular cavity system.

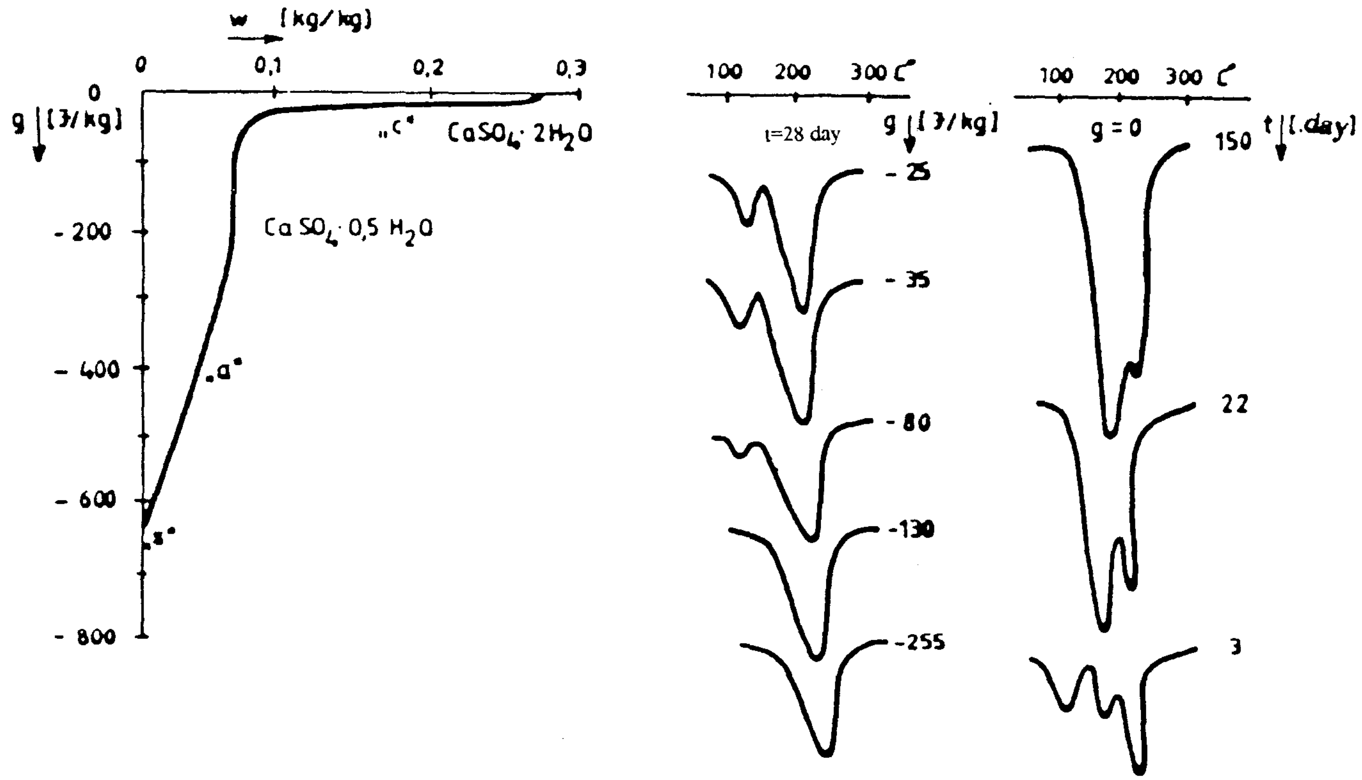

FIG. 2.

Water vapour adsorption of $CaSO_4$-III (left), DTG-curves of samples with different equilibrium water content (centre) and demonstration of water vapour adsorption as a function of time on DTG-curves (adsorption from saturated sample) (right).

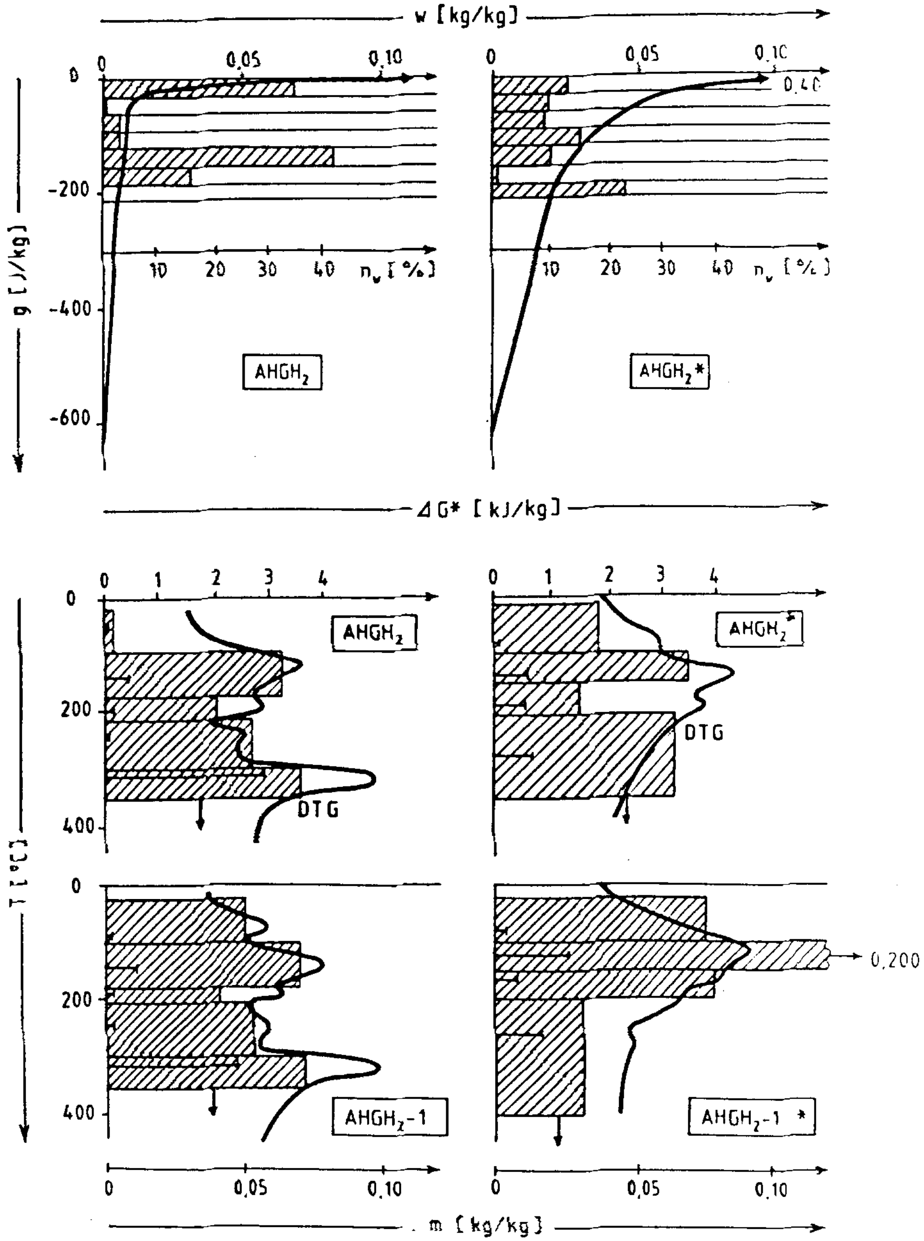

FIG. 3.
Experimental curves of mixtures of $Al(OH)_3$ and $CaSO_4.2H_2O$.

As far as mechanical activation of various modifications of $CaSO_4$ is concerned, we concluded in a previous publication [5] that by using anhydrite for grinding one can achieve much higher specific surfaces than with pure gypsum. During grinding, the crystal structure of gets decomposed, whereas that of gypsum not. The reason for this is that the crystal water

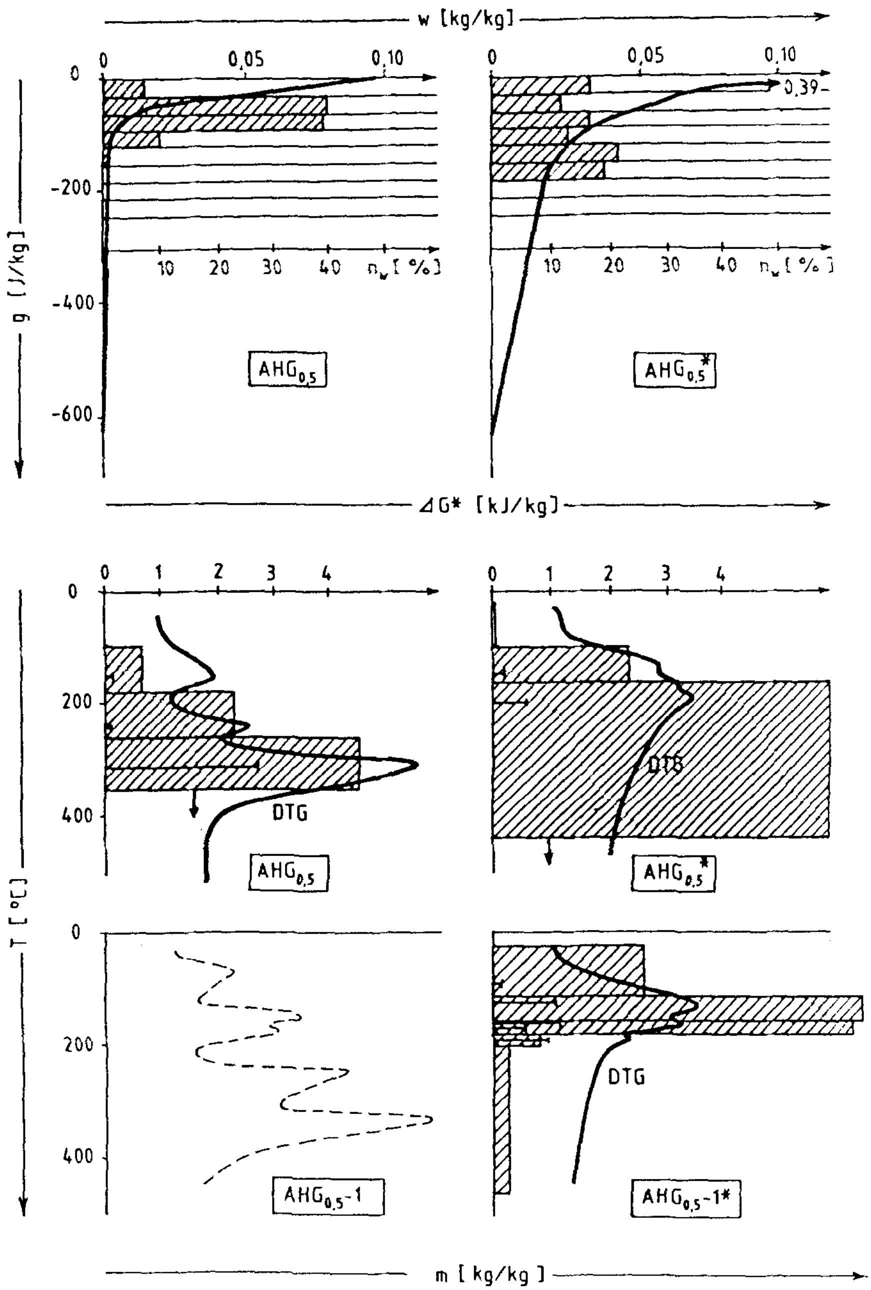

FIG. 4.
Experimental curves of mixtures of $Al(OH)_3$ and $CaSO_4.0.5H_2O$.

is easily removed due to mechanical ingressions and penetrates in the intergranular spaces where it dissolves calcium sulphate and re-crystallises.

Disproportionation of hemihydrate was observed:

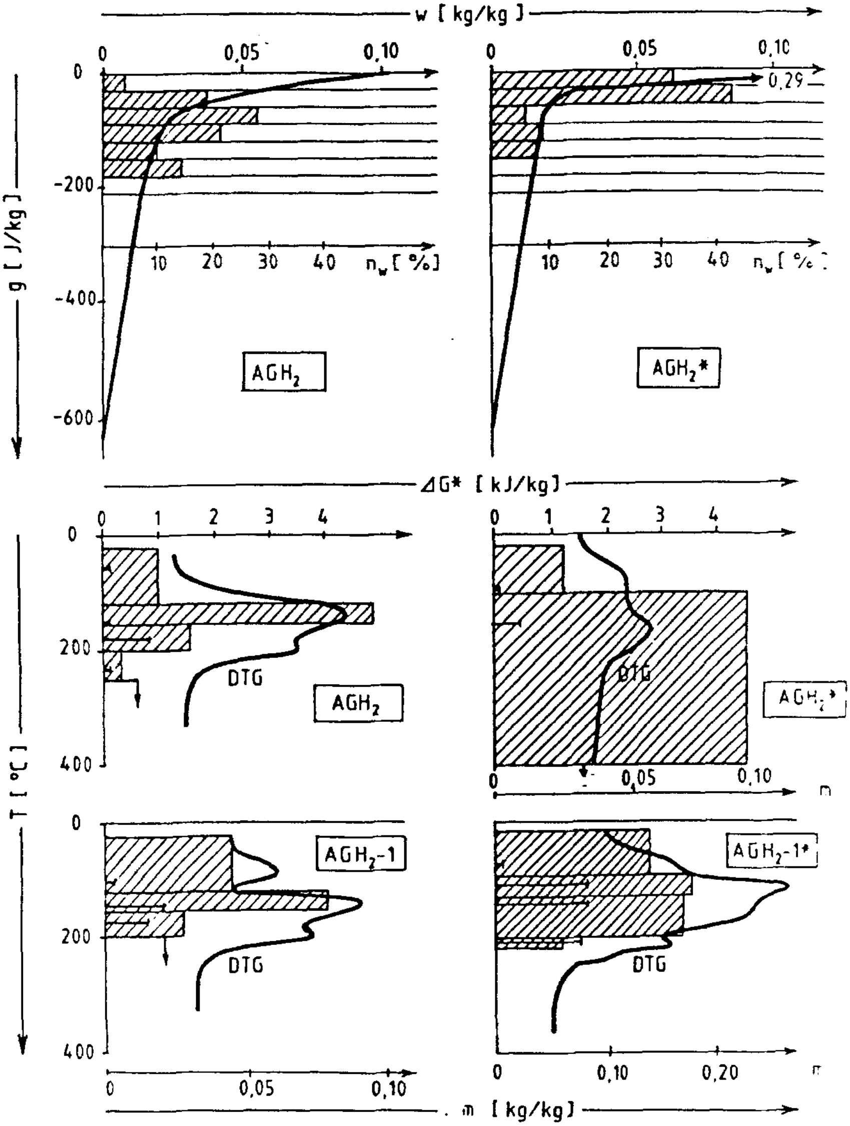

FIG. 5.
Experimental curves of mixtures of Al_2O_3 and $CaSO_4.2H_2O$.

$$4CaSO_4 \cdot 0.5H_2O = CaSO_4 \cdot 2H_2O + 3CaSO_4$$

As a result of the above reaction, pastes of plaster of Paris with water may lose their binding capacity after mechanical activation.

Experimental details of samples **AHGH**$_2$, **AHG**$_{0.5}$, **AGH**$_2$ and **AGH**$_{0.5}$ are given in Figs. 3-6. The adsorption potential curves are indicated on the top of the figures, while the thermoanalytical curves are in the centre and the thermoanalytical results of the samples kept in saturated water vapour for 2 months are in the bottom.

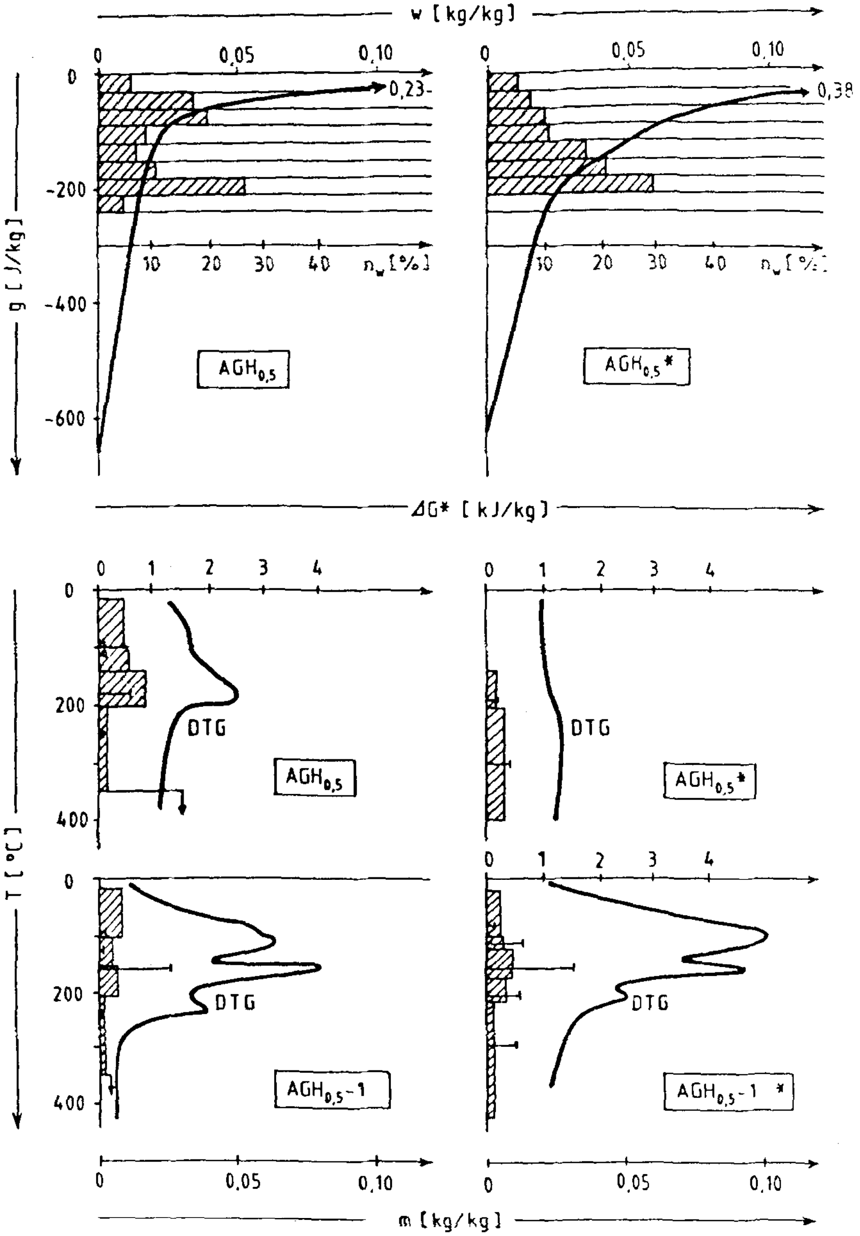

FIG. 6.
Experimental curves of mixtures of Al_2O_3 and $CaSO_4.0.5H_2O$.

Some observed phenomena:

- The water adsorption capacity generally increased; in activated material (of lower potential) even the share of fine pores increased

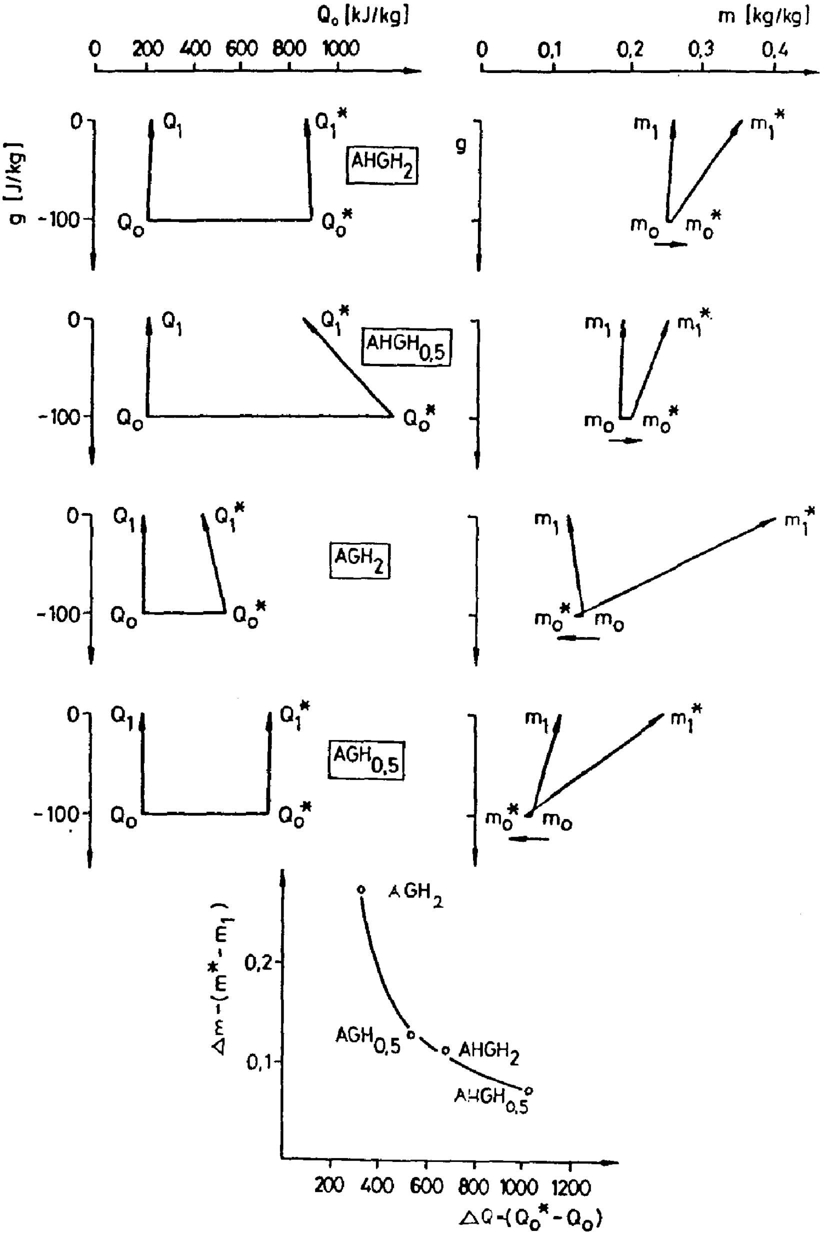

FIG. 7.

Changes of heat of dissolution (Q) and that of structural water (m) after mechanical activation and water vapour adsorption.

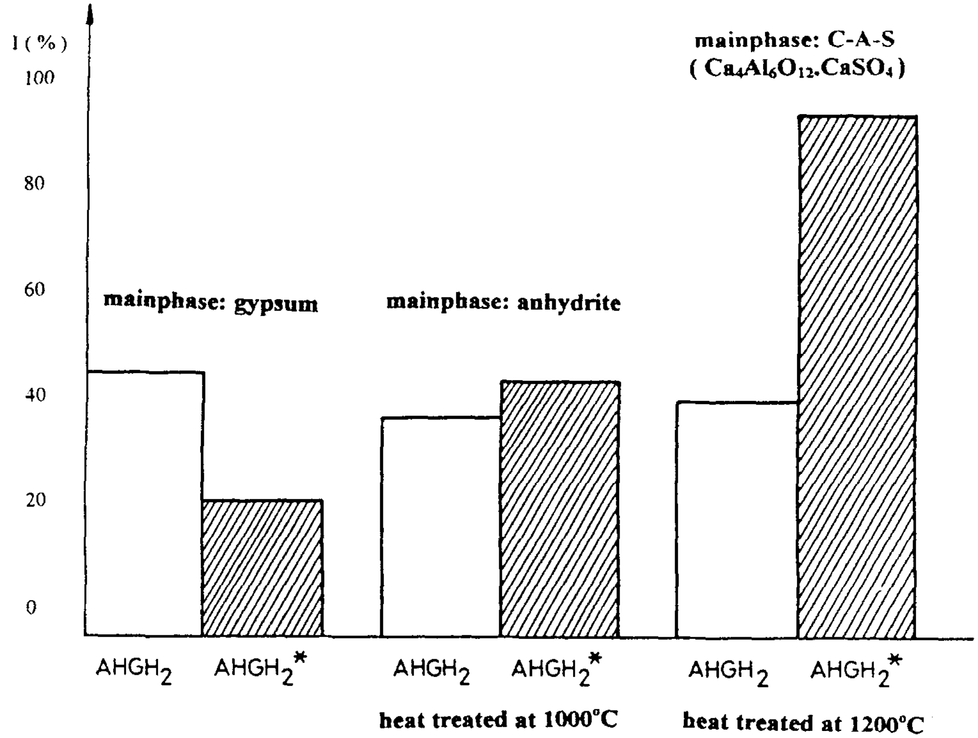

FIG. 8.

Diffraction maxima of crystalline components of mixtures of $Al(OH)_3$ and $CaSO_4.2H_2O$ in original state and after mechanical activation as well as after heat treatment.

- As a result of mechanical activation, the originally well separated water elimination thermal steps overlapped and the activation energy of dehydration usually decreased.
- The blurred thermal valleys of the activated samples split into distinguished water elimination steps, which suggests re-crystallisation (formation of dihydrate). (Because of the large amount of amorphous material present, nuclei of crystallisation could not be detected by XRD.)
- Significant differences were seen between the aluminium-hydroxide and the alumina containing powder mixtures. Adsorption capacity and specific surface of the former were largely increased, its pores became finer and increased in number. In the case of the alumina containing mixtures, however, the adsorption capacity and specific surface were only slightly increased, their pores became coarser and decreased in number. This means that in the aluminium hydroxide containing materials the rate of dispersion increased, whereas in the presence of alumina a pronounced aggregation occurred. The aluminium hydroxide as "internal grinding aid" promotes grinding, while gypsum hinders grinding and causes agglomeration.

Changes in the heat of dissolution and quantity of structural water (m) after mechanical activation and water vapour adsorption can be observed in Fig. 7. The heat of dissolution of the starting (untreated) materials, as it was expected, has hardly changed just after water vapour adsorption ($Q_0 \rightarrow Q_1$ transitions from potential level g = -100 to g = 0). After mechanical activation, however, the change was surprisingly large ($Q_0 \rightarrow Q_1^*$ transition within the g = -100 J/kg level). When the activated materials were stored in saturated water vapour atmosphere, greater of smaller decrease in heat of dissolution was found ($Q_0^* \rightarrow Q_1^*$ transitions between the bands), which corresponds to the re-crystallisation phenomena shown thermoanalytically.

- It is observed generally for the activated materials that larger amount of water is incorporated into the structure during storage in vapour atmosphere (right hand side drawings in Fig. 7.). Mechanical activation, however, caused hardly any changes in total amount of structural water.
- Fig. 7. also includes a drawing to compare the two series of measurements. It is obvious from the experimental results that after mechanical and subsequent adsorption treatments the mixtures containing gypsum dihydrate are more active for interactions (ΔQ_0 is higher) than are the mixtures containing hemihydrate (ΔQ_0 is lower). It is also to be concluded that the samples with hemihydrate incorporate more structural water in their lattice during water vapour adsorption (Δm is lower) than do samples containing dihydrate (Δm is higher). Nevertheless, activated mixtures containing aluminium hydroxide show a larger water uptake than do the ones containing alumina.

Fig. 8. shows selected XRD results for the sample **$AHGH_2$**

- Intensities of reflections of all components generally decreased as a consequence of mechanical activation. Especially remarkable is the decomposition of crystal structure of gypsum, which, as was indicated earlier, could not be achieved using pure gypsum.
- After heating to 1000°C and cooling to 20°C XRD peaks of anhydrite, CaO, MgO and, with reduced intensity, of γ-Al_2O_3 were observed. However, the figure shows that the amount of anhydrite (judged upon the intensity of its strongest reflection) is much higher in the activated sample than in the original one.
- After heat treatment at 1200°C for 2 hours, a calcium-alumino-sulphate crystalline phase appears, whose quantity is much larger after mechanical activation and vapour adsorption than was in the original mixture. (Al_2O_3 has re-crystallised to corundum; products arising from contamination were ignored.)

Findings, Conclusions

If surfaces and pores between particles of components in the investigated system are filled up with water not by adsorption from the vapour phase, but from the opposite direction i.e. from the solid phase by elimination of structural water as an effect of mechanical activation, can be observed mechanical *chemisorption* and *mechano-chemical capillary reactions*. These involve processes based on types of reactions not yet fully known, if not unknown, in chemistry.

During grinding, water is eliminated from the particles under mechanical stress (source: crystal water or H_2O molecules produced by internal condensation from OH-groups) and diffuses into the capillaries between the particles of the components. These capillaries and pores are of submicroscopic size [6, 14] as a result of agglomeration, thus are suitable for capillary condensation. Water appears especially at the critical mechanical tension of one of the components i.e. of the *donor*. Such donor may be the gypsum dihydrate or aluminium hydroxide.

The eliminated water on the one hand is adsorbed on the surface of the particles constituting the wall of the capillaries, but, when amounting to sufficient quantity or reaching a required vapour pressure, it also condenses and remains as pore water. On the other hand, the eliminated water can be confined in another component i.e. *acceptor* (by chemisorption, re-hydration). Such acceptor may be the anhydrite and alumina in the investigated system.

Capillary water can dissolve material from the surface of particles of one of the components and this saturated solution can attack the particles of another component e.g. that of aluminium hydroxide and oxy-hydroxide. This latter process is considered as mechanochemical capillary reaction. As a consequence of this interaction, various complex compounds can form from the supersaturated solution, which compounds are mostly gel-like phases or of extremely small particle size. Water molecules, eliminated under stress during mechanochemical reactions, are confined in the reaction products. Therefore, on interruption of the mechanical treatment, water molecules eliminated under mechanical stress cannot be built back into the dehydrated component. If neither suitable reaction partner is present, not water-containing product can appear (e.g. if gypsum is ground on its own), re-building of water or maybe its crystallisation in the pores are real options, and thus transformations in the structure of the materials will not occur.

Attention is called to the fact that gels, produced during mechanical capillary reactions, as nuclei for crystallisation, greatly affect thermal reactions. These effects become pronounced especially in determination of the quantity of products during thermal reaction in the investigated $CaSO_4$-H_2O-Al_2O_3 system.

Summary

From solid materials, which contain crystal water and OH-groups directly incorporated in the crystal structure with various binding energies, water can be eliminated not only by thermal energy, but also by mechanical activation e.g. by intensive grinding. These water molecules diffuse through the capillary system of the lot of particles to the gaseous phase. During diffusion water molecules are adsorbed, condense in the submicroscopic pores and also may induce chemical reactions. These reactions are called mechanochemical capillary reactions.

Present work demonstrates conclusions of the experiments intended to clarify the aforementioned reactions using model powder mixtures composed of gypsum and alumina.

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