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Thermochimica Acta 332 (1999) 89–96

thermochimica
acta

Dehydration behaviour of a natural gypsum and a phosphogypsum during milling

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Received 9 February 1999; accepted 30 March 1999

Abstract

The paper describes an investigation into the dehydration behaviour of a natural and a phosphogypsum under isothermal conditions. The purpose of the work was to assess whether there is a difference in the dehydration behaviour and what effects it could possibly have in practical applications in the cement industry. It was found that there is a significant difference in the amounts of moisture loss from the two materials under the same temperature conditions as well as their respective surface areas after dehydration. The results of the investigation indicate that great care should be exercised under production conditions when changing from the use of a natural gypsum as set retarder for cement to using a phosphogypsum. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Gypsum; Dehydration; Milling; Phosphogypsum; Surface area

1. Introduction

After cement clinker is cooled down to ambient temperature, it is usually ground in a ball mill. Ball mills consist of large steel tubes rotating around their axes. The inside is usually divided into a least two chambers, containing different size steel balls to grind the clinker ranging from lumps with diameters as large as 60 mm to small pieces with diameters of 13 mm or less [1,2]. Prior to entering the mill between 3% and 5% gypsum is added to the clinker to retard the hydration of the tricalcium aluminate phase and to optimise the strength-giving properties of the calcium silicates [2]. Upon addition of water to cement, the tricalcium aluminate phase (C_3A) reacts very quickly with the water, turning the mix into an unworkable solid mass. The process is referred to as ''Flash Setting'' of cement [1]. Gypsum or $CaSO_4{\cdot}2H_2O$ is slightly soluble in water and reacts with C_3A to form an insoluble sulphoaluminate hydrate, ettringite ($C_3A{\cdot}3CaSO_4{\cdot}32H_2O$) [1,3]. The ettringite forms a boundary layer between the individual C_3A crystals and thus controls the setting process.

Naturally occurring gypsum, phosphogypsum (a by-product of various industries) or synthetic gypsum can all be added to the cement clinker. All these gypsum types consist of various amounts of $CaSO_4{\cdot}2H_2O$ (calcium sulphate dihydrate), $CaSO_4{\cdot}(1/2)H_2O$ (calcium sulphate hemihydrate) and $CaSO_4$ (calcium sulphate anhydrite). The ratios in which these calcium sulphate forms occur in the gypsum can have a profound effect on the setting behaviour of the cement, because their respective solubilities in water are significantly different from one another. The dihydrate form is the preferred form

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PII: S0040-6031(99)00083-0

required in the cement. Hewlett reported that at grinding temperatures between 115°C and 130°C, the dihydrate form can dehydrate to the hemihydrate form and to a lesser extent to calcium sulphate anhydrite, which upon mixing with water forms a supersaturated solution with respect to the dihydrate form. This leads to gypsum precipitation and some rigidity or stiffening of the concrete or mortar, making it necessary to add more water for workability and resulting in a lowering of the strength properties. This process is referred to as ''False Setting'' [2,3]. The ratios between the different calcium sulphate forms in the final product are thus crucial for the cement industry.

It was decided to investigate the degree of dehydration of a naturally occurring gypsum and a phosphogypsum at various isothermal conditions between 90°C and 140°C in a first effort to simulate milling conditions. By far the largest source of gypsum is from the manufacture of phosphoric acid by the reaction of phosphate rocks with sulphuric acid [4]. Unreacted phosphates and other impurities combine with the calcium sulphate compounds and the whole residue is called phosphogypsum. The change in surface area during milling and subsequent partial dehydration of the compounds can be an indication of the reactivity of the compounds, as an increase in surface area also increases the number of surface active points or nuclei, where reaction, in this case dissolution in water, starts [5].

2. Experimental

2.1. Samples

The naturally occurring gypsum was obtained from Gypsum Industry's deposit in the Northern Cape Province, through PPC, and the phosphogypsum from Omnia Fertiliser's plant in Rustenburg, Northwestern Province.

2.2. Thermogravimetric analysis

Analysis to obtain the percentages dihydrate, hemihydrate and anhydrite of the samples was performed on a NETZSCH STA 409 simultaneous TG/DSC instrument. Temperature calibration was achieved using the ICTAC recommended DTA standards. Sample sizes varied between 15 and 25 mg. A heating rate of 5°C min^{-1} was used in a static air atmosphere. All data were obtained using covered sample pans.

For the dehydration studies mass-loss curves were obtained using a Leco 601 thermogravimetric analyser (TGA). Sample sizes between 2 and 3 g were used. In order to obtain the maximum dehydration at the various constant temperatures, sample pans were not covered.

2.3. X-ray powder diffraction analysis

X-ray powder diffraction analyses were performed on a Siemens D5000 XRD spectrometer using Cu K_α radiation. The PDF-1 database from ICDD was used to analyse the data.

2.4. XRF analysis

X-ray fluorescence analyses were performed on a Siemens SRS 330 wavelength-dispersive XRF spectrometer. Table 1 summarises the XRF analysis of each sample.

According to these results, the impurities other than hemihydrate and anhydrite in the natural gypsum sample is approximately 5.9% and for the phosphogypsum it is 2.6%.

Table 1
XRF analysis of the natural gypsum and the phosphogypsum

Compounds	Natural gypsum (%)	Phosphogypsum (%)
SiO_2	3.7	0.2
Al_2O_3	0.3	0.1
Fe_2O_3	0.2	<0.1
Mn_2O_3	<0.1	<0.1
TiO_2	0.1	<0.1
CaO	31.0	37.0
MgO	1.0	0.1
P_2O_5	<0.1	1.5
SO_3	43.8	52.2
Cl	0.1	<0.1
K_2O	0.1	<0.1
Na_2O	0.1	<0.1
SrO	0.2	0.3
Loss on ignition	19.4	8.5
Total	100.0	99.9

2.5. Surface areas

The gypsum samples were heated for periods of 5–120 min in a Term-O-Mat laboratory oven at temperatures of 90°C, 100°C, 110°C, 120°C, 130°C and 140°C. The surface areas were immediately determined on a Micromeritics FlowSorb II 2300 BET instrument, using nitrogen gas as an adsorbant.

3. Results and discussion

3.1. Composition of the gypsums

Literature reports two methods to determine the percentages of the hydrates of calcium sulphate. In the first method differential scanning calorimetry was used, with the prerequisite that sample pans must be closed [6]. The second method describes the analysis by thermogravimetry in an atmosphere containing a water vapour pressure of at least 88 Torr [7]. It is known that the pure β-hemihydrate form of calcium sulphate can only be synthesised under a water vapour pressure at temperatures above 100°C. Under higher pressure, also in a water vapour saturated atmosphere, it is possible to obtain the α-hemihydrate of calcium sulphate [8].

To obtain approximations of the percentages of the dihydrate, the hemihydrate and the anhydrite, thermogravimetric analysis of the samples were performed using closed crucibles. Fig. 1 shows the mass loss and differential scanning calorimetric curves for the natural gypsum and the phosphogypsum. Using the XRF, thermogravimetric and differential scanning calorimetric data, it is calculated that the natural gypsum sample mainly consists of the dihydrate form of calcium sulphate (94%). The phosphogypsum sample contains 16% dihydrate, 66% hemihydrate and 15% anhydrite of calcium sulphate.

X-ray diffraction data confirm that the natural gypsum sample mainly consists of the dihydrate of calcium sulphate and that the phosphogypsum has the

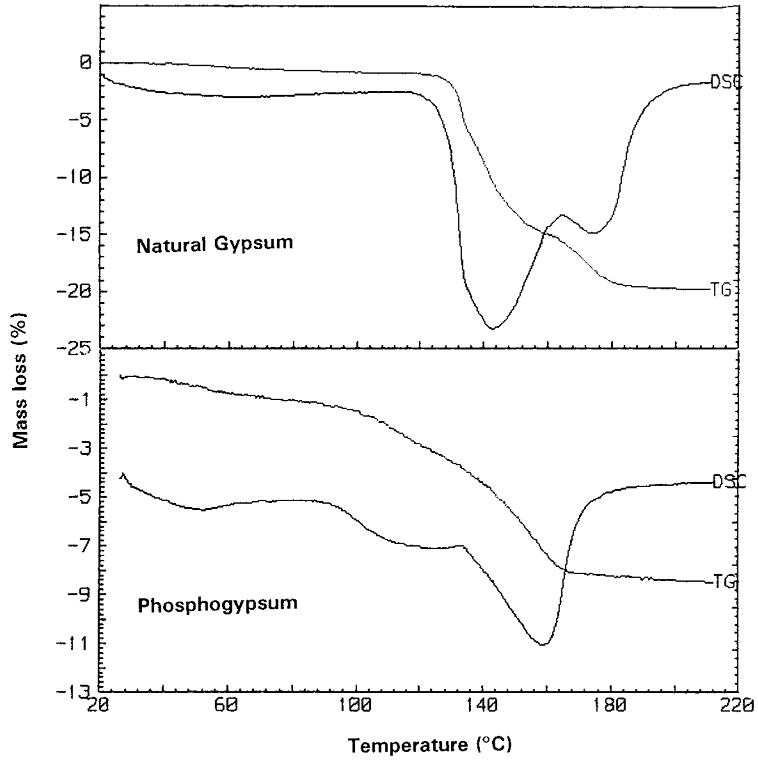

Fig. 1. Mass loss and differential scanning calorimetric curves for the gypsum samples using a heating rate of 5°C min^{-1}.

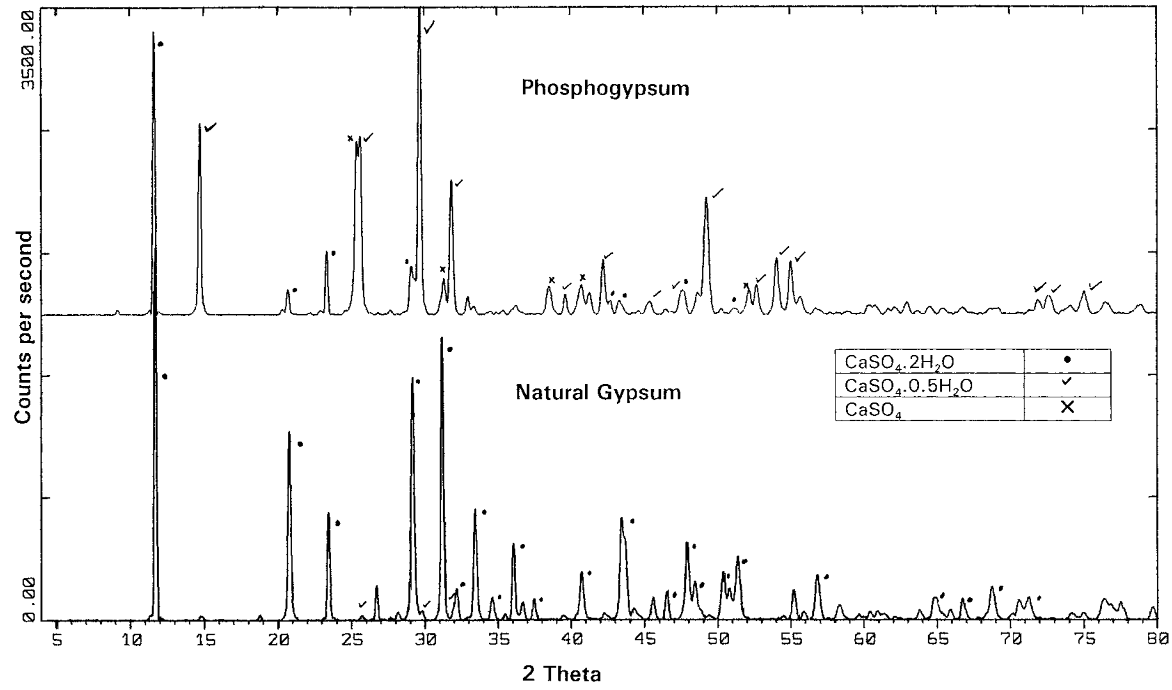

Fig. 2. XRD scan of natural gypsum and phosphogypsum.

di-, hemi and anhydrite forms of calcium sulphate (Fig. 2).

3.2. Surface area changes during dehydration

Fig. 3 gives the change in surface area with time at the different temperatures for the natural gypsum and Fig. 4 that for the phosphogypsum. As is expected from the difference in chemical composition between these two compounds, the change in surface area for the phosphogypsum is overall smaller than that for the natural gypsum. Isothermal dehydration of $CaSO_4 \cdot 2H_2O$ is reported to be controlled by two reaction mechanisms; up to 100°C it is dominated by first-order kinetics and above 110°C, it is dominated by a two dimensional phase boundary mechanism [9]. The first-order mechanism seems to consist mainly of the external diffusion of water molecules, evaporated from the surface of the solid, as the rate determining step. The change in surface area with time at the different temperatures for the natural gypsum seems to confirm this tendency as the curves clearly form two groups, one group of slow change at temperatures of 100°C and lower and another group at

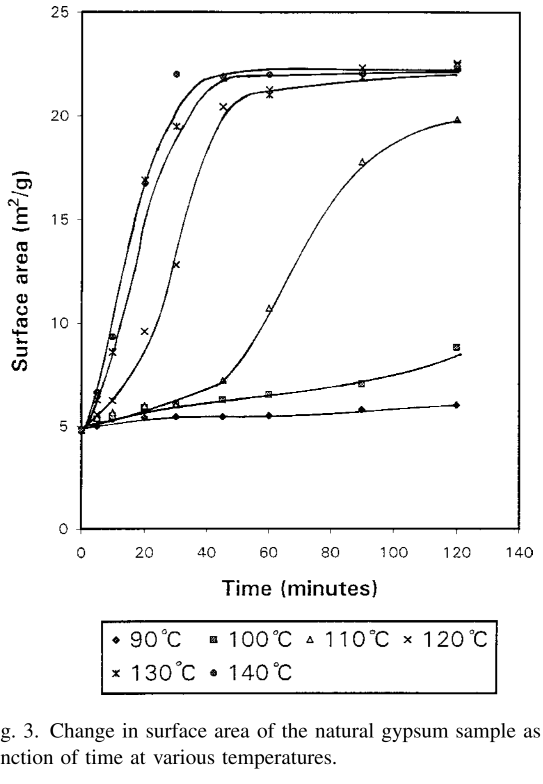

Fig. 3. Change in surface area of the natural gypsum sample as a function of time at various temperatures.

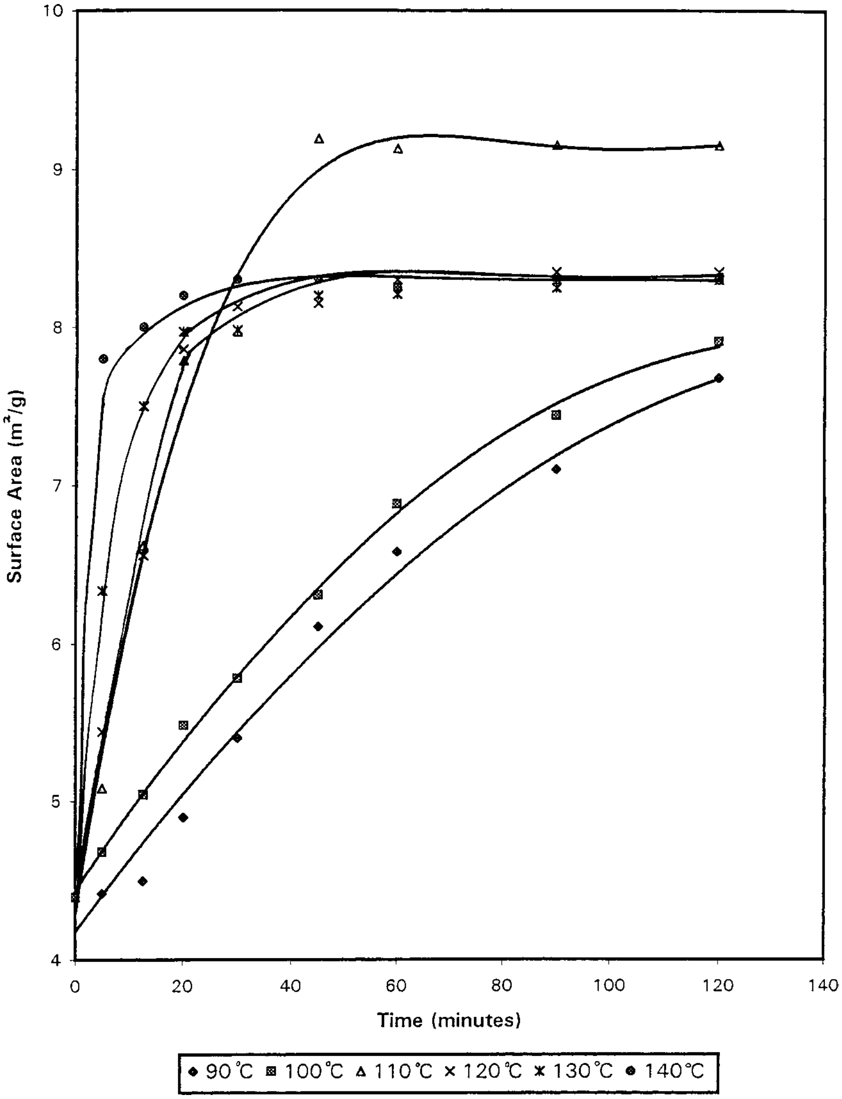

Fig. 4. Change in surface area of the phospogypsum sample as a function of time at various temperatures.

temperatures above 110°C. As expected, the higher the temperature, the faster the increase in surface area, until a maximum of approximately 22.5 $m^2 g^{-1}$ is reached for the natural gypsum sample.

The change in surface area with time for the phosphogypsum sample (Fig. 4) indicates the same tendencies as for the natural gypsum sample up to 20 min. For longer exposure times to the different temperatures, however, it was observed that a maximum surface area is obtained for heating at 110°C (9.2 $m^2 g^{-1}$), after which the surface area drops off to a value of 8.3 $m^2 g^{-1}$ as a maximum for all temperatures above 110°C. This clearly indicates that the mechanisms involved in the dehydration of the phosphogypsum sample are different from that of the natural gypsum, and that some of the impurities in phosphogypsum could influence the dehydration mechanism.

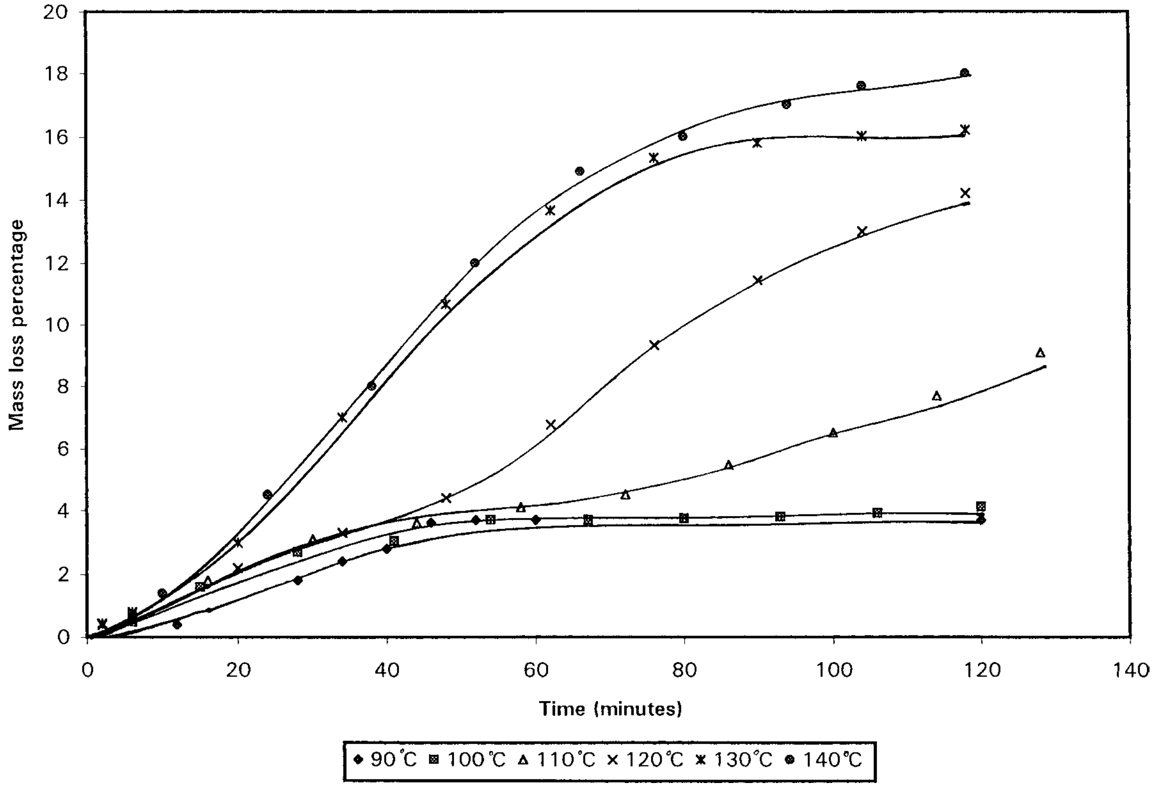

Fig. 5. Mass-loss curves at various constant temperatures against time for the natural gypsum sample.

3.3. Isothermal dehydration thermogravimetric analysis

Fig. 5 gives the mass-loss curves at various constant temperatures against time for natural gypsum and Fig. 6 the values for the phosphogypsum. For the natural gypsum it seems that dehydration at temperatures of less than 100°C reaches a maximum value of approximately 4% mass loss, indicating a remaining dihydrate content of approximately 80%. Maximum dehydration is only obtained after heating the natural gypsum sample for more than 120 min. at 140 °C, the value of 18.0% mass loss still being lower than the mass-loss percentage obtained for the complete dehydration of this natural gypsum sample (19.6%). These values were obtained under much lower humidity conditions than those normally existing in cement mills into which water is sprayed to control the milling temperatures. This means that under normal milling conditions in a cement plant most of the natural gypsum in the cement produced should remain in the preferred dihydrate form, provided that the temperature inside the mill does not get too high and is controlled well.

Much lower mass-loss percentages were observed for the phosphogypsum sample, as the sample contains much less calcium sulphate dihydrate (approximately 16% as determined by the dynamic thermogravimetric method). The maximum dehydration after 120 min at 140°C is 7.4%. The use of such a material in cement production will necessarily entail more elaborate quality control measures to ensure that the material used in mills consist mostly of the preferred dihydrate form and remains so during milling. Furthermore the different mechanism of dehydration will probably also necessitate more strict and maybe even slightly different mill control procedures.

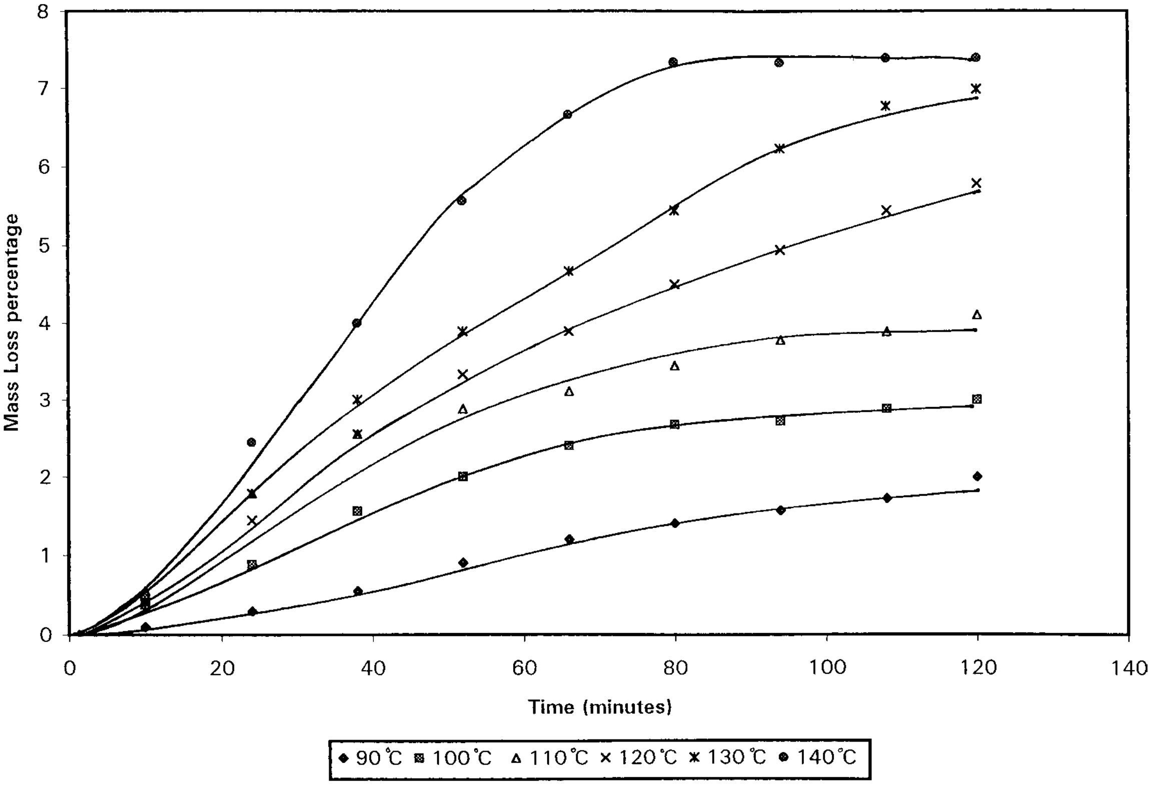

Fig. 6. Mass-loss curves at various constant temperatures against time for the phosphogypsum sample.

4. Conclusions

The mass-loss curve obtained at the various constant temperatures (Figs. 5 and 6) can be used as an indication of the percentage calcium sulphate dihydrate left after cement clinker with the added gypsum were milled for a certain time at a known temperature. The values obtained from the figures are optimum values, as small sample sizes in comparison to the mill sizes were used. The water vapour pressure in a mill will also be higher than for the small sample sizes and thermogravimetric analyser set-up.

The percentages of the dihydrate, hemihydrate and anhydrite of calcium sulphate in the gypsum samples can vary significantly among different gypsum types, especially the phosphogypsums originating from different process routes, plants and operating conditions and can influence the dehydration behaviour of the gypsums. Therefore, it seems necessary that the dehydration behaviour of each material used in industry must be studied separately to obtain an indication of the dihydrate composition of a gypsum in a milled cement sample, as the latter would have a major effect on the setting behaviour of the final product. It would also be beneficial if sensitive enough measurement methods are developed to quantitatively determine the various forms of calcium sulphate in cement after milling. The quantification of the residual amount of calcium sulphate hemihydrate that could result in "Flash Set" problems also requires attention.

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