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KINETICS OF THE THERMAL DECOMPOSITION OF $C_4A_3\overline{S}$ IN AIR

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ABSTRACT

In this paper a study on the thermal behaviour of $C_4A_3\overline{S}$ (in an open system and up to 1500ºC) is presented as well as the kinetics of decomposition of this compound. At temperatures higher than 1300ºC, the thermal decomposition of C_4A_3S starts. Such a process is linked to a loss of SO_2 simultaneously with a production of CA and CaO. After that CA and CaO reacts giving $C_{12}A_7$. If the temperature is lower than 1400ºC or even being higher than 1400ºC (between 1400 and 1500ºC) although only during the first moments, the decomposition process of C_4A_3S occurs through a solid-gas reaction. This reaction is controlled by a first order kinetic and can be represented by the following equation:

$$F_1\ (\alpha) = \mathrm{Ln}\ (1-\alpha) = -\ kT$$

having a energy of activation E_a = 538 Kj mol. When the temperature surpasses 1400ºC then a melting of at least $C_{12}A_7$ and CA phases takes place. It occurs in such a way that when $\alpha > 0,5$, the $C_4A_3\overline{S}$ decomposition is produced in the presence of a quantity of liquid enough for considerably modifying its kinetic.

Introduction

3 $CaO.3Al_2O_3.CaSO_4$ ($C_4A_3\overline{S}$) is the alumina-bearing compound in expansive cement type K. This cement was developed in 1966 by Klein (1), and is made by grinding together a portland cement clinker and an expansive clinker with gypsum and/or anhydrite.

Expansive clinkers, contain, besides $C_4A_3\overline{S}$, alite, belite, C_4AF, $CaSO_4$ and some free lime. They are made in rotary kilns at a 1300º -1400ºC temperature interval.

The first evidence of the existence of $C_4A_3\overline{S}$ appears in 1957, when Ragozina(2) studying the CaO-Al_2O_3 -SO_3 ternary system, found a new compound with formulae 1.6-3.6 ($CaO.4Al_2O_3.3SO_3$).

Klein and Troxell (3) prepared an expansive cement from a mixture of $Ca(OH)_2$, gypsum and bauxite at 1350ºC and demonstrated that a ternary phase ($5CaO.2Al_2O_3.SO_3$ or $9CaO.4Al_2O_3.3SO_3$) occurred.

Fakuda (4), in 1961, indicated that the resulting product from the mixture of bauxite, gypsum and lime at 1350ºC, was $3CaO.3Al_2O_3.CaSO_4$.

$C_4A_3\bar{S}$ is one of the main phases of the sulphoaluminate belite cements (5, 6, 7).

Halstead and Moore (8) made a very extensive study of $C_4A_3\bar{S}$ determining its density (2.6 grs/cc), refractive index (1.57), melting point in a closed system (≈1600ºC) and lattice constants. C_4A_3S has a body-centered cubic crystalline structure with a_o = 18.39 Å.

More recently, Zhang et al (9), studying the monomineral, have indicated that C_4A_3S belongs to the tetragonal system, having the lattice constants $a_o = b_o = 13.031$ Å and $c_o = 9.163$ Å and space group $D^62^d - P_4C_2$.

In 1991, Feng Xiuji (10) showed that the lattice constant obtained after the X-ray diffraction analysis of a C_4A_3S monocrystal was $a_o = 9.167$ A, while in powder samples this constant was more similar to 2 a_o.

The thermal stability of $C_4A_3\bar{S}$ was found by Halstead and Moore (8) to be better than expected, as at synthesis temperature, 1350ºC, the pressure of dissociation of SO_3 in $CaSO_4$, is 29 mmHg. This seems to indicate, according to these authors, that SO_3 in C_4A_3S is more strongly fixed than in $CaSO_4$.

At 1350ºC, Halstead and Moore demonstrated by means of thermogravimetry that the decomposition velocity (loss of SO_3) of $CaSO_4$ was thirty times higher than $C_4A_3\bar{S}$. These authors did not give data related to the mechanism and kinetics of the decomposition process of this compound.

Gang-Soon and Glasser (11) measured the vapor pressure of some sulfated compounds, important for the cement chemistry, up to 1400ºC. This authors reported that C_4A_3S vapour pressure is lower than $CaSO_4$ one.

The aim of this work is to study the thermal stability of $C_4A_3\bar{S}$ in an open system and high temperatures (in a 1300º-1500ºC range), determining the kinetics of the decomposition process.

Experimental

The compound $C_4A_3\bar{S}$ was synthesized from stoichiometric amounts of reagent grade CaCO3, Al_2O_3 and $CaSO_4$. The mixture was homogenized in an agate mortar using ethanol as dispersing medium. The resulting mixture was thermally treated, in a laboratory furnace, at 1300ºC for 2h 30′. Some homogenizations during the thermal treatment were made, in order to facilitate the reaction.

The degree of purity of synthetic $C_4A_3\bar{S}$ was evaluated by using XRD and IR spectrocopy.The thermal behaviour of the compound was studied using high-temperature microscopy and DTA-TG.

The studies on thermal stability were carried out on a Mettler thermobalance, by means of developing isothermal treatments at temperatures of 1300ºC, 1350ºC, 1400ºC, 1450ºC and 1500ºC. The heating of the sample was performed at a velocity of 8ºC/min., until reaching the selected final temperature and maintaining it for twenty one hours. The TG sensitivity was 10 mgrs. The analyses were made in air atmosphere.

The solids obtained after the isothermal experiments were analyzed through XRD.

Results and Discussion

The diffraction pattern of $C_4A_3\bar{S}$ only presents the reflections of this phase. Its IR spectrum shows the characteristic absoptions of this phase. Neither anhydrite nor other sulfated compounds were found.

From high temperature microscopy it can be deduced that the specimen deformation starts at 1400ºC and its volume decreases as temperature increases. At 1500ºC, the area observed in the photographs is approximately 35% lesser than the initial one. However, the melting point of $C_4A_3\bar{S}$ has not still been reached.

Volume shrinkage observed cannot be only justified because of the loss of SO_2, under temperature effects, according to reaction [1]:

$$3CaO.3Al_2O_3.CaSO_4 \xrightarrow{T^a} 3(CaO.Al_2O_3) + CaO + SO_2 + 1/2\ O_2 \qquad [1]$$

The visual observation of the sample after this high temperature microscopy test indicates that a partial melting has taken place.

Table I shows the results of XRD analyses of the samples isothermally treated in the range of 1300º-1500ºC (at 50º C intervals) for twenty-one hours.

As a consequence of the thermal treatment, tetracalcium sulphoaluminate, $C_4A_3\bar{S}$, decomposes eliminating SO_3 and obtaining CA and CaO. These phases are not compatible, and by solid state reaction produce $C_{12}A_7$. Consequently the presence of this aluminate is detected in the diffractogram patterns of the samples. The increasing intensity in the characteristic diffraction lines of these compounds (d = 2.97 Å for CA and d = 2.68 Å for $C_{12}A_7$), is simultaneous with the decreasing intensity of the main reflections due to C_4A_3S. Above 1400ºC, CA and $C_{12}A_7$ appear to be the major phases, although some $C_4A_3\bar{S}$ is still observed.

TABLE I

XRD of samples after isothermal treatments during 21 hours

SAMPLES	IDENTIFIED PHASES (XRD)
$C_4A_3\bar{S}$	$C_4A_3\bar{S}$ +++ CA o
$C_4A_3\bar{S}$ TG 1300ºC	$C_4A_3\bar{S}$ +++ CA o $C_{12}A_7$ o
$C_4A_3\bar{S}$ TG 1350ºC	$C_4A_3\bar{S}$ +++ CA + $C_{12}A_7$ +
$C_4A_3\bar{S}$ TG 1400ºC	$C_4A_3\bar{S}$ ++ CA ++ $C_{12}A_7$ ++
$C_4A_3\bar{S}$ TG 1450ºC	$C_4A_3\bar{S}$ ++ CA +++ $C_{12}A_7$ +++
$C_4A_3\bar{S}$ TG 1500ºC	$C_4A_3\bar{S}$ + CA +++ $C_{12}A_7$ +++

+++ = Abundant
++ = Moderate
+ = Little
o = Trace

Figure 1 shows the DTA - TG $C_4A_3\bar{S}$ curves during the heating until 1500ºC and subsequent cooling. No endothermic sign typical of melting appears in the DTA curve during the heating. However, an exothermic peak is observed in the cooling curve at 1360ºC, as a result of the solidification of a melt.

Chatterjee and Zhmoidin (12) studied the $CaO-Al_2O_3$ binary system, indicating the existence of a binary eutectic point between CA and $C_{12}A_7$ at approximately 1390ºC; with a composition of about 25% CA and 75% $C_{12}A_7$.

So, during the thermal treatment of $C_4A_3\bar{S}$ in an open system at temperatures higher than 1300ºC, the decomposition of $C_4A_3\bar{S}$ is produced according to reaction [1]. The subsequent reaction of CA and CaO produces $C_{12}A_7$. Above 1400ºC a melted phase appears as a

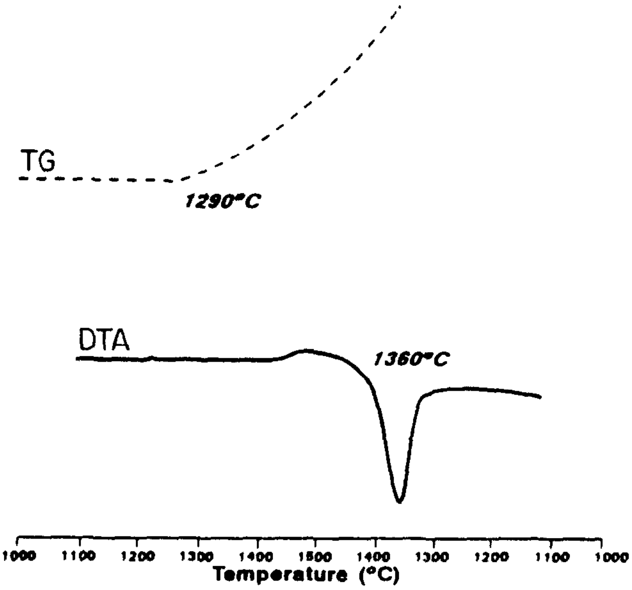

Figure 1

DTA and TG curves of $C_4A_3\bar{S}$

consequence of the binary eutectic $C_{12}A_7$-CA, although C_4A_3S might participate in the melting.

Kinetics of the Decomposition of $C_4A_3\bar{S}$

Figure 2 represents α (the decomposed fraction of $C_4A_3\bar{S}$) versus time at the different temperatures studied.

At 1300ºC an induction period of almost four hours, after which C_4A_3S starts to lose weight, was observed. After that, C_4A_3S continues losing weight progressively until the end of the experiment 21 hours later.

In the experiments carried out above 1300ºC the induction period is not observed. C_4A_3S is losing weight while the dynamic heating up to 1500ºC is taking place (see figure 2).

From the isothermal curves it is deduced that above 1400ºC, the decomposition of this phase evolves through two different mechanisms.

It is convenient in comparing experimental data to transform the curves from the type $\alpha = f(t)$ into the form $\alpha = f(t/t_{0.5})$, where $t_{0.5}$ corresponds to the time at which the half of the reaction has been produced. The curves obtained are shown in figure 3.

Experimental data obtained at 1300º, 1350º and 1400ºC are well adjusted to a single curve which corresponds to a first order

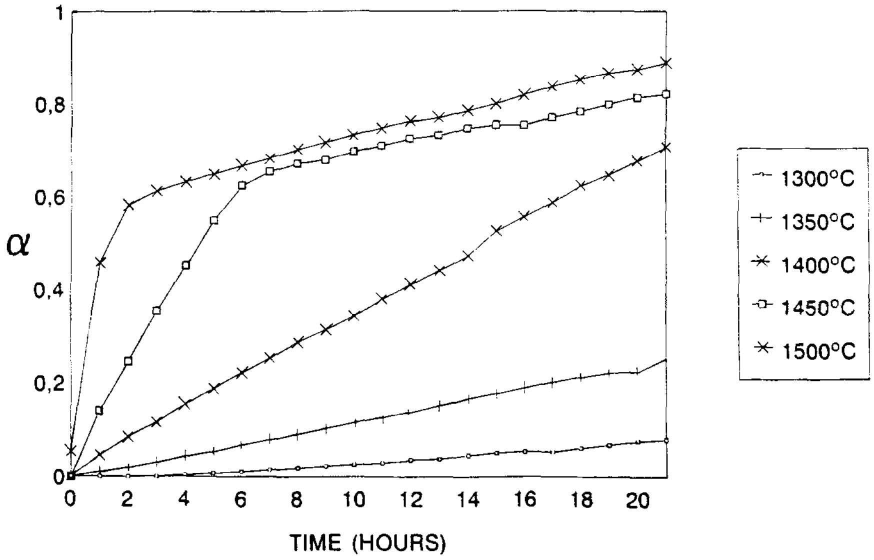

Figure 2

Fraction decomposed α vs.time for isothermal decomposition of $C_4A_3\bar{S}$

kinetic equation (13).

$$F_1\ (\alpha) = Ln\ (1-\alpha) = -kt \qquad [2]$$

Experimental data obtained at 1450º and 1500ºC do not conform to a single curve. These curves show two parts; the first one,

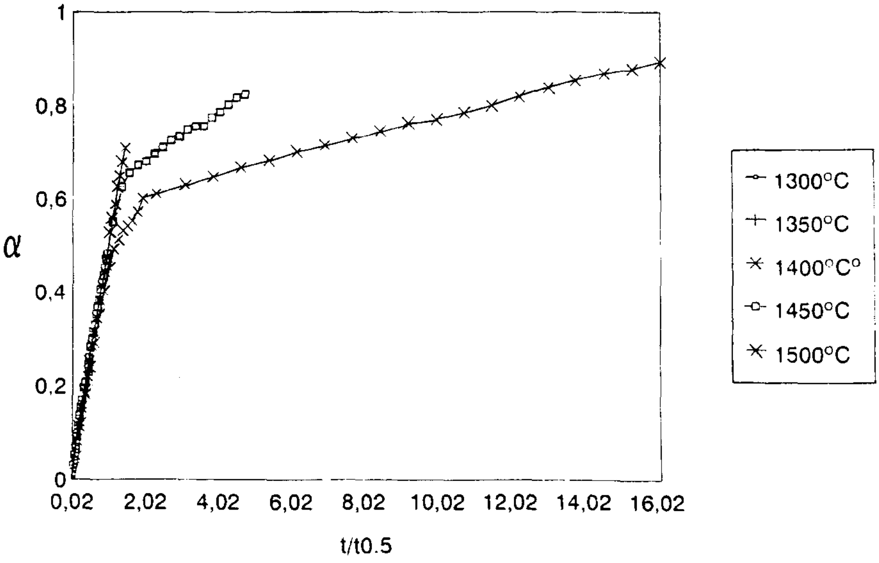

Figure 3

Fraction decomposed α vs. reduced time $t/t_{0.5}$

until α = 0.5 -0.6, where the experimental data coincide with those obtained at lower temperatures, being also fitted to a first order kinetic equation [2]. The second part of the curve obtained at 1450ºC, that is to say, for α values higher than 0.5 - 0.6, fits with moderate precision to the kinetic equations given by Ginstling and Brounshtein (14) for diffusion-controlled reactions in a sphere, but that obtained at 1500ºC does not adjust conveniently.

From the results, it can be deduced that when the process of decomposition of $C_4A_3\underline{S}$ develops according to the reaction [1], that is to say, in a solid-gas heterogeneous system, at a 1300ºC-1500ºC temperature interval, the kinetics of the process are in good agreement with a first order reaction (and can be described by the equation [2]).

As a consequence of this decomposition process, a melt is obtained. The presence of this liquid in relatively high quantities modifies the decomposition process mechanism considerably.

Supposing the composition of the melt that of the binary eutectic described by Chatterjee and Zhmoidin between CA and $C_{12}A_7$ and that $C_4A_3\underline{S}$ do not operate in the process, the quantity of liquid phase present for values of α = 0.5, would be 25% in weight. This liquid proportion seems to be critical, modifying the SO_3 vapor pressure in $C_4A_3\underline{S}$ and decreasing its decomposition velocity.

Hanic et al. [15], studying the kinetics of decomposition of $CaSO_4$, describe equally two kinetic models; the first at subeutectic temperatures which corresponds to a first order kinetic equation and the second in presence of a melt, which is controlled by a phase boundary reaction in which an interphase moves at a constant velocity.

Figure 4 shows the value of the first order kinetic equation [2] for the experimental values of the decomposed fraction α and time, at temperatures of 1300º, 1350º and 1400ºC, as for the first step at temperatures of 1450º and 1500ºC.

The linear representation allows one to measure the temperature coefficients of the rate constants. These parameters are needed for the calculation of the activation energy Ea.

The temperature coefficients of the rate constants were obtained by applying the least square methods, and then used in the representation of the Arrhenius equation shown in figure 5.

The activation energy for reaction [1] at temperatures lower than 1400ºC and for the first decomposition step (up to α = 0.5) at temperatures between 1400-500ºC is 538 KJ mol^{-1}.

Conclusions

The main conclusions which can be extracted from this study are:

1.- In an open system and at temperatures higher than 1300ºC

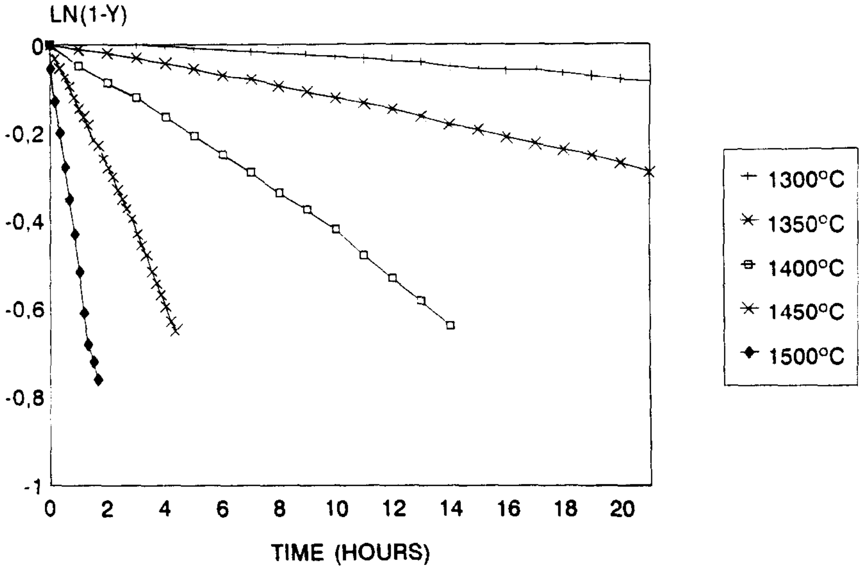

Figure 4

The plot of experimental conversion of α by the first order kinetic ecuation vs. time

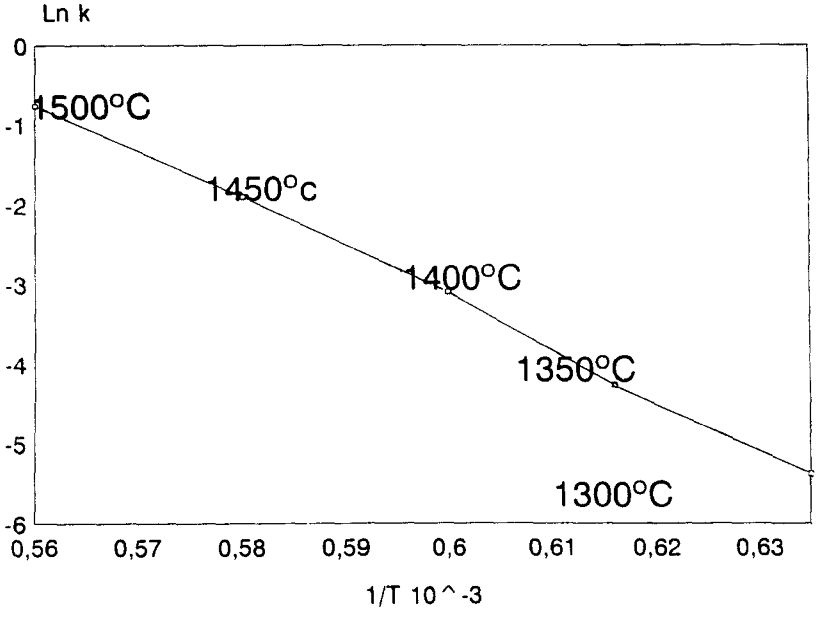

Figure 5

Arrhenius plot for the isothermal decomposition of $C_4A_3\overline{S}$

the decomposition of C_4A_3S is produced according to the reaction [1]. The subsequent reaction products react to form $C_{12}A_7$. When the treatment temperature is higher than 1400ºC a melt occurs due to the binary eutectic $C_{12}A_7$ - CA, although it is not denied that $C_4A_3\bar{S}$ might also operate in that process.

2.- In the absence or low proportion of a melting phase, that is to say, at temperatures lower than 1400ºC or when the decomposition degree α is lower than 0.5 (in the 1450ºC-1500ºC temperature interval), the thermal decomposition of C_4A_3S obeys a first order kinetic, represented by the equation:

$$F_1\ (\alpha) = Ln\ (1-\alpha) = -\ kT$$

in which activation energy, Ea is 538 Kj mol^{-1}.

3.- For values of $\alpha > 0.5$ and temperatures higher than 1400ºC, the liquid phase proportion is near 25% in weight. This proportion seems to be critical, modifying SO_3 vapor pressure in C_4A_3S and decreasing its decomposition velocity. A transformation in the kinetics of the process similar to a decomposition controlled by a diffusion mechanism through a liquid is developed.

aknowledgement

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