Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 1021-1029

MINERAL COMPOSITION OF BUILD-UP IN CEMENT KILN PREHEATER

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Abstract

Use of a short rotary kiln with a cyclone preheater allowed the internal recirculation of volatile constituents, essentially consisting of compounds of potassium, chlorine and sulphur. These compounds underwent partial condensation on the raw material grains, composed mainly of calcite. The increasing concentration of volatile constituents created convenient conditions for the crystallization of new phases, particularly sylvite. Beautiful crystals of this phase were formed, probably by the VLS mechanism. Thermal analysis revealed that a liquid phase was formed in the system at the relatively low temperature of about 630°C, which enhanced the reaction of silica with calcium carbonate, and spurrite was formed. Thus, the build-ups were composed mainly of calcite, sylvite and spurrite, and in some cases also of calcium oxide and anhydrite. Sulphospurrite, gehlenite, calcium langbeinite, dicalcium silicate and calcium aluminate, $12CaO \cdot 7Al_2O_3$ were found as minor components.

Keywords: anhydrite, build-up, calcite, preheater, rotary kiln, spurrite, sylvite

Introduction

In a modern cement plant, rotary kilns with cyclone preheaters are used. These kilns are very economical, with a low heat consumption of about 3000 kJ kg^{-1} of clinker and with an efficiency coefficient higher than 60%. However, these kilns have the disadvantage: build-up formation. It is the result of the increase in concentration of some components with a relatively high vapour pressure, which therefore evaporate in the sintering zone of the rotary kiln and condense on the surface of the grains of the raw meal in the preheater at lower temperatures. These components, called volatile constituents, are reintroduced into the kiln with the raw meal. Repeated evaporation and condensation, forming an internal circuit in the kiln, causes the increase in concentration of these elements in the raw meal in the preheater. The main volatile elements are potassium, chlorine and sulphur.

The increased concentrations of volatile elements in the raw meal result in the formation of liquid phase and new compunds, chiefly melting at low tempera-

* Presented at CETTA'97, Zakopane, Poland.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ture, which are the reasons for the agglomeration of calcite grains, the increased adhesion of these grains to the wall of the preheater and build-up formation [1].

Independently of the universality of this behaviour of a short modern kiln, the mechanism of build-up formation is not well understood, and only a few works deal with the mineralogical study of these accretions [2-4].

The present paper describes the results of a study of build-ups in a single cement kiln. A knowledge of the build-up phase composition can facilitate an understanding of the mechanism of their formation.

Materials and methods

The build-up samples were collected from the cyclone preheater after the kiln had been stopped for refractory lining repairs. The sites at which the samples were collected are presented in Fig. 1.

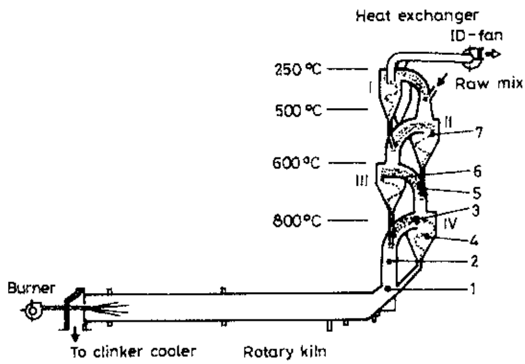

Fig. 1 Scheme of cement kiln with sites of sample collection

The phase compositions of the samples changed to some extent during the cooling of the kiln, under the influence of the gaseous atmosphere. These changes, however, did not influence the understanding of the primary phase composition of the accretions because they concerned the transformation of CaO to $Ca(OH)_2$ and that of $CaSO_4$ to $CaSO_4 \cdot 2H_2O$.

The determination of the phase composition of the build-up was based principally on two methods: X-ray and DTA, supplemented by SEM.

Results and discussion

The X-ray analysis of the sample of the build-up formed at the bottom of the riser duct showed the presence of calcium hydroxide and spurrite. Strong peaks of calcite were also present in the X-ray pattern. Additionally, weak peaks of clinker phases were found in the X-ray pattern. DTA, TG and DTG curves are shown in Fig. 2.

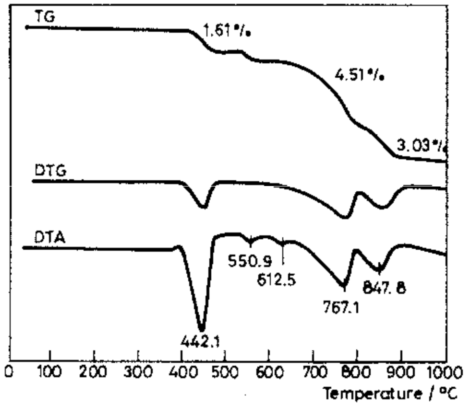

Fig. 2 Thermal analysis of accretion sample from bottom of riser duct

Besides the endothermic peaks of decomposition of $Ca(OH)_2$ at about 440°C, of $CaCO_3$ at about 770°C and of $Ca_5([SiO_4]_2, CO_3)$ at about 850°C, the DTA curve exhibited two small endothermic effects. The first, at about 550°C, was accompanied by a small mass loss. It seems that this involves the decomposition of montmorillonite. The presence of montmorillonite in the sample is supported by the presence of the 1.39 and 0.501 nm lines in the X-ray pattern.

The small peak at 613°C is due to the formation of a eutectic in the sample during heating. We prepared a synthetic mixture containing 30% CaO + 20% $CaCO_3$ + 20% SiO_2 + 20% K_2SO_4 + 10% KCl, which showed liquid phase formation at a very similar temperature, i.e. 583°C (Fig. 3), with subsequent spurrite formation.

The accretion sample from the bottom of the riser duct revealed the presence of conglomerates of elongated crystals of spurrite (Fig. 4a) and their intergrowth with belite (Fig. 4b). The content of belite was below the threshold value detect-

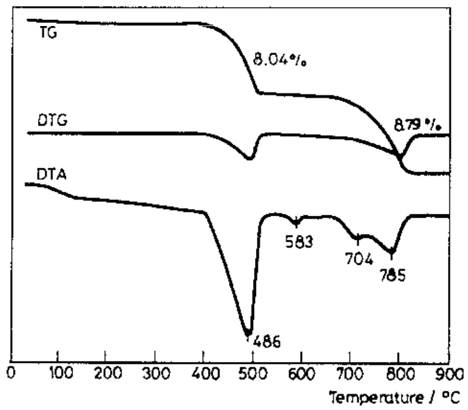

Fig. 3 Thermal analysis of the mixture 30% CaO+20% $CaCO_3$+20% SiO_2+20% K_2SO_4+ 10% KCl

able by X-ray means, but its formation in this preheater zone is quite possible. Belite formation occurs very quickly on the decomposition of spurrite [5].

a b

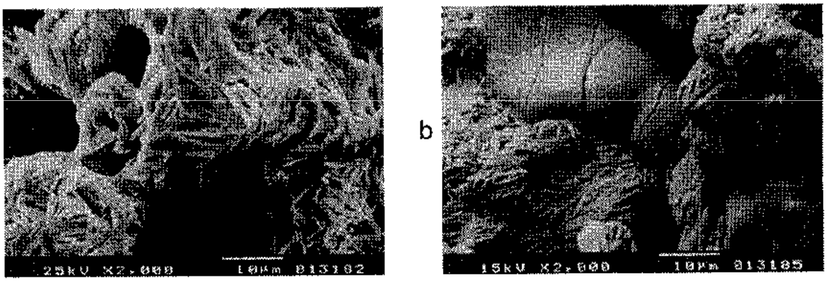

Fig. 4 a) SEM showing crystals of spurrite in sample from bottom of riser duct; b) the same sample: spurrite and belite grains

The build-up sample formed in the middle of the riser duct had a very similar phase composition. The DTA curve (Fig. 5) showed only a low presence of fluxes in the sample, i.e. alkalis and chlorine, because no liquid phase formation was observed.

An X-ray analysis of the accretion of the top of the riser duct revealed the presence of calcium hydroxide, calcite, spurrite and smaller quantities of sylvite and anhydrite. Four strong endothermic peaks were present in the DTA curve of this sample (Fig. 6). They relate in turn to $Ca(OH)_2$ decomposition at about 440°C, the decomposition of calcite at 730 and at about 800°C, and the decomposition of spurrite at 852°C. This gradual decomposition of calcite proves that the formation of spurrite took place during the thermal analysis. Such behaviour is typical for samples containing $CaCO_3$, SiO_2 and chlorine [5].

The formation of spurrite during the thermal analysis proves that the accretion was in the preheater zone where the temperature was lower than about 700°C, and in this condition only a small quantity of primary spurrite was formed in the sample. A small peak at about 624°C was due to liquid phase formation, as in the previous sample, from the bottom of the riser duct. The sample also contained a small quantity of gypsum (peak at 264°C), formed from anhydrite during the cooling of the kiln.

The accretion from cyclone B-54 contained high quantities of three phases: calcium carbonate, calcium oxide and spurrite. X-ray examination also showed the presence of a small content of sylvite. Small peaks at 147 and 303°C in the DTA curve are connected with the decomposition of gypsum and brucite–$Mg(OH)_2$, respectively.

The sample from cyclone B-53 was rich in calcite and also contained significant amounts of spurrite and sylvite. The small endothermic peak at 667°C is linked with the fusion of KCl. The gradual decomposition of $CaCO_3$ is identical with the behaviour of the sample from the top of the riser duct.

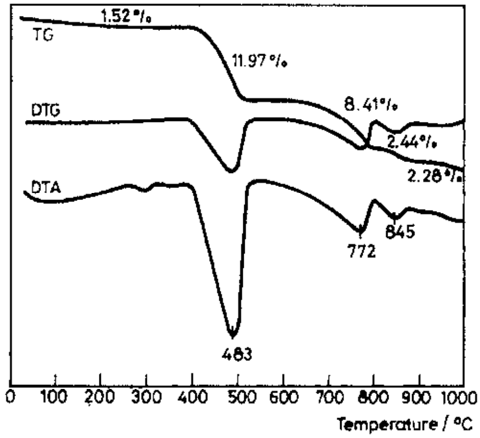

Fig. 5 Thermal analysis of accretion sample from middle of riser duct

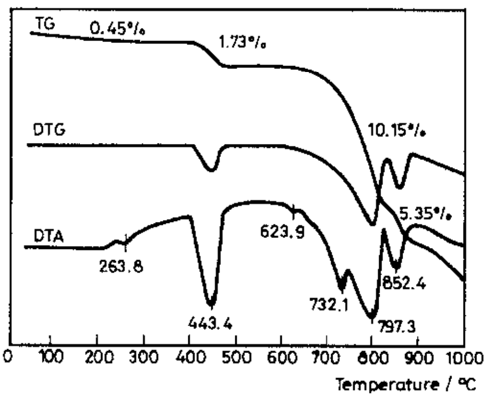

Fig. 6 Thermal analysis of accretion sample from top of riser duct

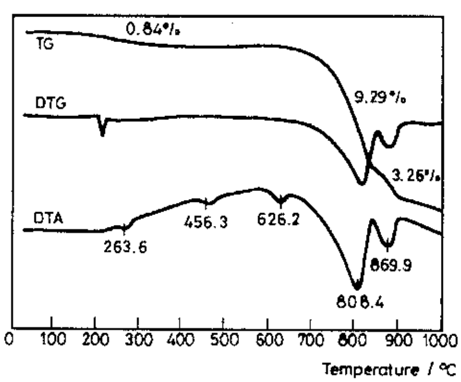

Fig. 7 Thermal analysis of accretion sample from gas duct connecting cyclone IV with cyclone III

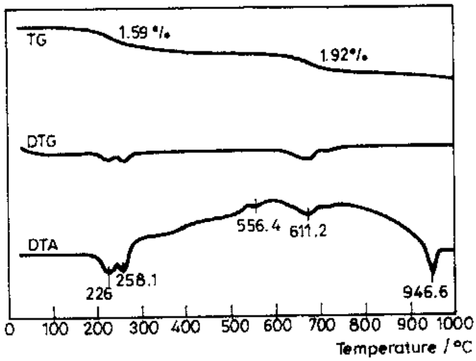

Fig. 8 Thermal analysis of accretion sample from cyclone B-52

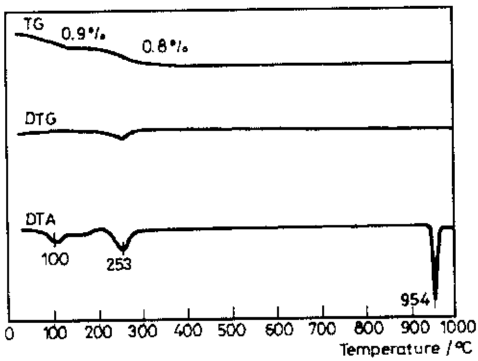

Fig. 9 Thermal analysis of mixture 50% $Ca_2K_2[SO_4]_3$ + 50% $CaSO_4$

The build-up sample from the gas duct connecting cyclone IV with cyclone III (Fig. 7) had a phase composition very similar to that of the sample from cyclone B-54. It contained calcite, spurrite and smaller quantities of free calcium oxide, sylvite and anhydrite. The X-ray pattern also revealed a small quantity of calcium langbeinite, $Ca_2K_2[SO_4]_3$. All peaks in the DTA curve were explained as for the previous samples.

The accretion sample from cyclone B-52 had a completely different composition. According to the X-ray analysis, the main phase was anhydrite, with calcite, calcium langbeinite and belite in smaller quantities. A strong endothermic peak was present at about 947°C in the DTA curve (Fig. 8), due to the eutectic formation between $Ca_2K_2[SO_4]_3$ and $CaSO_4$ (Fig. 9). The small peak at 611°C is linked with the small quantity of $CaCO_3$. In turn, a very small bend at 556°C is due to formation of the liquid phase in the mixture $CaSO_4$, K_2SO_4 and KCl. The small peaks at 226 and 258°C are caused by the decomposition of gypsum.

The phase compositions of the accretions revealed that two zones can be distinguished in the preheater: The lower zone, with a higher temperature, where the KCl–K_2SO_4–$CaSO_4$ liquid phase enhances the agglomeration of limestone

Fig. 10 SEM, showing crystals of sylvite

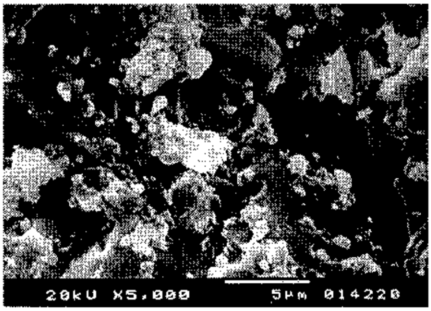

Fig. 11 SEM of solidified chloride liquid phase

grains, with adherence to the wall of the cyclone and the formation of build-up. The simultaneous and subsequent formation of elongated crystals of spurrite strengthens the agglomeration and the accretion becomes stable. In the phase composition of the accretions in this lower zone, calcite prevails, the complementary compounds being spurrite and sylvite and a variable quantity of calcium oxide. This zone can be called a sylvite-spurrite zone.

Quite a different situation occurs in the higher zone in the temperature range 600-400°C. In the upper part of the preheater, the concentrations of chlorine and potassium are much lower and the chlorine mechanism of accretion formation is less important. In this zone, therefore, anhydrite prevails and the mechanism of accretion formation is different. Due to the sorption of SO_2 from the gaseous phase, calcium sulphate is formed, and with K_2SO_4 and sylvite the liquid phase is formed at about 560°C. This causes the limestone grains to stick to the gas duct wall, but the process is much slower than in the lower part of the preheater. The sorption of SO_2 plays an important role, and calcite is converted to anhydrite. The reaction with K_2SO_4 results in calcium langbeinite.

Under the SEM, the accretion samples revealed the presence of beautiful regular crystals of sylvite (Fig. 10). The dimensions of some crystals attained 100 μm. As a rule, they formed a layer covered with limestone grains. In several build-ups, sintering due to the formation of chloride liquid phase is typical (Fig. 11).

Analysis of the experimental results led to the following conclusions concerning the sylvite crystallization model (Fig. 12):

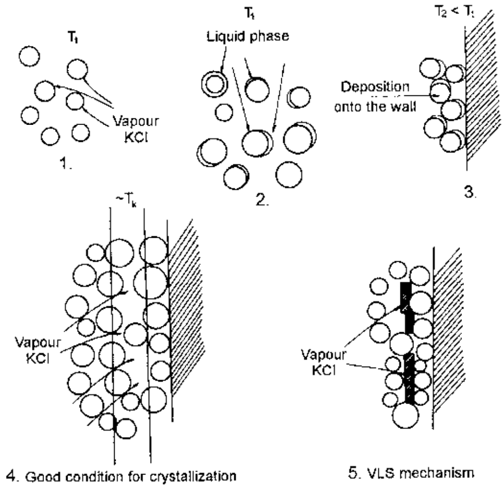

Fig. 12 Model of sylvite crystallization

Three initial steps are typical for accretion formation: condensation of volatile elements on the grains of limestone, formation of agglomerates in the presence of liquid phase, and their sticking to the walls of the gas ducts, with a further increase in thickness of the limestone layer.

Then, in the accretion formed, the conditions are created for sylvite crystallization, i. e. KCl vapour pressure and a temperature close to the melting point of sylvite (step four). Under these conditions, crystals of sylvite probably grow according to the VLS mechanism. Thus, sylvite crystallization is secondary to accretion formation, and takes place when the accretions are stable.

Conclusions

Two zones with different accretion phase compositions can be distinguished: the first at a higher temperature, in which spurrite and sylvite are the reasons for the build-up stability, while in the second one anhydrite prevails.

Sylvite crystallization is secondary to build-up formation and probably takes place by the VLS mechanism.

References

1 H. Ritzmann, Zement-Kalk-Gips 34 (1971) 408, 338.
2 A. A. Gristiakowa and W. W. Michajlow, Cement (in Russian) 7, (1974) 16.
3 M. Katsioti, V. Kusselouri, Ch. Fticos and G. Parissakis, World Cement 67, October 1995.
4 H. J. Schmidt and B. E. Driscoll, VDZ - Kongress '85, 471, Berlin 1987.
5 W. Kurdowski and A. Garbacik, Ceramika (in Polish) 30, s. 47, PAN Krakow 1980.