ELSEVIER

Thermochimica Acta 373 (2001) 173–180

thermochimica acta

www.elsevier.com/locate/tca

# Aluminosilicates transformations in combustion followed by DSC

M.C. Mayoral*, M.T. Izquierdo, J.M. Andrés, B. Rubio

*Instituto de Carboquímica, CSIC., María de Luna, n. 12, 50015 Zaragoza, Spain*

Received 24 November 2000; accepted 15 January 2001

**Abstract**

The behavior of quartz, kaolinite and calcite, as main components of coal mineral matter, has a direct impact on slags formations and development in pulverized coal combustion. The mineral transformations along temperature can be followed by differential scanning calorimetry (DSC), provided that the formation and crystallization of mullite ($3Al_2O_3{\cdot}2SiO_2$) are exothermic phenomena. Peak heights and areas allow to quantify the occurrence and extent of those mineral transformations for pure kaolinite and its mixture with calcite as fluxing agent. On the other hand, sinterization time at temperatures bellow mullite formation has a clear impact on the onset and the shape of the peaks. In this way, it is demonstrated that mineral transformations at solid state have a direct effect on the final structure of mineral species generated by slagging.


*Keywords:* Slagging; DSC; Mullite

## 1. Introduction

One of the most frequent operational problem in pulverized coal boilers is due to the uncontrolled deposition of fused ash material onto heat transfer surfaces within the furnace, in areas which are directly exposed to flame radiation. This phenomenon, referred as slagging, involves time-consuming unplanned shut-downs and a reduction in thermal conductivity. The extent of ash related problems depends on the quality and nature of the inorganic constituents present in the coal, as well as on the combustion and plant operating conditions and system geometry [1]. Most engineering research on full-scale boilers has been intended to reduce the adverse effect of ash deposition by modeling the design of tube banks, optimization of sootblowers, and changes in operating conditions [2]. Prediction of slagging can be based on the chemical composition of the ash, from which a number of empirical indices may be calculated. These include laboratory ash analysis, standardized ash fusibility temperatures and the base/acid, Fe/Ca and silica/alumina ratios in laboratory ash. For many years these have been the principal basis of assessing the probability of ash deposition in a boiler [3]. In an effort to improve repeatability and reliability, new methods have been developed, based on physical characteristics that change when melting or sintering begins: dimensional changes of ash pellets, compressive strength, electrical conductance and pressure drop across pellets [4]. Precise determination of the onset of fusion can also be provided by thermal analysis as an endothermic phenomenon [5]. Nevertheless, these techniques are based on ash that is no representative of pulverized fuel combustion conditions, and thus, cannot accurately predict the slagging potential.

* Corresponding author. Tel.: +34-976-73-39-77; fax: +34-976-73-33-18.
*E-mail address*: mayoral@carbon.icb.csic.es (M.C. Mayoral).

0040-6031/01/$ – see front matter 
PII: S0040-6031(01)00459-2

Research efforts have been focused to enhance slagging prediction taking into account the different ash formation mechanisms of excluded and included mineral matter in coals, as well as the impact of reducing environment during char particle combustion [6]. The mechanistic approach has identified a need for fundamental understanding of formation and mineral transformation in the deposits. XRD [7] and SEM [8] have been used to study the distribution of inorganic matter in deposits to provide a basis for predictive models of the deposition process.

Provided that quartz, kaolinite and calcite are the main components of coal mineral matter, their behavior under combustion has a direct impact on slags formations and development. It is well known that the incorporation of the lime in molten clays forms anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), which is a lower melting point silicate brought about by the fluxing action of calcite on the clay minerals. The aluminosilicate glass can adhere to the initial sticky deposit layers contributing to deposit build up. This is why the mechanism of the decomposition of kaolinite and the ternary system $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ have been studied extensively [9]. The thermal decomposition of the individual mineral species was investigated using differential thermal analysis (DTA) methods [10]. Calcite as an additive has been used over ash mixture to determine the change in fusion temperatures by XRD and DTA [11].

We have approached this system in a different way, studying the influence of calcite and sinterization time over the reactions of aluminosilicates in solid state. Sintering, which is referred to as the bonding or welding of adjacent particles under the influence of excess surface tension, rather than melting, is the responsible of the increase of the adhesive force of ash [12]. Explicit tracking of the extent of sintering as a function of time will be required for the prediction of properties through the deposit as equilibrium is not reached [13]. On the other hand, crystals formation may be a highly desirable phenomenon for amorphous ashes because it displaces the densification process to higher temperatures [14]. For this propose, differential scanning calorimetry (DSC) and DTA were set-up to monitor the evolution of aluminosilicates with temperature and sintering time, as thermal analysis is proving an invaluable help in the assessment of coal properties and ash-related implications [15].

## 2. Experimental

In order to characterize ash behavior, standard minerals representative of the most commonly occurring minerals in coal were selected for this study: kaolinite as a representative of aluminosilicates, quartz, and calcite. The samples were ground and sieved to $d < 80\,\mu m$, and kept in inert atmosphere. For binary mixtures, the corresponding weights of each component were mixed in an agate mortar, and pressed as pellets to ensure interparticle contact.

Simultaneous differential thermal analysis and thermogravimetry were performed in a STD 2960 from TA instruments, which allows temperatures up to 1500°C. A flow of 80 ml $min^{-1}$ of argon was used in all these experiments. Although a standard 20°C $min^{-1}$ ramp is recommended by the thermobalance user manual, resolution in mineral transitions peaks was studied at different heating ramps (80 and 120°C $min^{-1}$). After these studies, for DSC experiment, a ramp of 20°C $min^{-1}$ was chosen for calibration and a heating ramp of 80°C $min^{-1}$ for the experiments. This high heating rate implies errors in quantification of decarboxilation of dehidroxilation areas (in general, in all decomposition which involves mass loss), but it seemed to be highly desirable for detecting mineral transitions and fusions with small heat exchange, and without weight change. Nevertheless, and as expected, onsets and maxima in peaks are higher as heating ramp is increased. Pt pans were preferred for these studies because alumina pans suffered great damage when calcite was used.

Different thermal treatments were performed over the samples. They were held for long periods (1, 2, 4 and 8 h) at different high temperatures (750, 800, 850 and 900°C) and shorter sinterization times (3′, 8′, 15′, 30′ and 45′) at 950°C, and after these isothermal stages 1500°C were reached at 80°C $min^{-1}$.

Scanning electron microscopy was performed in a Jeol SM6400 apparatus.

## 3. Results

The evolution of kaolinite with thermal treatment, as a representative of aluminosilicate minerals in coal inorganic matter, is shown in Fig. 1. Kaolinite losses the combined water from the hydroxyl groups

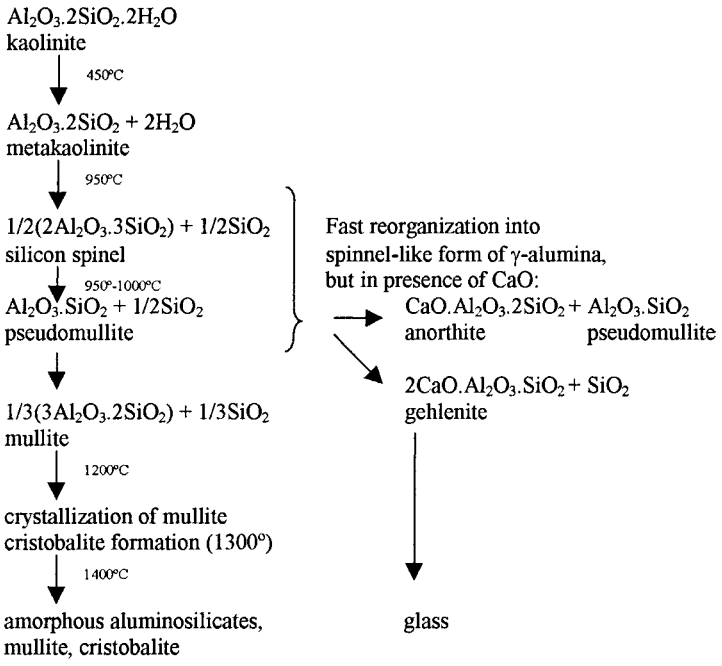


Fig. 1. Major mineral transformations of the aluminosilicate phase during the combustion of coal depending on the calcium content (after [7]).

surrounding the Al atoms, yielding in the formation of an amorphous phase, metakaolin at around 400°C. It remains unaltered till 950–1000°C, when a fast reorganization of oxide ions in the lattice structure develops into a spinnel-like form of γ-alumina, and further formation of mullite ($3Al_2O_3{\cdot}2SiO_2$). The final form of aluminosilicates is a mixture of cristobalite and crystallized mullite.

The two crystallographic transformations, i.e. the formation of the spinnel or mullite precursor, and mullite crystallization, can be followed by differential thermal analysis since these reorganizations involve changes to more stable phases with energy liberation. The amount of energy and the shape of exothermic peaks can be quantified by DSC if experimental conditions are optimized.

As mentioned in Section 2, for these experiments, fast heating rates in DSC furnace were chosen as they yielded better resolution of peaks, as can be seen in Fig. 2 for kaolinite from 950 to 1400°C. Spinnel

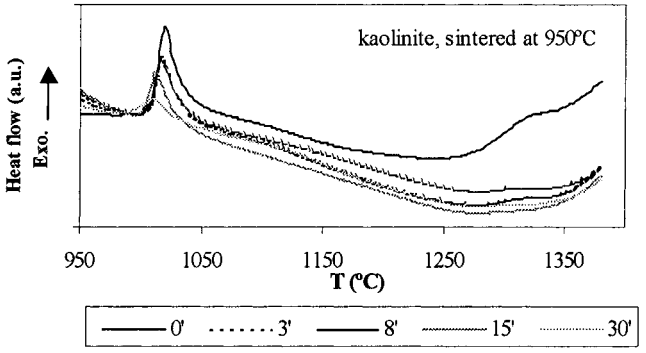


Fig. 2. DSC runs at 80°C $min^{-1}$ to 1400°C, with holding times at 950°C of 3, 8, 15 and 30 min.

formation is clearly indicated for the first exothermic peak that starts at 1000°C. The presence of mullite is confirmed by the crystallization peak at 1300°C, although its shape is quite flat. Higher temperatures involve the tetragonal modification of silica excess yielding cristobalite, although such effect could not be monitorized in these DSC runs.

A complete set of DSC experiment were carried out to study the crystalline structures at those temperatures which mineral particles find when they impact on the tube banks inside burners. The heating ramp was stopped at 950°C, and this temperature was held for 3, 8, 15 and 30 min. After the sinterization time, runs were completed at 1400°C at 80°C $min^{-1}$. The main effect over metakaolinite transformation can be seen on the exothermic peak of Al–Si spinnel formation: peak areas in J $g^{-1}$, what it is to say, transformation heats, decrease, and a decrease in onset and maxima temperatures is detected (Fig. 2). In fact, a sinterization time of 45 min involved the absence of such peak. Similar effects were detected in mullite crystallization peaks at 1300°C for each experiment, as can be seen in the figure.

The extent of mullite crystallization can be followed from peak areas and shapes at 1300°C. Although quantitative measurement of peak height would be a better indication of crystallinity, the values are less reliable due to peak flatness observed for these experiments. Areas were calculated with tangential adjustment of baselines. Under the experimental thermal conditions, it is not possible to ensure complete crystallization of mullite. Nevertheless, the values of peak areas could be considered as an indicative of portion of mass that has reached the crystalline organization. In this way, the decrease in peak area as a function of sinterization time can be considered as an indication of how short holding times at 950°C have a great impact over the portion of mass that reach crystallinity (Fig. 3).

On the other hand, the extent of mullite crystallization reached at 1300°C should be related to the degree of organization of the mullite precursor as spinnel achieved at 1100°C. As mentioned above, peak area and specially peak height could be an indicative of crystalline order in the spinnel structure. Fig. 4 shows the values of both the area and height of mullite precursor peak versus mullite crystallization peak area. There is clear relationship between both structures, almost linear for crystallization areas higher than 5 J $g^{-1}$. This linear relationship between peaks shape is lost at sinterization times higher than 10 min. These results imply that sinterization time at 950°C, before the spinnel formation, hinders the formation of that spinnel or mullite precursor, which involves that the final state is highly amorphous rather than crystalline mullite. None of these effects (decrease in peak area and $T_{onset}$ for mullite transformation) were detected when the sample was sintered at 1150°C, which indicate that the sinterization time affect the sample only before the spinnel formation.

### 3.1. Binary mixtures

Calcite was added to kaolinite in two different proportions: 33% calcite over kaolinite, which is a ratio 1:1:2 in Ca:Al:Si in the final form of stoichiometric

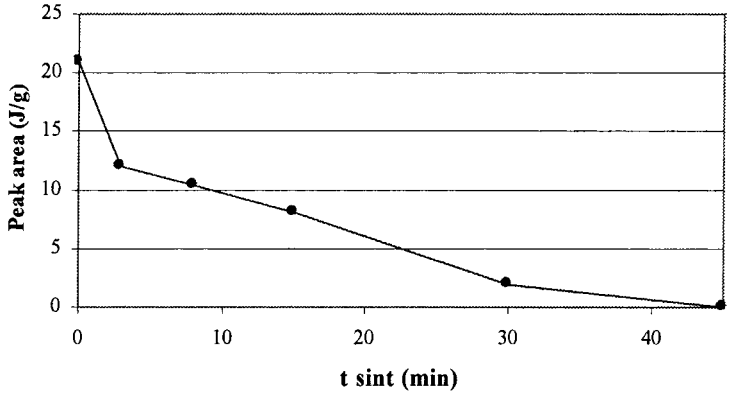


Fig. 3. Peak area of mullite crystallization as a function of sinterization time.

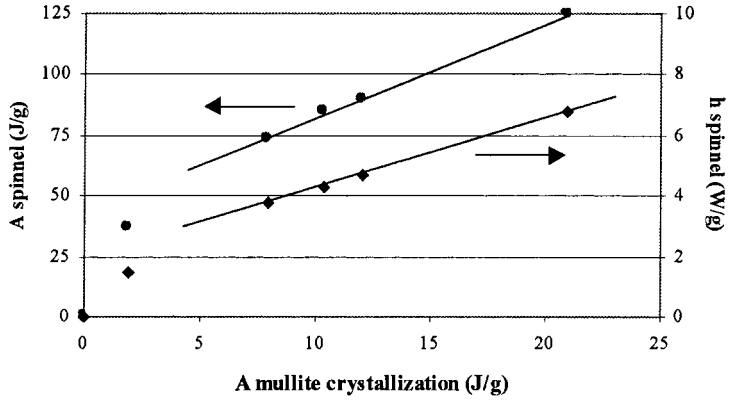


Fig. 4. Values of area and height of spinnel peak vs. mullite crystallization peak area.

anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), and a 50% in calcite, which is a mixture with an excess of lime over the estequiometric anorthite has a clear effect over kaolinite heat treatment. Pellets were prepared with agate mortar and press shaped to ensure mixture and contact of particles. Calcite as a fluxing agent has a clear effect over kaolinite heat treatment. In Fig. 5, a broad endothermic peak appears at 1250°C for a 50% calcite addition. It is compatible with anorthite fusion, in fact samples resemble vitreous blue drops. If sample is let to cool and then the heating–cooling cycle is repeated, the peak of spinnel formation disappears as expected, but two different fusion peaks appear at 1200 and 1300°C, which indicates that amorphous material has a biphasic composition, probably due to the line excess.

The effect of calcite addition is clear not only in co-melting at high temperatures, but also over the Al–Si spinnel reorganization at 1000°C: peak decreases in area and height as sinterization time (no sinterization time, 15′ and 30′) and calcite addition (no calcite, 33% calcite, 50% calcite) increase, as can be seen in Fig. 6. Area values can give an indication of the initial mass of kaolinite that develops spinnel structure, and peak height could be an indication of order degree in the spinnel structure. Therefore, DSC allows to quantify the relationship between the extent of the mineral transformation and the degree of order in Al–Si structure. The ratios of peak height/peak area for kaolinite and its mixtures, at the three sinterization times studied, are shown in Table 1. These results indicate that the sinterization stage for pure kaolinite involves a degree of disorder in the mineral phases similar to that achieved as effect of calcite addition.

On the other hand, onset temperature of exothermic peak decrease as well with sinterization time and

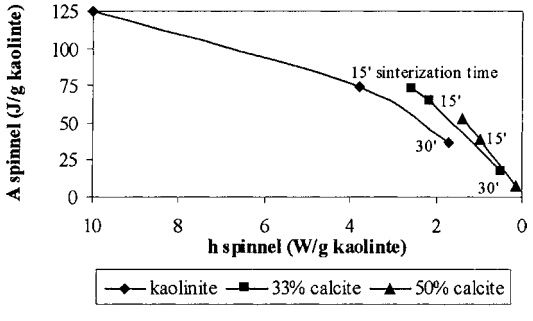


Fig. 5. DSC run at 80°C $min^{-1}$ to 1400°C of a mixture 50% kaolinie–50% calcite with three cooling–heating cycles.

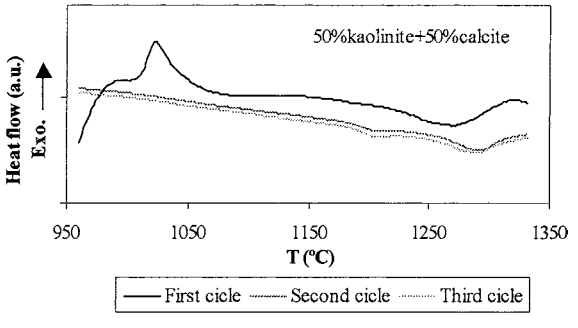


Fig. 6. Relationship between peak area and height for spinnel formation depending on the addition of calcite and on sinterization time.

Table 1

| Sinterization time at 950°C | Ratio (*h*/*A*) | | |
|---|---|---|---|
| | Kaolinite | 33% Calcite | 50% Calcite |
| 0 | 1 | 0.7 | 0.5 |
| 15′ | 0.9 | 0.6 | 0.5 |
| 30′ | 0.8 | 0.5 | 0.4 |

Table 2

| Sinterization time at 950°C | Kaolinite | | 33% Calcite | | 50% Calcite | |
|---|---|---|---|---|---|---|
| | $T_{onset}$ | $T_{max}$ | $T_{onset}$ | $T_{max}$ | $T_{onset}$ | $T_{max}$ |
| 0 | 1008.8 | 1019.5 | 1009.9 | 1020.2 | 1006.5 | 1018.9 |
| 15′ | 1002.3 | 1012.1 | 997.2 | 1011.3 | 995.1 | 1011.3 |
| 30′ | 990.0 | 1009.8 | 990.7 | 1012.8 | 991.7 | 1012.7 |

calcite addition, see Table 2, which indicates that time and fluxing agent decrease the temperature of mineral transformation at solid state.

Fig. 7 shows the effect of sinterization temperatures before spinnel formation (850, 900 and 950°C) held for 1 h, over a mixture of 50% clacite/50% kaolinite. Fig. 8 shows the effect of long sinterization (4 and 8 h) times at 900°C over the mixture. From these results, it can be inferred that low sinterization temperatures partially destroy spinnel structure provided that sinterization times are long enough. On the other hand, 1 h at 950°C imply the complete destruction of spinnel structure. In all cases, the broad endothermic peak starting at 1200°C indicates a high degree of fusion. The extremely exothermic peak detected above

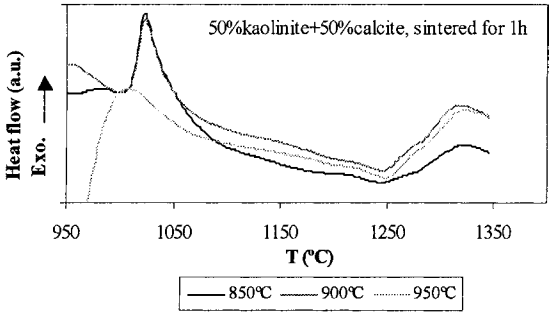


Fig. 7. DSC runs at 80°C $min^{-1}$ to 1400°C mixtures 50% kaolinie–50% calcite, effect of 1 h sinterization temperature (850, 900 and 950°C) over spinnel formation.

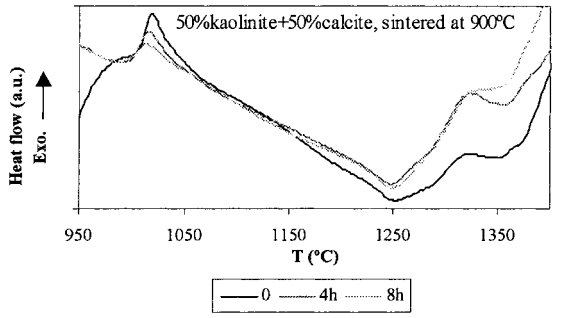


Fig. 8. DSC runs at 80°C $min^{-1}$ to 1400°C mixtures 50% kaolinie–50% calcite, effect of sinterization time (4 and 8 h) at 900°C over spinnel formation.

1300°C for mixtures seem to offer support for the concept of changes in thermal conductivity of slags that can be related to phase transformation [11]. Both are very difficult to quantify because there is no clear baseline.

To study the degree of sintering and the final mineral structures, SEM–EDX was applied to some of the samples. Heating treatment of kaolinite to 1500°C yielded a certain degree of fusion between discrete particles. When kaolinite is sintered for 30 min at 950°C before reaching 1500°C at 80°C $min^{-1}$, SEM shows a great degree of fusion. The expected small crystals of mullite were shown by SEM, although EDX was unable to establish their composition due to their small size.

SEM photographs of binary mixtures are shown in Fig. 9, where it is possible to see the effect of sinterization time over the mixtures. Picture (a) shows 50% calcite over kaolinite heated to 1500°C at 80°C $min^{-1}$, is a fused glassy matrix of Al:Si:Ca in a proportion 1:1:1 with some granules rich in calcium. When this mixture is let to sinter for 30 min at 950°C, the final form; (b) is a matrix of Al:Si:Ca in a proportion 1:1:1, with needle shaped crystals of anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$). The formation of anorthite needles is clear when there is not an excess in calcium, for mixtures 33% calcite over kaolinite (pictures c and d). For these samples, differences between sintered and not sintered samples are not so big. It is worthwhile to comment that similar pictures were obtained with SEM of slags obtained in drop tube of a coal with the same Ca/Al ratio that this mixture [16]. On the other hand, no single crystals of mullite were detected by SEM–EDX for any of the

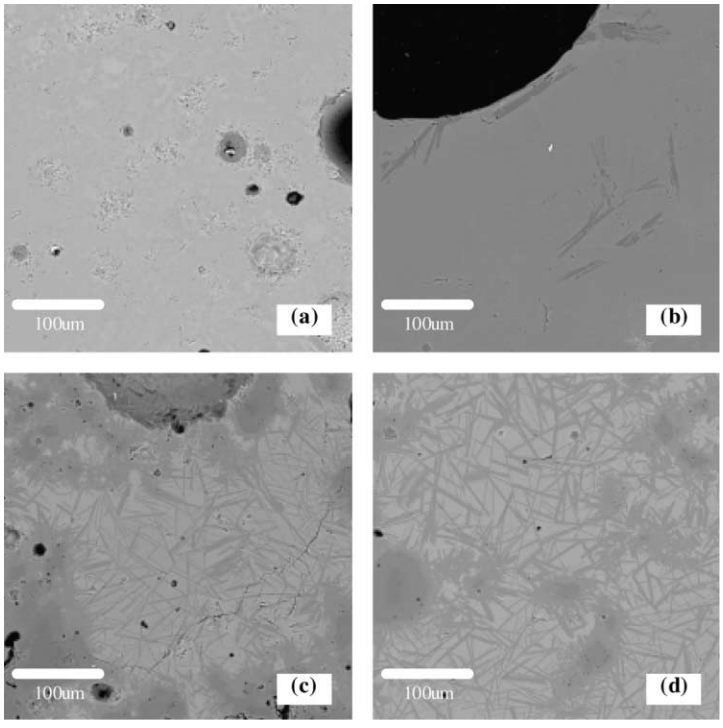


Fig. 9. SEM photographs of: (a) 50% calcite over kaolinite heated to 1500°C at 80°C $min^{-1}$; (b) 50% calcite over kaolinite heated to 950°C at 80°C $min^{-1}$, 30 min holding time, and heated to 1500°C at 80°C $min^{-1}$; (c) 33% calcite over kaolinite heated to 1500°C at 80°C $min^{-1}$; (d) 33% calcite over kaolinite heated to 950°C at 80°C $min^{-1}$, 30 min holding time, and heated to 1500°C at 80°C $min^{-1}$.

samples. Other works confirmed that well-crystallized mullite crystals are only present when equilibrium condition have been reached, which only happens in outer layer of deposits, whereas middle layers present a highly sintered nature with only trace amounts of mullite [8]. In this study, mullite determination should require the use of XRD, and results will be shown in future works.

Fig. 10 shows the comparison between kaolinite (a) and a mixture of kaolinite with calcite (b), both samples cooled down after sinterization at 950°C, what it is to say, before any fusion effect could be

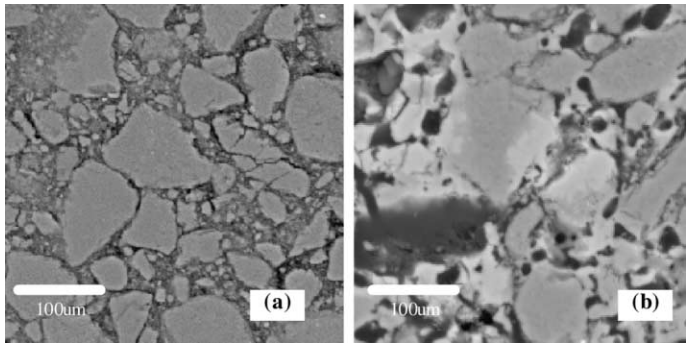


Fig. 10. SEM photographs of: (a) kaolinite and (b) 50% calcite over kaolinite, heated to 950°C at 80°C $min^{-1}$ and sintered for 12 h at this temperature.

detected by DSC. In picture b, SEM identifies gray areas as aluminosilicates, and white areas as rich in calcite. Apart form this interaction, the picture shows a sort of interparticle fused matrix, with a composition 1:1:1 in Si:Al:Ca. From these results, it is clear that the sinterization time involves reactions at solid state that at higher temperatures, have a direct effect over the final state of slag.

## 4. Conclusions

DSC is a useful tool to follow the mineral transformations of aluminosilicates in combustion conditions. The quantification of area and height of the exothermic peaks allowed the study of the influences of sinterization time and temperature on the final mineral phase. Using this approach, it is confirmed that the reactions at solid state, at temperatures bellow any mineral transformation, have a direct effect on the crystallization degree of mineral species on combustion slags.

## Acknowledgements

Authors acknowledge the European Commission for the financial support by contract no. ECSC 7220-PR/048. M.C.M. and M.T.I. are thankful to the Ministry of Science and Technology.

## References

[1] J.R. Gibbins, J. Williamson, Proc. Instin. Mech. Engrs. 212, 12.
[2] R.W. Bryers, Prog. Energ. Combst. Sci. 22 (1996) 29.
[3] G. Couch, IEACR/72, IEA Coal Research, London, 1994.
[4] D.H. Scott, CCC/24, IEA Coal Research, London, 1999.
[5] L.A. Hansen, F.J. Frandsen, K. Dam-Johansen, H.S. Sorensen, Thermochim. Acta 326 (1999) 105.
[6] A.R. McLennan, G.W. Bryant, B.R. Stanmore, T.F. Wall, Energ. Fuels 14 (2000) 150.
[7] X. Querol, J.L. Fernandez-Turiel, A. Lopez-Soler, Mineral. Mag. 58 (1994) 119.
[8] H. Wang, J. West, J.N. Harb, Energ. Fuels 13 (1999) 570.
[9] J.R. Qiu, F. Li, Y. Zheng, C.G. Zheng, H.C. Zhou, Fuel 78 (1999) 963.
[10] J.W. O'Gorman, P.L. Walker, Fuel 52 (1973) 71.
[11] Y. Ninomiya, A. Sato, Energ. Convers. Mgmt. 38 (1997) 1405.
[12] A.Y. Al-Otoom, G.W. Bryant, L.K. Elliot, B.J. Skrifvars, M. Hupa, T.F. Wall, Energ. Fuels 14 (2000) 227.
[13] H. Wang, J. West, J.N. Harb, Energ. Fuels 13 (1999) 570.
[14] J.W. Nowok, S.A. Benson, M.L. Jones, D.P. Kalmanovich, Fuel 69 (1990) 1020.
[15] S.St.J. Warne, Thermochim. Acta 272 (1996) 1.
[16] L.S.K. Pang, A.M. Vasallo, D. Phong-Anant, M.A. Wilson, Fuel Proc. Technol. 33 (1993) 13.