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Thermal Decomposition of Zinc Carbonate Hydroxide

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This study is devoted to the thermal decomposition of two zinc carbonate hydroxide samples up to 400 °C. Thermogravimetric analysis (TGA), boat experiments and differential scanning calorimetry (DSC) measurements were used to follow the decomposition reactions. The initial samples and the solid decomposition products were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infra-red (FTIR) and laser particle size analyzer.

Results showed that zinc carbonate hydroxide decomposition started at about 150 °C and the rate of decomposition became significant at temperatures higher than 200 °C. The apparent activation energies 'E_a' in the temperature range 150-240 °C for these two samples 132 and 153 kJ/mol. The XRD analyses of the intermediately decomposed samples and the DSC results up to 400 °C suggested a single step decomposition of zinc carbonate hydroxide to zinc oxide with not much change in their overall morphologies.

Key Words: Zinc carbonate hydroxide, thermal decomposition, zinc oxide

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1. Introduction

Preparation of different grades of zinc oxide has been the subject of many recent researches [1-3]. This is due to the diversified applications of ZnO which include manufacture of varistors, used as protection elements in electric and electronic appliances, as a polymer dispersant and heat absorbant in tyre industry, in cosmetics as UV light absorber and in paints and pigment industry as a color hue [4-6]. This compound is commercially produced by zinc vaporization and its subsequent oxidation (French and American Processes), but majority of lab scale R & D activities are focused on precursor calcination methods. Zinc oxides from the decomposition of hydroxy-carbonates are energetically favorable due to their lower decomposition temperature in comparison to other zinc oxide precursors (such as hydroxides, carbonates, acetates, oxalates, etc.). Further, it is well known that the composition and the properties of zinc carbonate hydroxides are largely dependent on the precipitation conditions, variation of which led to different grades of ZnO[7, 8].

Thermal decomposition is an essential step for preparation of ZnO from the precipitated precursors. The mechanism and kinetics of thermal decomposition of zinc carbonates (anhydrous, hydrated and hydroxy or basic carbonates) were reported by several authors [9-14]. Recently, thermal decomposition kinetics of anhydrous ZnCO_3 was studied by Gotor *et al.* [9], in the temperature range of 330-452 °C. They suggested two different 'nucleation and growth' mechanisms at different temperature ranges by comparing the results of isothermal TG and constant rate thermal analysis (CRTA). The estimated apparent activation energy ' E_a ' was found to be 224 kJ/mol and 140 kJ/mol in the temperature ranges of 347-402 °C and 402-452 °C, respectively. Heide and Knorr [10] reported a value of ' E_a ' equal to 113 kJ/mol for the decomposition of smithsonite (ZnCO_3) in the temperature range of 269-434 °C. Galvez and Arana [11] had studied the kinetics of non-isothermal decomposition of ZnCO_3 by constant heating rate TGA. They reported a value of ' E_a ' = 88.6 kJ/mol within the temperature range of 175-462 °C. Similarly, one of the earlier studies on the thermal decomposition of hydrated zinc carbonate ($\text{ZnCO}_3 \cdot 2\text{ZnO} \cdot 2\text{H}_2\text{O}$) was performed by Dollimore *et al.* [12]. They suggested that the decomposition proceeds through two thermally overlapping stages with a constant reaction interface area. On the basis of isothermal TG between 200 to 260 °C they reported an activation energy 94 ± 9 kJ/mol. The non-isothermal decomposition of a PROLABO zinc carbonate sample was reported by Gadalla [13] by using TG and DTA under different heating rates. He obtained an average activation energy of 97 kJ/mol. Recently, only one report by Jianxun *et al.* [14] on the decomposition kinetics of precipitated $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ is available. Based on the DTA results under different heating rates (4-20 °C/min) they suggested a single step decomposition process with an activation energy of 113 kJ/mol. The large discrepancy in the value of the activation energies reported by the above authors could be attributed to different sample origins, methods employed for kinetic studies and the poor characterization of the studied samples in most of the cases.

This paper is focused on the thermal decomposition behavior of two well- characterized zinc carbonate hydroxide samples. This work was carried out in the frame of an integrated research program for clean and cost effective treatment of electric arc furnace dust (EAFD). The objective of this research is to produce commercial grade ZnO from EAFD. Zinc carbonate hydroxide was precipitated by Na_2CO_3 under ambient conditions from the purified dust leach liquor and subsequently thermally treated. The thermal decomposition behavior of this zinc carbonate hydroxide sample was compared with a chemically pure reference PROLABO sample.

2. Materials and Experimental Procedure

Two zinc carbonate hydroxide samples were used in this study. One chemical grade supplied by PROLABO and designated as reference sample 'RFS'. The other one was obtained by purification / precipitation of ZnCl_2 solution from leaching of electric arc furnace dust. This sample is designated as the industrial sample 'INS'. The characterization of these samples were done by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray unit (EDS), X-ray diffraction (XRD), Fourier transform infra-red (FTIR) in the range of $700\text{-}4000\text{ cm}^{-1}$ and chemical analyses.

Thermogravimetric decomposition tests were performed using 60 mg of sample and a SETARAM microbalance having a sensitivity of $10\text{ }\mu\text{g}$. All the experiments were carried out with constant flow of inert gases (N_2 , Ar, dried by P_2O_5 columns) inside the reactor,. Experimental tests were carried out under non – isothermal and isothermal conditions. The maximum temperature of the isothermal treatment was chosen so that the weight loss during non-isothermal period did not exceed 7 % that is about 28 % of the decomposition reaction.

Boat experiments in isothermal conditions were performed using about 2 grams of samples. The final decomposed products obtained at several temperatures were subjected to SEM and XRD analyses as well as particle size measurements.

3. Results and Discussion

3.1. Characterizations of Zinc Carbonate hydroxides :

The XRD patterns of the two zinc carbonate hydroxide samples are shown in Figure 1. In both the samples all the major peak positions correspond to either $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (hydrozincite) or $\text{Zn}_4(\text{CO}_3)(\text{OH})_6\cdot\text{H}_2\text{O}$ phase [15]. From this figure it seems that the sample obtained from EAFD (INS) is less crystalline than the PROLABO (RFS) sample. Laser particle size analysis suggest two

size distributions for PROLABO sample with a d_{50} of 12.7 μm , while the industrial sample have a uniform size distribution with a d_{50} of 25.5 μm . Chemical and SEM-EDS (Figure 2) analysis of INS showed the presence of Na, Ca and Cl as the major impurities. The total impurity percentage of INS is less than 5 % with Cl as the major one (2 %). Chemical analysis of this sample showed a Zn content of about 50 % in contrast to 59 % in hydrozincite. The hydrozincite phase was further confirmed from the FTIR spectra (Figure 3) of the PROLABO sample. The strong and broad band centered at about 3317 cm^{-1} is the characteristic $-\text{OH}$ stretching vibrations in hydrozincite [16]. These type of bands correspond to $-\text{OH}$ groups co-ordinated to the metal ions indicating the absence of free / loosely bound water molecules. The other peaks in this spectrum can be assigned as: at 1517 and 1390 cm^{-1} (ν_3 mode of carbonate), at 1047 , 954 and 890 (sh) cm^{-1} ($-\text{OH}$ liberation modes), at 835 cm^{-1} (ν_2 mode of carbonate), at 737 (sh) and 710 cm^{-1} (ν_4 mode of carbonate) and the satellite peaks between 1750 - 2950 cm^{-1} region are due to various combination modes in hydrozincite [16].

3.2. Non Isothermal TG Treatment :

A series of non isothermal tests of the reference sample (RFS) and the sample obtained from EAFD processing (INS), was carried out from room temperature up to $400\text{ }^\circ\text{C}$ with an heating rate of $5\text{ }^\circ\text{C}/\text{min}$ and steady flow of argon as carrier gas. Results are shown in Figure 4 as evolution of % weight loss (% WL) Vs temperature. This figure also contains the calculated % WL (25.88 %) for the decomposition of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ to ZnO. The shape of these curves for both samples is similar. However, the INS seems to be more affected by temperature than RFS. As shown by Figure 4, the weight loss increase slightly with temperature up to $200\text{ }^\circ\text{C}$, since then, the decomposition rate becomes fast and almost full decomposition is reached at about $350\text{ }^\circ\text{C}$.

The decomposition of the reference sample in nitrogen was studied using different heating rates from 1 to $10\text{ }^\circ\text{C}/\text{minute}$ and the results obtained are shown in Figures 5. With increasing heating rate the decomposition temperature increased appreciably. This indicates the slow kinetics nature of the thermal decomposition reaction of zinc hydroxy-carbonate into zinc oxide.

3.3. Isothermal TG Analysis :

Isothermal decomposition studies on both the samples were performed in the temperature range 150 to $240\text{ }^\circ\text{C}$ under flow of nitrogen. Figure 6 (a and b) shows the data obtained during the treatment of RFS in the above-mentioned conditions. They represent the evolution of % WL Vs time. The weight loss observed at time "zero" correspond to the decomposition of sample from room temperature ($20\text{ }^\circ\text{C}$) up to the fixed temperature of the isothermal treatment. As shown by Figure 6 a, more than 160 hours are required to achieve 17 % WL of the sample at $150\text{ }^\circ\text{C}$. While,

about 1 hour is sufficient for the full decomposition at 240 °C (Figure 6 b). The sigmoid shape of the obtained curves indicate a most probable nucleation and growth processes. However, suggestion of a mechanism will be of over simplification with present experimental data. Similar curves were also obtained in case of the industrial sample (Figures 7 a & b). By comparing Figures 6 and 7 it is observed that INS takes longer time in comparison to RFS to achieve same weight loss at same temperature, indicating a slower kinetics of decomposition of the former. The slower decomposition rate of INS may be either due to their larger particle size or due to the presence of impurities notably Cl. The Arrhenius diagram obtained with the data of Figures 6 & 7 are presented in Figure 8. The apparent activation energy calculated from the slopes of these straight lines are 132 ± 5 and 153 ± 4 kJ/mol for RFS and INS respectively.

3.4. Isothermal Boat Experiments and Characterization of Decomposed Products :

Isothermal boat experiments (with about 2 g of samples) under air flow were carried on RFS from 200 to 275 °C . The decomposed products obtained at several temperatures were subjected for XRD, SEM, DSC, and particle size analyses. The evolution of % WL with time at four different temperatures is presented in Figure 9. The shape of the curves is almost similar to that obtained in case of vertical TG analysis. It is observed that full decomposition is achieved within 30 minutes at 275 °C, whereas about 70 % decomposition is achieved at 200 °C for 3 hours. This suggests the highly dependence of this decomposition reaction on temperature.

The X-ray diffraction patterns of two typical samples, one fully decomposed obtained at 250 °C (WL = 25.85 %), and another intermediately decomposed sample obtained at 200 °C (WL = 15.29 %) is shown in Figure 10. The XRD pattern of the fully decomposed sample shows the peaks for only ZnO while for the sample obtained at 200 °C shows the presence of both ZnO and hydrozincite phases [15]. The presence of anhydrous ZnCO₃ was not detected in the latter sample. The DSC plot of RFS (Figure 11) up to 400 °C with a heating rate of 1 and 10 °C/min show only one sharp endothermic peak at about 230 and 248 °C respectively. Combining both the XRD and DSC observations it can be concluded that the decomposition most probably occurs in a single step with simultaneous de-hydroxylation and de-carboxylation.

Laser particle size measurements were done on RFS and two samples obtained after decomposition of RFS at 250 and 400 °C. These samples were dispersed ultrasonically in ethanol medium prior to their size measurements. The curves are shown in Figure 12. The size distribution of the initial and the 250 °C treated samples are almost same, having two distinct distributions whereas, the 400 °C treated sample shows more uniform distribution. The d₅₀ of this sample is also decreased a little in comparison to the initial and 250 °C treated sample.

SEM micrographs of the reference sample (RFS) and the sample obtained after its decomposition at 250 °C are compared in Figure 13. No noticeable change in their morphology is observed. In both the cases the particles are in a highly agglomerated state making it difficult to measure their sizes. These results are in agreement with that of Castellano and Matijevic [17] on calcination of hydrozincite to zinc oxide. This result further confirmed the iso-morphological thermal transformation of zinc carbonate hydroxides to zinc oxides.

4. Conclusions

From the above study, the following conclusions can be drawn on the thermal decomposition behavior of zinc carbonate hydroxide (hydrozincite):

1. Although, the thermal decomposition was started at lower temperature (150 °C) but the reaction rate was appreciable only above 200 °C.
2. Presence of minor amounts of impurities in the sample 'INS' resulted a slower decomposition rate in comparison to the chemically pure 'RFS' sample.
3. The apparent activation energies obtained from the isothermal TG tests within the temperature range of 150-240 °C are 132 ± 5 kJ/mol for the reference sample and 153 ± 4 kJ/mol for the industrial sample.
4. XRD results of samples obtained in boat experiments at different extent of decomposition as well as the DSC analysis of RFS sample up to 400 °C suggested a most probable single step transformation of zinc carbonate hydroxides to ZnO.
5. The morphological aspects during the decomposition was more or less unchanged. A minor decrease in the particle size was observed at relatively higher decomposition temperature (400 °C).

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FIGURE CAPTIONS

- Figure 1 : XRD results of zinc carbonate hydroxide samples.
- Figure 2 : SEM-EDS spectra of the zinc carbonate hydroxide samples
(a) : Reference sample,
(b) : Industrial sample.
- Figure 3 : FTIR of the reference sample.
- Figure 4 : TG non isothermal treatment of samples.
- Figure 5 : Treatment of RFS at different heating rates.
- Figure 6 : Isothermal treatment of RFS between 150 and 240 °C.
- Figure 7 : Isothermal treatment of INS between 150 and 215 °C.
- Figure 8 : Arrhenius diagrams of decomposition of both samples.
- Figure 9 : Treatment of RFS between 200 and 275 °C at different times.
- Figure 10 : XRD result of RFS treated at 200 and 250 °C.
- Figure 11 : DSC results of the reference sample.
- Figure 12 : Evolution of the particle sizes during the treatment of RFS at 250 and 400 °C.
- Figure 13 : SEM micrograph of the reference sample
(a) : Non treated,
(b) : Decomposed at 250 °C.

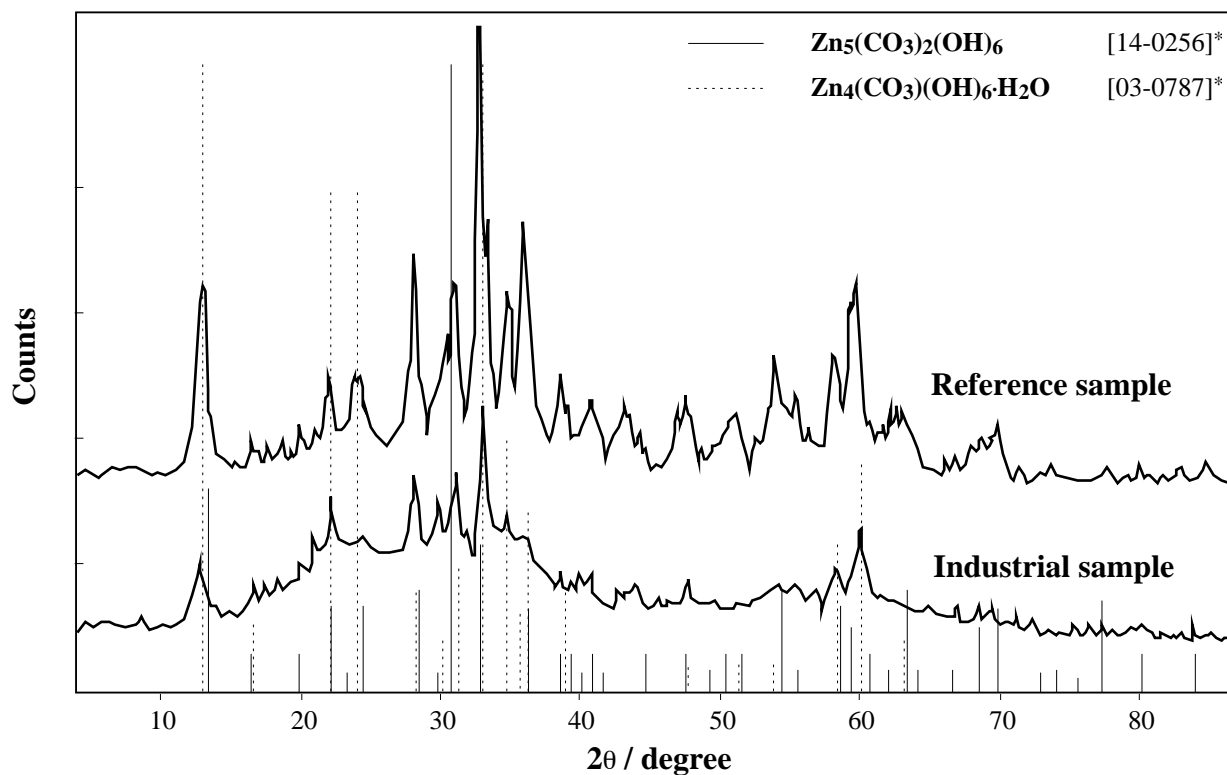


Fig. 1 : XRD results of zinc carbonate hydroxide samples.

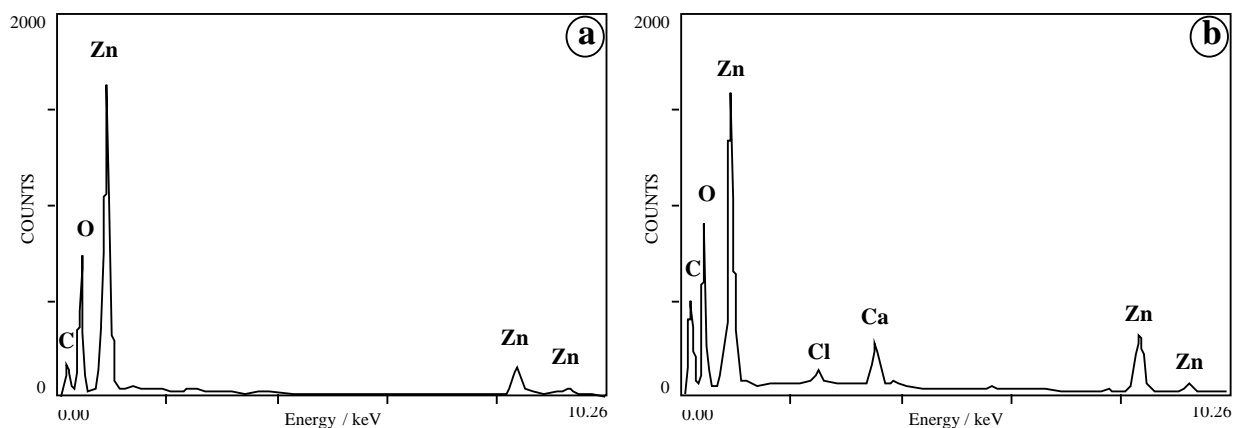


Fig. 2 : SEM-EDS spectra of the zinc carbonate hydroxide samples
 (a) : Reference sample,
 (b) : Industrial sample.

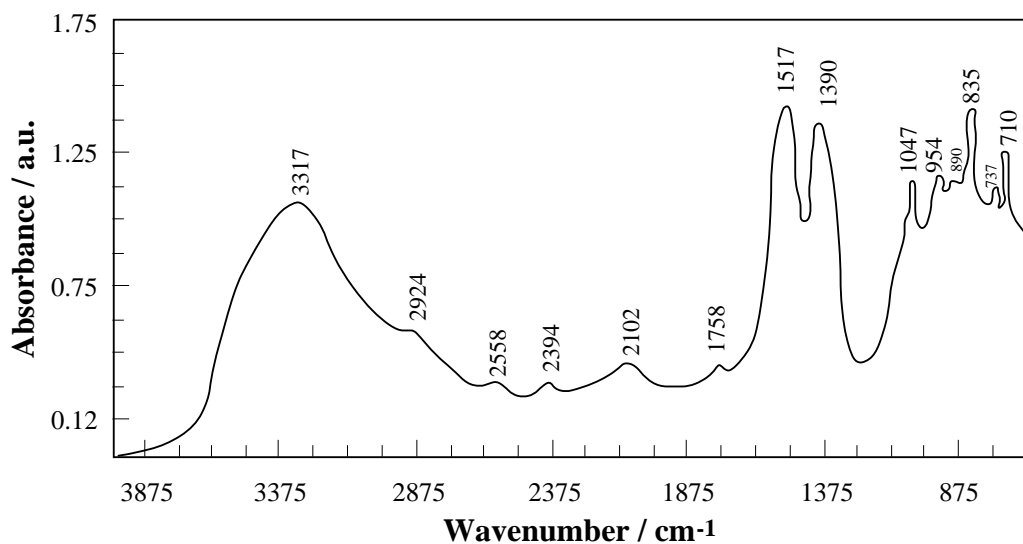


Fig. 3 : FTIR of the reference sample.

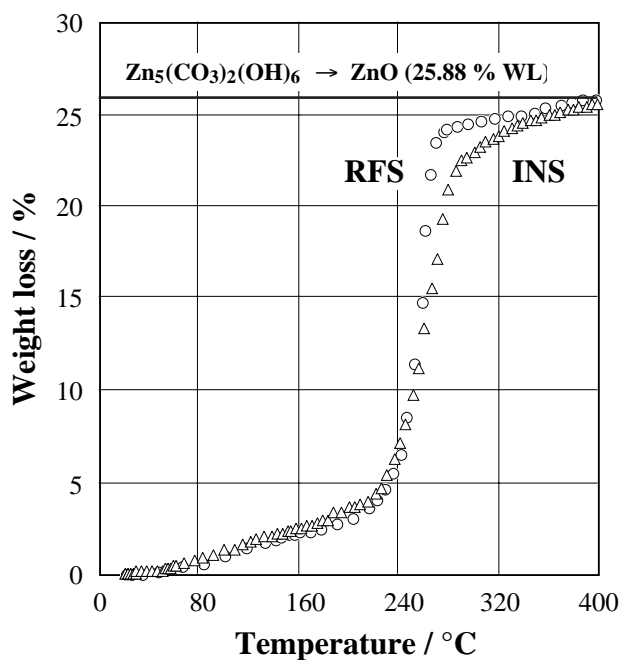


Fig. 4 : TG non isothermal treatment of samples.

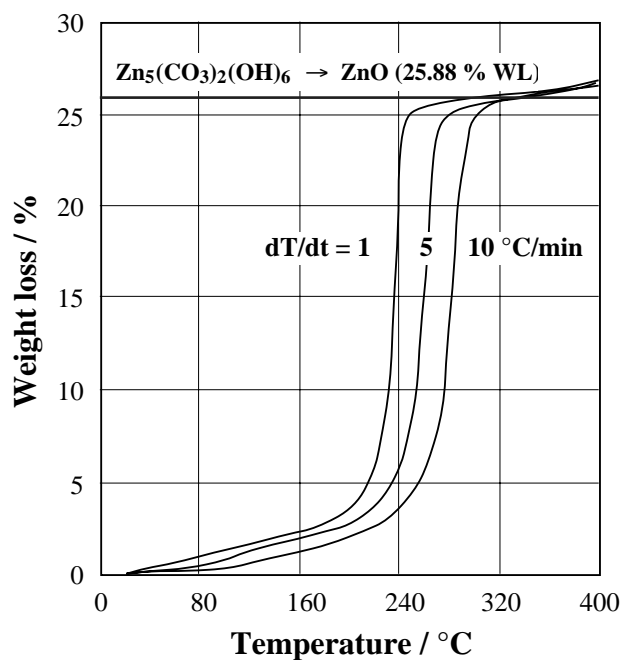


Fig. 5 : Treatment of RFS at different heating rates.

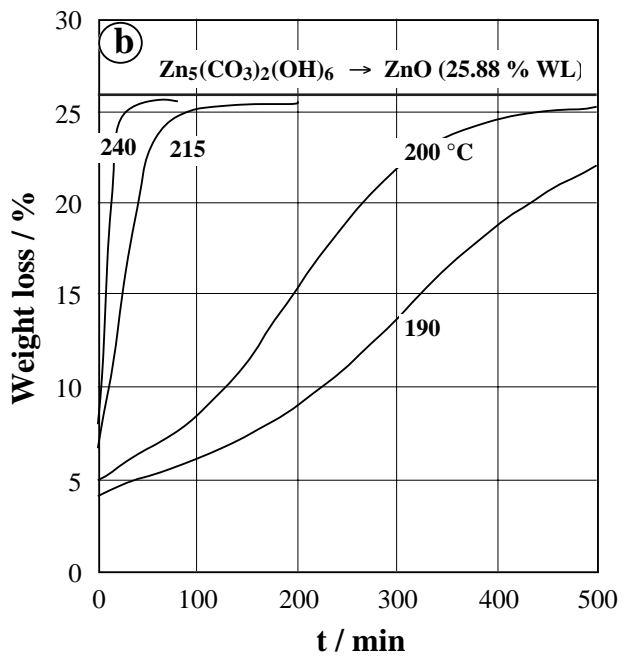
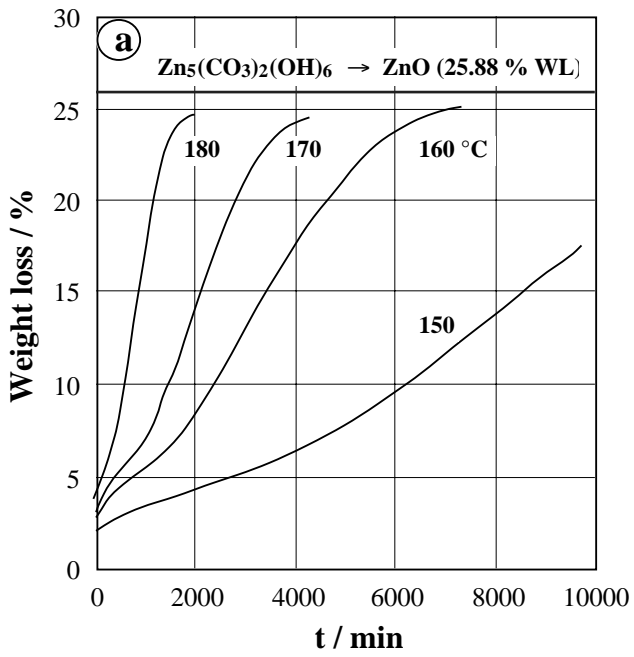


Fig. 6 : Isothermal treatment of RFS between 150 and 240 °C.

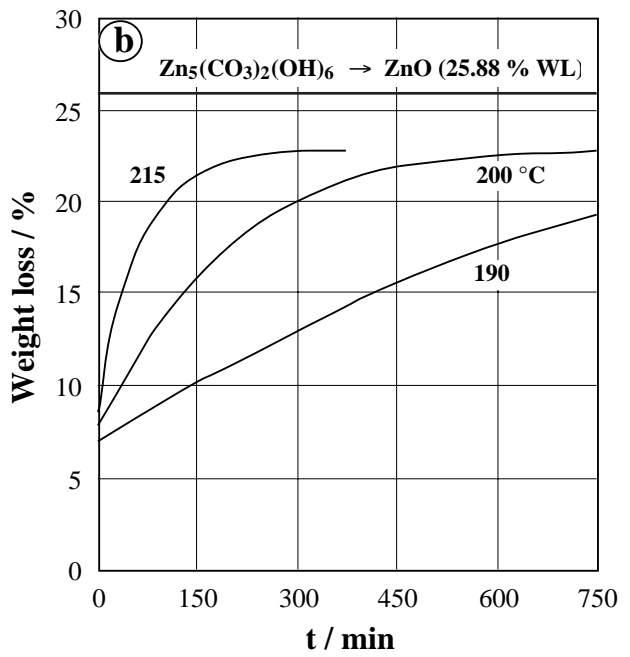
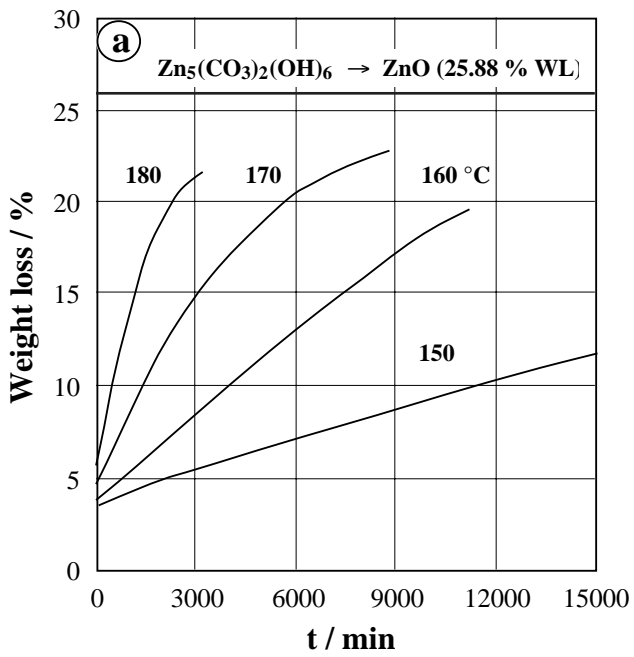


Fig. 7 : Isothermal treatment of INS between 150 and 215 °C.

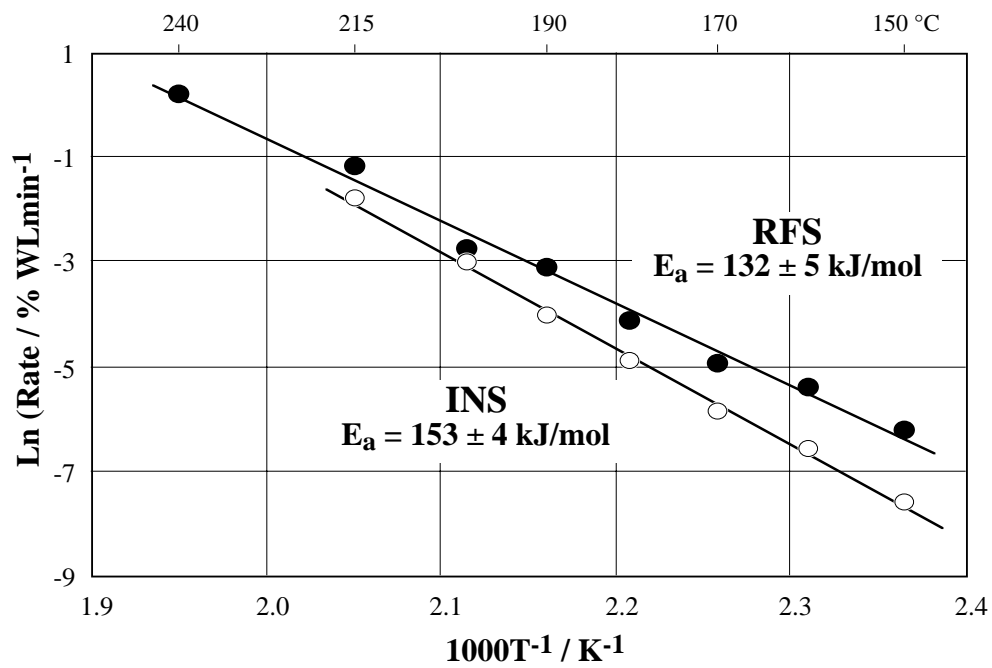


Fig. 8 : Arrhenius diagrams of decomposition of both samples.

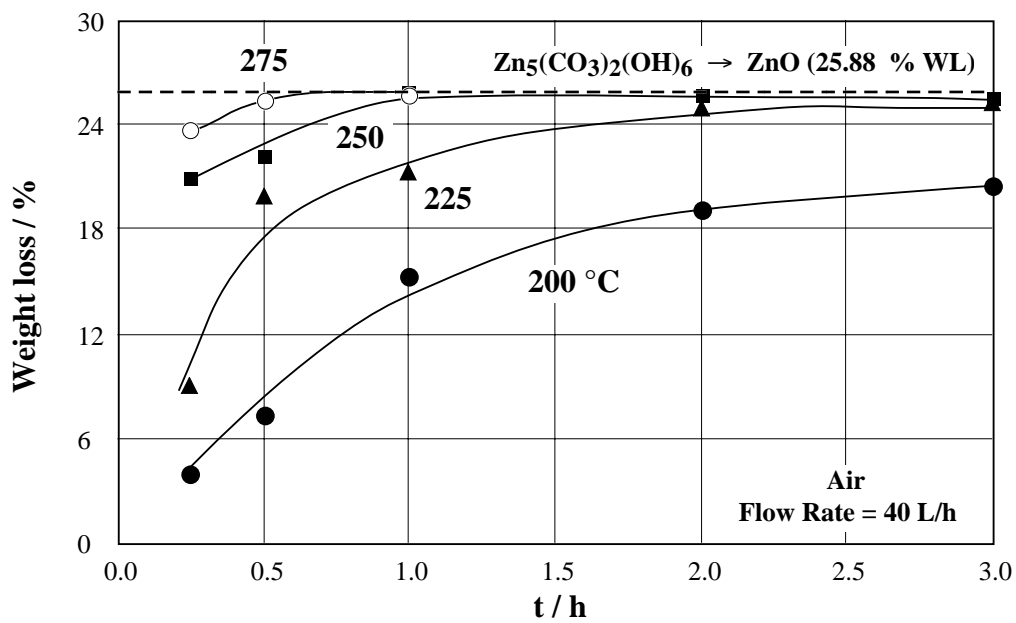


Fig. 9 : Treatment of RFS between 200 and 275 °C at different times.

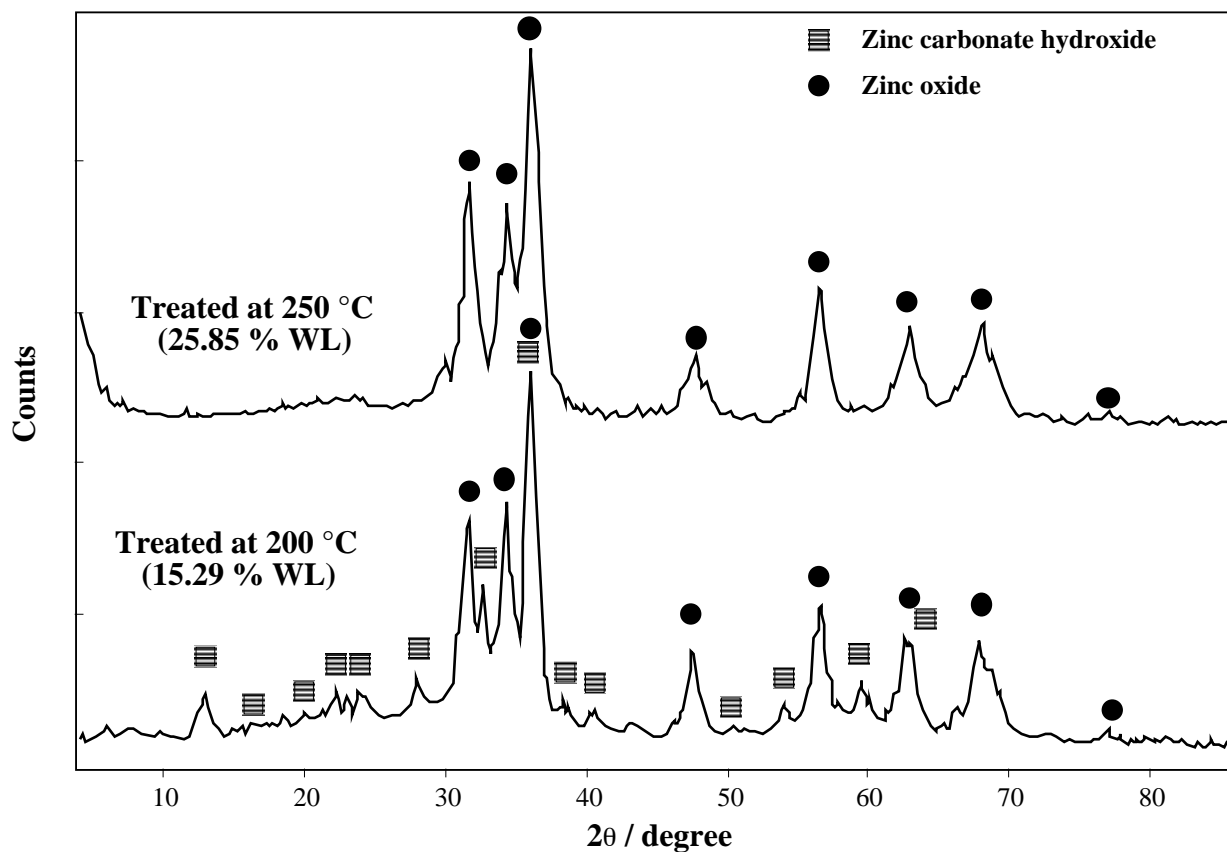


Fig. 10 : XRD result of RFS treated at 200 and 250 °C.

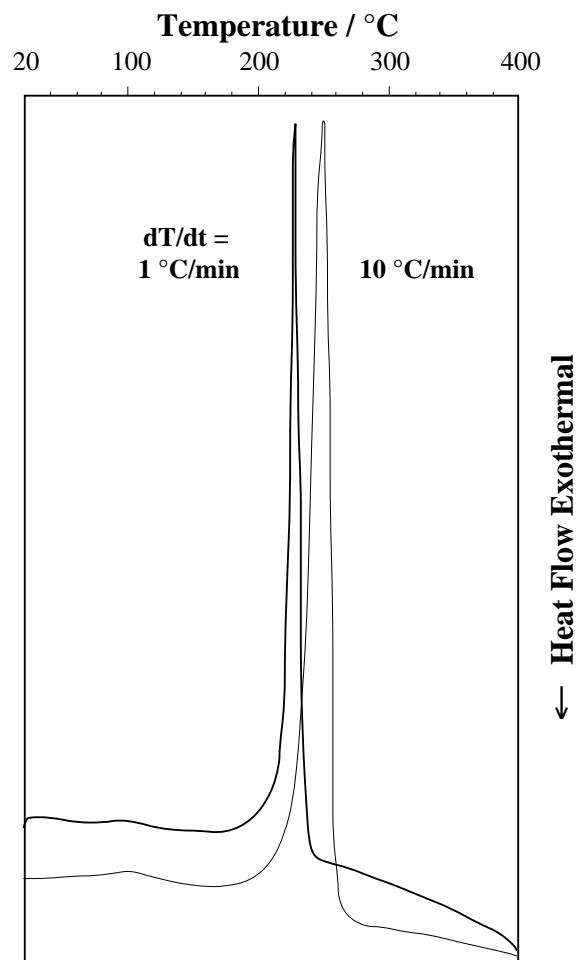


Fig. 11 : DSC results of the reference sample.

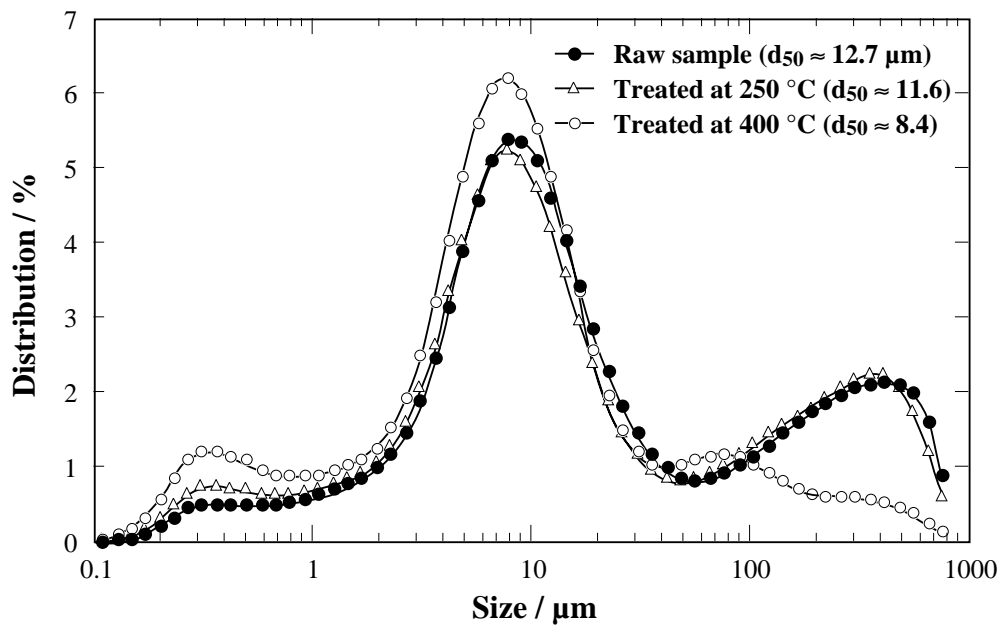


Fig. 12 : Evolution of the particle sizes during the treatment of RFS at 250 and 400 °C.

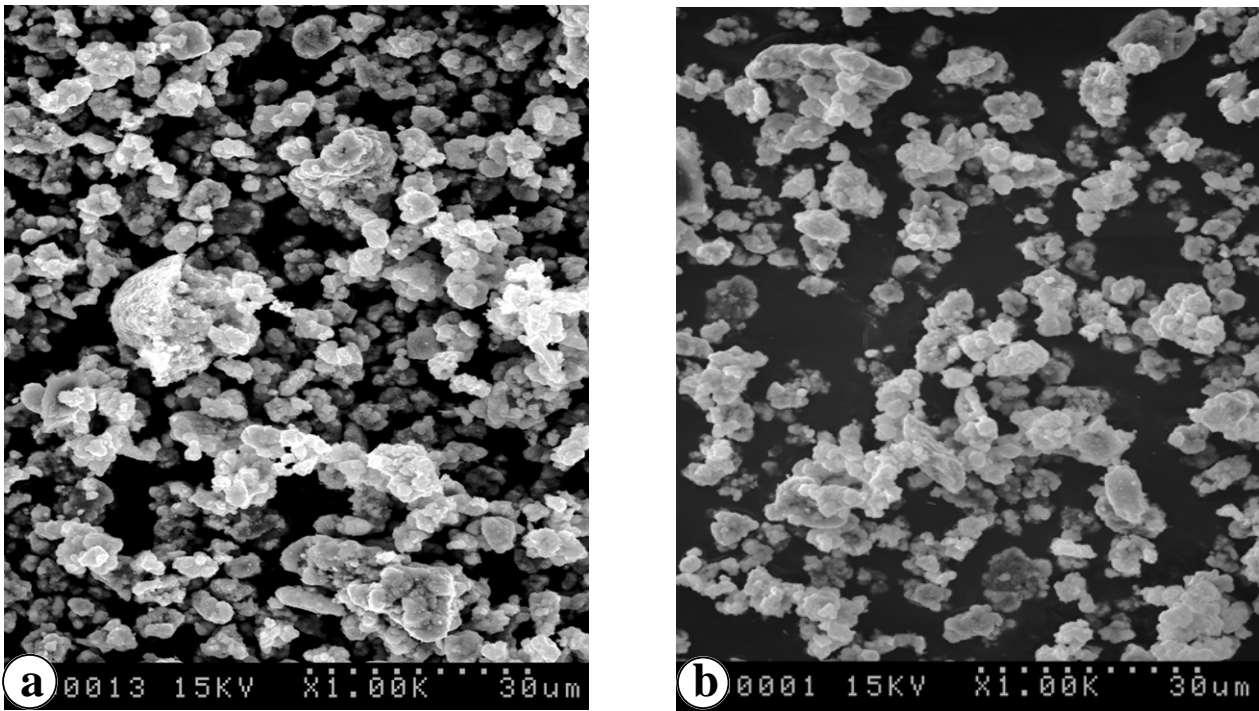


Fig. 13 : SEM micrograph of the reference sample

(a) : Non treated,

(b) : Decomposed at 250 °C..