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Thermogravimetric analysis of the reaction between carbon and $CaSO_4{\cdot}2H_2O$, gypsum and phosphogypsum in an inert atmosphere

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Abstract

Heating stoichiometric amounts of carbon and pure $CaSO_4$, synthetic gypsum or phosphogypsum in a nitrogen atmosphere, results in the formation of CaS between 700°C and 1100°C. Different heating rates were used to investigate the reaction, and the amount of CaS formed depends on the heating rate used. A quantitative XRD method was used to determine the amounts of $CaSO_4$, CaS, CaO and C in the samples. More CaS formed with increasing heating rate. Addition of 5% Fe_2O_3 and 5% ZnO as catalysts lowers the temperature range, as well as the activation energy of the reaction. The relationship between the activation energy values and degree of conversion (α) for the reaction between carbon and $CaSO_4$ indicates that it is a complex reaction, and that simultaneous competitive reactions are taking place. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Calcium sulphide has many industrial applications, one of which involves the increased mechanical strength of cement. Gypsum and phosphogypsum are widely available to use on industrial scale and can therefore be applied in the synthesis of CaS.

Phosphogypsum is a by-product of the production of wet phosphoric acid during which phosphate rock (usually fluorapatite) is reacted with sulphuric acid [1]

$$\begin{aligned}&Ca_5(PO_4)_3F(s) + 5H_2SO_4(aq) + 10H_2O(l)\\&\quad\rightarrow 5CaSO_4 \cdot 2H_2O(s) + 3H_3PO_4(aq)\\&\quad + HF(aq)\end{aligned}$$

The reduction of gypsum and phosphogypsum using reducing gases, such as CO, H_2S, H_2 and CS_2, suffers from some disadvantages. One disadvantage is that a large excess of gaseous reductants is required, with no oxygen at all present. The nature of the solid and gaseous products varies depending on the reaction conditions and reducing gases, making the process difficult to control. Gypsum and phosphogypsum are also reacted with different types of carbon such as coke, coal, charcoal, etc. For the maximum conversion to CaS, the molar ratio $CaSO_4 : C$ should be a minimum of $1 : 2$. The nature of the products varies with change in this ratio [2].

Synthesizing pure CaS from carbon and gypsum in air would not be possible, since the carbon reacts with the oxygen in air at lower temperatures than those at

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which the solid state reaction occurs and leaves the mixture depleted in carbon [3]. It was decided to investigate the reaction of gypsum and phosphogypsum with carbon in a nitrogen atmosphere and to determine the temperatures at which the reactions occur.

2. Experimental

2.1. Sample preparation

Synthetic gypsum, obtained from the PPC plant in Cleveland, Johannesburg, was prepared via the reaction of limestone with sulphuric acid [4]. Samples were ground to a fine powder and thoroughly mixed to obtain an almost homogeneous sample with the composition as constant as possible. Phosphogypsum was available as "agricultural gypsum" and was obtained from a South African phosphoric acid producer (Omnia). Pure chemicals were obtained from Fluka, Merck and Saarchem. The X-ray fluorescence analyses (XRF) of the chemicals used are summarised in Table 1. XRD spectra were also obtained for $CaSO_4 \cdot 2H_2O$, gypsum, phosphogypsum and graphite.

Stoichiometric mixtures consisting of 2 : 1 molar ratios of pure graphite to $CaSO_4$, phosphogypsum and synthetic gypsum respectively were used for thermogravimetric measurements, kinetic studies and XRD analysis. Five percent (m/m) Fe_2O_3 and ZnO were investigated as possible catalysts for the reduction.

2.2. Thermogravimetric analysis and differential scanning calorimetry

A Netzsch STA 409 EP simultaneous TG/DSC instrument was used to collect the thermogravimetric data. Nitrogen and air were used as dynamic atmospheres, using a flow rate of 50 $cm^3\ min^{-1}$ for nitrogen and 20 $cm^3\ min^{-1}$ for air. Platinum sample pans were used. A temperature calibration was achieved using the ICTAC recommended DTA standards. Sample masses of between 20 and 25 mg were used for kinetic analysis, while sample masses up to 50 mg were used for XRD analysis.

The software module for kinetic analysis of thermal measurements by means of multi-variant nonlinear regression developed by Netzsch was used to investigate the kinetic behaviour of the respective reactions [5]. Six different heating rates between 1°C/min and 10°C/min were used to investigate the kinetic behaviour of the samples.

2.3. XRD and XRF analysis

X-ray powder diffraction analyses were done on an automated Siemens D501 XRD spectrometer with a 40-position sample changer and monochromated Cu K_α radiation. The results were analysed with the use of the International Centre of Diffraction for PDF database sets 1–44. A quantitative method was used to determine the amount of analytes in the samples, and 20% (m/m) silicon was used as internal standard.

Table 1
XRF results of pure $CaSO_4 \cdot 2H_2O$, synthetic gypsum and phosphogypsum

Compounds	$CaSO_4 \cdot 2H_2O$ (%)	Synthetic gypsum (%)	Phosphogypsum (%)
SiO_2	0.9	0.5	0.5
Al_2O_3	0.0	0.4	0.1
Fe_2O_3	0.08	0.8	0.1
Mn_2O_3	0.0	0.1	0.0
TiO_2	0.02	0.1	0.02
CaO	33.4	32.2	31.7
MgO	0.4	0.6	0.1
P_2O_5	0.0	0.02	0.82
SO_3	46.3	45.4	44.8
Cl	0.0	0.0	0.0
K_2O	0.01	0.04	0.0
Na_2O	0.06	0.0	0.04
Loss on ignition	18.8	20.1	20.1

X-ray fluoresence analyses were performed on a Siemens MRS 400 MP wavelength–dispersive XRF spectrometer.

3. Results and discussion

3.1. Reaction between carbon and the calcium compounds in nitrogen

Fig. 1 gives the result of a typical TG curve obtained when stoichiometric amounts of carbon and the respective calcium compounds were heated up to 1300°C in nitrogen, using a heating rate of 5°C/min.

The mass loss observed between 80°C and 200°C is due to the loss of the hydrated water of calcium sulphate [6,7].

$$\mathrm{CaSO_4 \cdot 2H_2O(s) \rightarrow CaSO_4(s) + 2H_2O(g)}$$

The small mass loss between 650°C and 750°C occurs because of oxidation of some of the carbon in the mixture. The presence of oxygen in the reaction system is unwanted, therefore an inert atmosphere is used. However, because the instrument does not seal tightly, a small amount of oxygen is present. Carbon is oxidised to carbon dioxide between 600°C and 900°C, with the extent of oxidation depending on the availability of oxygen [3].

$$\mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}$$

The reaction between carbon and calcium sulphate takes place between 750°C and 1080°C [7–13]. The theoretical mass loss for this reaction due to the release of CO_2 is 44.9%.

$$\mathrm{CaSO_4(s) + 2C(s) \rightarrow CaS(s) + 2CO_2(g)}$$

From 1080°C to 1300°C, the TG curve is constantly descending due to the decomposition of $CaSO_4$ to CaO above 1000°C [2,13]

$$\mathrm{CaSO_4(s) \rightarrow CaO(s) + sulphur\ oxide\ gases.}$$

3.2. Effect of the heating rate

Thermogravimetric curves for the reduction of all three calcium sulphate compounds were obtained at heating rates between 1°C/min and 10°C/min. The results are summarised in Table 2.

The mass losses obtained for heating rates between 3°C/min and 10°C/min in the case of pure $CaSO_4$ compare very well with the theoretical value. Impurities contained in the phosphogypsum and synthetic gypsum have probably caused the lower mass losses observed for these compounds. The results obtained for the three calcium sulphate compounds are very similar, and in all three cases the value of the theoretical mass loss is not approached at heating rates lower than 3°C/min.

Differences in mass loss obtained at lower heating rates can possibly be caused by simultaneous reactions taking place at the temperature where the reaction between calcium sulphate and carbon must start. If there is any oxygen present in the system, oxidation of carbon will take place between 600°C and 900°C. This

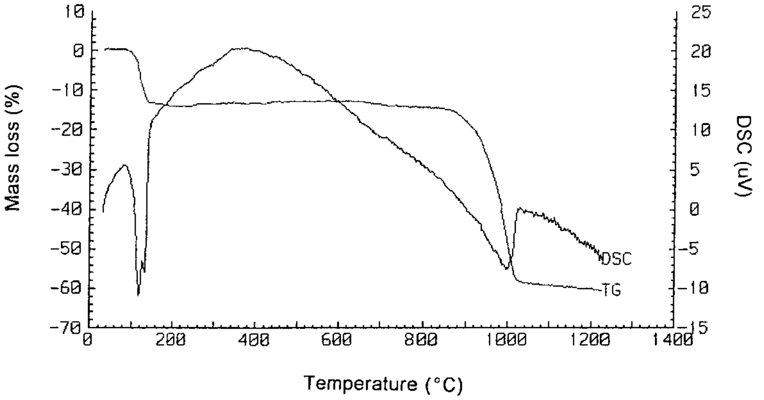

Fig. 1. TG and DSC curves when a stoichiometric mixture of carbon and calcium sulphate dihydrate was heated up to 1300°C in nitrogen, using a heating rate of 5°C/min.

Table 2
TG results for the reaction between carbon and the different calcium sulphate compounds

Heating rate (°C/min)	$CaSO_4 \cdot 2H_2O$ (mass%)	Phosphogypsum (mass%)	Synthetic gypsum (mass%)
1	−10.6	−13.6	−13.2
2	−29.0	−26.5	−28.0
3	−44.7	−41.6	−42.3
4	−44.9	−43.7	−40.9
5	−44.4	−43.5	−41.2
10	−44.4	−42.9	−41.5

reaction can overlap with the reduction of calcium sulphate at lower heating rates. XRD analyses were done to find an explanation for the lower mass loss at lower heating rates and will be discussed later.

3.3. Effect of catalysts

Fe_2O_3 has been used previously as a catalyst for the reaction between calcium sulphate and carbon [7]. For the higher heating rate (10°C/min), addition of Fe_2O_3 and ZnO as catalysts lowered the starting temperature of the reduction from 872°C to 854°C in the case of Fe_2O_3 and from 872°C to 832°C for ZnO. With a lower heating rate (2°C/min), the starting temperature was higher than was the case where no catalyst was used. There was not a considerable change in the starting temperatures when heating rates between 3°C/min and 5°C/min were used. The temperatures at which the reaction was completed were lower at all heating rates than when no catalysts were used. Therefore, addition of both Fe_2O_3 and ZnO as catalysts caused the reduction to proceed over a smaller temperature range.

It was not possible at this stage to decide which catalyst was best for the reduction of $CaSO_4$, and kinetic analyses had to be done to supplement these results.

3.4. X-ray diffraction analysis

XRD analyses were done on the samples used during thermogravimetry by taking samples from the furnace at different temperatures. The samples were taken from the hot furnace and immediately cooled to room temperature to prevent further solid state reactions while the furnace cools down slowly.

The amounts of CaS for each of the calcium sulphate compounds increase with increasing heating rates. Therefore, the best yield of CaS was obtained by using a heating rate of 10°C/min, while no CaS formed when the heating rate was 1°C/min. More CaS was formed when pure $CaSO_4 \cdot 2H_2O$ was used than when phosphogypsum and synthetic gypsum were used. This can be ascribed to the fact that there are impurities contained in these compounds. The lowest yield of CaS was obtained by using synthetic gypsum.

At low heating rates the competing reactions must be more prominent than when a higher heating rate is used. It is possible that $CaSO_4$ reacts quicker with CaS at lower temperatures with low heating rates [2,12,14–18]:

$$3CaSO_4(s) + CaS(s) \rightarrow 4CaO(s) + 4SO_2(g)$$

3.5. Kinetic analysis

Six different heating rates between 2°C/min and 10°C/min were used to calculate the activation energy values at different degrees of conversion (α), using the isoconversion method described by Ozawa [18] and Flynn and Wall [19]. The most important advantage of this method is that it provides a model-free approximation of the activation energy, by using multiple scan analysis [20]. The following equation is used to determine the activation energy values (E) at different degrees of conversion (α) [5]:

$$\ln\beta = \ln\left(\frac{A \cdot E}{R}\right) - \ln G(\alpha) - 5.3305 - 1.052 \cdot \frac{E}{RT}.$$

This model forms part of the kinetic analysis program described in the experimental part of this paper. Figs. 2–4 show the dependency of the activation energy on the degree of conversion for the different calcium sulphate compounds, with and without the catalysts.

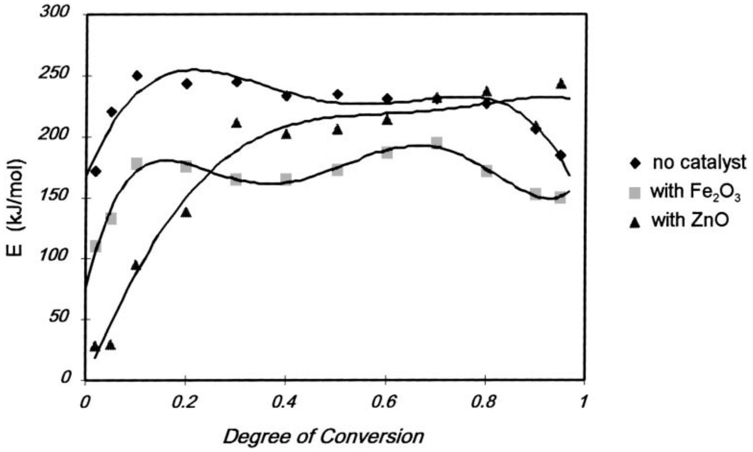

Fig. 2. Dependency of the activation energy on the degree of conversion for the reaction between carbon and pure $CaSO_4$·2H2O, with and without the catalysts, using heating rates between 3°C/min and 10°C/min.

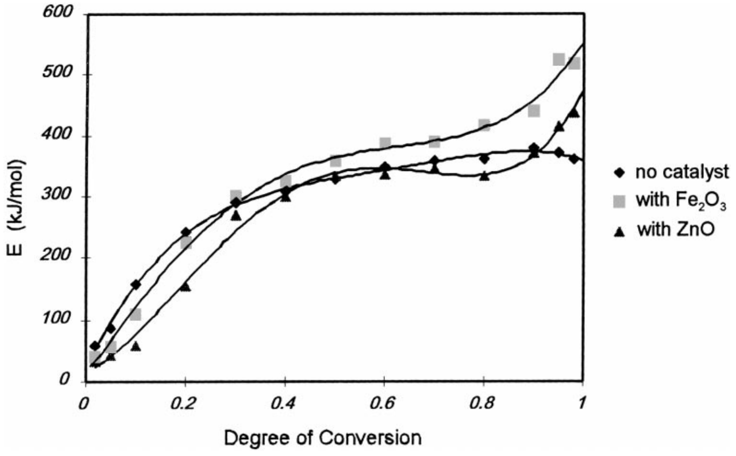

Fig. 3. Dependency of the activation energy on the degree of conversion for the reaction between carbon and phosphogypsum, with and without the catalysts, using heating rates between 3°C/min and 10°C/min.

If the determined activation energy is the same for different degrees of conversion (α_k), it can be concluded that the reaction is a single-step reaction. On the other hand, if E changes with increasing values of α_k, it suggests a complex reaction mechanism [21,22].

It can be seen from the figures that the reaction between carbon and calcium sulphate, with or without a catalyst, is a complex reaction. This can also be assumed from the fact that the mass loss is dependent on the heating rate (different mass losses for different heating rates). Isoconversional methods are based on the assumption that the Arrhenius parameters and the mechanism of the reaction do not change when the heating rate varies, but could with degree of conversion [23]. The requirement for a well-defined degree of conversion (α) is that the initial and final states for each heating rate must be the same. This is true when the simultaneous reactions are independent from each other, but competitive reactions cause problems [22].

Comparing the results for the mixtures of pure calcium sulphate, phosphogypsum and synthetic gypsum without a catalyst are compared with the corresponding mixtures with a catalyst, addition of the catalyst lowered the activation energies for pure cal-

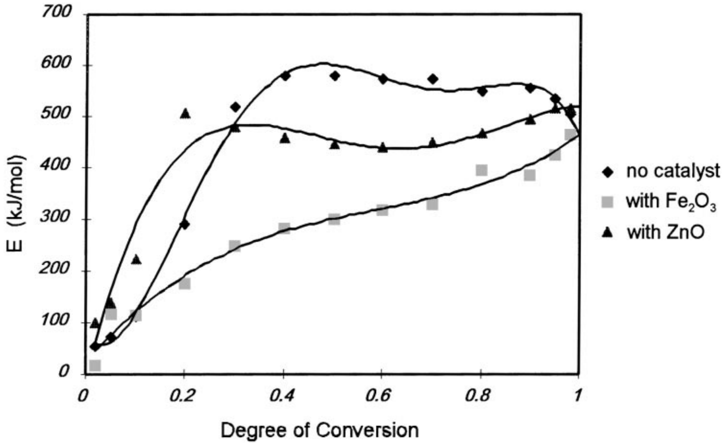

Fig. 4. Dependency of the activation energy on the degree of conversion for the reaction between carbon and synthetic gypsum, with and without the catalysts, using heating rates between 3°C/min and 10°C/min.

cium sulphate and synthetic gypsum, but did not have a noticeable effect on the reaction with phosphogypsum, probably due to the influence of impurities. It seemed that Fe_2O_3 lowered the activation energies more than ZnO, and is therefore more effective for use as a catalyst in the reaction between carbon and calcium sulphate.

The activation energies for the reaction with pure $CaSO_4$ were in each case lower than those with phosphogypsum and synthetic gypsum. This could be a result of impurities in phosphogypsum and synthetic gypsum, which can cause interference by means of side reactions.

4. Conclusion

The reaction between carbon and $CaSO_4$ in nitrogen atmosphere takes place between 700°C and 1100°C:

$$CaSO_4(s) + 2C(s) \rightarrow CaS(s) + 2CO_2(g)$$

The experimental mass losses indicated that the above reaction is not the only one, some CaO also forms. The higher the heating rate (up to 10°C/min) the higher the yield of CaS.

Fig. 5 shows the dependence of the percentage CaS formed on the heating rate for the different calcium sulphate compounds. The percentage CaS formed

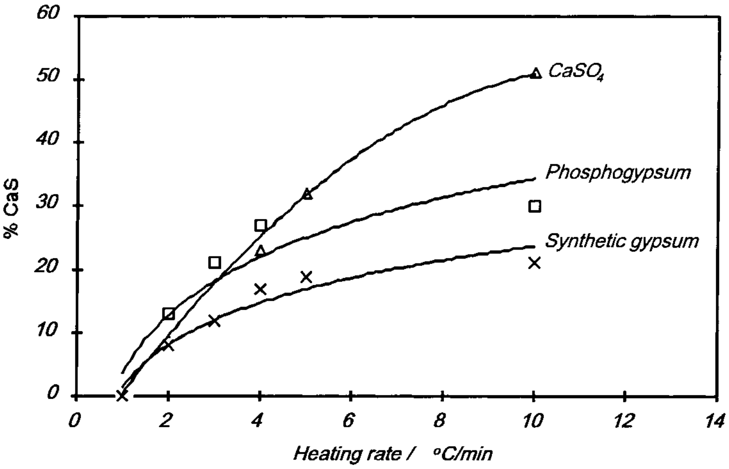

Fig. 5. Dependency of the percentage CaS formed on the heating rate for the different calcium sulphate compounds.

when pure $CaSO_4{\cdot}2H_2O$ was used is much higher than the calcium sulphate compounds. No CaS was observed for a heating rate of 1°C/min. It seems as if the competing reactions became more prominent at lower heating rates. There is also interference from the reaction between CaS and $CaSO_4$ from 900°C to 1100°C

$$3CaSO_4(s) + CaS(s) \rightarrow 4CaO(s) + 3SO_2(g).$$

Fe_2O_3 and ZnO are suitable catalysts for the reaction between carbon and the calcium sulphate compounds. Addition of both catalysts caused the reduction to take place over a smaller temperature range, when compared with the temperature ranges when no catalyst was added. Fe_2O_3 lowered the temperature range more than ZnO, and is therefore the better catalyst.

Increasing dependencies of activation energy on the degree of transformation (α) occur when parallel reactions are taking place. Decreasing dependencies are typical of intermediate reversible processes, or when a change in the limiting stage of a complex reaction (for example a change from the kinetic to the diffusion regime) takes place. In the first, the decreasing curve will have a concave shape, while the second will be convex. The differences in shapes of decreasing dependencies can probably be used in detailing the types of complex processes [23,24].

Kinetic analysis of the reaction between carbon and $CaSO_4$ indicates that the reactions occurring between carbon and the calcium sulphate compounds are complex. This could also be assumed from the fact that the mass loss is dependent on the heating rate. From the dependency of the activation energy on the degree of conversion it seemed as if competing parallel reactions were taking place in the beginning of the reaction interval (α between 0 and 0.2). The largest part of the curve (α between 0.2 and 0.8) is almost constant, and it seems as if the reactions are occurring at respectively constant rates, with each having a constant activation energy value, resulting in an almost constant overall E_a–value. The kinetic analyses have shown that both catalysts lowered the activation energy of the reaction, Fe_2O_3 more than ZnO.

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