

THERMOGRAVIMETRIC STUDIES OF THE SYNTHESIS OF CaS FROM GYPSUM, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ AND PHOSPHOGYPSUM

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Abstract

Using a heating rate of 2°C min^{-1} , CaS reacts with oxygen in air from 700°C to form CaSO_4 , with a complete conversion at 1100°C . Synthesis of CaS from the reaction between CaSO_4 containing compounds and carbon compounds in air would not be possible, as the carbon reacts from 600°C with oxygen in the air to give CO_2 . Heating stoichiometric amounts of carbon and pure CaSO_4 , synthetic gypsum or phosphogypsum in a nitrogen atmosphere, results in the formation of CaS from 850°C . Using a heating rate of $10^\circ\text{C min}^{-1}$, the formation of CaS is completed at 1080°C . Addition of 5% Fe_2O_3 as a catalyst lowers the starting temperature of the reaction to 750°C . Activation energy values at different fraction reaction values (α) differ between 340 and 400 kJ mol^{-1} . The relationship between the activation energy values and conversion (α) indicates that the reaction proceeds via multiple steps.

Keywords: calcium sulphide, gypsum, oxidation, phosphogypsum, reduction, stability, thermogravimetry

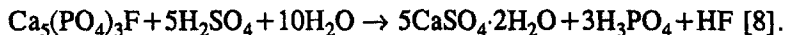
Introduction

Calcium sulphide is used in phosphors and electron emitters [1]. It is a depilatory in leather manufacturing. Luminous CaS, called Canton's phosphor, is used in luminous paints and varnish, and is synthesised by igniting a mixture of calcium carbonate and sulphur with tiny amounts of bismuth or manganese salts [2]. Calcium sulphide has been used medically to treat acne and boils, and in veterinary practice to treat chronic lesions. It is an industrially important chemical, used in the production of sulphur by the Chance-Claus process, in the treatment of waste liquor from paper mills, as an insecticide and germicide [3]. In cement, CaS is used to achieve an increase in mechanical strength with time [4].

Calcium sulphate in the form of natural deposits of gypsum and anhydrite represents a large source of sulphur. Gypsum and phosphogypsum are also produced as waste byproducts of the chemical and fertilizer industries. While some byproduct gypsum from forced oxidation flue gas desulphurization systems is being converted into wallboard, the supply of waste gypsum greatly exceeds the demand [5]. The main chemical use of gypsum and phosphogypsum is in the manufacture of sulphuric acid [6]. The first step involves the decomposition of calcium sulphate to cal-

cium sulphide, which is achieved by reducing it at high temperatures with coke, coal or reducing gases [6, 7]. During the next steps calcium sulphide is used as main reagent to obtain sulphuric acid. Another use of gypsum is as an additive to cement clinker to prevent flash-setting of cement.

Phosphogypsum is a byproduct of the production of wet phosphoric acid whereby phosphate rock (usually fluorapatite) is reacted with sulphuric acid:



The predominant species in the phosphoric acid solution, from which the phosphogypsum is crystallized, are H^+ , $\text{H}_5\text{P}_2\text{O}_8$ and HSO_4^- . It seems however more likely to find HPO_4^{2-} ions in the crystals, since these ions and SO_4^{2-} ions are similar in size and share the same affinity towards Ca^{2+} . A possible formula for phosphogypsum could therefore be $\text{Ca}(\text{SO}_4)_x(\text{HPO}_4)_y \cdot z\text{H}_2\text{O}$, with $y \ll x$ [9].

The reduction of gypsum and phosphogypsum using reducing gases, such as CO, H_2S , H_2 and CS_2 suffer from some disadvantages. One disadvantage is that a large excess of gaseous reductants is required, with no oxygen at all present [6]. The nature of the solid and gaseous products vary 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, wood charcoal, etc. For the maximum conversion to CaS, the molar ratio $\text{CaSO}_4:\text{C}$ should be a minimum of 1:2 [6]. Again the nature of the products varies. It was decided to investigate the reaction of gypsum and phosphogypsum with carbon in both air and nitrogen atmospheres, and to determine the temperatures at which the reactions occur. The thermal stability of CaS in air was also investigated.

Physical changes like sintering during the course of reduction may affect the reaction rate considerably, hence the use of a catalyst to bring down the reduction temperature. Fe(III) oxide was determined to be an effective catalyst for the reduction of calcium sulphate anhydrite to calcium sulphide in a carbon monoxide atmosphere [10].

Experimental

Sample preparation

Synthetic gypsum was prepared via the reaction of limestone with sulphuric acid [11], obtained from the PPC plant in Cleveland, Johannesburg. Samples were ground to a fine powder and thoroughly mixed to obtain an almost homogeneous sample with as constant a composition as possible. Phosphogypsum was available as "agricultural gypsum" and was obtained from a South African phosphoric acid producer (Omnia). Pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Fe_2O_3 were obtained from Fluka. XRF analysis of the synthetic gypsum and phosphogypsum are summarized in Table 1.

Stoichiometric mixtures consisting of 2:1 molar ratios of carbon to CaSO_4 , were heated at 800 and 1000°C under a nitrogen atmosphere in a Carbolite furnace for 2, 5 and 24 h respectively and XRD analysis performed on the products. XRD spectra were also obtained for gypsum and phosphogypsum.

Table 1 XRF results of synthetic gypsum and phosphogypsum

Compounds	Synthetic gypsum/%	Phosphogypsum/%
SiO ₂	0.5	0.5
Al ₂ O ₃	0.4	0.1
Fe ₂ O ₃	0.8	0.1
Mn ₂ O ₃	0.1	0.0
TiO ₂	0.1	0.02
CaO	32.2	31.7
MgO	0.6	0.1
P ₂ O ₅	0.02	0.82
SO ₃	45.4	44.8
Cl	0.00	0.00
K ₂ O	0.04	0.0
Na ₂ O	0.0	0.04
Loss on ignition	20.1	20.2

5% Fe₂O₃ was added to the stoichiometric mixtures of carbon and calcium sulphate compounds to investigate the influence of Fe(III) oxide as a catalyst on the reaction.

Thermogravimetric analysis

A Netzsch STA 409 simultaneous TG/DSC instrument was used to collect thermogravimetric data. Nitrogen and air were used as dynamic atmospheres using a flow rate of 50 cm³ min⁻¹. Platinum sample pans were used. Temperature calibration were achieved using the ICTAC recommended DTA standards. Sample masses of less than 20 mg were heated. The software module for kinetic analysis of thermal measurements by means of multivariant non-linear regression developed by Netzsch was used to investigate the kinetic behaviour of the reaction between carbon and CaSO₄.

XRD and XRF analysis

X-ray powder diffraction analyses were performed on a Siemens D501 XRD spectrometer using CuK_α radiation. X-ray fluorescence analyses were performed on a Siemens MRS 400 MP wavelength-dispersive XRF spectrometer.

Results and discussion

Stability of CaS in air

Pure CaS was heated in air using a heating rate of 2°C min⁻¹ up to a temperature of 1400°C (Fig. 1). From 700°C CaS reacts with the oxygen in the air to form CaSO₄, with a complete conversion to CaSO₄ at 1100°C. Taking the mass of CaSO₄ as the 100% level, a mass gain of 50% is observed, which is comparable to the

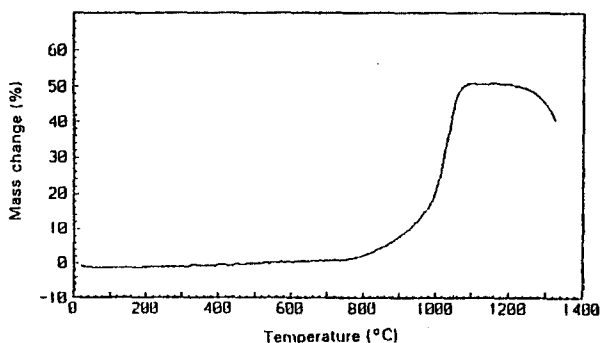


Fig. 1 TG curve for CaS heated in air using a heating rate of $2^{\circ}\text{C min}^{-1}$

theoretical mass gain of 47.0%. The mass gain CaSO_4 starts to decompose to CaO above 1200°C using this heating rate.

XRD analysis of samples heated in furnace

Heating the mixtures of carbon and gypsum or phosphogypsum in a nitrogen atmosphere at 1000°C for 2 h, results in a reaction mixture consisting of mainly CaS, with some CaO and C (Fig. 2). The reaction mechanism is still under investigation. No CaSO_4 was detected on the XRD spectra. Heating the mixtures for 5 and 24 h in a nitrogen atmosphere gave the same results. When the mixtures were heated at 1000°C for 2, 5 or 24 h in an air atmosphere, neither CaS nor C were detected, but only CaSO_4 and CaO.

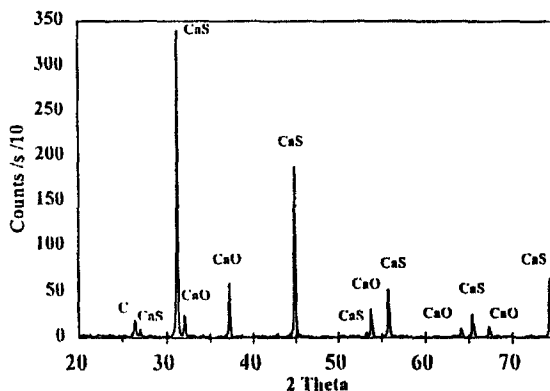


Fig. 2 XRD spectrum of the products of the reaction between CaSO_4 and C after 2 h at 1000°C in nitrogen

Heating of carbon-calcium sulphate mixtures in air

The TG curve, when stoichiometric amounts of carbon and pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are heated using a heating rate of $10^{\circ}\text{C min}^{-1}$, is given in Fig. 3. The first mass loss

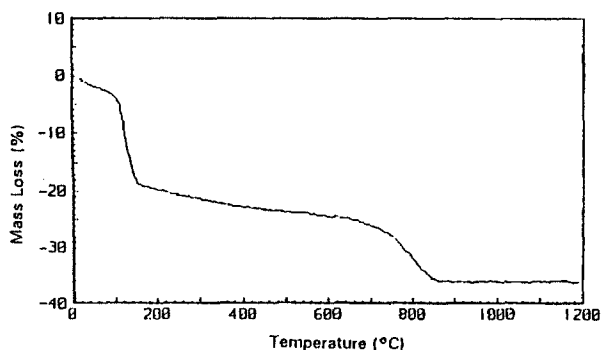


Fig. 3 TG curve when stoichiometric amounts of carbon and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were heated in air using a heating rate of $10^\circ\text{C min}^{-1}$

up to 200°C is due to the dehydration of calcium sulphate hydrate, while the mass loss of 12.2% between 600 and 900°C is due to the oxidation of all the carbon (theoretical value 12.9%). As also indicated by XRD, the reaction mixture at temperatures higher than 900°C consists of CaSO_4 and CaO . No solid state reaction between carbon and CaSO_4 is thus possible in the presence of enough oxygen to react with the carbon, since the last reaction takes place at a lower temperature. Using a heating rate of $10^\circ\text{C min}^{-1}$, CaSO_4 only decomposes to CaO at temperatures higher than 1200°C in air and nitrogen atmospheres.

Reaction between carbon and the calcium sulphate compounds in nitrogen

Figure 4 gives the TG curves when stoichiometric amounts of carbon and synthetic gypsum, with and without the presence of 5% (mass) Fe_2O_3 , were heated in nitrogen. Using a heating rate of $10^\circ\text{C min}^{-1}$, the reaction between carbon and pure CaSO_4 , or carbon and synthetic gypsum, or carbon and phosphogypsum, becomes detectable at 850°C and is completed at 1080°C in all cases. The mass loss of 44%

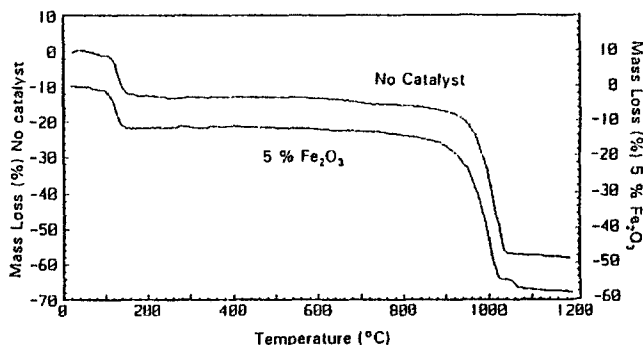
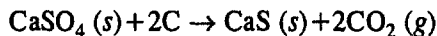


Fig. 4 TG curves when stoichiometric amounts of carbon and synthetic gypsum were heated with and without the presence of 5% Fe_2O_3 in nitrogen using a heating rate of $10^\circ\text{C min}^{-1}$

observed in the case of pure CaSO_4 compares very well to the theoretical value of 44.9%, while the mass losses of 42 and 43% for respectively synthetic gypsum and phosphogypsum are lower as expected. These mass losses indicate that the following reaction is taking place:



Addition of 5 mass percentage Fe_2O_3 as a catalyst, decreases the starting temperature in all cases to approximately 750°C . The mass losses observed all indicate the formation of CaS, but an additional 3% mass loss is observed between 1050 and 1200°C using the heating rate of $10^\circ\text{C min}^{-1}$ (Fig. 4).

Kinetics of the solid state reaction of carbon with pure CaSO_4

The mixtures (2:1) of pure CaSO_4 and carbon were heated using heating rates between 2 and $10^\circ\text{C min}^{-1}$ to obtain the mass loss curves. The data were used to calculate the activation energy values at different fraction reaction values (α), using the isoconversion method described by Ozawa [12] and Flynn and Wall [13]. The following equation is used to determine the activation energy values (E) at different α -values without the knowledge of the reaction model that describes the reaction [14]:

$$\ln\beta = \ln\left(\frac{AE}{R}\right) - \ln g(\alpha) - 5.3305 + 1.052\frac{E}{RT}$$

This method forms part of the kinetic analysis program are described in the experimental part of this paper. Figure 5 is obtained for the reaction between CaSO_4 and carbon. From this figure, it is clear that the reaction is complex, with the activation energy values varying between 340 and 400 kJ mol^{-1} . The aspect is under further investigation.

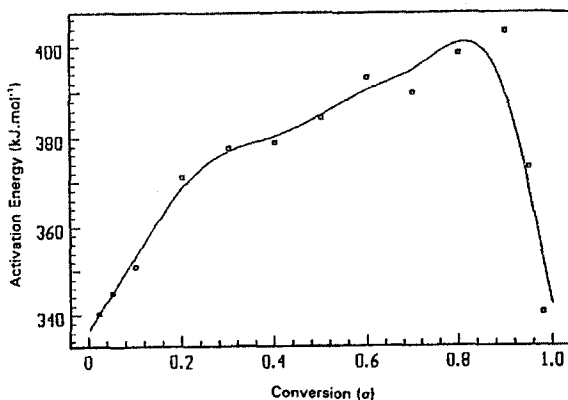


Fig. 5 Activation energy values (E) at different degrees of conversion (α) for the reaction between carbon and pure CaSO_4

Conclusion

It would not be possible to synthesize pure CaS from carbon and CaSO₄ compounds in air, since the carbon reacts with the oxygen in air at a lower temperature than the solid state reaction and leaves the mixture depleted in carbon. CaS proved also not to be stable in air at the temperatures at which the solid state reaction occurs, since it reacts with oxygen to form CaSO₄ from 700°C upwards. Depending on the amount of oxygen present and heating rate, the reaction mixture, after being heated to 1200°C, consists of CaO and CaSO₄.

Heating stoichiometric amounts of CaSO₄, synthetic gypsum or phosphogypsum and carbon in a nitrogen atmosphere, with a heating rate of 10°C min⁻¹ results in the formation of CaS from 850°C. Addition of 5% Fe₂O₃ lowers the starting temperature to 750°C.

Kinetic analysis of the reaction between CaSO₄ and carbon indicates that the reaction does not occur in a single step, but that it is a multiple-step reaction.

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