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Note

EFFECT OF CARBON AND SILICA ON THE REDUCTION OF CALCIUM SULFATE

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Numerous studies have been conducted on the reduction of calcium sulfate by carbon or carbon monoxide gas [1–5] with or without silica addition. It was established that the formation of various solids and gases could be controlled by adjusting the composition of the initial solid mixtures or by changing the surrounding atmosphere. Thermogravimetric analysis (TGA) of the reduction of calcium sulfate by carbon at a low heating rate (2°C min^{-1}) has allowed the consecutive reactions to be defined. Data from the X-ray diffraction analysis (XRD) of the reaction products further provide supporting evidence for the proposed reaction mechanism.

EXPERIMENTAL

Mixtures of high purity calcium sulfate, carbon, and silica of different molar ratios were pelletized in a hydraulic press (2000 psi). A thermogravimetric analyzer (Cahn Electrobalance 1000A) was used to monitor the weight loss and the rate of weight loss of these pellets continuously under either a nitrogen or carbon monoxide atmosphere at a slow heating rate of 2°C min^{-1} (20–1400°C). At such a slow heating rate, some stable solid intermediates corresponding to the weight loss plateaus were isolated. These stable solid intermediates and the final residues were then subjected to X-ray analysis. The information generated from these TGA tests and X-ray analyses was later used to verify the postulated reaction mechanism reported earlier.

RESULTS AND DISCUSSION

Table 1 summarizes the results of the effect of carbon and silica on the decomposition of calcium sulfate. By altering the molar ratios of the ingredients in the initial mixtures, various solid phases formed during the

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TABLE 1

Effect of carbon and silica on the reduction of calcium sulfate in nitrogen

($CaSO_4$: C : SiO_2) molar ratios of initial mixtures (M)	TGA test reaction temp. (°C)	XRD analysis		Reaction schemes based on TGA and XRD data
		Stable solid intermediates	Final residues	
1 : 0 : 0.5	920–1300	none	Ca_2SiO_4	$2\ CaSO_4 + SiO_2 \rightarrow Ca_2SiO_4 + 2\ SO_3$
1 : 0.5 : 0.5	760–1180	$CaSO_4$, C, CaS	Ca_2SiO_4	I. $CaSO_4 + 2\ C \rightarrow CaS + 2\ CO_2$ II. $3\ CaSO_4 + CaS + 2\ SiO_2 \rightarrow 2\ Ca_2SiO_4 + 4\ SO_2$
1 : 1.5 : 0	760–1060	$CaSO_4$, C, CaS	CaS, CaO	I. $0.75\ CaSO_4 + 1.5\ C \rightarrow 0.75\ CaS + 1.5\ CO_2$ II. $0.25\ CaSO_4 + 0.08\ CaS \rightarrow 0.33\ CaO + 0.33\ SO_2$
1 : 2 : 0	760–1060	none	CaS	$CaSO_4 + 2\ C \rightarrow CaS + 2\ CO_2$
1 : 3 : 0	760–1060	none	CaS, C	$CaSO_4 + 2\ C \rightarrow CaS + 2\ CO_2$

reaction were observed. From the TGA and XRD data, it is believed that calcium sulfate was reduced by carbon to form calcium sulfide first, starting near 760°C in a nitrogen atmosphere. When the molar ratio of carbon to calcium sulfate was greater than or equal to 2, all of the calcium sulfate was reduced to calcium sulfide. There were no weight loss plateaus (TGA curves) corresponding to the stable solid intermediates observed. The total weight loss was equal to the weight loss from the release of carbon dioxide. When the ratio was between 0 and 2, only part of the calcium sulfate was reduced to form calcium sulfide. The remaining unreacted calcium sulfate then reacted with the calcium sulfide to form calcium oxide and sulfur dioxide. This was previously reported by Yang and Shen [4]. When no carbon was present, calcium sulfate did not start decomposing until the temperature was above 920°C. The decomposition was complete at 1300°C.

Silica was believed to function simply as a scavenger for the removal of calcium oxide in the form of calcium silicates. It provided a driving force to facilitate the reaction between calcium sulfate and calcium sulfide. For example, there were two consecutive reaction stages involved if the molar ratios of $CaSO_4$ to C to SiO_2 are 1 : 0.5 : 0.5. They are suggested as follows:

Stage I: $CaSO_4 + 2C \xrightarrow{(760\text{–}985^\circ\mathrm{C})} CaS + 2CO_2$

Stage II: $3CaSO_4 + CaS + 2SiO_2 \xrightarrow{(1000\text{–}1180^\circ\mathrm{C})} 2Ca_2SiO_4 + 4SO_2$

A weight loss plateau corresponding to the formation of calcium sulfide was observed in the temperature range 985°C–1000°C. The kinetic parameters for these two reactions using the semi-empirical nth order equation

$$\frac{d\alpha}{dt} = k_0(1-\alpha)^n \exp(-E/RT) \tag{1}$$

are listed in Table 2. The overall reaction is formulated as

$$2CaSO_4 + C + SiO_2 \rightarrow Ca_2SiO_4 + 2SO_2 + CO_2$$

When the surrounding atmosphere was changed from nitrogen to carbon monoxide, all of the calcium sulfate was found to be reduced to calcium sulfide starting at a lower temperature (690°C). The initial composition of

TABLE 2

Kinetic parameters of the reduction of calcium sulfate by carbon

Stage of reactions	Reaction order, n	Activation energy, E (kcal g-mol^{-1})	Frequency factor, k_0 (s^{-1})	Std. Error (%)
I	1	36.4±0.4	5.02×10^3	2.7
II	1	59.9±0.8	5.65×10^6	4.3

TABLE 3

Effect of carbon and silica on the reduction of calcium sulfate in carbon monoxide

($CaSO_4$:C:SiO_2) molar ratios of initial mixtures (M)	TGA test reaction temp. (°C)	XRD analysis		Reaction scheme based on TGA and XRD data
		Stable solid intermediates	Final residues	
1:0:0	690–910	none	CaS	$CaSO_4 + 4\,CO \rightarrow CaS + 4\,CO_2$
1:1.5:0	690–910	none	CaS, SiO_2	
1:0:0.5	690–910	none	CaS, SiO_2	

these solid mixtures had no effect on the reduction scheme of calcium sulfate. No weight loss plateaus were observed in the TGA curves. The reaction rates appeared to be independent of carbon and silica. The reaction scheme is

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2$$

The results from TGA and XRD data are shown in Table 3.

NOTATION

E	activation energy
k_0	frequency factor (s^{-1})
n	order of reaction
R	gas constant (1.987 cal g-mol^{-1} K^{-1})
t	reaction time (s)
T	reaction temperature (K)
α	percent reduction of calcium sulfate

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