REACTION MECHANISM STUDIES IN LIMESTONE SULPHATION USING SEM-EDS TECHNIQUE

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SUMMARY

The gas-solid reaction between sulphur dioxide and limestone in flue gas atmosphere produces solid reaction product which consists of calcium oxide and calcium sulphate. Small amount of calcium carbonate may be present in the end product depending on the sulphation conditions. The effect of temperature, residence time and limestone particle size on the sulphation of the particles was studied by SEM-EDS technique. The principle of the SEM-EDS procedure and main results are described.

INTRODUCTION

Dry flue gas desulphurization is an interesting technique when reducing sulphur dioxide in energy production. Dry injection technology is a low capital cost process compared to wet and spray drying processes and it is supposed to be commercially available in the beginning of 1990's (ref. 1). The main disadvantage with dry injection is the relatively poor sorbent utilization.

The most common sorbent used in high temperature sulphation is limestone which is economical and common mineral, and which produces stable end product, calcium sulphate. Major operating expense of limestone injection process is the cost of the sorbent and therefore it is important that as large amounts of injected sorbent as possible will react with SO_2. This means that the fundamentals of the sulphation process should be studied to be able to optimize the conditions for sulphur removal.

A number of studies have been performed to describe the effect of different parameters on sulphur removal with the limestone under fluidized bed combustion (FBC) environment. The studies include both laboratory and pilot scale experiments (refs. 2-4).The results achieved are not adaptable to limestone injection process because the sulphation temperature and the particle size of the sorbent are different.

High-temperature limestone injection is a process where the sorbent is injected to temperatures of 1000-1250 °C, the reaction time for sulphur removal is 0.1-1.0 seconds and the particle size of limestone is below 100 μm. Studies in this environment are being performed but the reaction conditions are impossible to achieve in a thermobalance and thus special reactors are needed. Fundamental research is being performed (refs. 5-6)

but the current knowledge and the literature base are not adequate, however. The results achieved have been conflicting and created a demand for further experiments.

The SEM-EDS (scanning electron microscope combined with energy dispersive spectral analysis) technique has been used in FBC sulphur capture experiments to get information about the microstructure of the sorbent samples (refs.7-8). SEM-EDS technique has not much been utilized in sorbent injection experiments because the analysis is more difficult to perform due to small size of the particles.

The study described herein is part of the fundamental approach to the mechanism and capacity of sulphation of certain limestones available in Finland. The SEM-EDS technique was used to get information about the morphology of the samples and the distributions of sulphur in the samples after they have been reacted with sulphur dioxide under controlled reaction conditions.

EXPERIMENTAL

Limestone used in these experiments was sedimentary limestone from Gotland, Sweden. The limestone was ground and sieved to fractions of 0-10 μm, 10-30 μm, 30-40 μm and 50-60 μm. The calcium carbonate contents of the fractions were 95.6 %, 91.8 %, 91.7 % and 93.4 %, respectively. The impurity in the samples consists of silica.

Sulphation of the particles was carried out using a specially designed isothermal flow reactor (ref. 9).The reaction conditions were adjusted close to full scale boiler conditions and the adjustable parameters were:

- temperature   850-1150 °C
- residence time 0.09-0.32 s

The gas atmosphere was simulated flue gas atmosphere (15 % CO_2, 8 % H_2O, 5 % O_2, 0.1 % SO_2 and balance N_2) and the calcium to sulphur mole ratio (Ca/S) was adjusted to 2.

Solid samples were collected after the reactor and transferred to SEM-EDS analysis. Samples for SEM-EDS were prepared by mounting reacted particles into brass ring filled with epoxy resin and hardener. After hardening the particle cross-sectioning was carried out by grinding the sample ring with carborundum disc and polished with diamond pastes. The specimen's surface was coated with thin, uniform conductive carbon layer. The sample for the SEM-EDS analysis is shown in Figure 1.

The SEM-EDS analysis was carried out with JEOL JSM 6400 scanning electron microscope equipped with energy dispersive X-ray analyser LINK AN 10/85. The exitation voltage used was 12 kV. The measured X-ray intensities were converted to weight % using LINK ZAF-4/FLS program and the virtual standards pack.
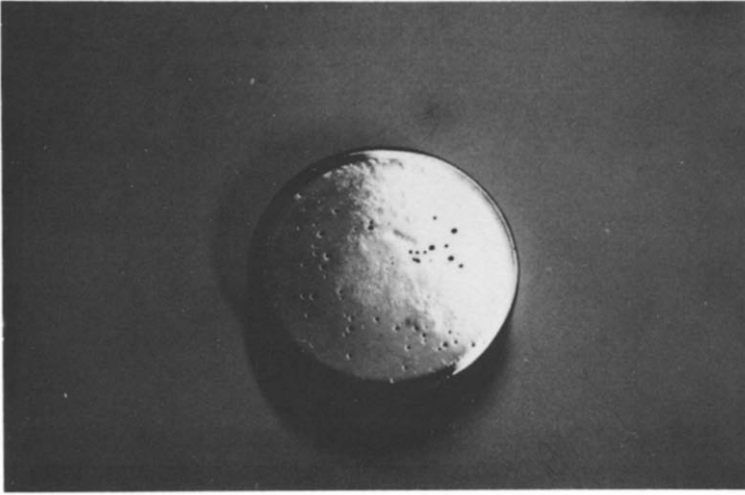
Fig. 1. Sample for SEM-EDS analysis

RESULTS AND DISCUSSION

When the limestone particles are introduced to the high temperature conditions the particles are shock-heated to the surrounding temperature. The heating of below-50-μm-diameter particles to the reaction temperature occurs within 20 milliseconds and the calcination of the particle starts immediately . The carbon dioxide evolves rapidly and the formed calcium oxide reacts with sulphur dioxide. The efficiency of the reaction is dependent on the surface area of calcium oxide. The surface area development during calcination possibly occur through pore formation or creation of small particles because of shock-heating.

The visual examination of the samples was carried out by taking scanning electron micrographs without cross-sectioning the samples. Stated small particle formation is not the reason for high surface areas according to our experiments and can be seen in Figures 2-3, where both unreacted limestone and sulphated limestone are presented. The particle size in both cases is 30-40 μm and sulphation conditions have been: temperature 1040 °C, residence time 0.24 s and SO_2-concentration 0.1 %. The particle size of the samples has remained unchanged. The surface of the samples is shown in Figures 4-5, where small cracks can be noticed in the sulphated particles. This is supposed to be the result of shock-heating and carbon dioxide pressure within the particle. The progress of sulphation can be seen in Figure 6, where a fully sulphated, brain-like particle surface is shown.
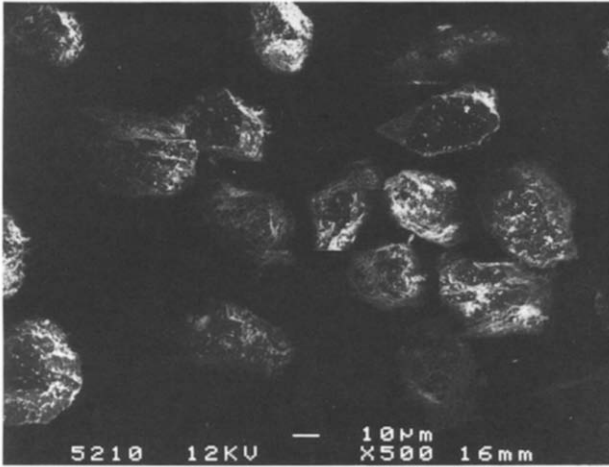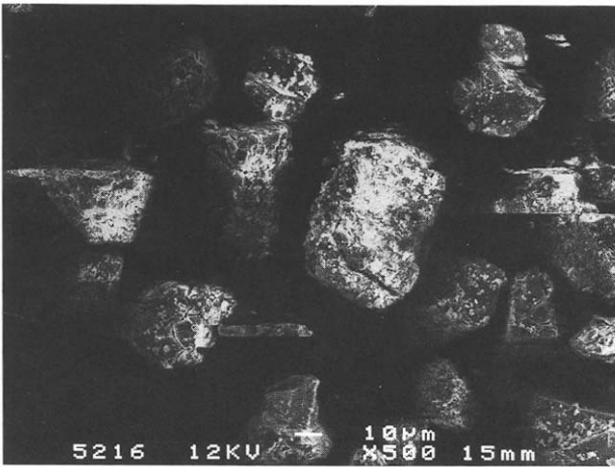
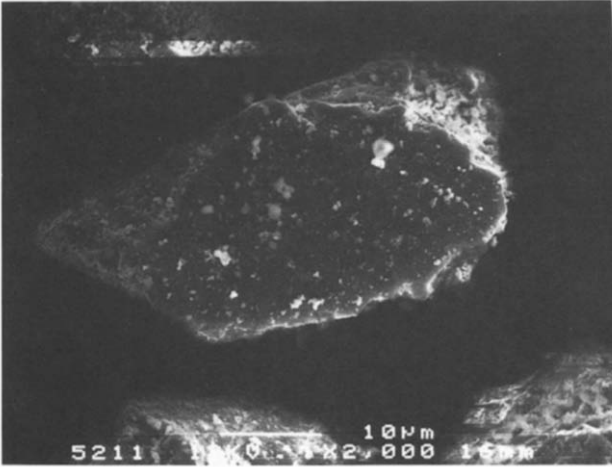Fig. 2. Unreacted limestone

Fig. 3. Sulphated limestone

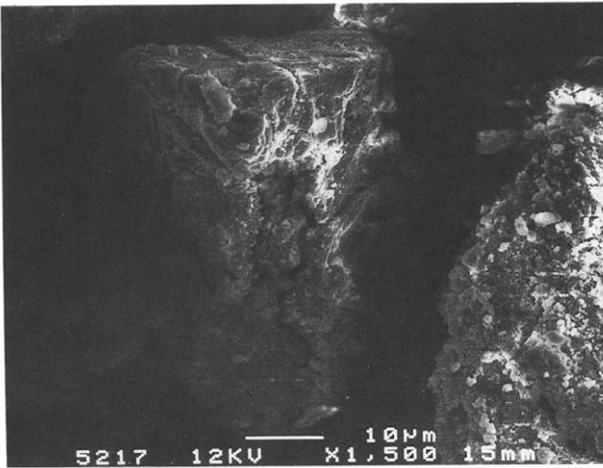Fig. 4. Surface of unreacted limestone

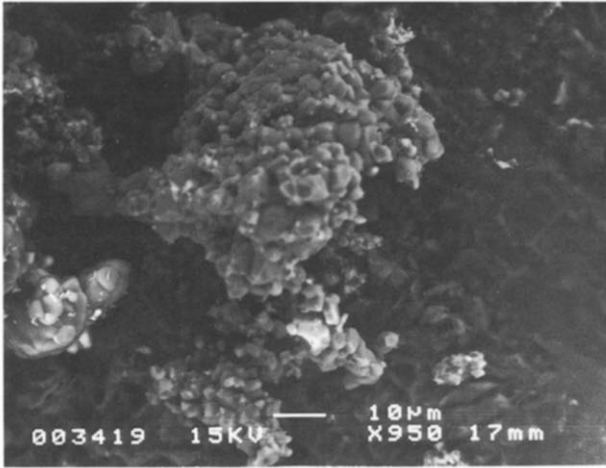Fig. 5. Surface of sulphated limestone

Fig. 6. Surface of totally sulphated limestone

The cross-sectioned samples were placed in the microscope and the sample area which corresponds to the microstructure of the specimen was selected from the backscattered electron image which is shown in Figure 7. The backscattered electron image gives the same information about the morphology of the samples; they have maintained their ordinary sizes and shapes.
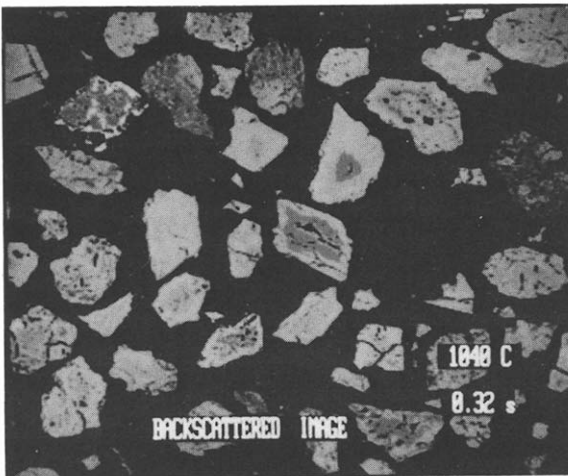

Fig. 7. Backscattered electron image of sulphated limestone

With the aid of the mapping procedure necessary information about the composition of the particles was achieved. In Figures 8-9 calcium and sulphur maps of the selected sample are presented. The particle size of the sample is 30-40 µm and the sulphation conditions have been temperature 1040 °C, residence time 0.32 s and SO2-concentration 0.1 %. The silicon maps of the samples showed that the impurities were as separate particles and could be neglegted when analysing the sulphur distribution in the selected particles. The selection of the representative particles for further analysis was carried out from the calcium and sulphur maps.
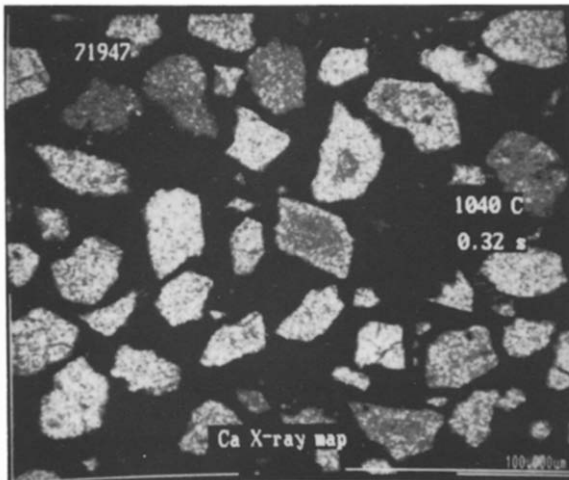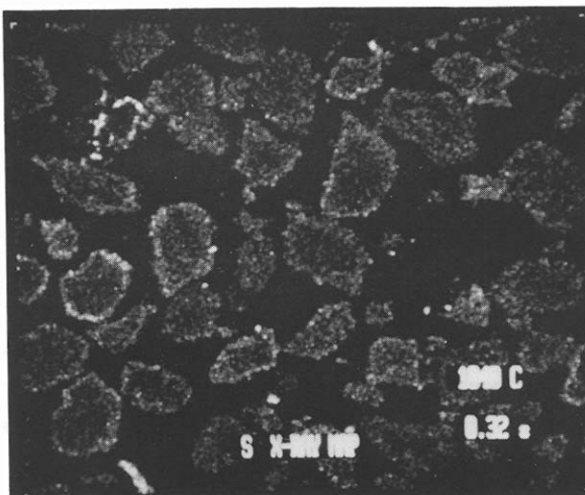

Fig. 8. Calcium map of sulphated limestone

Fig. 9. Sulphur map of sulphated limestone

The main information by SEM-EDS was achieved when analysing the sulphur penetration within the particles and the effect of different process parameters on the sulphur penetration. The studies were carried out with LINESCAN- analysis, where sulphur, calcium, silicon, etc concentration along selected line across the particle was analysed. The particles for the analysis had to be properly cross-sectioned and thus a lot of emphasis was put on the selection of the particle from the sample mass. The resolution in our equipments limited the experiments to particle sizes over 10 μm.

In Figure 10 LINESCAN-analysis for a 15 μm particle which has been sulphated at 1040 °C, 0.32 s and 0.1 % SO_2 is shown. The results reveal a 3 μm thick sulphur core around the particle. IR-, TG- and X-ray diffraction studies confirm that no calcium sulphide or calcium sulphite is present, so the resulting sulphur compound in the core is calcium sulphate. The core surrounding the particle is not totally calcium sulphate but contains also unreacted calcium oxide. The thickness of the sulphate core remains below 4 μm at the reaction conditions examined.
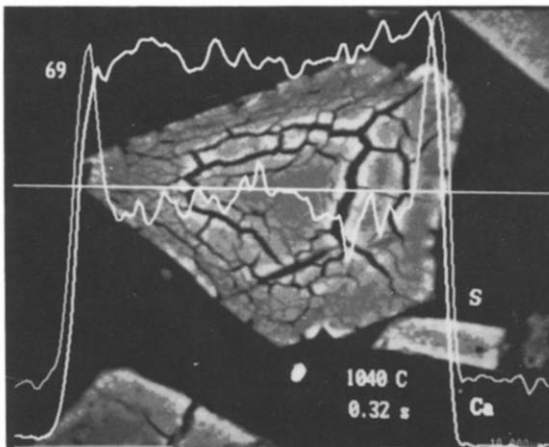

Fig. 10. LINESCAN of sulphated particle

In Figure 11 a particle of 15 μm which has been sulphated at 1150 °C, 0.24 s and 0.1 % SO_2 is shown. The penetration of sulphur within the particle is comparable with the results achieved at lower temperatures (Fig. 10). The effect of temperature does not increase the efficiency of sulphur capture because of faster chemical reaction. This confirms the fact that the rate determining step in limestone sulphation is not the chemical reaction. The possible rate determining step is pore diffusion or product layer diffusion. The results reveal that the pores within the particle remain unused, so the

diffusion within the pores seems to be slow compared to the chemical reaction on the particle surface. The diffusion through the product core is very slow and to get increased utilization of the particles with reaction time, it should be increased to minutes or hours.
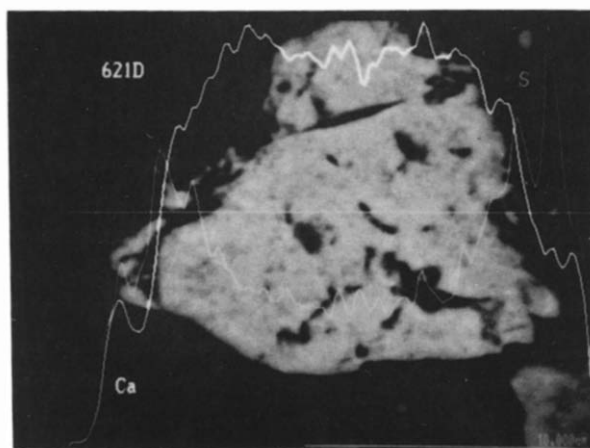

Fig. 11. LINESCAN of sulphated particle

The sintering of the particles was not detectable under conditions examined. The sintering tendency of the samples should be determined together with sulphur capture and porosity development data. The results of sulphur capture and porosity development will be discussed elsewhere (ref. 10). It is also believed that SO_2 diffusing into pores and its reaction with CaO would decrease the sintering tendency by interfering with the solid-state diffusion-related exhange of lattice vacancies and migrating reactant species at the pore surface (ref. 11).

CONCLUSIONS

Scanning electron microscopy combined with energy dispersive X-ray spectral analysis (SEM-EDS) is a useful tool when examining the behaviour of limestone particles in dry sorbent injection. The method is suitable in examining sulphur distribution within single particle if the particle is over 10 μm in diameter. The important information about the sulphur distribution within the particle was achieved by cross-sectioning the particle and analysing sulphur , calcium and silicon concentration profiles along selected line across the particle.

The following observations can be made about the sulphur dioxide reaction with selected limestone at high temperature:

- The shock- heating of the sample does not blow up the particles, so the evolution of carbon dioxide produces porous calcium oxide.
- When reacting with sulphur dioxide the pores on the particle surface are blocked and calcium sulphate around the particle is formed.
- The pores inside the particle are unused, so the diffusion within the pores is slow compared to the chemical reaction on the surface.
- The diffusion through the product layer is slow and to increase the utilization of the particles reaction time should be increased to minutes, which is not possible during limestone injection.
- The sulphate core surrounding the particle is below 4 μm wide and cannot be increased under conditions examined. This means that the utilization of these 10-32 μm particles in diameter remains poor.
- No visible changes in surface properties could be noticed, so the sintering of the particles was not detectable. Possible reason may be the effect of sulphur dioxide on the sintering tendency noticed earlier.

The results achieved show that the sulphation of limestone is a complex gas-solid process where surface properties are of great importance. Porosity development and chemical reaction rates are specific for each limestone and should be studied separately. SEM-EDS is a tool to get information about the particle behaviour during the process but great emphasis should be put on the sample preparation and particle selection for EDS-analysis.

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