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AN APPROACH TO SOLID PHASE IDENTIFICATION IN A Ca-S-O SYSTEM BY QUANTITATIVE ENERGY DISPERITIVE X-RAY MICROANALYSIS

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Abstract

Solid phases formed in the limestone sulphation reaction were identified by scanning electron microscopy with backscattered electron (BSE) imaging and by quantitative energy dispersive X-ray (EDX) microanalysis of calcium and sulphur. Since calcium and sulphur can form several compounds in the Ca-S-O system, two quantities, the sum of oxides ($\text{CaO}+\text{SO}_3$) and the molar ratio (CaO/SO_3), were used to calculate empirical formulae for the compounds actually present.

A method for analysing the experimental results is proposed, the mathematical expressions employed are presented and the numerical coefficients tabulated. It is shown with some examples that the method used here provides useful criteria for the identification of limestone sulphation products.

Introduction

Chemical processes for removing sulphur oxides from fuel gases by means of Ca-based sorbents are of great interest. Although the concept is simple, the kinetics and the elementary steps involved have not yet been fully elucidated. Many physical and chemical factors, not always independent ones, influence both the reactivity of the sorbents and the composition of the final products (Reid, 1970; Chang and Thodos, 1984).

Thermoanalytical methods have been of great help in analysing model systems attempting to simulate conditions during the sulphation process in a fluidized bed coal combustor (Ulerich et al., 1980; Wieczorek-Ciurowa et al., 1981). These methods are limited, however, as they give direct information only on the degree of conversion of CaO to CaSO_4 or CaSO_3 (TG curve) and the transformation rate (DTG curve), and such data alone are insufficient for a full description of the process.

The phase composition of samples from the sulphation process can be determined by other conventional methods, e.g. IR spectroscopy and X-ray diffraction, but the results are often distorted by the presence of undetected inclusions, so that these methods should be employed for tentative identifications only. Moreover, to detect a phase by means of X-ray diffraction, it must be present in from 1 to 5 % of all material being X-rayed. In contrast to these, back-scattered electron imaging combined with X-ray microanalysis can provide very detailed information on limestone sulphation products, because single limestone particles can be imaged and analysed with a spatial resolution of a few tenths of a micron in an image and a few microns in an analysis. BSE images and elemental dot maps form one possible and fairly popular technique that nicely reveals the distribution of the elements being analysed (Ulerich et al., 1979; Freeman, 1984). The drawback is that no chemical formulae for the phases present in samples can be calculated by means of these maps.

Key Words: limestone, sulphation, Ca-S-O system, phase identification, backscattered electron imaging, energy dispersive X-ray microanalysis

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This paper describes the use of quantitative X-ray microanalysis to identify the solid phases CaCO_3 , CaO , and $\text{Ca}(\text{OH})_2$ and the sulphur-bearing phases CaSO_4 and CaS in the products formed in limestone sulphation reaction. The kinetics and mechanism of the formation of the products during SO_2/SO_3 capture by limestone under different conditions lie beyond the scope of the paper.

Materials and Methods

Sample preparation

Natural limestone quarried in Zabierzów near Cracow (Poland) was used. The material has previously been studied as a potential SO_2/SO_3 sorbent for use during the fluidized bed combustion of coal (Bulewicz et al., 1981). The samples were crushed and sieved to the desired size range (0.5-0.6 mm). The weight loss on calcination (from TG curves) was $43.70 \pm 0.09\%$, and chemical analyses carried out with a Philips PW1400 X-ray fluorescence spectrometer showed their average composition to be CaO 57.4 %, MgO 0.4 %, SiO_2 0.5 % and Al_2O_3 0.1 %.

Limestone samples with NaCl were obtained by adding an aqueous solution of the required amount of NaCl to the prepared limestone particles, mixing the resultant slurry and drying it at about 420K.

Calcination and sulphation were carried out in a Mettler TA-2 Thermoanalyser equipped with a corrosive gas atmosphere accessory designed by one of the authors, as described in detail previously (Wieczorek-Ciurowa, 1988).

As an analytical procedure for identifying solid phases in a Ca-S-O system, polished cross-sections of the following selected samples were prepared:

sample A - raw limestone,

sample B - pre-calcined limestone with 2 % NaCl sulphated at 1100K,

sample C - raw limestone sulphated dynamically up to 1100K.

Specimens for microstructural examination and elemental microanalysis were prepared by mounting a few dozen limestone particles on a brass ring of diameter one inch with epoxy resin. After hardening overnight, the specimens were first ground with 800 mesh carborundum on a cast iron disc and then polished successively with 3 and 1 μm diamond pastes. Due to the hygroscopic character of the samples, xylene and butyl alcohol were used to make the paste instead of water. Specimen preparation was completed by vacuum-evaporating a thin layer of carbon (about 25 nm) onto the specimen surface to make it electrically conductive.

Experimental procedure

An electron microprobe (JEOL JCXA-733)

equipped with an energy dispersive X-ray spectrometer system (Link An10/85) was used for microstructural examination and elemental microanalysis.

Microstructural information on the phases appearing in the samples was obtained using back-scattered electron (BSE) imaging followed by quantitative energy dispersive (EDX) microanalysis. The average atomic numbers for the phases of interest being 18.2 for CaS , 16.6 for CaO , 14.3 for $\text{Ca}(\text{OH})_2$, 13.4 for CaSO_4 and 12.6 for CaCO_3 , the backscattered electron image provided a sufficient contrast difference for fairly easy visual discrimination of the matrix phases in most cases. The average atomic number was calculated as an average of the atomic numbers of the elements multiplied by their weight fractions in the phase (Yakowitz, 1975). A divided solid state BSE detector allowing separate observation of a composition image and a topography image was used.

Backscattered electron imaging and energy dispersive elemental analysis were carried out at an electron beam voltage of 15 kV. Link ZAF-4/FLS software and simple compound standards as commonly used for the X-ray microanalysis of minerals were used for quantification of the EDX spectra acquired using both a spot and a raster mode. Since oxygen and carbon could not be determined by the energy dispersive spectrometer used here, the amounts of calcium and sulphur were first calculated as elemental concentrations and then either as oxides or as stoichiometric carbonate depending on the contrast in the BSE image and on total of the analysis. The accuracy of the analysis results was certainly reduced to some extent by the porosity and fine-scale heterogeneity of the samples.

Results and Discussion

By determining the elemental concentrations of calcium and sulphur at different points in the limestone particle, one can calculate the chemical formulae for compounds in which calcium and sulphur appear. The calculated weight percentages of the oxides, CaO and SO_3 , denoted in the following discussion by y_1 and y_2 , their sum, denoted by s , and their molar ratio, denoted by r , are utilized in these calculations. Elemental calcium and sulphur are both represented by the weight percentages of their oxides in the first calculation. The values of s and r are then used as guides when calculating and identifying the compounds actually present at the point analysed.

Let us first consider the case of single compounds. Characterizations of CaSO_4 , CaS , CaO , $\text{Ca}(\text{OH})_2$ and CaCO_3 , which may be present in limestone sulphation products, are given in Table 1.

By combining the grey tone information in the BSE

Identification of limestone sulphation products

Table 1. Compounds present in limestone sulphation products, characterized by the elemental and oxide concentrations of Ca and S and their grey tone level appearances in the BSE image. The terms in parentheses are the variables in equations 1-3. Concentrations are expressed in terms of weight percentage.

Compound	Elemental concentration		Oxide concentration		Sum of oxides (s)	Molar ratio (r)	Grey tone level in BSE image
	Ca	S	CaO (y ₁)	SO ₃ (y ₂)			
CaSO ₄	29.4	23.6	41.2	58.8	100.0	1	grey
CaS	55.6	44.4	77.7	111.0	188.7	1	bright
CaO	71.5	0	100.0	0	100.0	∞	very light
Ca(OH) ₂	54.1	0	75.7	0	75.7	∞	light
CaCO ₃	40.0	0	56.0	0	56.0	∞	dark

Table 2. Theoretical results obtainable in X-ray microanalysis of the two-component system CaO-CaS. The terms in parentheses are variables in equations 1-3. Concentrations are by weight percentage.

Composition		Elemental concentration		Oxide concentration		Sum of oxides	Molar ratio
CaO (x)	CaS (100-x)	Ca	S	CaO (y ₁)	SO ₃ (y ₂)	CaO+SO ₃ (s)	CaO/SO ₃ (r)
100	0	71.5	0.0	100.0	0.0	100.0	∞
80	20	68.3	8.9	95.5	22.2	117.7	6.1
60	40	65.1	17.8	91.1	44.4	135.5	2.9
40	60	61.9	26.7	86.6	66.6	153.2	1.9
20	80	58.7	35.6	82.2	88.8	171.0	1.3
0	100	55.6	44.4	77.7	111.0	188.7	1.0

image with the result of the quantitative microanalysis one can identify single compounds quickly, and most probably reliably, but if more than one compound is present, then the procedure is more complicated. Let us next consider the case when both CaO and CaS are present. Their proportions are reflected in the values of s and r, as indicated in Table 2. Hence, if these compounds are expected to be present in the particle analysed and the concentrations of Ca and S are measured, the calculated values of s and r can be used to determine the ratio between CaO and CaS.

In a two-component system, s and r are given by the equations

$$s = y_1 + y_2 \quad (1)$$

$$r = c * y_1 / y_2 , \quad (2)$$

in which y_1 and y_2 represent the amounts of CaO and SO₃ respectively, and c is a numerical coefficient given by the equation

$$c = M(SO_3) / M(CaO) = 1.43 , \quad (3)$$

in which M(SO₃) and M(CaO) are molar masses. y_1 can be expressed as

$$y_1 = a_1 + b_1 * x , \quad (4)$$

in which x is the percentage of the first component in the system. Correspondingly

$$y_2 = a_2 + b_2 * x . \quad (5)$$

Note that the expressions for y_1 and y_2 are both linear functions of x, and thus the coefficients a_1 , a_2 , b_1 and b_2 can easily be determined. The expressions for s and r (equations 1 and 2) are

$$s = f_1(x) = a + b * x , \quad (6)$$

in which $a = a_1 + a_2$ and $b = b_1 + b_2$, and

$$r = f_2(x) = c * (a_1 + b_1 * x) / (a_2 + b_2 * x) . \quad (7)$$

s and r are obtained from the experimental data, and x can be resolved from the reciprocal functions in the following way.

$$x = \phi_1(s) = (-a/b) + (1/b) * s , \text{ and} \quad (8)$$

$$x = \phi_2(r) = (c * a_1 - a_2 * r) / (-c * b_1 + b_2 * r) . \quad (9)$$

The equations and values for the numerical coefficients in six model systems are summarized in Table 3.

This table together with observations on the contrast in the BSE image can be used as a guide for determining the phase system and its composition.

To illustrate the procedure for the phase analysis presented above, typical results for the quantitative microanalysis of calcium and sulphur at different points in three samples are shown in Table 4.

Without doubt sample A belongs to system IV, in Table 3 $\text{CaO}-\text{CaCO}_3$. This is seen more easily if one compares the measured values in Table 4 with the calculated values for CaCO_3 in Table 1. In this case a dark BSE image is observed, Figure 1a.

Analysis point 1 in sample B gives values for s and r which can only match system III, $\text{CaSO}_4-\text{Ca}(\text{OH})_2$. This allows us to calculate the CaSO_4 fractions, from $\phi_1(s)$ and $\phi_2(r)$, as being 93.0 % and 94.7 %, respectively, which means that x should lie between these estimated values. This is confirmed by the grey BSE image, which is typical of CaSO_4 , Figure 1b.

In the case of point 2 in sample B, two systems satisfy the experimental results: IV $\text{CaO}-\text{CaCO}_3$ and V $\text{CaO}-\text{Ca}(\text{OH})_2$. In order to establish which one corresponds to the real composition the BSE image observation has to be used. The high lightness indicates system V, in which the value of x can only be established from function $\phi_1(s)$, for which we have $x = 35.5$ % for CaO .

The values of s and r for point 3 in sample B show that this case matches system I, CaSO_4-CaS . Using the function $\phi_1(s)$ we obtain $x = 22.3$ % for CaSO_4 , which means that the major component at the point measured is CaS . The values of s and r also match system VI, $\text{CaO}-\text{CaS}$, in which we have $x = \phi_1(s) = 22.3$ % and $x = \phi_2(r) = 0.8$ %. The considerable difference between the values indicates that system VI can be eliminated.

The BSE image of sample C is shown in Figure 1c. Two analysis points lie in pure phases: point 1 in CaCO_3 and point 3 in CaSO_4 . The analysis results for point 2 match system I, CaSO_4-CaS , with $\text{CaSO}_4 = 95.0$ % (calculated from $\phi_1(s)$), while at point 4 one can expect to find system III, $\text{CaSO}_4-\text{Ca}(\text{OH})_2$. The values for $\phi_1(s)$ and $\phi_2(r)$ lead us to the conclusion that CaSO_4 is present at a concentration of around 88 %.

Conclusions

A scanning electron microscope equipped with a good backscattered electron detector and an energy dispersive X-ray spectrometer is a very powerful tool for investigating porous solids in great detail. It is shown that simultaneous use of backscattered electron imaging and X-ray microanalysis makes it possible to utilize variations in calcium and sulphur concentrations measured along cross-sections of limestone particles to distinguish solid phases occurring within limestone

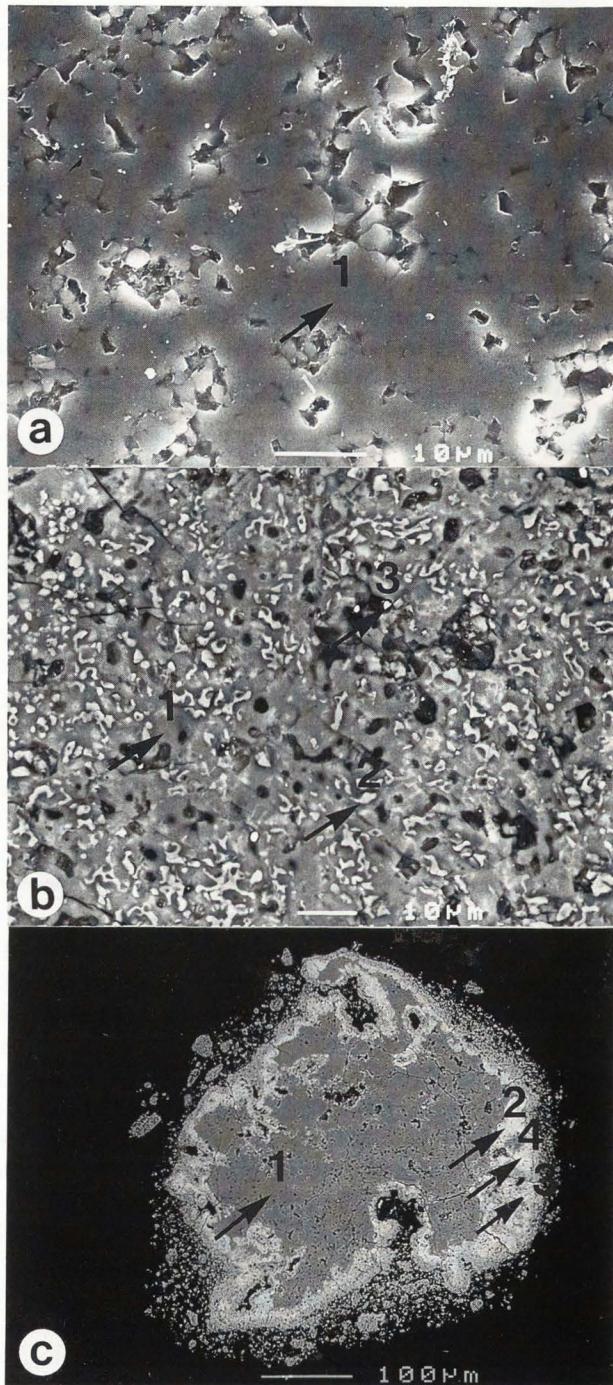


Figure 1. Backscattered electron micrographs of polished cross-sections of three limestone particles. **a)** Raw limestone, sample A, **b)** sulphated (pre-calcined) limestone with 2 % NaCl, sample B, **c)** sulphated limestone, sample C. The arrows indicate the points from which the microanalyses shown in Table 1 were obtained. Magnification markers are at the bottom of each figure.

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Table 3. Equations and numerical coefficients for calculating the percentages of the components in six compound combinations in the Ca-O-S system. Initial values for the calculations are the concentrations of Ca and S determined by X-ray microanalysis.

$$\begin{aligned} I &= \text{CaSO}_4 \cdot \text{CaS} \\ IV &= \text{CaO} \cdot \text{CaCO}_3 \end{aligned}$$

$$\begin{aligned} II &= \text{CaSO}_4 \cdot \text{CaO} \\ V &= \text{CaO} \cdot \text{Ca(OH)}_2 \end{aligned}$$

$$\begin{aligned} III &= \text{CaSO}_4 \cdot \text{Ca(OH)}_2 \\ VI &= \text{CaO} \cdot \text{CaS} \end{aligned}$$

	$y_1 = \text{CaO}$ $y_1 = a_1 + b_1x$	$y_2 = \text{SO}_3$ $y_2 = a_2 + b_2x$	$s = \text{CaO} + \text{SO}_3$ $s = a + bx$	$r = \frac{M(\text{SO}_3) y_1}{M(\text{CaO}) y_2}$ $r = 1.43 \frac{(a_1 + b_1 x)}{(a_2 + b_2 x)}$	$x = \phi_1(s)$ $x = -\frac{a}{b} + \frac{1}{b}s$	$x = \phi_2(r)$ $x = \frac{(1.43a_1 - a_2r)}{(-1.43b_1 + b_2r)}$
I	$a_1 = 77.7$ $b_1 = -0.365$	$a_2 = 111$ $b_2 = -0.522$	$a = 189$ $b = -0.887$ $100 \leq s \leq 189$	$r = 1$	$x = 213 + 1.13s$	(*)
II	$a_1 = 100$ $b_1 = -0.588$	$a_2 = 0$ $b_2 = 0.588$	$s = 100$	$r = \frac{(143 - 0.840x)}{0.588x}$ $1 \leq r < \infty$	(*)	$x = \frac{143}{(0.840 + 0.588r)}$
III	$a_1 = 75.7$ $b_1 = -0.345$	$a_2 = 0$ $b_2 = 0.588$	$a = 75.7$ $b = 0.243$ $75.7 \leq s \leq 100$	$r = \frac{(108 - 0.492x)}{0.588x}$ $1 \leq r < \infty$	$x = -311 + 4.11s$	$x = \frac{108}{(0.493 + 0.588r)}$
IV	$a_1 = 56.0$ $b_1 = 0.440$	$y_2 = 0$	$a = 56.0$ $b = 0.440$ $56.0 \leq s \leq 100$	$y_2 = 0$ $r \rightarrow \infty$	$x = -127 + 2.27s$	-
V	$a_1 = 75.7$ $b_1 = 0.243$	$y_2 = 0$	$a = 75.7$ $b = 0.243$ $75.7 \leq s \leq 100$	$y_2 = 0$ $r \rightarrow \infty$	$x = -311 + 4.11s$	-
VI	$a_1 = 77.7$ $b_1 = 0.223$	$a_2 = 111$ $b_2 = -1.11$	$a = 189$ $b = -0.887$ $100 \leq s \leq 189$	$r = \frac{(111 + 0.318x)}{(111 - 1.11x)}$ $1 \leq r < \infty$	$x = 213 - 1.13s$	$x = \frac{(111 - 111r)}{(-0.318 - 1.11r)}$

(*) no reciprocal function

Table 4. Results obtained in energy dispersive X-ray microanalyses of three limestone samples: A - raw limestone; B - pre-calcined limestone with 2 % NaCl sulphated at 1100K; C - raw limestone sulphated dynamically up to 1100K. Concentrations are by weight percentage. Analysis points are shown in Figure 1.

Sample	Analysis point	Elemental concentration		Oxide concentration		Sum of oxides	Molar ratio	Grey tone level in BSE image
		Ca	S	CaO	SO ₃			
A	1	39.6	0.0	55.5	0.0	55.5	∞	dark
	1	30.7	22.2	42.9	55.4	98.3	1.10	grey
B	2	60.1	0.1	84.1	0.2	84.3	∞	light
	3	49.9	39.7	69.8	99.0	168.8	1.00	bright
C	1	40.0	0.3	56.0	0.6	56.6	∞	dark
	2	30.8	24.6	43.1	61.4	104.5	1.00	light grey
	3	29.0	23.2	40.6	58.0	98.6	0.99	grey
	4	32.4	20.8	45.4	51.9	97.3	1.24	grey (*)

(*) with bright spots

sulphation products. The proposed method gives a rapid and most probably a reliable identification of the compounds in the Ca-S-O system.

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References

Bulewicz EM, Janicka E, Wieczorek-Ciurowa K, Kandefer S, Jurys Cz (1981) Desulphurization during the fluidized combustion of coal using limestone-based sorbents. *Arch. Comb.* 1, 121-129.

Chang EY and Thodos G (1984) Complex nature of the sulphation reaction of limestones and dolomites. *AICHE J.*, 30, 450-457.

Freeman GB (1984) The sulphation reaction and bed ash characterization. *Scanning Electron Microsc.* 1984; III: 1147-1160.

Reid WT (1970) Basic factors in the capture of sulfur dioxide by limestone and dolomite. *J. of Eng. for Power, Trans. ASME, Ser. A*, 92 (1), 11-16.

Ulerich NH, Newby RA, Keairns DL (1980) A thermogravimetric study of the sulphation limestone and dolomite - prediction of pressurized and atmospheric fluidized-bed desulphurization. *Thermochim. Acta* 36, 1-16.

Ulerich NH, O'Neill, Alvin MA, Keairns DL (1979) Criteria for the selection of SO₂ sorbents for atmospheric pressure fluidized bed combustors. EPRI FP-1307, 2, Project 721-1 Final Report.

Wieczorek-Ciurowa K (1988) Solid-gas reactions: study of sulphation of limestone using thermogravimetry. *J. Therm. Anal.* 33, 407-411.

Wieczorek-Ciurowa K, Paulik F, Paulik J (1981) Influence of foreign materials upon the thermal decomposition of dolomite, calcite and magnesite. Part III: The effect of the thermal dissociation and sulphation conditions on the capture of sulphur dioxide. *Thermochim. Acta* 46, 1-8.

Yakowitz H (1975) Methods of Quantitative X-Ray Analysis Used in Electron Probe Microanalysis and Scanning Electron Microscopy, in: Practical Scanning Electron Microscopy, Goldstein JI and Yakowitz H (eds), Plenum Press, New York, 327-372.

Discussion with Reviewers

J.M. Vleeskens: The calculations are based on the assumption that dense recrystallized phases result from gas-solid surface reactions. The paper should discuss the question "re-ordered or topochemical (surface) reaction product" before starting the maths.

Authors: The aim of this paper, as mentioned in the introduction, is to present a method which is useful for phase analysis of the products of the reaction between CaO/CaCO₃ and sulphur oxides. Phase identification and localization of the phases within the grain is an essential aspect when describing the mechanism of the topochemical process (Boldyrev, 1975). Limestone sulphation is one example of this, although the topic would require too long a discussion in this connection.

G. Bonifazi: Reading the text it seems that all the analyses have been conducted using samples resulting from a laboratory scale preparation and not on "true" samples resulting from a process of SO₂ removing from real fuel gases. Could this kind of approach be influenced in some evidence when applied to a real case and how could the methodology proposed in the paper be modified when applied to a real case? What should be the differences expected on the subsequent results?

Authors: It is true that the sulphated samples of limestone/lime were prepared by a thermal analysis method, but we believe that this simulates the fluidized bed conditions sufficiently. Furthermore, they were derived from exactly the same natural material as had previously been used as a SO₂/SO₃ sorbent during the combustion of coal. Thus there should be in principle no differences in sulphation resulting from these two techniques (TGA and FBC). The method described above was used to identify solid phases in samples from the fluidized combustor too, but only the most characteristic samples were chosen for illustrating the method here.

G. Bonifazi: One of the basic assumptions reported in the paper is the existence of a correspondence between the grey tones detectable in a region of the backscattered electron image (BSEI) and the content of the chemical compounds formed after the reaction (Ca-S-O system). Have the authors developed this approach using only the human eye capability to separate different grey tone levels or have they performed some determinations using different approaches, based on more objective procedures, e.g. image analysis procedures? Try to establish a correspondence between the grey tone levels associated in a BSEI by means of image processing procedures and the chemical content or the phase composition of the area investigated in the sample could be, in fact, of great interest in a large field of applications.

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G. Remond: The contribution of the backscattered electron imaging to the EDX analyses - is it only a qualitative use or a quantitative image analysis of the BSE?

Authors: The backscattered electron imaging and X-ray microanalysis were carried out using constant gain settings in the BSE amplifier and a constant electron beam current, thus providing fairly well the same grey tone level for the same compound from day to day. The levels were also regularly checked and adjusted using single compound particles. The phases with different grey tone levels were indeed separated subjectively by eye. We agree that more objective procedures for evaluating grey tone levels in BSE images are needed, and image analysis, including accurate measurement of the BSE signal, is unquestionably a very attractive method.

I. Geuens: Because you are working with porous material, is it not possible that the density varies a lot in the sample and this gives rise to problems for quantification with ZAF correction procedure? By the way: do you have any trouble with the polishing paste that gets into the porous sample?

Authors: We tried to avoid density problems by analysing only points or small areas which were compact in appearance in the backscattered and secondary electron images. Some polishing paste can always be found in the pores, of course, but that did not cause any trouble. The pores were not analysed and the BSE contrast from the paste (diamond) particles was so low that they could not have been analysed as particles of interest by mistake.

I. Geuens: You used the ZAF correction method for quantification of the X-ray spectra. How do you take the interaction volume into account? Because you are working with small particles in the specimen (e.g. in Figure 1b spot 3: ~2 μm diameter) the interaction volume can be important for quantitative results. What is the average error for the results?

Authors: Of the several expressions available for calculating the diameter of the interaction volume, we use here the equation developed by Andersen and Hasler (Goldstein, 1975). This enables one to calculate that at an accelerating voltage of 15 kV the X-ray source sizes for calcium and sulphur are 2.5 and 2.6 μm in CaS, and slightly lower or higher in the others depending on the density of the compound. These values mean that quantitative results for particles with a diameter of about 3 μm or more should correctly represent the composition whereas the results for smaller particles will include some error, since the X-ray source size will contain not only the particle itself but also a small amount of the surrounding matrix. The error in the quantitative results increases very rapidly with decreasing particle size. The

interaction volume was taken into account in the sense that only "large" particles were selected for quantitative analysis. The example mentioned in the question, a CaS particle in the CaSO_4 matrix, is an unusual one. In this particular case the particle and the matrix have the same Ca/S ratio, and therefore the only possible error in the analysis results is that CaS is present at a higher concentration than indicated. The situation in the other particle-matrix combinations is not that simple.

J.M. Vleeskens: Your data show different values of x as derived from the sum function or the ratio function. Using good standards and applying ZAF corrections, these values should be equal. Could you explain the reason for this discrepancy?

Authors: Good standards and a good ZAF correction method were used, but the samples were not equally good. Porosity, and especially fine-grained secondary phases, undoubtedly caused some inaccuracy in the analyses, and this inaccuracy is then reflected in a small discrepancy between the values of x calculated from the two functions.

I. Geuens: In the case of point 2 of sample B, two systems satisfy the experimental X-ray results: CaO-CaCO_3 and CaO-Ca(OH)_2 . It is said that a high BSEI brightness indicates system V, CaO-Ca(OH)_2 . When one calculates the atomic number (according to Danguy & Quivy, *Le Journal de Physique et le Radium*, 17 (1956), 320-325.), one finds:

for CaO-CaCO_3 , $Z = 14.9$ (IV)

for CaO-Ca(OH)_2 , $Z = 15.5$ (V).

Indeed the atomic number for CaO-Ca(OH)_2 is higher. But for point 1B the authors found the composition $\text{CaSO}_4\text{-Ca(OH)}_2$, with the average atomic number 13.8. Both systems (CaO-Ca(OH)_2 and CaO-CaCO_3) have a higher atomic number than in point 1B. It is therefore not possible to exclude system IV, CaO-CaCO_3 . Furthermore, if one calculates the fraction CaO for both systems, one finds:

for CaO-Ca(OH)_2 : 35.5 %

for CaO-CaCO_3 : 64.4 %.

Calculating the average atomic number again, one finds:

for CaO-Ca(OH)_2 : 15.1

for CaO-CaCO_3 : 15.4: becomes higher?

Authors: Using the values 35.5 % and 64.4 % for the weight fraction of CaO in the CaO-Ca(OH)_2 and CaO-CaCO_3 systems, respectively, we calculate that the average atomic number at point 2B is 15.1 for both systems. This means that neither the grey tone level in the BSE image nor the analysis result indicates which system should be selected, and some other information is needed. The small difference in average atomic number calculations between the question and the answer is not

important. It is more important to note that the differences between the phase candidates are so small that some quantitative method for accurately determining the grey tone levels in BSE images would be of great importance.

I. Geuens: We made some calculations of the back-scattered electron coefficient according to Hunger and Küchler (with minor corrections by August and Wernisch, Phys. Stat. Sol. (a), 114 (1989), 629-633) for the proposed compositions at certain points in the sample. If it were possible to read the grey values at the different points, it would have been possible to estimate whether point 2B corresponds to CaO-CaCO₃ or CaO-Ca(OH)₂.

Authors: We fully agree that if the grey tone levels are accurately measured, phase identification becomes more straightforward and above all more reliable. Your figures enclosed with the question illustrate this nicely.

I. Geuens: For point 3B, two systems are possible (I and VI). System VI is eliminated because of the considerable difference between the values estimated from $\phi_1(s)$ and $\phi_2(r)$. What about the difference of x estimated from $\phi_1(s)$ and $\phi_2(r)$, which cannot be calculated for System I? How do you explain the very bright spot in Figure 1b?

Authors: There is one marked difference. When the value of r is close to 1, the numerator of $\phi_2(r)$ in system VI is almost 0, while in system I it is the denominator that is almost 0. In the latter case the values of x calculated from $\phi_2(r)$ are naturally of no significance. The bright spot is probably a tiny piece of debris from some other sample of a different type polished on the same polishing cloth.

I. Geuens: What is the reason to conclude that point C3 is pure CaSO₄? For system III one can calculate $x = 94.2\% - 100.4\%$.

Authors: You are right, a very small amount of Ca(OH)₂ can be calculated to exist in system III. The analysis result for point C3 (Table 3) is so close to that of CaSO₄, however (Table 1), that it is quite reasonable to call it pure CaSO₄.

G. Remond: Are some comparisons available between the present data and analyses including quantitative determination of the oxygen concentrations?

Authors: We do not know of any microanalysis data with oxygen determinations, and the corresponding results obtained by bulk analysis methods cannot be compared with those of microanalyses.

Additional References

Boldyrev VV (1975) Topochemical reactions. Particularities of their research. Part I. J. Therm. Anal. 7, 685-694.

Goldstein JI (1975) Electron Beam-Specimen Interactions, in: Practical Scanning Electron Microscopy, Goldstein JI and Yakowitz H (eds), Plenum Press, New York, 49-94.