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THE GROWTH OF CALCIUM AND STRONTIUM SULFATES ON  
BARIUM SULFATE SURFACES

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Abstract

The crystallization of calcium sulfate dihydrate (gypsum) and strontium sulfate (celestite) induced by the presence of barium sulfate (barite) surfaces has been studied using a Constant Composition kinetic method. In contrast to calcium sulfate, strontium sulfate appears to grow epitaxially on barium sulfate surfaces. However, barium sulfate induces calcium sulfate dihydrate precipitation from metastable supersaturated solutions of the salt. Following nucleation, the rate of growth of strontium sulfate was found to be a second order with respect to supersaturation indicating a surface dislocation growth mechanism. The observed epitaxial growth is in agreement with calculations based on crystal lattice mismatch.

Introduction

The formation of scale is a serious problem in areas such as desalination (23), oil production (2,3,24) and in cooling water technology (3). The calcium carbonate polymorphs (22,25), calcium sulfate hydrates (12,13,19,21,26), barium sulfate (7,27,28), and strontium sulfate (6,10,16,18) are all involved as scale forming minerals. The kinetics of crystallization of these minerals have been well studied using, as seed crystals, the phase to be precipitated (1,5,8,11,14,15,20). The growth of gypsum crystals on barite and calcite has also been reported (9).

One of the most important parameters involved in scale formation is the adherence of precipitates to surrounding surfaces. This leads to the development of nucleation sites on surfaces for subsequent crystal growth and resulting scale build-up. The growth of the primary scales would, in turn, support the further growth of the secondary scales by heterogeneous nucleation or epitaxial growth mechanisms (18). While barium and strontium sulfates are predominant in the thin primary scale layers, calcium sulfate and calcium carbonate are often observed in secondary scales. As the least soluble of the scale forming minerals, barium sulfate would have the greatest tendency to form in the primary-scale layers, perhaps serving as substrate for the heterogeneous nucleation of the strontium and calcium sulfates. However, little attention has been given to the study of the possible epitaxial growth of calcium or strontium sulfate on barium sulfate or of calcium sulfate on strontium sulfate. This may be due not only to the very low solubility of these minerals, making it difficult to achieve appreciable growth extents by conventional crystallization experiments, but also to the difficulties of simulating field conditions in which parameters such as fluid dynamics and changes in pressure and temperature may also play important roles.

In the present study, the heterogeneous nucleation of calcium and strontium sulfates has been investigated on barium sulfate surfaces using a Constant Composition (CC) technique. Energy dispersive X-ray analysis was used in order to determine if the phase precipitated was growing on the seed crystals.

Materials and Methods

Reagent grade chemicals, triple distilled carbon dioxide free water, and grade A glassware were used throughout. Barium, strontium, and calcium ion

**KEY WORDS:** Heterogeneous Nucleation, Epitaxial Growth, Scale Formation, Crystal Growth, Growth Rate, Induction Time, Constant Composition Technique, Calcium Sulfate, Barium Sulfate, Strontium Sulfate.

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concentrations were determined by exchanging for hydrogen ion on a Dowex-50 ion exchange column in the hydrogen form and titrating the liberated acid against standard potassium hydroxide solution. Sulfate was analyzed using high performance ion chromatography (Dionex QIC Analyzer). Barium sulfate seed crystals were prepared by the slow mixing of  $2 \times 10^{-3}$  mol L<sup>-1</sup> barium chloride and  $2 \times 10^{-3}$  mol L<sup>-1</sup> sulfuric acid at 80 C. The crystals were washed free of chloride ions with a saturated solution of barium sulfate. A scanning electron micrograph (Amray 1000 A scanning electron microscope) of the seed material is shown in Fig.1. The particle sizes, determined by an Electrozone/Celloscope (Particle Data Inc.) indicated that about 80% were between 9 and 12  $\mu$ m. The specific surface area (BET nitrogen adsorption, Quantasorb II, Quantachrome, Greenvale, N.Y., 30-70 nitrogen/helium mixture) was 0.44 m<sup>2</sup>g<sup>-1</sup>. The seed crystals were characterized by X-ray powder diffraction (Phillips XRG 3000, X-ray diffractometer, CuK $\alpha$  radiation with Ni filter) and by chemical analysis.

Supersaturated solutions for the growth experiments were prepared by mixing either strontium chloride and sodium sulfate or calcium chloride and sodium sulfate solutions to yield stable supersaturated solutions of strontium sulfate or calcium sulfate, respectively. The ionic strength was maintained at 0.15 mol L<sup>-1</sup> during the reaction by the addition of sodium chloride as inert electrolyte. Experiments were made in a double walled Pyrex glass vessel of 300 mL capacity. Thermostatted water was circulated in the space between the walls in order to maintain the temperature at 25 $\pm$ 0.02 C. All experiments were made in a nitrogen atmosphere to exclude carbon dioxide. Crystal growth was induced in the supersaturated solutions by the addition of barium sulfate seed crystals. The activities of the calcium and strontium ions during the experiments were maintained constant by the addition of titrant solutions from mechanically coupled motor driven burets (pH-stat model 3D Metrohm Brinkmann, Brinkmann Instruments, Westbury, New York). In the case of calcium sulfate precipitation, titrant solutions consisted of calcium chloride and sodium sulfate in 0.15 mol L<sup>-1</sup> sodium chloride solution, and the activity of the free calcium ions in the solution was monitored by means of a calcium selective ion electrode (Radiometer Model F 2112) coupled with a silver/silver chloride reference electrode. Calibration of the calcium electrode was made before and after each experiment by the method of standard addition using calcium chloride solutions.

For strontium sulfate crystallization experiments, the titrant solutions consisted of strontium chloride and sodium sulfate in 0.15 mol L<sup>-1</sup> sodium chloride. The

activity of the strontium ions was monitored by using a calcium selective electrode which responds to the activity of strontium ions [ $25\text{mv}(\text{pSr})^{-1}$ ] with sufficient sensitivity to monitor the reactions up to approximately 10% growth with respect to the original amount of seed crystals. After this time, the rate of growth was too fast and the response of the electrode was insufficient to maintain constant composition. Calibration of the calcium electrode for use in strontium sulfate solutions was made before and after each experiment by the method of standard additions using strontium chloride solution. During the experiments, aliquots were withdrawn periodically, filtered (0.22  $\mu$ m filter, Millipore, Bedford, Mass.), and analyzed for calcium or strontium by atomic absorption (Perkin Elmer Model 503) and sulfate by ion-exchange chromatography (Dionex QIC Analyzer). The air-dried solid phases were also examined by scanning electron microscopy, energy dispersive X-ray analysis (EDAX 9100/70) and X-ray powder diffraction.

### Results & Discussion

The results of experiments of the heterogeneous nucleation and subsequent growth of strontium sulfate on barium sulfate surfaces are summarized in Table 1. The overgrowth of the new phase can be seen in Figs. 2 and 3 which were taken 4h and 5h following seed inoculation, respectively, (Expt. E-36). The marked change in morphology to that typical of strontium sulfate is immediately apparent. The results of the energy dispersive X-ray analysis (EDXA) of the crystals (Fig.4) show the appearance of the strontium peak and at the same time, the decreasing intensity of the barium peaks (Expt. E-37). The EDXA results in Figs. 5 and 6 for samples 1, 3 and 6 of Expt. E-36 taken after 5 min, 1.5h and 3h following seed inoculation also showed increasing intensity of the strontium peak and decreasing intensity of the barium peaks. From the SEM micrographs, EDXA analysis and the lattice registry parameter,  $\delta$ , (Table 2) calculated from crystallographic data for strontium sulfate, it may be concluded that strontium sulfate may grow epitaxially on barium sulfate surfaces.

Typical plots in Fig.7, of titrant uptake following the addition of barium sulfate seed crystals, show marked induction periods,  $\tau$ , reflecting the nucleation time, which decreased as the supersaturation increased.

Plots of  $\log \tau$  against  $(\log S)^{-2}$ , where  $S = (M^{2+})(SO_4^{2-})/K_{SO_4}$ , give a straight line (Fig.8), the slope of which,  $\alpha_t$ , is related to the surface energy,  $\sigma_E$ , through Equation 1 (17):-

$$\sigma_E = kT(\alpha_t/2\beta n a^6) \ln 10 \quad (1)$$

Table 1  
Epitaxial Growth of Strontium Sulfate on Barium Sulfate Experimental Conditions

Exp. No.	$T_{Sr} = T_{SO_4}$ $\times 10^{-3}$ mol/L	$S$ $\sigma$	Induction time hr.	Rate $\times 10^{-6}$ mol/min m <sup>2</sup>	$\Delta g \times 10^{-3}$
E-30	3.0	2.69 3.698	28.00	7.06	2.19
E-39	3.5	3.31 4.315	8.17	14.50	2.69
E-37	3.9	3.80 4.808	3.39	19.10	3.09
E-36	4.3	4.30 5.301	1.42	20.40	3.49
E-32	4.8	4.92 5.917	1.20	34.6	3.99

Crystallization of Alkaline Earth Surfaces

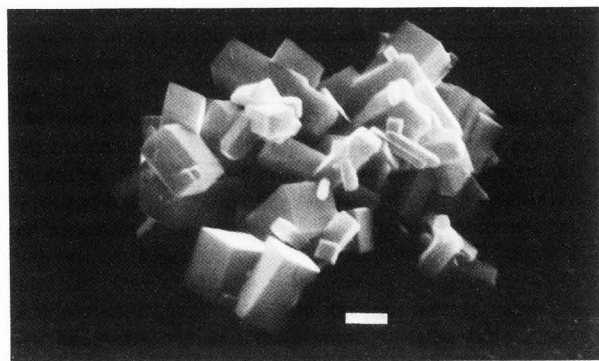


Fig.1. Scanning electron micrograph of barium sulfate seed crystals. Bar = 1  $\mu$ m

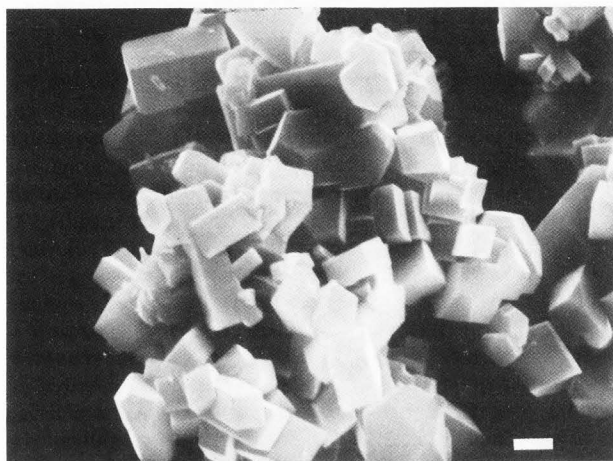


Fig.2. Scanning electron micrograph of solid sample at 4h in expt. E37 (Table 1). Bar = 1  $\mu$ m

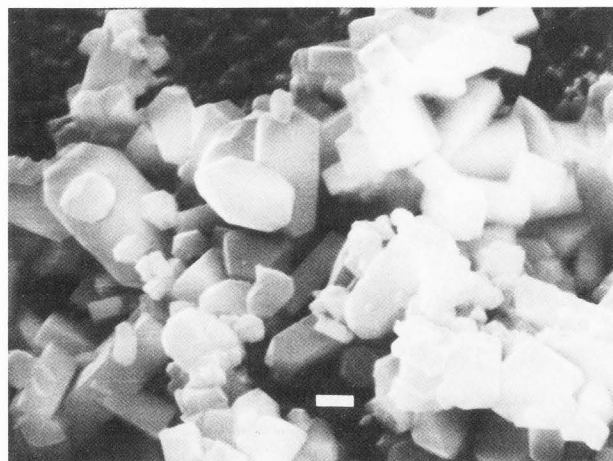


Fig.3. Scanning electron micrograph of solid sample at 5h in expt. E37. Bar = 1  $\mu$ m

RATE: CPS TIME 50LSEC  
 00-20KEV: 10EV/CH PRST: 50LSEC  
 A: BASD4 B: SR/BA  
 FS= 571 MEM: A/B FS= 538

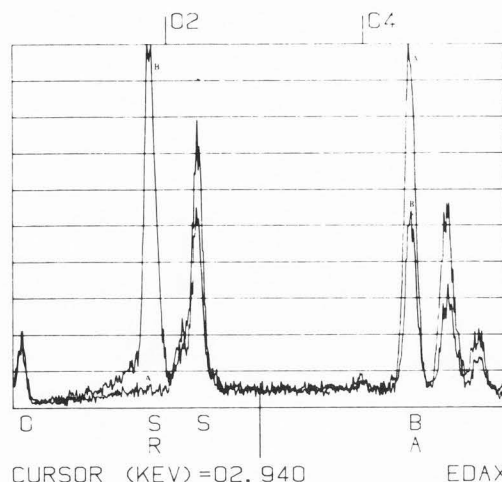


Fig.4. EDXA of initial and final solid phases in Expt. E37.

Table 2. Crystallographic Data and Disregistry Calculation for the Growth of Strontium Sulfate on Barium Sulfate

	Strontium Sulfate	Barium Sulfate
Crystal System:	Orthorhombic	Orthorhombic
Space Group:	Pnma (62)	Pnma (62)
Z	4	4
Molar Volume (cm) <sup>3</sup>	46.25±0.06	52.10±0.06
a <sub>0</sub>	8.359±0.005 Å	8.878±0.005 Å
b <sub>0</sub>	5.352±0.005 Å	5.450±0.005 Å
c <sub>0</sub>	6.866±0.005 Å	7.152±0.003 Å

$$\delta_a = (8.878 - 8.359) / 8.359 = 0.062$$

$$\delta_b = (5.450 - 5.352) / 5.352 = 0.018$$

$$\delta_c = (7.152 - 6.866) / 6.866 = 0.041$$

Solubility of strontium sulfate in 0.15 M NaCl =  $8.112 \times 10^{-4}$  mol/L. (4)

The ideal disregistry  $\delta_i$  is defined as

$$\delta_i = (\alpha_1^o - \alpha_2^o) / \alpha_2^o$$

where  $\alpha_1^o$  and  $\alpha_2^o$  are the equilibrium atomic spacing in free 1 and free 2 crystalline phases, respectively.

The constant  $\beta_n$  was assumed to have a value, 32, corresponding to cubic nuclei. The surface energy,  $93 \times 10^{-3} \text{ J m}^{-2}$  was comparable to the values for barium and strontium sulfate,  $135$  and  $85 \times 10^{-3} \text{ J m}^{-2}$ , respectively (17). The kinetic plots of  $-\log(\text{rate})$  against  $\log \Delta g$ , where

$$\Delta g = (M^{2+})(SO_4^{2-})^{1/2} - k_{50}^{1/2}$$

RATE: CPS TIME 50LSEC  
 00-20KEV: 10EV/CH PRST: 50LSEC  
 A: #1 B: #3  
 FS= 560 MEM: A/B FS= 475

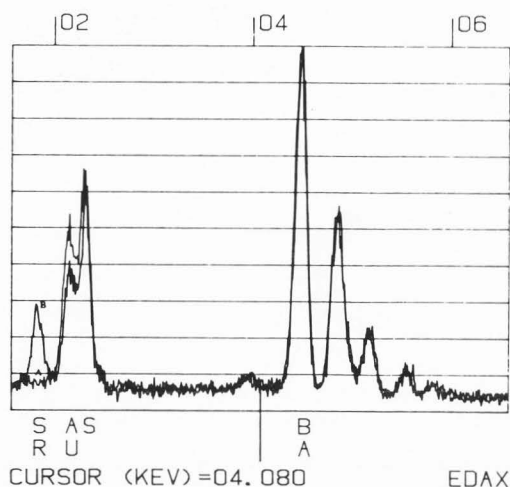


Fig.5. EDXA of solid phase after 5 min (A) and 1.5h (B) following seed inoculation (exp. E36, Table 1).

RATE: CPS TIME 50LSEC  
 00-20KEV: 10EV/CH PRST: 50LSEC  
 A: #3 B: #6  
 FS= 475 MEM: A/B FS= 373

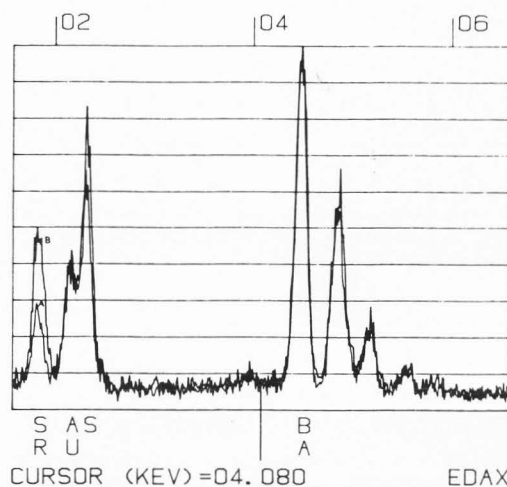


Fig.6. EDXA of solid phase after 1.5h (A) and 5h (B) following seed inoculation (exp. E36).

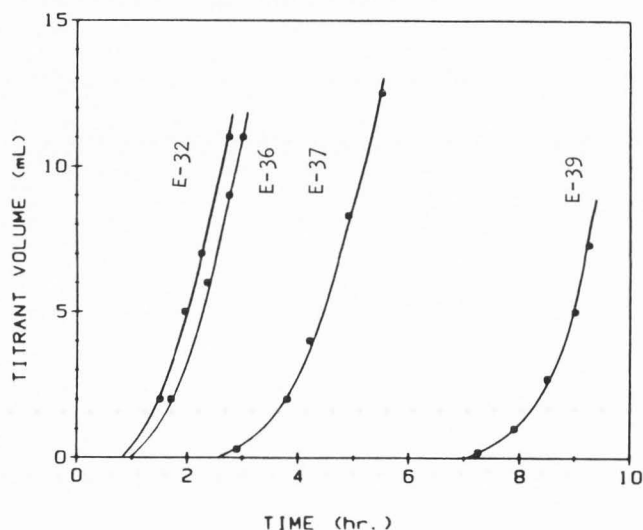


Fig.7. Plot of titrant volume against time during the growth of strontium sulfate on barium sulfate. (Curve numbers refer to experiments in Table 1).

are shown in Fig.9. The value of the slope, 2.2, suggests that following nucleation, the rate of crystallization may be represented by a parabolic rate law similar to that reported for the growth of the pure phase (1).

Table 3 shows the experimental conditions for the growth of calcium sulfate when using barium sulfate seed crystals. During these experiments, the induction period preceding the growth was irreproducible, (eg. varying from 9-13h in Experiments E-41, E-42, and E-45). Scanning electron micrographs (Figs. 10 to 12) indicate that although the calcium sulfate did not grow on the barium sulfate surfaces, the addition of barium sulfate

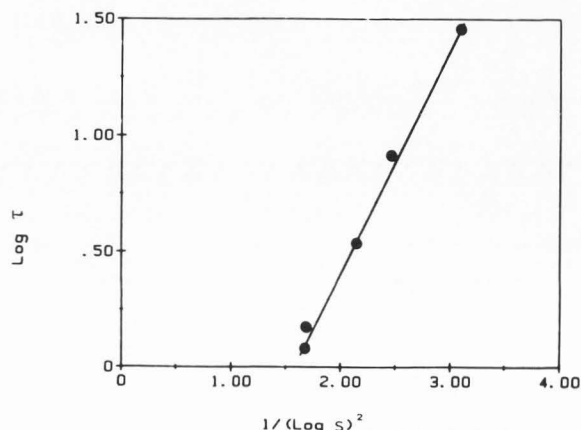


Fig.8. Plot of induction time ( $\tau$ ) against  $(\log S)^{-2}$ .

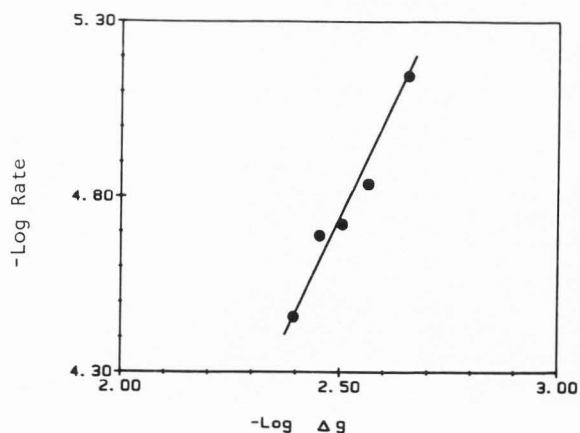


Fig.9. Logarithmic plots of rate against  $\Delta g$ .

## Crystallization of Alkaline Earth Surfaces

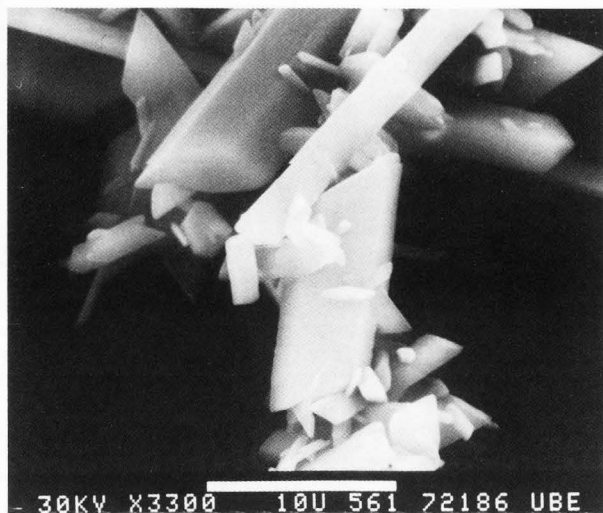


Fig.10. Scanning electron micrograph of calcium sulfate induced by presence of barium sulfate seed. Exp. E43 (Table 3). Bar = 10  $\mu$ m



Fig.11. Scanning electron micrograph of calcium sulfate induced by barium sulfate seed. Note the typical twinned crystals formed between calcium and barium sulfate observed in all experiments (Table 3). Bar = 10  $\mu$ m

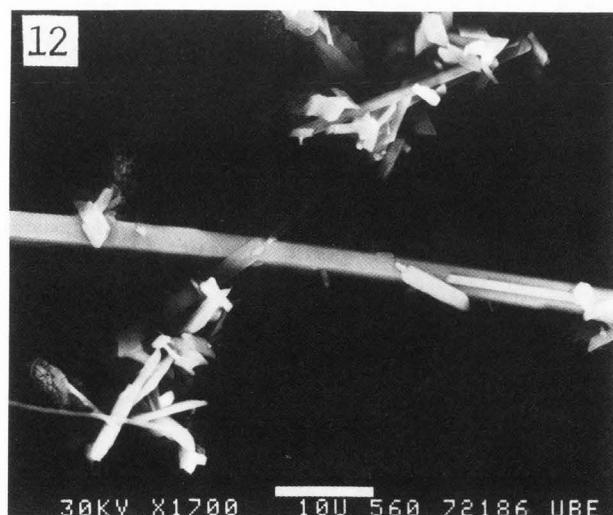


Table 3. Experimental Conditions for the Heterogeneous Nucleation of Calcium Sulfate on Barium Sulfate

Exp. No.	$T_{Ca} = T_{SO_4}$ $\times 10^3$ mol/L	Induction time hr.
E-40	3.70	29
E-41	4.20	13
E-42	4.20	9
E-43	4.60	7
E-45	4.20	10.6
E-47	4.60	7
E-49	4.40	9

seed crystals induced a precipitation of calcium sulfate in a time frame considerably shorter than the demonstrated stability of the supersaturated solutions. Precipitation may have been induced by imperfections on the barium sulfate surface and it is important to note that Nancollas and Gill (9) reported the growth of calcium sulfate dihydrate on dendritic barium sulfate. The results of EDXA analysis of the precipitated material (Fig. 13) suggest that epitaxial growth of calcium sulfate did not take place. In the analysis of those crystals with calcium sulfate morphology, barium peaks were absent from the spectra. Likewise, the crystals with barium sulfate morphology showed no calcium peaks. The barium sulfate seed crystals remained with the same morphology and size during the experiments while at the same time, the calcium sulfate crystals grew larger. The absence of epitaxial growth of calcium sulfate on barium sulfate may also be expected on the basis of the lattice matching calculations outlined in Table 4. The disregistry parameter,  $\delta$ , is considerably greater than that between strontium sulfate and barium sulfate.

In general, it can be concluded that in contrast to

Table 4. Crystallographic Data and Disregistry Calculation for the System Calcium Sulfate - Barium Sulfate.

	Calcium Sulfate	Barium Sulfate
Crystal System:	Monoclinic	Orthorhombic
Space Group:	C 2/C	Pnma (62)
Z	4	4
Molar Volume ( $\text{cm}^3$ )	74.68	52.10
$a_o$	$5.58 \pm 0.01 \text{ \AA}$	$8.878 \pm 0.005 \text{ \AA}$
$b_o$	$15.18 \pm 0.01 \text{ \AA}$	$5.450 \pm 0.005 \text{ \AA}$
$c_o$	$6.29 \pm 0.01 \text{ \AA}$	$7.152 \pm 0.003 \text{ \AA}$
$\delta_a$	$= (8.878 - 5.68) / 5.68 = 0.56$	
$\delta_b$	$= (5.450 - 15.18) / 15.18 = 0.64$	
$\delta_c$	$= (7.152 - 6.29) / 6.29 = 0.13$	

Fig.12. Back scattering micrograph of calcium growth in the presence of barium sulfate seed crystals showing twinned crystals in more detail. Bar = 10  $\mu$ m

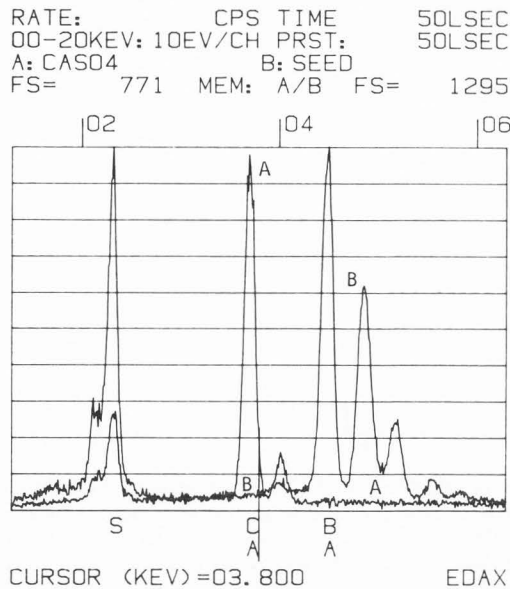


Fig.13. EDXA of final solid phases showing both calcium sulfate, A, and barium sulfate, B, spectrum.

calcium sulfate, strontium sulfate may grow epitaxially on barium sulfate surfaces. However, barium sulfate may induce calcium sulfate precipitation perhaps due to surface imperfections. The growth of the mixed phases may have important consequences for the control of oilfield scale in which both phases may be involved.

#### Acknowledgments

We thank Marathon Oil Company for a grant in support of this work. We also thank Mr. Peter Bush for helpful discussions.

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Discussion with Reviewers

H.C. Eaton: How did the authors coat their samples prior to examination in the SEM?

Authors: The samples were coated with gold for a 2 minute period at an applied current of 20mA.

H.C. Eaton: The live time for the EDX analyses should have been at least 50 seconds. Can the authors comment on how the low live time might affect their results?

Authors: In all our spectra the live time was 50 seconds. A lower live time would make the results unreliable since the count per second would be very small.

B.B. Tomazic: The authors pointed out the difficulties of simulating field conditions where fluid dynamics or pressure and temperature changes may play an important role in scale formation. Did they produce any information to illustrate the affect of changeable parameters such as fluid dynamics or changes in pressure and temperature?

Authors: Not yet. However, we have been working in our laboratory on the simulation of oilfield conditions. The results of these experiments will be published shortly.

B.B. Tomazic: The authors used a calcium selective ion electrode to monitor CC crystallization of  $\text{SrSO}_4$ . The electrode had a response limitation after about 10%  $\text{SrSO}_4/\text{BaSO}_4$  growth. Since the rate of precipitation depends on the seed/solution weight ratio, perhaps the electrode limitation can be avoided by using a lower original amount of seed. What seed/solution ratio was used in the present study?

Authors: The seed/solution ratio was  $150\text{mg L}^{-1}$ . We did not study the influence of seed concentration but this is a useful suggestion.

B.B. Tomazic: The authors indicate that  $\text{CaSO}_4$  growth initiates after an induction period that is irreproducible, as shown in Table 3. Table 1 shows induction periods for  $\text{SrSO}_4$  growth. It would be useful to point out the constancy or spread of these values, which would be another indication that  $\text{CaSO}_4$  and  $\text{SrSO}_4$  grow by different mechanisms.

Authors: In the case of  $\text{SrSO}_4$  growth the reproducibility of the induction period ranged from  $\pm 10$  minutes for the higher supersaturation (E32) to  $\pm 40$  minutes for lower supersaturation (E39).

Reviewer III: The chemical technique used in this paper follows that developed over years of careful research by the second author, on which he is a leading authority. Its validity is without question. However, the gravity of the content is a bit questionable. After all, two materials of identical structures and differing only in cations, those being in the same group in the periodic table, would be expected to grow epitaxially on one another. And two of different structures and quite different atomic lattice parameters would not.

Authors: It does not necessarily follow that materials with cations in the same Periodic Table group will grow epitaxially since there may be marked changes in other features such as the extent of hydration. It is therefore useful to make these analyses in terms of lattice matching.

Reviewer III: Particle size determination is a tricky thing, especially by one of many automated processes. Here the seeds are said to have a mean particle size between 9 and 12 micrometers. However, Figure 1 shows crystals of maximum size about 2.5 micrometers; in fact, the largest crystal shown on this page (Figures 1, 2 and 3) is about 5 micrometers in length. What does this say about growth rates? Are some of the new crystals heterogeneously nucleated on other surfaces?

Authors: The mean particle size was  $9-12\mu\text{m}$ . This does not imply that there were not a few smaller particles present as in Fig. 5. 1 and 2.

Reviewer III: Using seeds of greater than 1 Mm in size means that nucleation has nothing to do with  $\text{SrSO}_4$  growth process; its' growth on a substrate, and the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is heterogeneously nucleated somehow maybe having to do with the  $\text{BaSO}_4$  - but the authors only guess at that.

Authors: It is true EDXA is not a "surface" analytical technique and becomes more uncertain as the voltage is reduced in order to minimize penetration. However, if we observe that the Sr peak substitutes for the Ba peak during growth, it must mean that it has formed on the surface. This obviously involved a nucleation process as well as growth. Clearly the matching of crystal lattices is favorable for epitaxy but we cannot, without more surface molecular information, say that it is unequivocally epitaxial growth. The growth certainly has to do with the  $\text{BaSO}_4$  surface since the whole point of the study was to use conditions under which the supersaturated solutions would be stable if the foreign seed were not introduced.

\*Editor: Please provide availability information for references 7, 10, 12, 16, 19 and 25.

Authors: Reference 7 is available from U.S. Bureau of Mines, 4900 La Salle Road, Avondale, MD 20782. References 10, 12, 16, 19 and 25 can be obtained from the Society for Petroleum Engineers, P.O. Box 833836, Richardson, TX 75083.