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1. INTRODUCTION.

Sulfur emissions control is important for many fossil fuel applications, and mandatory to comply with environmental standards. Many techniques are available for the desulfurization of coal combustion processes. What is generally known as the LIMB process (Lime Injection Multistage Burner), however, carries great promises for an easy implementation and a low cost.

Temperatures found in coal-fired boilers are usually rather high (1500-2000°C), but the residence time is less than 2 seconds. The temperature history the limestone is subject to will have a determining effect on its reactivity. This can be attributed to changes in physical structure (sintering). Several investigators (Borgwardt, 1987; Sarofim et al, 1987) showed that the composition of the original stone is also very important: hydrates react much faster than carbonates, and, to a lesser extent, the concentration of other oxides affected the reaction.

Studies of the sulfation rate behavior show an initial fast rate followed by a rate decrease. This behavior has generally been interpreted as product layer diffusion limitations taking over after an initial kinetic rate regime. Many investigators tried to model this observed rate change, more or less successfully. No agreement has been reached, however, as to the value of the product layer diffusivity.

In this work we want to investigate the mechanism of this process. During the last quarter, most attention has been paid to analyzing the results obtained earlier. In the light of some unexpected results, we returned to the most fundamental question: what is the rate-limiting mechanism? It appeared that whatever the mechanism is, no rate "constant" could be used, since the rate is a function of the product layer composition, which changes during the reaction. When comparing the results obtained with different samples, however, it appeared that the best correlation was found if one assumes the limiting rate to occur at the $CaSO_4$ interphase. This point of view has never been presented before and requires therefore a more attentive analysis.

2. Experimental Results

2.1 Samples

A more detailed description of the various samples that were used, and a motivation for their use is found in the previous technical report. We want to discuss here the conversion behavior of these different samples and the information they provide.

This behavior is shown in Figure 1. The synthetic lime gives the most useful results (easier to measure), but must be compared with other stones for validation. The single crystals provide useful information in the long run (even though the time scale is much longer). The early time information, however, is not reliable due to the easy hydration of this material, which affects the superficial pore structure.

The Iceland Spar reacts very fast in the beginning, but the rate drops dramatically once a conversion of approximately 36% is achieved. The reason for this behavior is pore plugging, also easily observable on micrographic pictures. Because of this fast rate, probably limited by pore diffusion, no attention was paid to the early time results of the Iceland Spar runs. After pore plugging has occurred, the sample becomes non-porous and reacts only at the external surface. This rate is then very similar to the single crystal results.

The submicron ash particles, finally, react extremely fast, because of their small size. That is why, on Figure 1, the conversion behavior of this material is given at 600°C. The hydration problem, however, present in all CaO samples, is even worse here: the entire sample was systematically hydrated. As a result, the nonporous character of this material can no longer be guaranteed, and its surface area is probably much higher than the estimate made on basis of TEM pictures.

6.2 Initial Rate

This rate, on a virgin CaO surface, is easiest to measure because we know it is a surface phenomenon, and thus the kinetic rate simply equals the measured rate divided by the surface area. The dependence of this rate can then be investigated as a function of temperature and SO_2 gas concentration (oxygen is kept constant at 5%). The results are listed in Table 1.

The initial rate was, as mentioned earlier, most accurately measured with the synthetic lime. The value is within the range of values published by other authors ($1.7*10^{-6}$ mol/s m^2, Hartman & Trnka, 1976 and $37*10^{-6}$ mol/s m^2, Ramachandran & Smith, 1977). As a measure of the importance of temperature, the activation energy is given. The value measured in this work is, again, close to other author's measurements, and is reasonable for chemical kinetics. The order of SO_2 has been previously measured by Borgwardt (1987), and reported to be 0.56. We found an order ranging from 0.3 to 0.6, depending on the sample.

2.3 High Conversion Mechanism

At higher conversions, most authors assume that product layer diffusion is the rate-limiting mechanism. A number of observations seem to contradict this assumption, however: The activation energy measured at these higher conversions is too low for diffusion through solid crystals (24kcal/mol instead of order 100kcal/mol); the absolute value of the diffusivity is too high (the lowest number calculated from the experiments is 10[illegible] cm^2/s instead of order 10^{-12} cm^2/s) and the SO_2 order expected should be one.

In addition, it appeared that in order to have the rate measurements for the various samples correspond, one must take them to be proportional to the surface area, rather than to the square of the surface area, as in the case of a product layer diffusion limited regime. This points to a kinetically controlled regime. There are two interphases where a chemical reaction can give rise to such a kinetic regime. It can occur at the solid-solid interphase where the oxide reactant is in contact with the sulfate product. This would mean that the surface where the reaction occurs is the internal surface, very large in the case of porous limestone, independently of the pore plugging phenomenon. This doesn't concur with our observations that show a clear rate decrease after pore plugging occurs. Taking this observation together with the low SO_2 reaction order, we must conclude that the ad-(or chemi-)sorption is the rate-limiting mechanism.

Figure 2 shows, then, how the chemisorption rate constant obtained in this case looks evolves as a function of time, and for the various samples. When observing this figure, however, we notice a decrease in rate "constant" which, so far, cannot be explained. A similar decrease would have been observed using other rate-controlling mechanisms. The rate at zero conversion on a virgin CaO surface is faster than the rate on the $CaSO_4$ surface. The second part of Table 1 shows the value of this latter rate , its activation energy and its dependence on SO_2 concentration at given time and conversion levels. The SO_2 order is essentially the same, the activation energy is slightly higher and the rate at 800°C is lower.

2.4 Product Layer

Figure 3 shows how the product layer composition was observed to change with conversion. Initially, an amorphous-type blanket is formed on top of the Calcium Oxide. Calcium Sulfate crystals then appear on the surface. First scattered, then they multiply and cover the entire surface. Finally, the grains coarsen and the final product is obtained. It is very likely that this evolution influences the rate of sulfation, and thus provide an explanation for the rate decrease mentioned earlier.

Apart from the sulfation time, the composition of the product layer may also vary as a function as a function of temperature or SO_2 concentration. As a result, measurements performed under different conditions produce rates that are affected by a different product layer composition as well as by the actual change in conditions. This is why two stage, or 'combination' experiments were performed.

The procedure followed in this type of experiments is illustrated in Figure 4. After an initial heatup and equilibration period, a first, short, sulfation is performed under standard conditions. This way, a product layer is formed that can be reproduced under the same conditions. Next, the temperature is changed to the value under investigation. When sulfation is resumed under these conditions, the product layer has kept its known and reproducible form, and the rate (slope) is a sole measure of the temperature effect. Results of these type of experiments are shown in the third section of Table 1.

The order of SO_2 was measured using this type of experiments. First, the product layer was prepared under standard conditions (3000ppm SO_2 and 800°C), and then the gas concentration was changed in a range from ·30 to 10,000ppm. As indicated in Table 1, the order was found to be slightly lower than in direct runs. This would indicate that at low concentration, the product layer formed is less active than at high concentration.

Similar experiments were performed for investigating the effect of the temperature. The process was reversed: first, the surface was prepared at different temperatures; then, sulfation was resumed at 800°C. Figure 5 illustrates very clearly how the composition of the product layer affects the sulfation rate. This effect is easily understood when SEM pictures of the samples prepared at these different temperatures are observed (Figure 6): the product layer formed at low temperature consists of much smaller grains than the product layer prepared at high temperature (same conversion). From this, we are tempted to conclude that smaller grains result in a more active surface. In any case, the high temperature has a neutralizing effect on the rate.

3. Chemisorption as the Rate-Limiting Mechanism: Literature Discussion

As argued in the previous section, the only way found to reconcile the rate measurements of the different samples, is to take a chemical reaction at the outer $CaSO_4$ surface as rate-limiting. This is a point of view that has never been presented earlier in the literature, and that requires therefore a more detailed discussion.

Two mechanisms are usually taken into account in the literature. Initially, the kinetic rate of SO_2 reacting with virgin CaO is of course the only possible mechanism. After a while, as the $CaSO_4$ product layer builds up, the diffusion of reagents through this layer starts dominating the rate. Most authors use this approximation, to obtain, using a pore model and mathematical curve-fitting techniques, values for the two constants involved: the kinetic rate k and the solid-state diffusivity D_s. Using these numbers, and assuming order one, we can calculate the product layer thickness as follows:

$$k * C = D_s * C/\delta$$

or:

$$\delta = D_s/k$$

Simons (1986) noted that the value of this critical thickness obtained with the available data is approximately 5nm (at 800°C). This is of the same order of magnitude as the pore radius in most of the limestones used. This would mean that in fact, one never reaches the point where product layer diffusion takes over, but that the pores get filled long before.

Even though this point is well taken, many limestones used for sulfation experiments have larger pore sizes (e.g.: 0.42μm average pore size , Borgwardt, 1972, limestone #9), and as a result, significant values for D_s could be gathered

A few other inconsistencies are present in this traditional method. Indeed, physically it seems hard to believe that a similar mechanism will rule the sulfation at the CaO-$CaSO_4$ solid-solid interphase as is occurring on the virgin CaO surface. This observation is only of little interest if the product layer diffusion rate takes over very early on, but, if Simons' observation is correct, this might not always be the case. A simple calculation, however, shows that with a surface area of 30 m^2/g, a product layer thickness of 5 nm corresponds to 18%

conversion. This is no longer a negligible amount. A similar physical problem is present in the way product layer diffusion is handled. The unstated assumptions made in all publications is that: 1) The product layer is a homogeneous and isotropic layer of constant thickness

2) Sulfur dioxide gas is the diffusing compound, so that the driving force for diffusion is directly proportional to the SO_2 concentration and the diffusivity can be quantified using the SO_2 gas concentration.

The first point was already shown in the previous section to be inaccurate. The second point takes that the large SO_2 units (approximately 3 times as large as the O^{--} ions) diffuse through a crystalline lattice that is very well packed. That this cannot be the actual mechanism is easily proven by the fact that the SO_2 order is not one.

Borgwardt (1986) attempted to prove the product layer diffusion mechanism by measuring the rate as a function of surface area for limestones calcined under different conditions. When plotting the time needed to reach 20% conversion versus surface area, he found a quadratic relationship, which should agree with the mechanism suggested. However, as we pointed out earlier, due to important changes in surface area composition at early times, the kinetic parameters are not constant. Hence, the technique applied by Borgwardt, that assumes a constant value of D_s, is not applicable at early times.

These points, however, are not enough to reconcile the many studies performed on the sulfation reaction with the mecvhanism that is suggested in this work. It is therefore planned to use a simple model to investigate whether the existing literature data can also be explained using the chemisorption model.

4. Adsorption Isotherm

The chemisorption is composed of two stages: first, the gaseous components must adsorb on the surface and second, these adsorbed species further react to their final product. Hence, the rate can be expressed as

$$r = k * S * \theta \qquad (1)$$

Where k is the rate constant, S the surface area, and θ the surface coverage of adsorbed species.

In order to find an expression for the surface coverage as a function of the partial pressure of SO_2 in the gas, the Langmuir-Hinshelwood theory can be used. It states

$$\theta = Kp / (1+Kp) \qquad (2)$$

This equation provides a first order relationship between surface coverage and gas partial pressure at low pressure, and exhibits a saturation phenomenon (i.e. 0th order) at high pressure. Hence it doesn't explain the fractional order the we observed. This theory, however, is based on the assumption that the heat of adsorption is a constant, independent of the surface coverage. In many real life systems, this is only true as a first approximation. The Freundlich isotherm, however, has been used succesfully in many cases. It postulates a different relationship between heat of adsorption (Q_a) and coverage (θ) (Szekely et al., 1976, Halsey, 1952):

$$Q_a = Q_m \ln(\theta) \qquad (3)$$

Equation (2) is still valid in this case, but only in differential form, i.e. in the range of coverage between θ and $\theta + d\theta$, where the heat of adsorption is constant. The equation must then be written as

$$d\theta = K / (1+Kp)^2 \ dp \qquad (4)$$

where K is an equilibrium constant:

$$K = K_o \exp(-Q_a/RT) \qquad (5)$$

therefore

$$K = K_o * \theta^{-Q_m/RT} \qquad (6)$$

When substituting K in (4):

$$d\theta = K_o*\theta^{-Q_m/RT} / (1+K_o*\theta^{-Q_m/RT}*p) \ dp \qquad (7)$$

At low pressure, far from saturation ($Kp<<1$), this equation simplifies to

$$d\theta = K_o*\theta^{-Q_m/RT} \ dP \qquad (8)$$

which can be integrated from 0 to p, to obtain

$$\theta = K_o * Q_m * p^{RT/Q_m} \qquad (9)$$

where $RT<Q_m$, thus providing a fractional order.

Whether this isotherm is correct in our case will still have to be investigated by observing the behavior of the reaction order with temperature. Other attractive features of this theory is that it provides an order that is independent of the conversion level, which corresponds with our observations. Furthermore, the introduction of a heat of adsorption, Q_m, could provide us some clues for the effect of the surface composition on the rate.

This explanation would allow us -but this also is still an hypothesis- to explain the effect of the surface crystal size by way of surface energy. Smaller crystals have a higher surface energy. The heat of adsorption will thus be higher (Q_m), and so the rate constant ($k*Q_m$). When the crystals grow, the surface energy decreases and so does the rate

It is good to notice also that even though the surface reaction was found rate limiting, diffusion of the components through the product layer must still occur. It is assumed that the diffusion of O^{--} or SO_4^{--} through the grain boundaries is sufficiently fast to explain the above observations.

7. FUTURE WORK:

As mentioned earlier, a first step towards validation of this model will be to compare, using a mathematical model, the literature data to the proposed mechanism.

In a second stage, we will investigate the dependence of the reaction order as a function of temperature, thus obtaining some evidence to determine what adsorption isotherm should be used.

Finally, the importance of the product layer crystal size will be investigated more quantitatively, trying to understand what effect the surface composition has on the reaction rate. This should provide a clue as to why the rate decreases with time, and how additives affect the rate.

TABLE 2: Experimental Results

(the Rates are given at standard conditions, i.e. 800°C and 3000ppm SO_2)

Samples:	Single Crystals	Submicron Ash	Iceland Spar	Synthetic Lime
Surface Area:	0.18 m^2/g	30 m^2/g	30m^2/g	3-6 m^2/g
Initial Rates				
Rate (mol/s m^2)	$7.3*10^{-6}$	$22*10^{-6}$	-	$8.4*10^{-6}$
E_a (kcal/mol)	39.8	20.8	-	16.2
SO_2 order	-	-	-	0.2-0.6
High Conversion Rates				
	15%, 240min		41%, 51min	62%, 96min
Rate (mol/s m^2)	$0.68*10^{-6}$	-	$0.34*10^{-6}$	$0.13*10^{-6}$
E_a (kcal/mol)	22.0	-	31.0	27.8
SO_2 order	0.2	-	-	0.3-0.5
Combination Runs				
	50%, 10min		36%, 5min	16%, 2min
Rate (mol/s m^2)	$2.89*10^{-6}$	-	$2.43*10^{-6}$	$2.6*10^{-6}$
E_a (kcal/mol)	-	-	24.0	-
SO_2 order	0.2	-	0.2	-

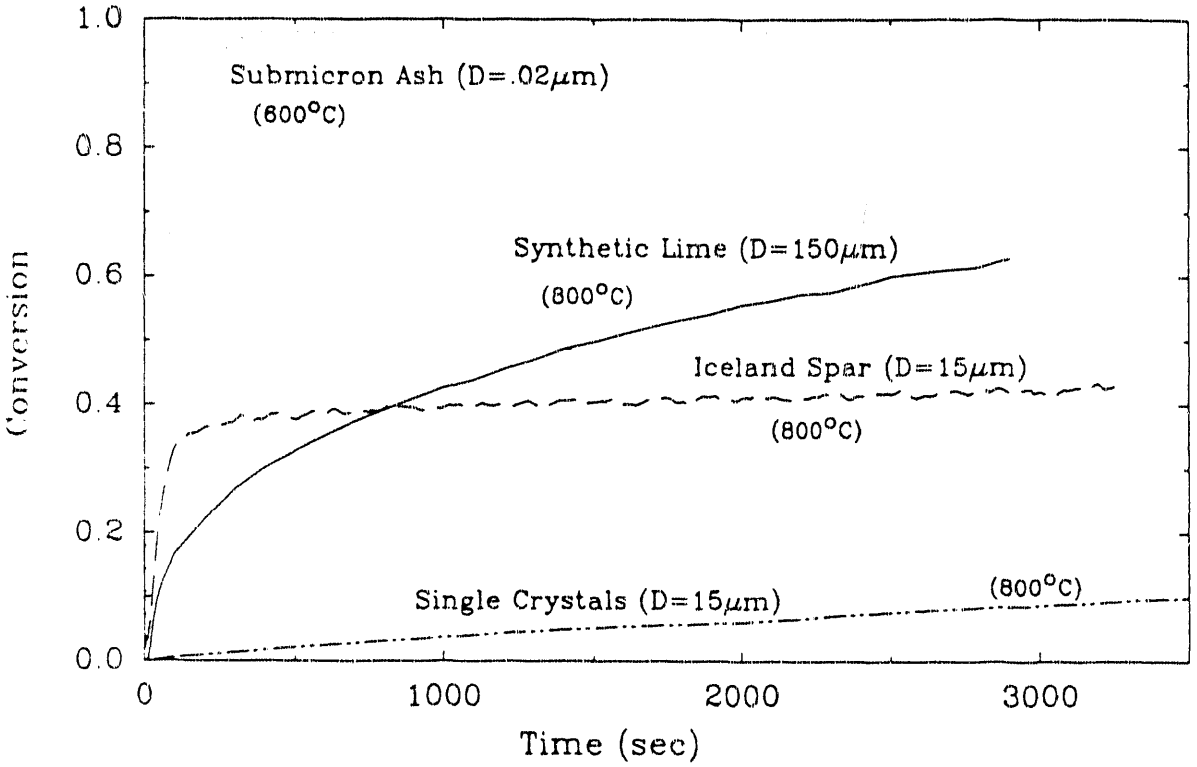

Figure 1. Conversion Behavior for Different Samples

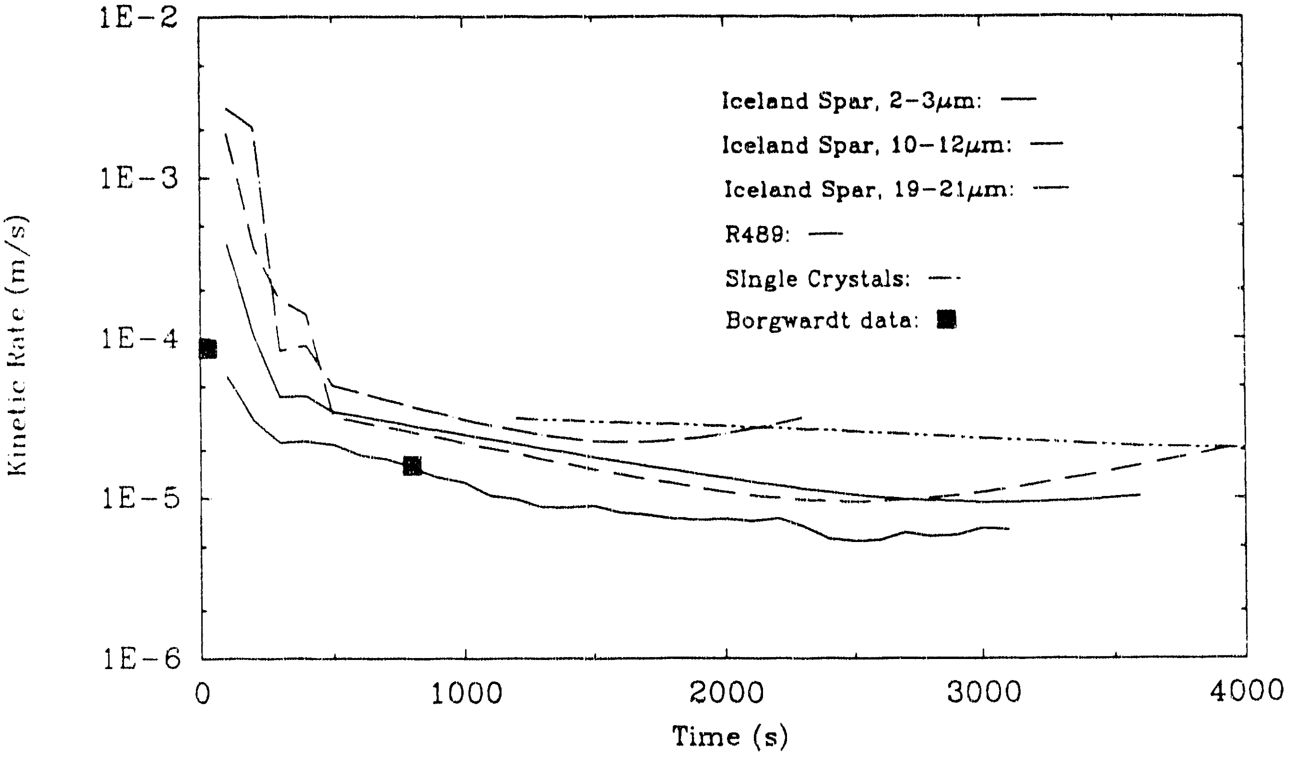

Figure 2. Kinetic Rate for Various Samples

Assuming that the Limiting Rate is Chemisorption at the Outer $CaSO_4$ Surface

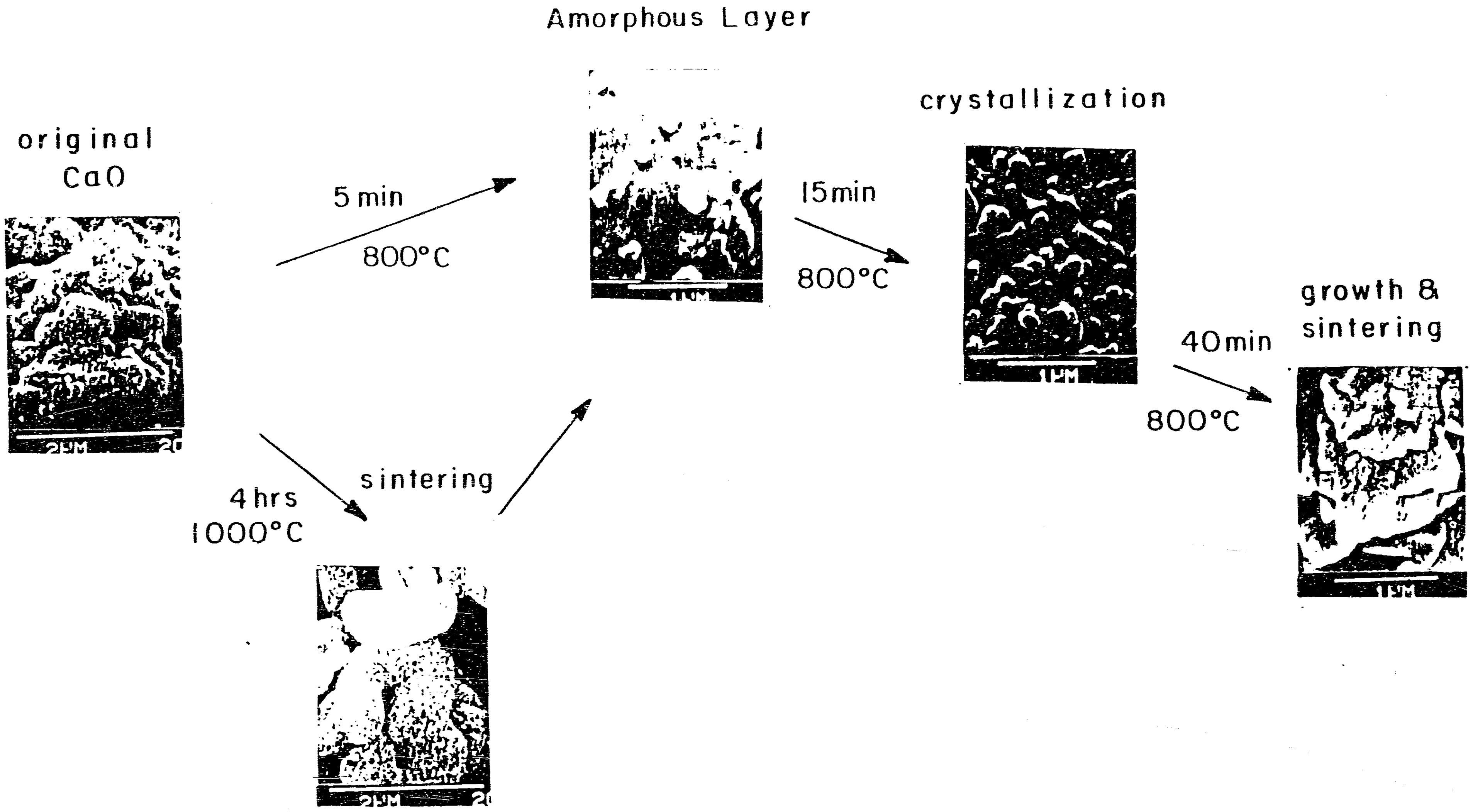

Figure 3 : Scheme of the reaction path

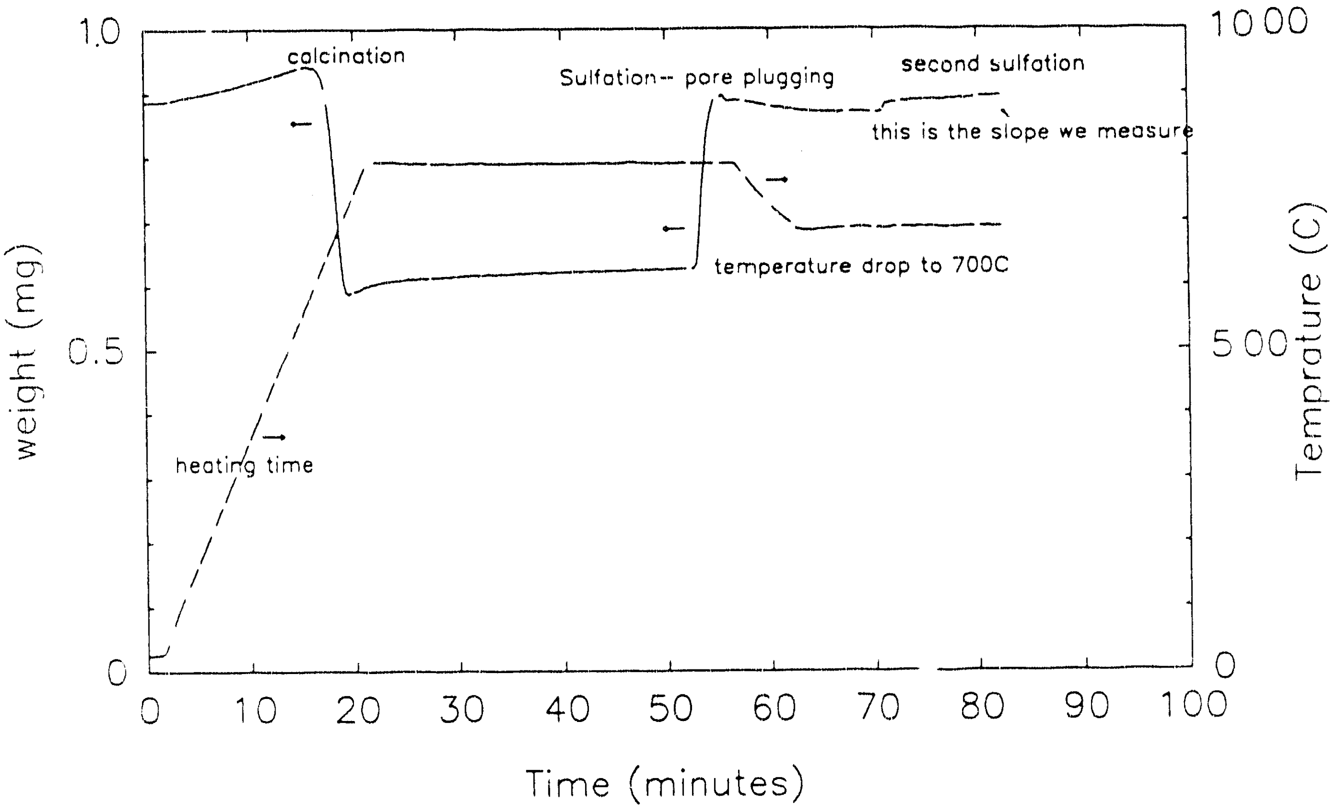

Figure 4. Combination run: example of weight and temperature profiles

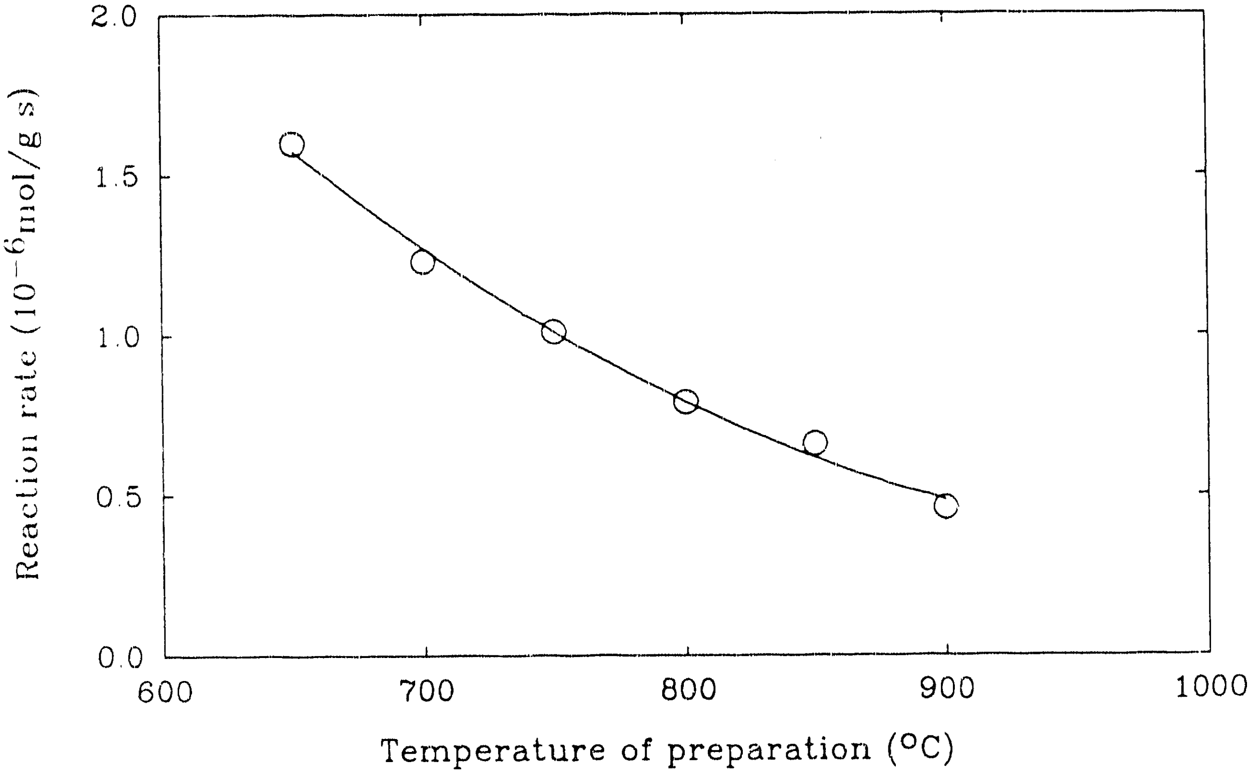

Figure 5. Reaction Rate at 800°C after Preparation at Diffferent Temperatures

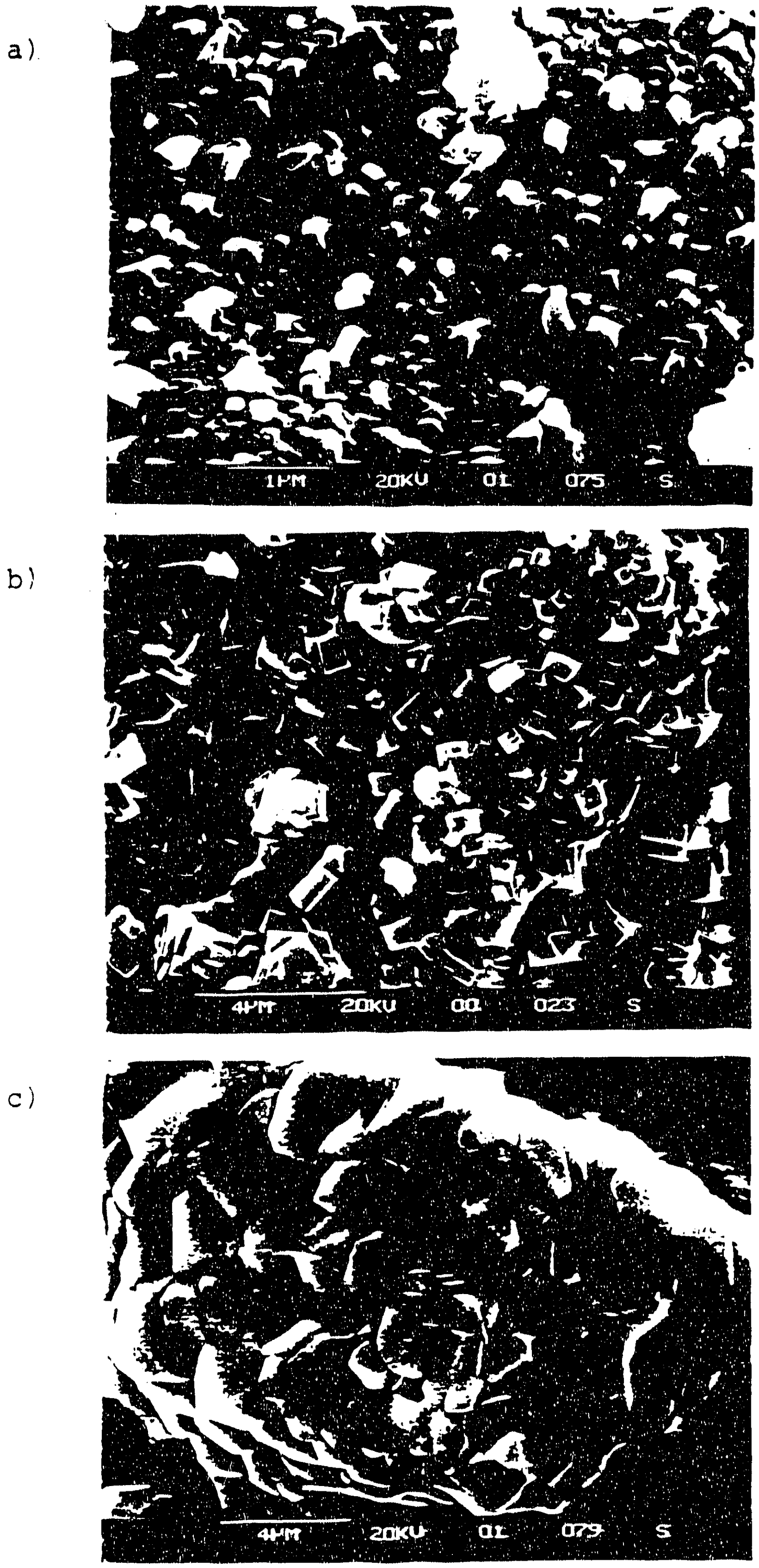

Figure 6. Micrographic Pictures of Samples Sulfated at Different Temperatures: a) 700°C; b) 800°C; c) 900°C

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