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Removal of H_2S and SO_2 by $CaCO_3$-Based Sorbents at High Pressures

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Prepared by:

Prof. Stratis V. Sotirchos

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Rochester, NY 14627

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EXECUTIVE SUMMARY

The theoretical and experimental investigation of the mechanism of SO_2 and H_2S removal by $CaCO_3$-based sorbents (limestones and dolomites) in pressurized fluidized-bed coal combustors (PFBC) and high pressure gasifiers, respectively, is the main objective of this study. It is planned to carry out reactivity evolution experiments under simulated high pressure conditions or in high pressure thermogravimetric and, if needed, fluidized-bed reactor (high pressure) arrangements. The pore structure of fresh, heat-treated, and half-calcined solids (dolomites) will be analyzed using a variety of methods. Our work will focus on limestones and dolomites whose reaction with SO_2 or H_2S under atmospheric conditions has been studied by us or other research groups in past studies. Several theoretical tools will be employed to analyze the obtained experimental data including a variable diffusivity shrinking-core model and models for diffusion, reaction, and structure evolution in chemically reacting porous solids.

During the first six months of the project, preparatory work was done on the development of a thermogravimetric analysis system for gas-solid reactions studies at high pressures. We also worked on adapting some algorithms developed in past studies for computing structural and transport properties in composite media to the porous structures encountered in calcines obtained from limestone or dolomite precursors. Since in the presence of high partial pressures of CO_2, the calcination of limestone – provided that it is thermodynamically possible – is expected to occur with rate much lower than that in the absence of CO_2, experimental reactivity evolution studies were carried out in a thermogravimetric analysis system on the simultaneous calcination and sulfation behavior of samples obtained from limestones of high calcium carbonate content ($> 95\%$), whose independent calcination, sulfidation, and sulfation reactions were investigated in detail in past studies. The results showed that, even when CO_2 is absent from the reactor, the behavior of the simultaneous calcination and sulfation process is markedly different from that inferred from the results of the sequential experiments. Simultaneous occurrence of calcination and sulfation has in general adverse effects on the effective capacity of limestone for SO_2 removal, which intensify as the particle size increases or the rate of calcination decreases. Effort is currently put into modifying a general reaction, transport, and structure evolution model developed by our research group in the past for describing the sulfation of calcined limestone particles for application to the simultaneous calcination and sulfation process. Once its development is completed, the model will be used to analyze the experimental data for simultaneous calcination and sulfation that were collected from our experiments.

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1. BACKGROUND INFORMATION

In a fluidized-bed combustor, a bed of combustible (coal) and noncombustible material is fluidized using air blown upward. Using dolomite or limestone as the noncombustible material, it is possible to have fuel combustion and flue gas desulfurization taking place simultaneously in the combustion vessel. If operation occurs under atmospheric pressure, the average partial pressure of carbon dioxide in the combustor (typically, 10-15% of the total pressure) is considerably lower than the equilibrium CO_2 pressure for decomposition of limestone ($CaCO_3$) or dolomite ($CaCO_3 \cdot MgCO_3$) at the temperatures usually encountered in FBC units (800-950 °C). In the high temperature environment of the AFBC unit, the limestone or dolomite particles undergo calcination, yielding a highly porous product (CaO or MgO), which reacts with the sulfur dioxide produced during coal combustion forming, mainly, calcium or magnesium sulfate. The sulfates occupy more space than the oxides they replace, and as a result, the pores of the calcine are completely plugged with solid product before complete conversion takes place. (The conversion for complete pore plugging is about 50% for the calcine of a stone consisting of $CaCO_3$ only.) Pores of different size are plugged at different conversion levels, and it is thus possible to have formation of inaccessible pore space in the interior of the particles when the small feeder pores of clusters of large pore are filled with solid product (Zarkanitis and Sotirchos, 1989). Moreover, under conditions of strong internal diffusional limitations, complete pore closure may first take place at the external surface of the particles while there is still open pore space left in the interior. For these reasons, ultimate conversions much lower than those predicted by the stoichiometry of the reaction for complete plugging of the internal pore space (less than 30-40%) are seen in AFBC units.

The reaction of calcined limestones (primarily) and dolomites with SO_2 has been the subject of extensive investigation. In accordance with the above remarks, the experimental evidence in most of the studies of the literature indicates strong effects of the pore size distribution on the overall reactivity of the calcined solids (Borgwardt and Harvey, 1972;

Wen and Ishida, 1973; Hartman and Coughlin, 1974, 1976; Ulerich et al., 1977; Vogel et al., 1977; Hasler et al., 1984; Simons and Garman, 1986; Yu, 1987; Gullett and Bruce, 1987; Zarkanitis and Sotirchos, 1989; Zarkanitis, 1991). Unfortunately, the immense volume of information that has been accumulated over the years on the reaction of calcined limestones and dolomites with SO_2 is not applicable to SO_2 emissions control by limestones and dolomites under PFBC conditions. PFBC units normally operate under a pressure of 16 atmospheres, and for an average CO_2 content of 15%, this implies that the partial pressure of CO_2 in the reactor is 2.4 atm. Thermodynamic calculations show that the temperature for $CaCO_3$ calcination in the presence of 2.4 atm of CO_2 must be larger than 980^o C, that is, well above the temperature range (750-950^o C) encountered in a PFBC unit. Nevertheless, even though formation of a highly porous material with a high specific surface area cannot take place under PFBC conditions, favorable desulfurization is known to occur in PFBC units (Bulewicz and Kandejer, 1986; Murthy et al., 1979). For dolomites, the situation is somewhat different since half-calcination (formation of an MgO-$CaCO_3$ product) is possible under 2.4 atm of CO_2. Even in this case, however, if the absorption of SO_2 occurred only in the pore space of the half-calcined solid, the utilization of the calcium content of dolomites should be much smaller than what is seen in practice under PFBC conditions.

The reaction of $CaCO_3$ with SO_2 may involve various reaction steps (Van Houte et al., 1981):

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \tag{1}$$

$$CaSO_3 + \frac{1}{2}O_2 \rightarrow CaSO_4 \tag{2}$$

$$CaSO_3 + \frac{1}{2}SO_2 \rightarrow CaSO_4 + \frac{1}{2}S \tag{3}$$

$CaSO_3$ decomposes at temperatures higher than 650 °C, and therefore, under typical operating conditions in a PFBC unit, the overall reaction may be written as:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2 \tag{4}$$

For dolomites, one should also address the question of the reaction of MgO with SO_2.

If the partial pressure of CO_2 within the bed varies, calcination of $CaCO_3$ may take place in regions where CO_2 pressures lower than the equilibrium pressure are prevailing. The calcination of $CaCO_3$ will yield a partially calcined product, the extent of calcination depending on the residence time of the solid in the low CO_2 concentration region. CaO formed in the solid will react with the SO_2 present in the bed in the same fashion as in the case of AFBC units:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{5}$$

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \tag{6}$$

If the partially calcined solid moves into regions rich in CO_2, where reaction (5) is favored to proceed from right to left, carbonation, i.e., recovery of $CaCO_3$, will take place, with reaction (4) competing with reaction (5) for CaO. Decomposition of $CaCO_3$ may also take place even if there is no variation of the CO_2 pressure in the reactor. Large variations in the temperature profile (100-140° C) within the combustor unit have been reported by Smith et al. (1982). Therefore, if the solid particles move into regions where the temperature of the reactor is above the temperature at which $CaCO_3$ is stable, at the average partial pressure of CO_2 in the reactor, decomposition of $CaCO_3$ will occur. However, only small amounts of CaO have been found in the reactor by Ljungstrom and Lindqvist (1982), suggesting that direct sulfation of limestones (eq. (4)) is the main reaction occurring in the combustor. Similarly, PFBC data from Exxon (Hoke et al., 1977) with uncalcined Grove limestone showed that most of the unreacted Ca in the bed for CO_2 partial pressures above the equilibrium value existed in the form of $CaCO_3$.

Studies of SO_2 removal at high pressures have been carried out both with carbonates and precalcined solids (Newby et al., 1980; Ulerich et al., 1982; Dennis and Hayhurst, 1984, 1987; Bulewicz et al., 1986). However, because of the aforementioned complexities, with the exception of the general conclusion that favorable desulfurization is possible under

PFBC conditions, there is not much agreement in the literature on the effects of the various parameters on the process. Dennis and Hayhurst (1984, 1987), for example, found that the reaction rate of precalcined limestones in a fluidized-bed reactor decreases with an increase in the operating pressure, both in the absence and presence of CO_2. Working with a laboratory-size PFBC, Bulewicz et al. (1986) observed an increase in the sorption capacity of Ca-based sorbents (chalk, limestone, and dolomite) with an increase in pressure up to 2 atm, but further increase in pressure caused a reduction in the sorption capacity of all samples. Similar observations were made by Jansson et al. (1982). PFBC studies at Exxon (Hoke et al., 1977) showed better sulfur retention for precalcined limestones, but Stantan et al. (1982) observed no improvement in sorbent utilization by precalcination. Stantan et al. also reported that under weakly noncalcining conditions, a feed of uncalcined limestone gave better sulfur retention than what kinetic studies performed in a thermogravimetric apparatus predicted.

A situation similar to that prevailing in PFBC units is encountered in desulfurization in gasifier at high pressures. Fixed-bed and fluidized-bed gasifiers typically operate around 850 °C with a temperature at the exit of around 500-800 °C. The pressure of operation is in most cases in the 200-300 psi range, and at an average pressure of 250 psi, it turns out that the CO_2 partial pressure in the reactor is about 1.8 and 4.3 atm for air blown and oxygen blown gasifiers, respectively (based on a typical CO_2 content (mole/mole) of 11% and 26%, respectively (Grindley et al., 1985). Almost all observations made for SO_2 removal in PFBC reactors apply to H_2S removal in high pressure gasifiers but with reactions (7) and (8) taking place (primarily) in a gasifier instead of (4) and (6):

$$CaCO_3 + H_2S \rightleftharpoons CaS + CO_2 + H_2O \tag{7}$$

$$CaO + H_2S \rightleftharpoons CaS + H_2O \tag{8}$$

Like in the case of sulfation, the main difference between the direct and indirect reactions is that a highly porous solid is involved in the indirect process while that participating in the direct reaction is essentially nonporous. In view of this difference, the information that is presently available on the sulfidation of limestone-derived calcines (e.g., see Borgwardt et al. (1984) and Efthimiadis and Sotirchos (1992)) and sulfidation of half-calcined dolomites (e.g., see Ruth et al. (1972) and Yen et al. (1981)) from studies in thermogravimetric analysis (TGA) systems and other types of reactors is inapplicable to the direct reaction of limestones with H_2S. Few fundamental studies have been presented in the literature on the direct reaction of limestones with H_2S, and most of those have been carried out under low pressures (Borgwardt and Roache, 1984) or under conditions where both sulfidation reactions ((7) and (8)) could take place (Attar and Dupuis, 1979).

The direct sulfation or sulfidation of calcium carbonate-containing sorbents can be studied under atmospheric pressure provided that there is enough CO_2 in the reactor to prevent decomposition of the carbonate (simulated PFBC or high pressure gasification conditions). Tullin and Ljungstrom (1989) performed sulfation experiments in a thermogravimetric analyzer (TGA) under conditions inhibiting calcination of $CaCO_3$ and found that the sulfation rate of uncalcined $CaCO_3$ was comparable with the sulfation rate of calcined material; they thus concluded that desulfurization in PFBC's is achieved by direct sulfation of limestones. Large amounts of sample and small particles (around 150 mg and 10-90 μm) were used by those authors in their experiments, and thus extracting any quantitative information is practically impossible (because of strong interparticle diffusional limitations). A similar procedure was employed by Snow et al. (1988) and Hajaligol et al. (1988), who also observed that the direct sulfation of $CaCO_3$ can reach for some precursors higher conversions than the sulfation of the calcines (CaO). High concentrations of CO_2 (70% CO_2 by volume) were also used by Borgwardt and Roache (1984) to study the direct reaction of limestone particles with H_2S at atmospheric pressure in a differential reactor. They employed a limestone precursor (Fredonia limestone) of relatively high porosity (about 8%), and thus, they were able to explain the behavior of the conversion-time trajectories for large particles (diameter greater than 15 μm) along the lines of the overall mechanism for the sulfidation of limestone-derived calcines (reaction (8)).

A detailed investigation of the direct sulfation of limestones with SO_2 and H_2S under simulated high pressure conditions was carried out by my research group (Krishnan and Sotirchos, 1993a,b,1994) using three limestone specimens of high $CaCO_3$ content. In accordance with the observations of Tullin and Ljungstrom (1989), Snow et al. (1988), and Hajaligol et al. (1988), our sulfation results (Krishnan and Sotirchos, 1993a,1994) showed that the direct reaction of calcium carbonate with SO_2, believed to be the dominant reaction in a PFBC, is qualitatively different from the reaction of limestone calcines. A similar conclusion was reached for the limestone-H_2S reaction (Krishnan and Sotirchos, 1994). These results reinforced our early conclusion that the accumulated knowledge in the literature from the extensive study of the reaction of calcined limestones and dolomites with SO_2 or H_2S cannot be used to derive any reliable conclusions for flue or coal gas desulfurization under high pressure conditions. Nevertheless, with the exception of the studies conducted under simulated high pressure conditions on a few limestones, no fundamental studies have been carried out in the literature on the reaction of limestones and dolomites with SO_2 or H_2S under true high pressure conditions (i.e., at high pressures and in the presence of CO_2). Moreover, even though the experimental data under simulated high pressure conditions have been extremely helpful in elucidating some of the phenomena encountered in the direct sulfation or sulfidation of limestones, it is questionable whether these results are directly applicable to reaction under true PFBC or high pressure gasification conditions, especially for solids with significant dolomitic content.

Based on the above observations, a research program has been proposed for the investigation of the mechanism of SO_2 and H_2S removal by limestones and dolomites at high pressures. Reactivity evolution experiments will be carried out using thermogravimetric and, if needed, fixed-bed and fluidized-bed reactor (high pressure) arrangements. Thermogravimetric experiments will be carried out under simulated high pressure conditions at atmospheric pressure using a unit currently available in our lab and at high pressures using a high pressure TGA proposed to be set up under this project. The pore structure of fresh, heat treated, and half-calcined solids (dolomites) will be analyzed using a variety of methods. Our work will focus on limestones and dolomites whose reaction with SO_2 or H_2S under atmospheric conditions has been in detail investigated by either us or other research groups. The obtained experimental data will be analyzed using various theoretical tools developed by my research group for studying gas-solid reactions, and will be used as basis for the development of predictive single particle models for use in design models of combustors or gasifiers.

2. WORK DONE AND DISCUSSION

During the first six months of the project, preparatory work was done on the development of a thermogravimetric analysis system for gas-solid reactions studies at high pressures. The turn-key high pressure units that are currently available in the market cost considerably more than the equipment funds available in the project, and as a result, our plan is to put together the system using a basic microbalance acquired from Cahn and parts from other vendors. We also worked on adapting some algorithms developed in past studies for computing structural and transport properties in composite media to the porous structures encountered in calcines obtained from limestone or dolomite precursors. Since in the presence of high partial pressures of CO_2, the calcination of limestone – provided that it is thermodynamically possible – is expected to occur with rate much lower than that in the absence of CO_2, experimental reactivity evolution studies were carried out in a thermogravimetric analysis system on the simultaneous calcination and sulfation behavior of samples obtained from limestones of high calcium carbonate content ($> 95\%$), whose independent calcination, sulfidation, and sulfation reactions were investigated in detail in past studies. Some of the obtained results are discussed in some detail next.

2.1. Computation of the Evolution of the Structural and Transport Properties of Reacting Porous Solids Using Stochastic Computer Algorithms

The distinguishing feature of the sulfation and sulfidation of calcined limestones as gas-solid reactions is the formation of a solid product that occupies more space than the solid reactant from which it results. This causes the size of the pores of the reacting solid to decrease and may lead to formation of inaccessible (locally) pore space. Among the structural models that are employed in representing the structure of calcined limestones in sulfation are grain models, in which an assemblage of solid particles is used to represent the solid phase. When a grain model is used as a structure model, the local evolution of the pore structure can be followed by allowing for grain growth on surfaces that are boundaries of the connected (accessible) part of the pore space. A stochastic simulation method was formulated for following formation of inaccessible pore space in structures of growing particles. It combines a gradual increase of the particle size with a random walk scheme, the latter used to determine whether a randomly chosen point in the unit cell of the two-phase structure lies in the particle phase or in the connected or isolated part of the matrix phase. The formulated algorithm was applied to structures of freely overlapping, unidirectional cylinders, and results were obtained both for the volume fractions and the specific surface areas of the accessible and inaccessible parts of the pore phase. A paper reporting on the simulation method and the results obtained from its application is under preparation.

The information on the trajectories of the random walkers as they travel in the pore space suffering collisions on the pore walls can be employed to determine the effective Knudsen diffusion coefficients of gases in the pore structure. If allowance is made for molecule-molecule collisions, effective diffusivities in the bulk and transition diffusion regimes can also be obtained. By allowing the walkers to enter the solid phase, it is also possible to use their trajectories to determine effective thermal conductivities and other transport properties of the porous material. A general stochastic simulation scheme was formulated on the basis of the above ideas for computing the effective transport properties of multiphase media in which the constitutive phases may be anisotropic. Its development was based on similar algorithms that had been formulated in past studies by my research group for computing effective transport properties in multiphase media possessing a single conductive phase (e.g., porous media). Computations were carried out using structures in which the transport problem is amenable to analytical treatment, such as structures consisting of parallel layers and regular arrays of cylinders, in order to validate the developed simulation scheme. Among our future goals is to use the method to determine the variation of the effective thermal conductivity of partially sulfated or sulfided calcined limestones with the extent of reaction. This parameter is needed in modelling the simultaneous calcination and sulfation or sulfidation of limestones since heat transport through the partially converted (sulfated or sulfided) layer may be among the controlling factors of the overall process. A presentation on the stochastic simulation algorithm for determining effective transport coefficient of multiphase media entitled "Stochastic Simulation Algorithms for the Computation of the Transport Properties of General Anisotropic Composite or Porous Media" is scheduled to be made at the ACerS Annual Meeting in Indianapolis in April 1996.

2.2. Simultaneous Calcination and Sulfation Studies

The subject of most studies, both theoretical and experimental, on limestone sulfation or sulfidation is the investigation of the sulfation behavior of samples which have been calcined completely in the absence of sulfur compounds. This is also the case with the studies that have been carried out by my research group on limestone calcination and sulfidation (Zarkanitis and Sotirchos, 1989; Efthimiadis and Sotirchos, 1992; Sotirchos and Zarkanitis, 1992). However, when desulfurization is carried out in a combustor or a gasifier in situ through limestone addition, both calcination and sulfation or sulfidation are carried out simultaneously. The argument that is usually made in justifying how experimental results obtained from sequential calcination and sulfuration (sulfation or sulfidation) experiments can be used to determine the performance of actual desulfurization systems in which these processes occur simultaneously is that calcination is so faster than sulfuration that in the time needed to achieve complete calcination the conversion of the calcined material to sulfide or sulfate is extremely low. However, the time needed to completely plug the pores at the external surface of the particles (during sulfation) or reach complete conversion (during sulfidation) is independent of the particle size, whereas the time needed for complete calcination increases strongly with increasing particle size. Therefore, the interaction between the calcination and sulfuration processes is expected to intensify as the particle size increases. Moreover, at high partial pressures of CO_2, as it is the case in high pressure reactors, the calcination of limestone – provided that it is thermodynamically possible – is expected to occur with rate much lower than that in the absence of CO_2. Therefore, it is possible the interaction of calcination and sulfuration to lead to sorbent performance in an actual unit much different from that revealed by sequential calcination and sulfuration experiments.

In order to examine the validity of the assumption of minimal interaction of calcination and sulfation during sulfur removal in a combustor, we investigated experimentally the simultaneous calcination and sulfation of limestones at atmospheric pressure using two limestone specimens. Experiments were carried out without CO_2 added in the reactant stream – except that resulting from the decomposition of calcium carbonate – in order to be able to compare our results with sequential calcination and sulfidation experiments that had been carried out under the same conditions in past studies using the same sorbents. The samples we used were: a limestone of very high $CaCO_3$ content distributed by Greer limestone Co. (Greer limestone) and a calcite (Iceland spar) distributed by Wards Inc. Chemical analysis of the solids showed that the calcium carbonate content was 99.19% in the Iceland spar and 97.89% in the Greer limestone. Detailed chemical analyses of the three solids are given elsewhere (Krishnan, 1993).

Simultaneous calcination and sulfation experiments were carried out in a thermogravimetric analysis (TGA) system operating at 1 atm. In order to avoid having significant interparticle diffusional limitations, a small amount of solid (1.4-4 mg) was used for reactivity experiments. Gas flow rates of 200 ml/min under standard conditions were used in all of the experiments. The effect of particle size on conversion vs. time results was studied by carrying out experiments with particles in two size ranges (53-62 and 297-350 μm) for each of the three solids. The temperature effect was also studied by performing experiments at two different temperatures, 750 and 850 °C. A gas mixture consisting of 3,000 ppm SO_2, 12% O_2 and the balance N_2 was used as reactant stream. Simultaneous calcination and sulfation experiments were started by heating the limestone sample to the reaction temperature under a stream of 70% CO_2 and the balance N_2 to prevent occurrence of decomposition, and switching to the SO_2-O_2- N_2 stream once the reaction temperature was reached.

Some of the results we obtained in our experiments are presented in Figure 1-4. In all these graphs, the reactivity vs. time data are presented as the ratio of the weight of the sample at time t, W_t, to the initial weight, W_0, as a function of time. This is done because the simultaneous occurrence of the two reaction does not permit us to determine which part of the total weight change is due to each process. In the same figures, we also present the weight change ratio vs. time curves that were determined in past studies for the same limestones (Sotirchos and Zarkanitis, 1992) for calcination and sulfation carried out independently of each other and the composite curves that are obtained by assuming that the interaction of the two processes as they occur simultaneously is unimportant.

We see from the results of Figures 1-4 that the total weight change vs. time curve for simultaneous occurrence of calcination and sulfation behaves qualitatively in the same way as the composite curve that is constructed using results from independent calcination and sulfation experiments, but there is not much quantitative agreement between the two curves in each case. Significant differences are observed even for particles with size in the range 53-62 μm, and this observation points to the conclusion that it is not possible to determine the performance of a limestone for in situ SO_2 removal from results obtained from sequential calcination and sulfation experiments. Both in the simultaneous (actual) and in the sequential (artificial) processes, the total weight of the sample decreases initially at a high rate, but after some time, it starts to increase, with the rate of increase being noticeably higher for the composite process. The weight change (drop) at the minimum is much larger in the sequential process. Since the decrease of the weight is due to the loss of CO_2 during calcination, one is led to conclude that the conversion of calcium oxide to sulfate impedes the progress of calcination in the simultaneous process. This effect must be a reflection of the reduction of the average pore size in the calcined shell of the particles by the occurrence of the sulfation reaction, which, as we pointed out before, forms a solid product that is bulkier than the solid reactant it replaces. The decreasing average pore size increases the diffusional limitations that CO_2 experiences as it is transported through the decomposed layer and thus slows down the calcination reaction.

In the case of the Greer limestone particles (Figures 1 and 2), the weight loss in the sequential process becomes eventually smaller than that in the simultaneous process, indicating that larger quantities of sulfur are removed per unit of weight of limestone in the former. For the Iceland spar, the sequential process shows larger weight loss than the simultaneous process at all times, but this does not mean that the sulfur uptake is larger in the latter. The analysis of the sulfation data of Greer limestone and Iceland spar (Sotirchos and Zarkanitis, 1992) showed that the mass transport limitations in the interior of the calcined particles are much higher in the case of Iceland spar. This is why much smaller weight changes are observed in the sulfation of Iceland spar calcines (compare Figures 3 and 4 with Figures 1 and 2). (Different reaction temperature was used for each of the two solids, but changing the reaction temperature from 750 to 850 °C does not lead to very large changes in the uptake vs. time curves.) Because of the smaller diffusion coefficient in the product layer, the calcination of Iceland spar particles requires more time to be completed than that of Greer limestone particles. As the calcined layer is sulfated and the effective diffusivity of CO_2 is decreased, the rate of calcination decreases faster than in the absence of the sulfation reaction, practically ceasing when the pores at the external surface becomes plugged with solid product. A significant fraction of the carbonate remains unreacted, and as a result, the simultaneous process curves stay above those of the sequential process at all times. Some unreacted material must also remain in the Greer limestone particles, and therefore, the difference between the sulfur uptake in the sequential process and that in the simultaneous process for this solid must be much larger than what the weight change vs. time curves of Figures 1 and 2 suggest.

The comparison of Figures 1 and 2 with Figures 3 and 4 reveals that the calcination of the Iceland spar particles takes much longer than that of the Greer limestone particles. This difference is a consequence both of higher mass transport limitations in the interior of the Iceland spar particles and of the lower reaction temperature used for samples of this solid. The same observation applies to differences observed between the curves for the other processes, and therefore, it is difficult to determine the effect of temperature on the sequential and simultaneous processes from the results of Figure 1-4. Conclusions on the effect of temperature may be extracted by comparing the results of Figure 1 with those of Figure 5 for Greer limestone particles reacted at 750 °C. It is seen that lower reaction temperatures lead to lower calcination rates and larger differences between the sequential and simultaneous processes. For the same limestone precursor, a reduction in the temperature increases the duration of the calcination process because it decreases the intrinsic rate of the calcination reaction and, as the analysis of the sulfation results showed (Sotirchos and Zarkanitis, 1992), the diffusion coefficient in the calcined layer. On the other hand, the reaction temperature does not influence significantly the intrinsic rate of sulfation, and thus, the time needed to plug the pores at the external surface with solid product remains about the same. Because of these two effects, a reduction in the reaction temperature increases the time of interaction between the calcination and sulfation reactions in the simultaneous process, leading to increased differences between the total weight change curves of the sequential and the simultaneous processes.

The comparison of Figure 1 with Figure 2 and Figure 3 with Figure 4 shows that an increase in the particle size decreases the rates of all processes and leads to larger, in a relative sense, differences between the sequential and simultaneous processes. The first effect is due to the existence of intraparticle diffusional limitations in the interior of the reacting particles, which tend to intensify with increasing particle size. On the other hand, the differences between the sequential and simultaneous processes increase with increasing particle size because – as when the temperature is decreased – the slowing down of the calcination reaction lengthens the time interval over which interaction of sulfation and calcination takes place. An increase in the particle size has a dramatic effect on the overall rate of sulfation of the calcine but it does not affect the intrinsic rate of the sulfation reaction and, therefore, the conversion vs. time curve at the external surface of the particles.

3. SUMMARY AND CONCLUSIONS

The following accomplishments were made under this project during the six-month period from August 1995 to January 1996 that is covered by this report: Computer simulation algorithms were formulated for computing structural properties and effective diffusion coefficients and their evolution with the conversion in porous structures of the type obtained from calcination of limestones and dolomites; simultaneous calcination and sulfation experiments were carried out using three limestone samples of well characterized sulfation, sulfidation, and calcination behavior; preparatory work was done on the development of a high pressure thermogravimetric analysis system.

Two limestone samples of high calcium carbonate content were used for simultaneous calcination and sulfation experiments. Comparison of the obtained weight change (overall reactivity) vs. time results with those obtained from sequential calcination and sulfation experiments revealed the existence of significant quantitative differences in the behavior patterns of the two processes even for small particle sizes. These differences increased with decreasing calcination temperature, increasing particle size and increasing diffusional limitations in the porous material formed during calcination. It is believed that the main cause for all these effects is the lengthening of the time required for completion of the calcination reaction, which leads to increased interaction between the calcination and sulfation reactions in the simultaneous process.

From the variation with time of the difference in weight change between the simultaneous and sequential processes, it was concluded that under simultaneous calcination and sulfation conditions, calcination is not completed and much smaller amounts of sulfur are absorbed by the solid. Since it is the simultaneous process that is encountered in practical applications, this suggests that it is not possible to obtain quantitative information on the performance of a limestone in an actual desulfurization process directly from studies of the sequential process. If a mathematical model is available for the simultaneous calcination process, one can use the results from the study of the sequential process to validate the model for the individual reactions and then use it to determine the performance of the limestone in the simultaneous process. A rigorous model that accounts for all the important phenomena that are encountered in the simultaneous process is currently under development.

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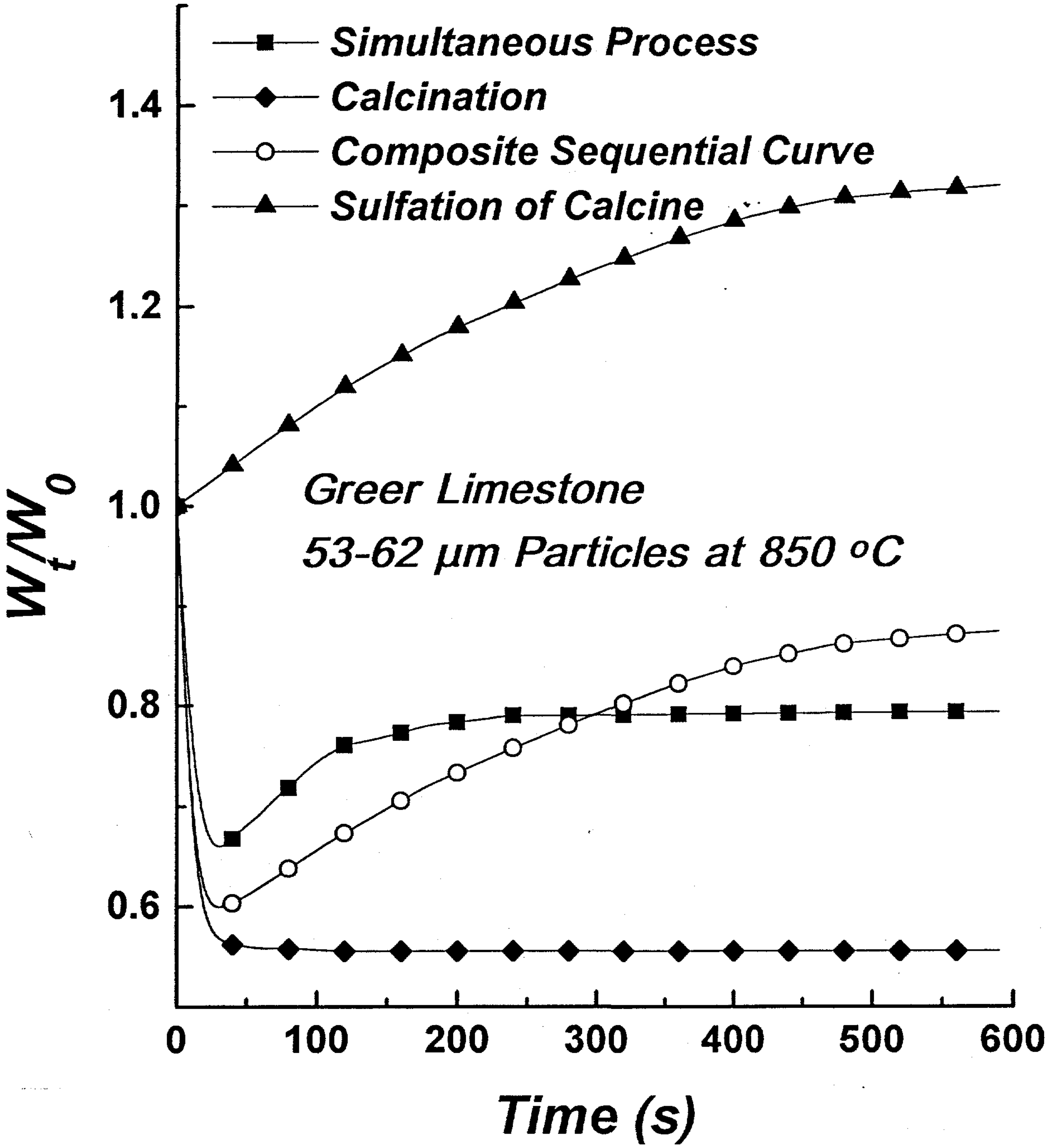

Figure 1. Weight change vs. time for Greer limestone 53-62 μm particles at 850 °C.

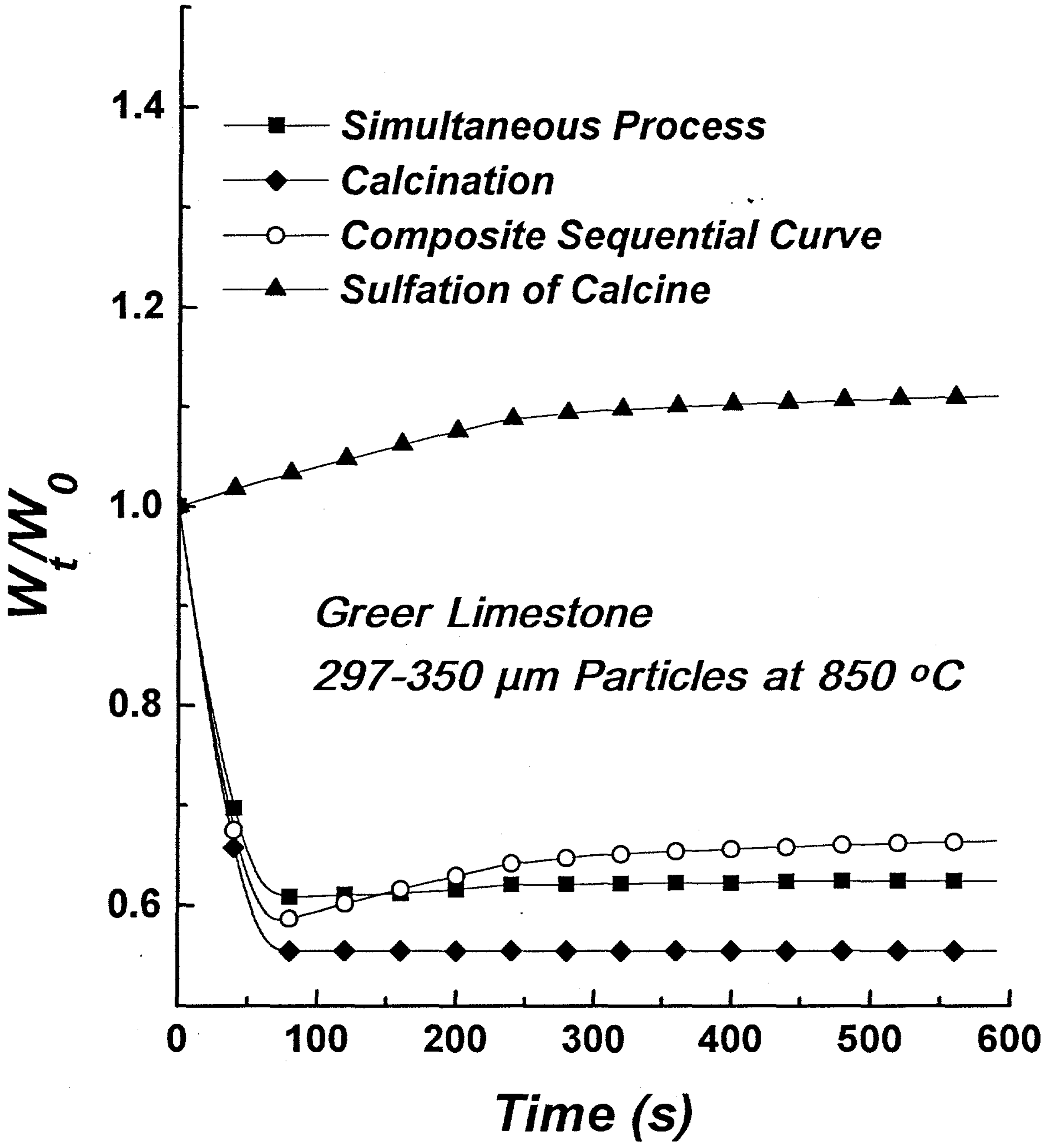

Figure 2. Weight change vs. time for Greer limestone 297-350 μm particles at 850 °C.

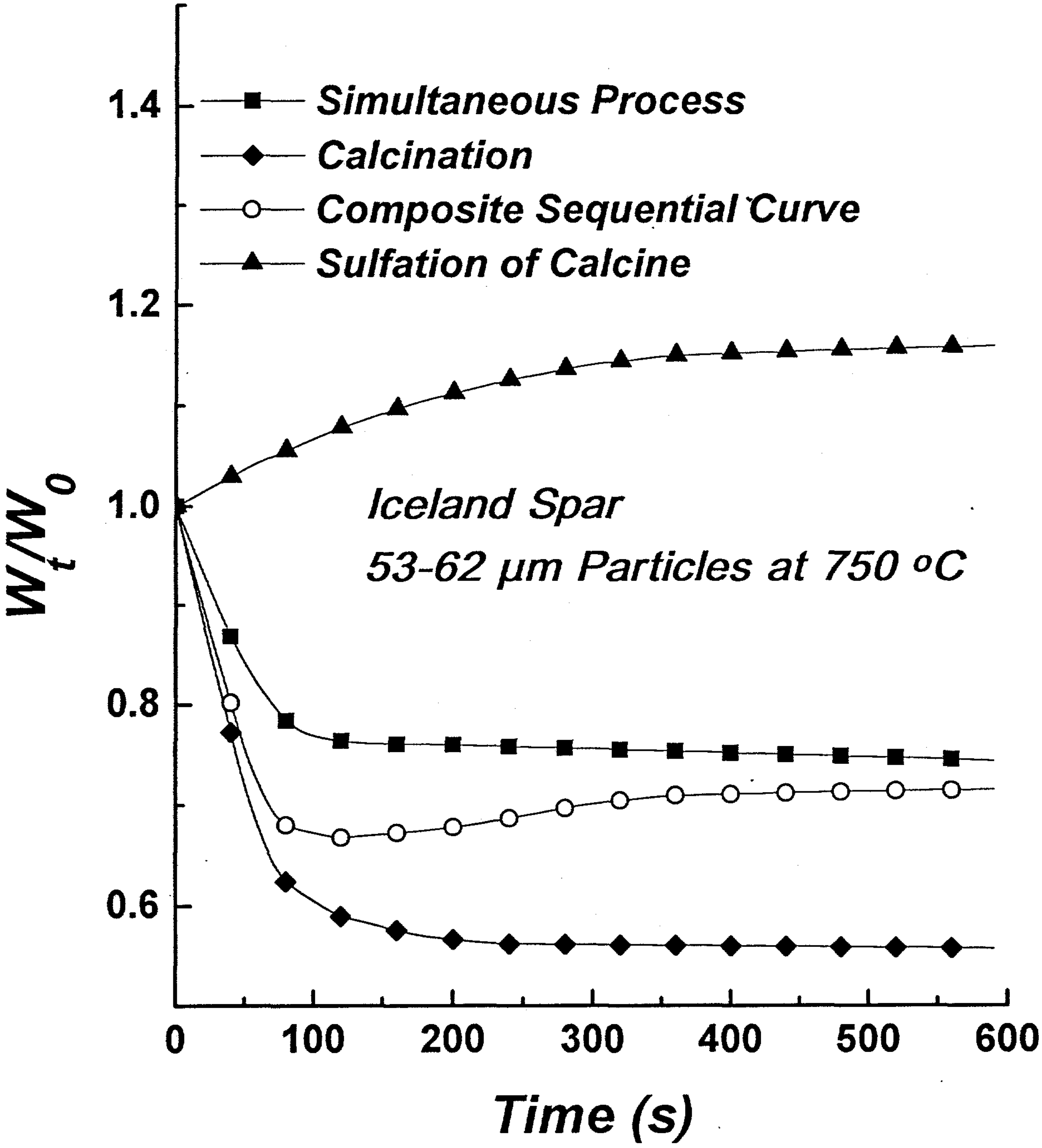

Figure 3. Weight change vs. time for Iceland spar 53-62 μm particles at 750 °C.

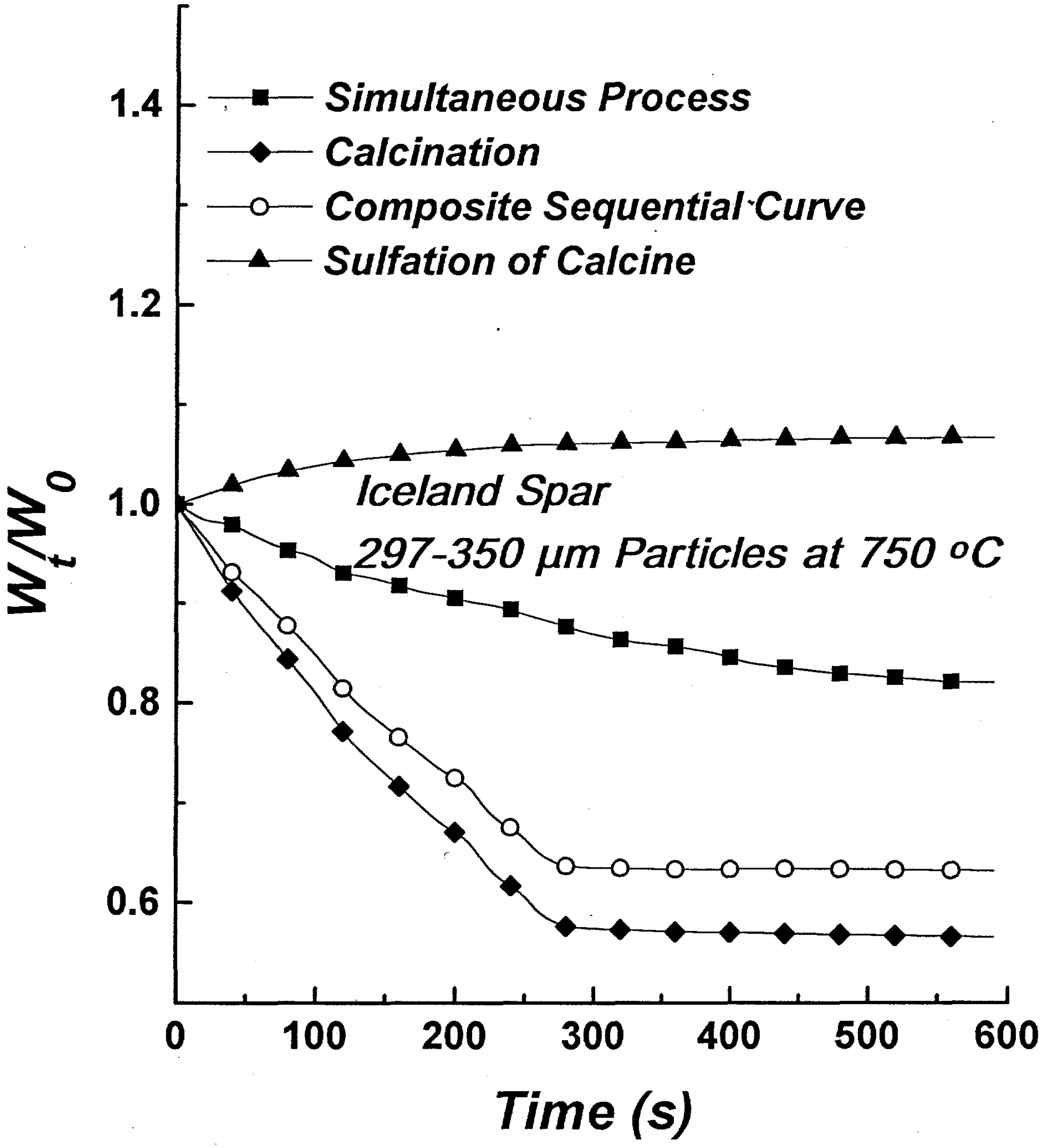

Figure 4. Weight change vs. time for Iceland spar 297-350 μm particles at 750 °C.

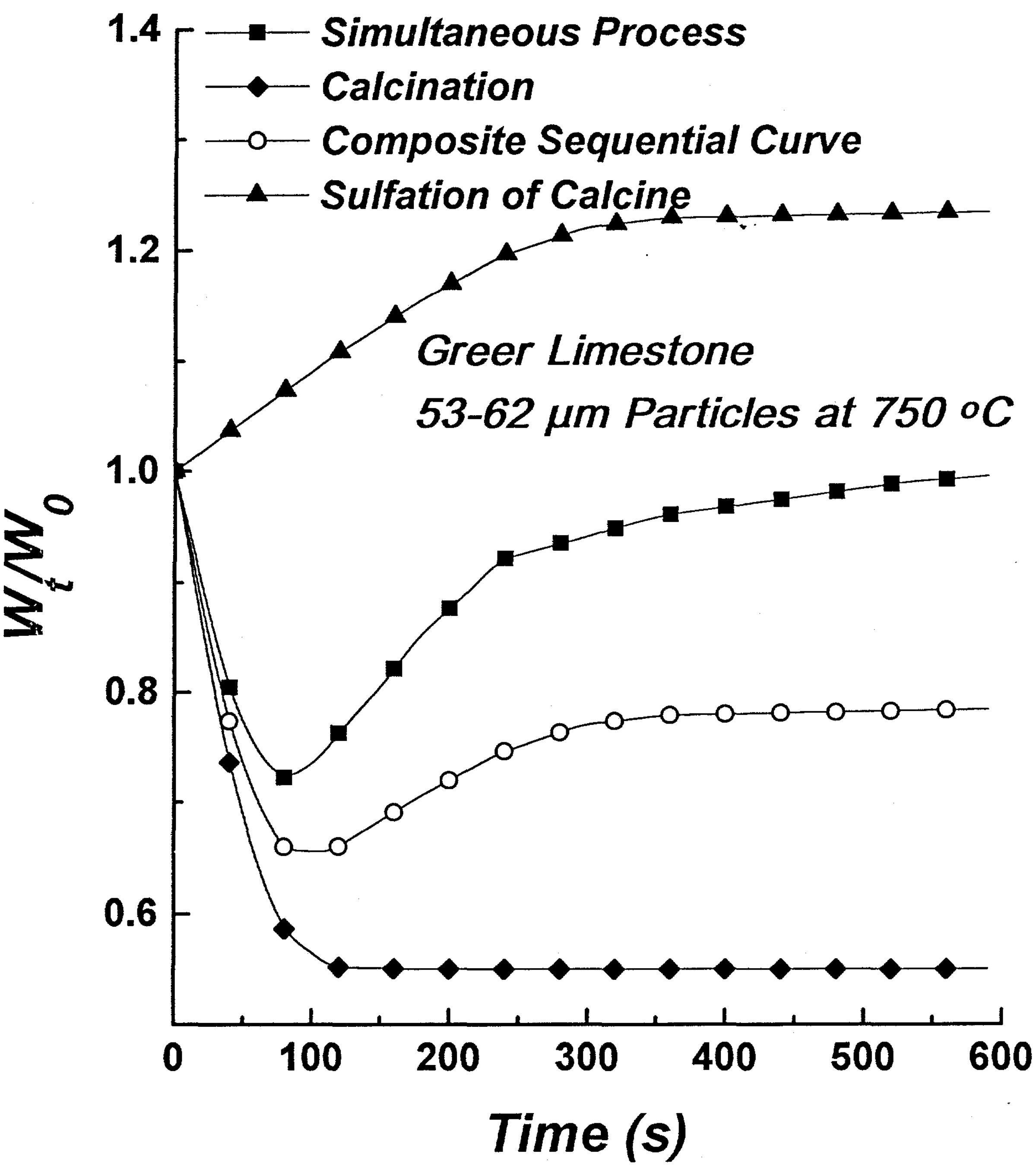

Figure 5. Weight change vs. time for Greer limestone 53-62 μm particles at 750 °C.