Comminution of Limestone During Batch Fluidized-Bed Calcination and Sulfation

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Batchwise fluidized-bed calcination and sulfation of a limestone were done to investigate particle comminution phenomena and their relation with parallel occurrence of reactions. Operating conditions of the bed were those typical of atmospheric bubbling fluidized-bed combustors. A general framework of comminution phenomena is outlined, which includes different types of fragmentations as well as attrition by abrasion. Comminution processes were characterized by following the modifications of bed sorbent particle-size distribution and the elutriation rates of fines throughout conversion. Mutual interactions between comminution processes and the progress of chemical reactions are assessed.

Scope

Sulfur oxide emissions control in fluidized-bed combustors is usually accomplished *in situ* by injection of limestone. Under conditions typical of atmospheric fluidized-bed combustion, limestone first undergoes thermal decomposition (calcination) and then sulfation. During their processing in the fluidized bed, sorbent particles are also subject to comminution phenomena. On the one hand, comminution determines the size distribution of sorbent particles established at steady state in the bed and the production of fines leaving the reactor in the flue gases. On the other hand, it may lead to the removal of the impervious layer formed at the external surface of the particles upon sulfation. The first aspect is related to the issues of losses of partially unreacted sorbent and of the environmental impact of the operation. The second aspect is closely connected to the kinetics and the effectiveness of sorbent utilization. Investigation on comminution of sorbents can be of paramount importance in optimizing the design and the operation of fluidized beds as tools for clean combustion of high sulfur fuels.

Different terminologies have been used by researchers to define the various mechanisms by which particles undergo comminution in fluidized beds (Blinichev et al., 1968; Bridgwater, 1987). In the present article the phenomenological framework proposed by Chirone et al. (1991) to analyze comminution of carbons in a fluidized-bed reactor will be assumed as a reference, after proper redefinition of terms (Figure 1 and Table 1). In the context of limestone comminution, *primary fragmentation* is that which occurs immediately after the injection of the particles in the bed, as a consequence of thermal stresses due to rapid heating of the particles, and of internal overpressures due to carbon dioxide emission after thermal decomposition. It results in the generation of either coarse or fine fragments. During their processing in the fluidized bed, sorbent particles are also subject to *attrition by abrasion* and *secondary fragmentation*. Both processes are determined by mechanical stresses due to collisions with other particles or with the internals of the reactor. According to Blinichev et al. (1968) these phenomena are classified on the basis of the typical size of the generated fragments: attrition by abrasion generates finer and quickly elutriable fragments; secondary fragmentation generates coarser and substantially nonelutriable fragments. Attrition by abrasion depends on the resistance of the bed particles to surface wear. Secondary fragmentation should rather be related to the resistance of the particles to the impacts on the walls and the internals of the bed or in the jetting region of fluidized beds (Ghadiri et al., 1995). *Percolative fragmentation* is associated with the loss of connectivity of the solid porous structure that occurs whenever particle voidage increases, by chemical reaction, beyond a threshold (Kerstein and Niksa, 1984). This results in the generation of either coarse or fine fragments, depending on the porous texture of the solid. In the framework of limestone processing in fluidized-bed combustors, occurrence of percolative fragmentation might be anticipated after calci-

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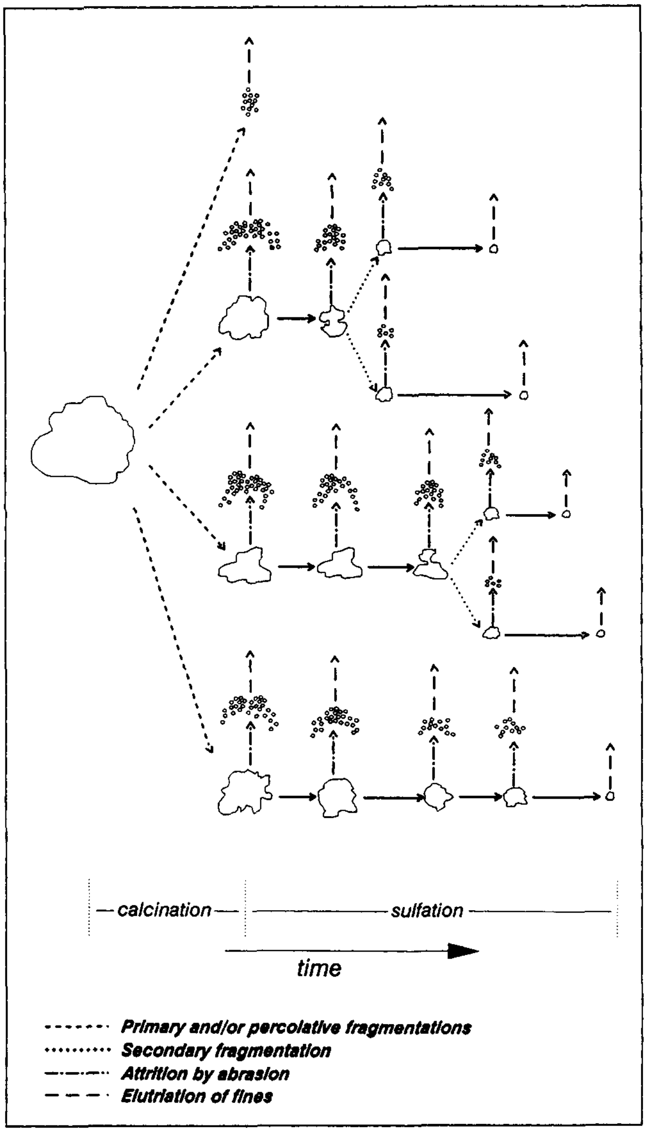

Figure 1. Series-parallel comminution phenomena occurring to limestone.

nation, as this process gives rise to an increase in particle voidage. On the other hand, sulfation of lime takes place with the generation of a coherent solid product and with decreasing voidage, and therefore it cannot lead to percolative fragmentation.

A limited number of studies on comminution of sorbents in fluidized beds are found in the literature. In particular the attrition tendency of limestone particles in fluidized bed was investigated at room and low temperatures (Franceschi et al., 1980; Vaux and Shruben, 1983; Ray et al., 1987), and after calcination at high temperatures (700–900°C) (Merrick and Highley, 1974; Vaux and Fellers, 1981; Vaux and Shruben, 1983; Chandran and Duqum, 1989). Lee et al. (1993) studied the attrition tendency of precalcined CaO at low temperatures (20–180°C). The only studies that considered sorbent attrition occurring during parallel calcination and sulfation were those of Chandran and Duqum (1989) and of Couturier et al. (1993). The fragmentation of calcium-based sorbents under high-heating-rate and short-residence-time conditions was recently characterized by Hu and Scaroni (1995).

The aim of this work is to investigate the relevance of comminution phenomena during calcination and sulfation of limestone particles in a bubbling atmospheric fluidized bed. In particular, we highlight the existence and the mechanisms of the mutual interactions between comminution phenomena and chemical reactions, in relation to changes in particle morphology and mechanical properties with conversion. Attention is also focused on the effect of some operating variables (fluidization gas velocity, size distribution of limestone and of inert particles in the bed, as well as relative amounts of limestone and inerts) on comminution during calcination and sulfation.

Conclusions and Significance

Comminution during fluidized-bed calcination and sulfation of a limestone has been characterized in batch experiments at 850°C. Attention has been focused on the occurrence and the extent of different comminution processes, namely primary fragmentation due to sudden particle heat up and release of carbon dioxide during calcination; percolative fragmentation due to loss of connectivity in the porous particle structure; secondary fragmentation (yielding relatively coarse nonelutriable fragments); and attrition by abrasion (yielding elutriable particulates) due to collisions and surface wear of sorbent particles with bed solids and reactor walls and internals.

Experiments were carried out under three reaction conditions: (1) calcination of limestone under inert atmosphere; (2) sulfation of precalcined limestone; and (3) simultaneous calcination and sulfation of fresh limestone in atmospheres containing SO_2 and O_2. Experiments were conducted to characterize the changes of the particle-size distribution of bed sorbent as well as the rate the elutriable fines were generated by comminution. All types of fragmentation proved negligible under each experimental condition. Attrition by abrasion was the dominant comminution mechanism and showed a strong dependency on the course of calcination and sulfation reactions and on the extent of particle rounding off. The fines

Table 1. Classification of Comminution Phenomena Occurring to Limestone

Comminution Phenomenon	Cause	Product
Primary fragmentation	Carbon dioxide release Thermal shock	Coarse and fine particles
Secondary fragmentation	Impacts	Coarse particles
Attrition by abrasion	Surface wear	Fine particles
Percolative fragmentation	Loss of particle connectivity	Coarse and fine particles

generation rate was maximum at the beginning of the calcination tests, then decaying to a steady value after conversion and particle rounding off were complete. Exposure of precalcined limestone to atmospheres containing SO_2 and O_2 further reduced attrition until a new, much lower steady level of fines generation rate was attained. The behavior observed during separate calcination and sulfation, as well as during simultaneous calcination and sulfation, was explained by a combination of particle rounding off and of the change in mechanical properties of the solid with the course of reaction.

The influence of main operating bed variables, namely superficial gas velocity, mass, and particle size of the sorbent and of inert bed solids (sand), on fines generation has been investigated. Experimental results confirm the validity of the relation.

$$E = k(U - U_{mf})m/d,$$

which has already been proposed and extensively applied to the attrition of carbon during the fluidized-bed combustion of coals.

Experimental Studies

Apparatus

The experiments were carried out in a stainless steel (AISI 312) atmospheric bubbling fluidized-bed reactor 40 mm ID and 1 m high (Figure 2). The fluidization column was heated by two 2.2-kW electric furnaces. The temperature of the bed, measured by means of a chromel–alumel thermocouple, was kept constant by a PID controller. The fluidization gas distributor was a perforated plate with 55 holes 0.5 mm in diameter disposed in a triangular pitch.

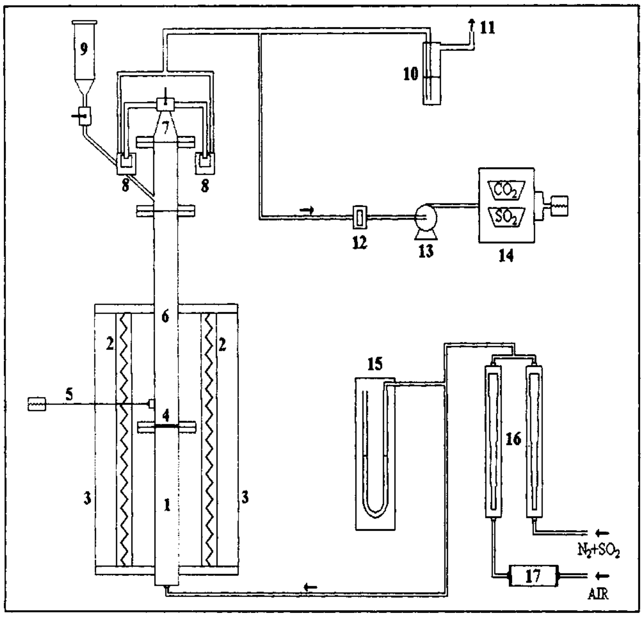

Figure 2. Experimental apparatus.

(1) Gas preheater; (2) electrical furnaces; (3) ceramic insulator; (4) gas distributor; (5) thermocouple; (6) fluidization column; (7) head with three-way valve; (8) sintered brass filters; (9) hopper; (10) SO_2 scrubber; (11) stack; (12) filter; (13) membrane pump; (14) gas analyzers; (15) manometer; (16) gas flowmeter; (17) air dehumidifier (silica gel).

Table 2. Chemical and Physical Properties of the Limestone

Mineralogical Analysis	100% Calcite
Chemical composition	
$CaCO_3$	96.8%
$MgCO_3$	2.4%
Others	0.8%
Loss on ignition (CO_2)	43.9%
Physical characteristics	
Porosity	
Initial rock	6.15%
After calcination	38.0%
Surface area, m^2/g	
Initial rock	0.247
After calcination	10.5
Density, g/cm^3	
Initial rock	2.42
After calcination	1.65

Batches of material could be fed to the reactor via a hopper connected sideways to the upper part of the freeboard. The latter was equipped with a three-way valve. By operating this valve it was possible to convey flue gases alternately to two removable filters of sintered brass. This device allowed time-resolved collection of elutriated fines. Analysis of CO_2 and SO_2 concentrations in the flue gas was accomplished by means of two on line Hartmann & Braun NDIR analyzers.

Materials

The bed material consisted of sorbent alone or in mixtures with an inert material, namely sand. Mixtures of limestone and sand were prepared starting from batches of the two materials independently sieved in given particle-size ranges prior to mixing.

The sorbent was an Italian limestone (Massicci), whose chemical and physical properties are reported in Table 2. In particular, values of the porosity and surface area of limestone and of precalcined limestone reported therein have been determined by nitrogen adsorption. Batches of sorbent were sieved in the three nominal size ranges—300–425 μm, 425–600 μm, 600–850 μm—with Sauter mean diameter of $d = 390, 570, 760$ μm, respectively. Minimum fluidization velocities of precalcined limestone at 850°C were experimentally found to be $U_{mf} = 0.03, 0.055, 0.10$ m/s, respectively.

Sand belonged to the four nominal size ranges 300–425 μm, 425–600 μm, 600–850 μm, and 850–1,000 μm. Minimum fluidizing velocities were 0.12, 0.17, 0.27 and 0.40 m/s, respectively.

Procedures

The reactor was charged with a bed made of limestone or sand (100–200 g), and then heated to 850°C prior to each experiment. The superficial velocity of the fluidizing gas varied between 0.57 and 1.45 m/s. Velocity excess with respect to the minimum for fluidization varied between 0.40 and 1.3 m/s.

Experiments were performed under three different reaction conditions: calcination, sulfation, and simultaneous calcination and sulfation.

Calcination Experiments. During the calcination tests a sample of fresh limestone was added to the bed made of sand or of previously calcined limestone, fluidized with air. Ten to

20 g of fresh limestone were added in each run. These amounts were a trade-off between the need to ensure significant quantities of fines collected as elutriated material and the requirement to limit cooling down of the bed after limestone injection, because of the strong endothermicity of calcination ($\Delta H = 183$ kJ/mole $CaCO_3$). Cooling down was of the order of 10–20°C, depending on the size of the limestone sample added to the reactor. The sample was calcined until complete conversion of $CaCO_3$ to CaO occurred, as indicated by the vanishing of CO_2 concentration in the flue gases.

Sulfation Experiments. Experiments were carried out by feeding a batch of 10 to 20 g of fresh limestone into a bed made of sand, fluidized with air. When calcination of the fresh charge and particle rounding off were complete, the fluidizing gas was switched from air to a mixture of dried air and SO_2 with an inlet concentration of 1,800 ppm of SO_2, and 8.5% by volume of O_2.

A limited number of runs (referred to as "differential" as opposed to the "integral" tests just described) were carried out where only 0.5 g of fresh limestone was fed to the bed. Such a limited quantity of limestone was small enough to consider the reactor differential with respect to SO_2. These experiments were especially designed to characterize the apparent kinetics of sulfation. The charge was calcined for 2 min in air before switching to the mixture containing SO_2 and O_2. Concentrations of SO_2 and of O_2 were kept at 1,800 ppm and 8.5% (v/v) at the reactor inlet in all tests. Elutriation rates during these runs were so small that they could be neglected in limestone balance.

Simultaneous Calcination and Sulfation Experiments. These experiments were carried out by feeding a 10- to 20-g batch of fresh limestone into a bed of sand while keeping in the reactor a flow of dry air containing sulfur dioxide (1,800 ppm) and 8.5% by volume of oxygen. Under these conditions calcination and sulfation occurred at the same time.

Monitoring the degree of conversion of the bed particles during calcination and/or sulfation in each batch was accomplished by recording the CO_2 and SO_2 concentration profiles in the flue gas. SO_3 concentration at the reactor outlet was not monitored continuously. However, it was noted that when the fluidizing gas containing SO_2 and O_2 passed through the reactor kept at 850°C without any sorbent, a loss of SO_2 between inlet and outlet was recorded. This loss was attributed to the oxidation of SO_2 to SO_3 inside the reactor by a homogeneous and/or surface catalyzed reaction (Dennis and Hayhurst, 1988). It was determined that under the experimental operating conditions the molar ratio SO_3/SO_2 at the outlet was ≈ 0.09, that is, smaller than the equilibrium value (0.15) calculated under the same conditions. It was assumed that this SO_3/SO_2 molar ratio also remained approximately constant during the sulfation experiments after the injection of limestone (Fieldes et al., 1979). Wet chemical analysis of a few samples of flue gases carried out batchwise during some experiments confirmed the validity of this assumption. In order to account for SO_3 not detected at the outlet of the reactor, the total concentration of sulfur oxides in the flue gases was evaluated as $[SO_2 + SO_3] = [SO_2](1 + 0.09)$.

In a limited number of tests the degree of calcium conversion evaluated from flue-gas analysis was compared with the value independently obtained by chemical analysis of samples of the bed, or by weighing the bed. In any case, agreement was satisfactory, the difference between the values being always smaller than 10%.

In any of the reaction conditions—namely, calcination, sulfation, and calcination/sulfation—two types of experiments were performed: the first (fines generation rate, or FGR, experiments) were designed to measure the rates of fines generation by comminution of the sorbent as it was reacted in the fluidized bed; the second (particle-size distribution, or PSD, experiments) were designed to follow the changes in particle-size distribution of the bed sorbent during conversion. Procedures followed in the two types of experiments differed and will be separately described in the following.

FGR Experiments. Fines generation rates by comminution of bed material were determined by measuring the amount of fines carried over by the fluidizing gas and elutriated from the reactor. The assumption underlying this procedure was that the residence time of elutriable fines in the reactor could be neglected and that the elutriation rate could be assumed to be equal to the rate of fines generation by comminution at any time during limestone conversion. Elutriated fines were collected by means of the two-exit head described in the Apparatus section by letting the flue gas flow alternately through sequences of filters (one being in use while the previous one was replaced) for definite periods of time (ranging from 0.5 to 10 min). In order to prevent hydration and/or recarbonation of the collected material, each filter was quickly put in a drier after each use, where it was cooled down before it was weighed. The difference in filter weights before and after operation, divided by the time interval during which the filter was in operation, gave the average fines generation rate relative to that interval. A limited number of tests repeated under the same experimental conditions indicated that the fines generation rate could be measured with an accuracy of ±10%.

Elutriated fines collected during a limited number of sulfation tests were chemically analyzed to determine the total amount of calcium and the amount of calcium sulfate in the sample.

The fines generation rate of silica sand was quantified separately in "blank" experiments in which only sand was charged in the reactor and fluidized under the same operating conditions as in the FGR experiments. The results of the blank tests led us to conclude that the contribution of fines produced by the attrition of sand never accounted for more than 5% of the total fines generation rate in experiments in which both limestone and sand were present.

PSD Experiments. Particle-size distributions of bed sorbent were determined by periodically retrieving the bed material from the reactor and subjecting it to particle-size analysis. The two-exit head was removed from the reactor since no fines collection was carried out. Limestone samples were fed to a bed of sand coarser than limestone (e.g., limestone with an average size of 0.57 mm was added to sand with an average size of 0.76 mm; similar additions were made for the other size cuts). Using this procedure, sorbent particles could be retrieved easily after calcination and/or sulfation by discharging the bed from the reactor and sieving the sorbent out of the sand. This operation was carried out gently to avoid further comminution of the particles, but rapidly, because of the propensity of calcined sorbent to absorb moisture when in contact with ambient air. The sorbent was eventually characterized from the standpoint of particle-size distribution. This was determined by image analysis with the aid of an optical microscope. Image analysis supplied the average projected area of the particles. The average particle diameter was calculated as the diameter of the sphere with the same projected area, multiplied by a coefficient (0.72) accounting for the nonsphericity of the particle. Image analysis was preferred to sieving in order to prevent hydration and recarbonation of the calcined and sulfated samples. For the same reason image-analysis was carried out while keeping the sorbent particles submerged in carbon tetrachloride.

Results

Sorbent comminution during calcination

PSD Experiments. Considering the rapid heat up of the particles and the associated release of carbon dioxide upon calcination, primary fragmentation of particles, in the meaning established in the Scope section, could be anticipated. At the same time, the increase of particle voidage associated with calcination might lead us to expect that percolative fragmentation could occur as well. Experiments have been purposely carried out to compare particle-size distribution before and after sorbent calcination in a fluidized bed. Figure 3 shows the cumulative size distributions of limestone particles before and after calcination at 850°C in a fluidized bed. Data refer to particles with initial sizes of 600–850 μm. A similar comparison was carried out for the other two particle sizes investigated. Analysis of the curves reported in the figure suggests that a 10% decrease of the Sauter mean diameter of the particles is associated with the calcination process. It is recalled here that calcination occurs with a decrease in the molar volume of the sorbent (from 36.9 cm^3/mol of $CaCO_3$ to 16.9 cm^3/mol of CaO; Dam-Johansen and Østergaard, 1991), but these variations are partially balanced by the increase in porosity from 6.2% to 38% (Table 2). According to these values, we would expect a decrease of about 8% in the mean diameter because of this effect. Other effects should be attributed to attrition by abrasion and possibly to fragmentation of the particles. On the whole, the occurrence of fragmentations, either primary, secondary, or percolative, during and after limestone calcination, cannot be inferred under the operating conditions tested from analysis of the particle-size distribution of the bed sorbent. This is consistent with results of previous studies (Merrick and Highley, 1974; Vaux and Fellers, 1981; Vaux and Shruben, 1983; Chandran and Duqum, 1989), where it was found that disintegration of limestone particles was a consequence only of attrition by abrasion (with generation of elutriable fines), and no appreciable fragmentation of the particles was observed. In particular, Hu and Scaroni (1995) found, by means of a laser heating technique, that limestone was able to withstand high heating rates, up to a temperature of 1600°C, without significant fragmentation.

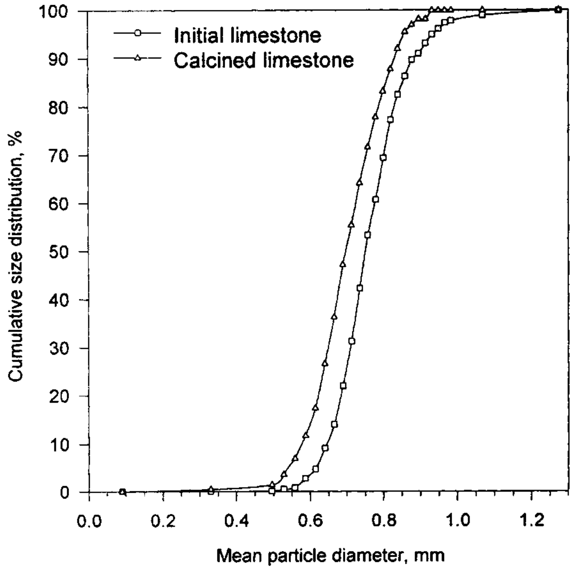

Figure 3. Cumulative size distribution of limestone particles of initial mean size 0.76 mm before and after calcination at 850°C in fluidized bed.

It is interesting to compare the results obtained in the present study with those reported by Lyngfelt and Leckner (1991). Negligible fragmentation of the sorbent could be inferred from the size distributions of fresh and bed material during the operation of an atmospheric fluidized combustor in the bubbling regime. On the other hand, large discrepancies between the average size of fresh limestone and that of bed material were observed in the fast fluidization regime. The same observation is reported by Couturier et al. (1993): significant limestone fragmentation was recorded by these authors in the early stage of limestone processing in a circulating transport reactor at large gas velocity. It is likely that the stronger impact loading of the particles under fluidization conditions typical of CFBCs favors secondary fragmentation of the particles.

FGR Experiments. Figure 4 reports the typical trend of the rate of fines elutriated from the bed E as a function of time during calcination of limestone. As already pointed out, E is assumed equal to the rate of fines generation by comminution. In the same figure the degree of conversion of calcium carbonate into the oxide, obtained by working out the CO_2 concentrations at the reactor outlet, has been reported. For comparison, Figure 4 also reports the fines generation rate and the degree of conversion measured during sulfation of the precalcined lime, which will be discussed later. The E vs. t curve during calcination shows a decreasing trend, until a steady-state value (E_∞) is reached. The initial higher fines generation rate might be due to two processes: the rounding off of the fresh particles by mechanical removal of surface asperities, and the occurrence of calcination. The progress of calcination might in turn be associated with the occurrence of primary and percolative fragmentations, as well as to the change in the morphological and mechanical properties of the solid upon loss of carbon dioxide. Comparing the curves in Figure 4 suggests, however, that decay of the fines generation rate to a steady value occurs over a time scale much longer than that necessary for the completion of calcination. It is therefore inferred that rounding off of initially rough lime particles prevails in determining enhanced attrition by abrasion in the early stage of their lifetime in the bed. The general data trend reported in Figure 4 is consistent with previous observations at low (Vaux and Shruben, 1983; Ray et al., 1987; Lee et al., 1993) and high temperatures (Vaux and Shruben, 1983; Chandran and Duqum, 1989; Couturier

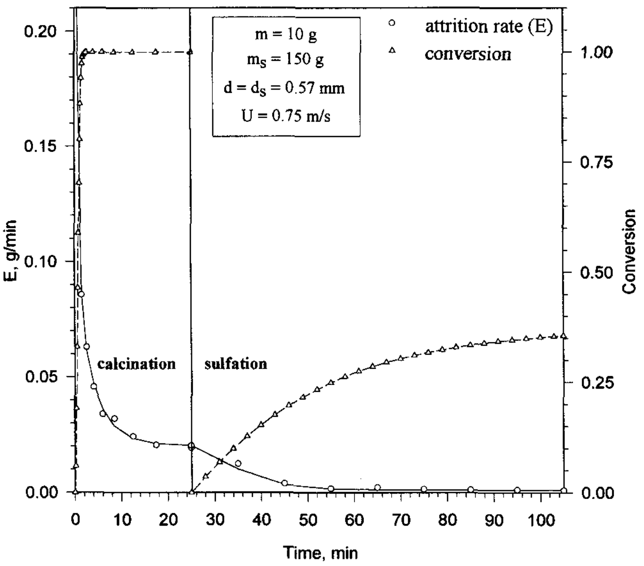

Figure 4. Fines generation rate and conversion degree as a function of time during calcination followed by sulfation of limestone in fluidized bed at 850°C.

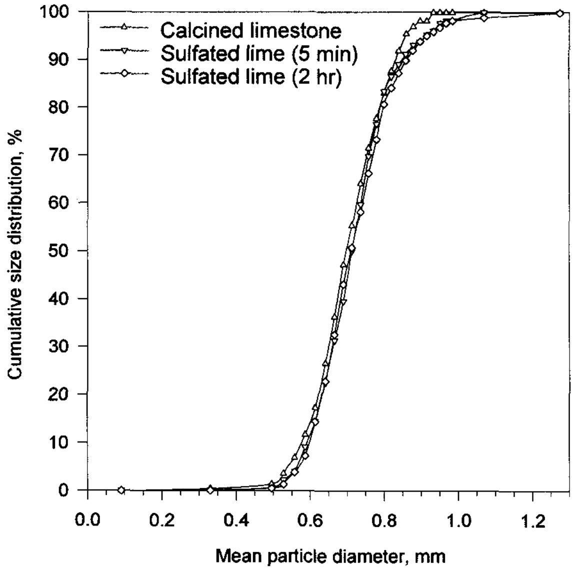

Figure 5. Cumulative size distribution of limestone particles of initial mean size 0.76 mm after calcination and after 5 min and 2 h sulfation at 850°C in fluidized bed.

et al., 1993). In particular, the results of low-temperature experiments, when calcination is not active, further support the conclusion that rounding off controls comminution. The morphology of lime particles, before and after different periods of fluidization, was observed by Lee et al. (1993): sharp edges initially present at the surface of raw lime gradually disappeared with time, while the particles maintained the same sphericity.

Characterization of the particle-size distribution of fines was carried out by sieve analysis of a limited number of samples collected in the filters. Results show that 50% by mass is below 40 μm, 90% below 100 μm, regardless of the size of the fresh sorbent initially charged to the bed. These figures are in line with results reported by Ray et al. (1987).

Integration of fines generation rates over the entire calcination test has been designed to calculate the size reduction of particles owing to attrition. Should attrition be the only mechanism of particle shrinkage, the decrease in particle size would be of the order of 2%. If this value is added to the contribution to shrinkage from volume reduction upon calcination, an overall reduction of particle size of about 10% is calculated. This is about the same reduction as that appearing from comparison of the curves in Figure 3.

Sorbent comminution during sulfation

PSD Experiments. Figure 5 compares the cumulative size distribution of limestone particles that are initially 600–850 μm precalcined in the fluidized bed with those of particles retrieved after 5 min and 2 h sulfation in the fluidized bed. Analysis of the data shows a slight (2%) increase in the Sauter mean particle diameter of the sample during sulfation. This increase occurs mainly during the early stage of the reaction, and should be attributed to the increase in the molar volume of the solid upon sulfation (from 16.9 cm^3/mol of CaO to 46 m^3/mol of $CaSO_4$; Dam-Johansen and Østergaard, 1991). This effect is partially balanced by the porosity decrease and by attrition of the particles in the bed. On the whole, the curves in Figure 5 suggest that secondary fragmentation of the sorbent particles during fluidized-bed sulfation does not take place under the conditions tested.

FGR Experiments. Figure 4 reports the typical trend of the fines generation rate as a function of time obtained during sorbent sulfation. In the same figure the degree of conversion of calcium oxide into the sulfate, obtained after working out the SO_2 *concentration profile at the reactor outlet,* is reported. The value of E at the beginning of sulfation coincides with the steady-state fines generation rate of lime, E_∞. As sulfation proceeds, the fines generation rate decreases until a new steady value E_∞ is reached, about one order of magnitude lower than that observed under calcination conditions. The fines generation rate decays, differently from what is observed during calcination, over a time scale comparable with that associated with the increase in calcium conversion. This finding supports the idea that the changes of the fines generation rate upon sulfation should be related to the progress of the reaction through the formation of a sulfate layer, harder than the oxide, on the particle surface. The observed phenomenology is substantially similar to that reported by Chandran and Duqum (1989) and by Couturier et al. (1993).

Figure 6 reports the degree of calcium oxide conversion to sulfate as a function of time during experiments in which 10 g of fresh limestone within the size ranges 300–425 μm, 425–600 μm, 600–850 μm were injected into a bed of sand. Maximum conversion degrees of the order of 35% are achieved. This value lies within the usual range of degrees of calcium sulfation (20%–50%) reported by previous studies in fluidized bed (Dennis and Hayhurst, 1984; Adanez et al., 1994), depending on the type of limestone, particle size and voidage, pore-size distribution, and surface area. The degree

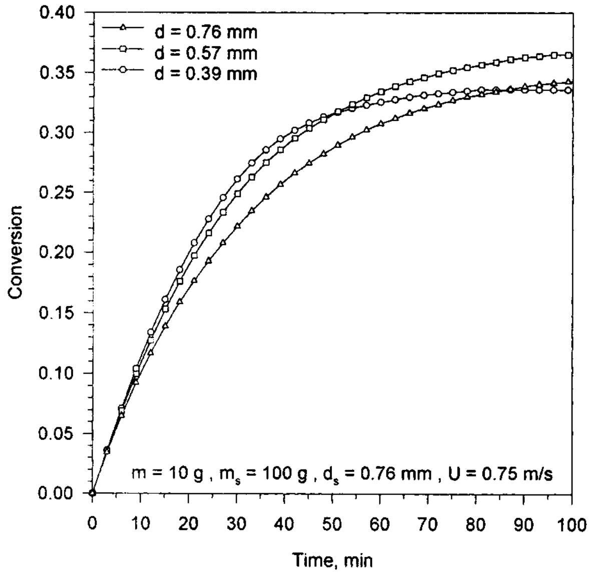

Figure 6. Conversion degree of calcium oxide into sulfate as a function of time for limestone particles of different mean sizes sulfated in fluidized bed at 850°C in integral conditions with respect to SO_2.

of sulfation increases faster at the beginning while at long times the curves flatten out as the maximum degree of conversion is approached. Notably, a nonmonotonic trend appears as one considers the dependence of the maximum degree of conversion on particle size: it increases as the average particle size increases from 390 μm (34%) to 570 μm (36%), but this tendency is reversed when increasing the average particle size from 570 μm to 760 μm (35%). This behavior is consistent with previous observations (Ford and Sage, 1991; Arsic et al., 1991) and has been interpreted to be a result of the conflicting effects of increased effectiveness of sorbent utilization and of augmented sorbent elutriation rate as particle size decreases.

Figure 7 shows the degree of sulfation of the elutriated material X_f as a function of the degree of conversion of bed sorbent to sulfate X. X_f is defined as the fraction of calcium present in the material as sulfate. In order to get a more reliable chemical analysis of the elutriated material, data in Figure 7 have been obtained from experiments carried out for that purpose by injecting 50 g of fresh limestone into a bed of 50 g of sand. As expected, the sulfation grade of the fines increased as X increased. X_f is larger than X for $X \leq 0.07$. Beyond this value X_f becomes smaller than X. In particular, the maximum sulfation grade of fines is about 15–20% when X is about 30-35%. The finding that $X_f < X$ is surprising if one considers that elutriated material results from the removal by abrasion of the surface layer of the particle where the sulfation grade $CaSO_4/(CaO+CaSO_4)$ should be equal to or larger than the average conversion degree X of the particle. The observed behavior could be explained by assuming that the softer CaO is more easily abraded from the surface than the harder $CaSO_4$. In that case, elutriated fines would be richer in unreacted CaO while the sulfate would accumulate on the particle surface.

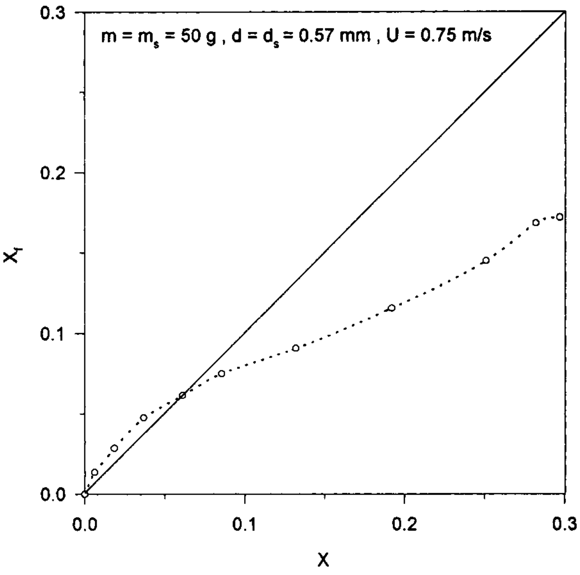

Figure 7. Sulfation degree of the elutriated fines X_f as a function of the conversion degree X of the bed sorbent during sulfation in fluidized bed at 850°C.

Sorbent comminution during simultaneous calcination and sulfation

On the whole, analysis of the results of PSD and FGR experiments when calcination or sulfation are active singly leads to the conclusion that fragmentations do not occur, and that attrition by abrasion is the main way comminution happens under these fluidization conditions. Comminution of limestone during simultaneous calcination and sulfation was therefore studied by FGR experiments only.

Figure 8 reports the fines generation rate as a function of time for the limestone calcined and sulfated simultaneously at 850°C. E vs. t curves obtained during calcination of limestone as well as during sulfation of precalcined limestone under comparable operating conditions are reported for comparison. It can be easily seen that the curve obtained during combined calcination and sulfation lies in between the curves obtained when the two reactions are active one at a time. The same value of attrition rate, E_∞, is obtained under sulfation and under calcination/sulfation conditions after the maximum degree of calcium conversion has been reached.

A general framework for interpreting the time dependence of the attrition rate is to express it as a function, $E = E[t, X(t)]$, embodying both the direct dependence of E on time (due to particle rounding off) and the indirect dependence due to the progress of the reactions (hardening by sulfation). With reference to findings of the present work, the following considerations apply:

1. Calcination is much faster than sulfation. The calcination time scale, t_c is shorter by about one order of magnitude than the sulfation time scale t_s: $t_c \ll t_s$.

2. The decay of the fines generation rate as calcination takes place alone (Figure 4) occurs over a time scale t_{dc} that is much longer than that required for the completion of calcination t_c: $t_{dc} \gg t_c$. Because of this finding, it has been concluded that such decay is mainly controlled by particle round-

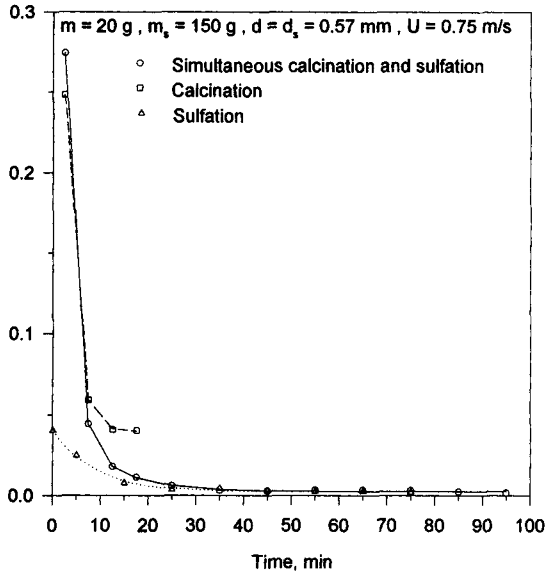

Figure 8. Fines generation rate as a function of time during calcination, sulfation, and simultaneous calcination and sulfation in fluidized bed at 850°C.

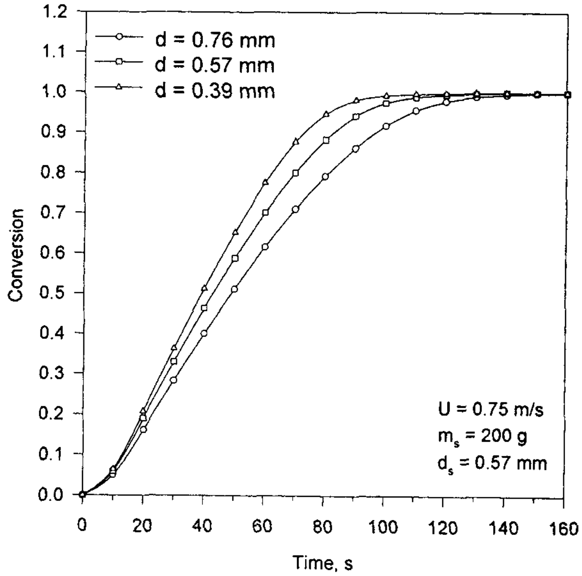

Figure 9. Conversion degree as a function of time for limestone particles of different mean sizes calcined in fluidized bed at 850°C.

ing off and that attrition is a time-dependent rather than conversion-dependent phenomenon.

3. The decay of the fines generation rate as sulfation takes place alone (Figure 4) occurs over about the same time scale t_{ds} as that required for completion of sulfation t_s: $t_{ds} \approx t_s$. Because of this, it has been concluded that the decay is mainly controlled by particle sulfation and that attrition is a conversion-dependent rather than a time-dependent phenomenon.

4. Under the experimental conditions of the present work the time scale of particle rounding off turns out to be about the same as the particle sulfation time: $t_{dc} \approx t_s$.

Attrition during combined calcination and sulfation is dependent on the relative magnitudes of t_c, t_s, t_{dc}, and t_{ds}. In particular if, as in this case, it is $t_{dc} \approx t_s \approx t_{ds}$, changes of the fines generation rate result from the parallel progress of particle rounding off and of sulfation, and it is virtually impossible to discriminate between the two contributions.

Apparent kinetics of calcination and sulfation

Apparent Kinetics of Calcination. Figure 9 shows the extent of calcination as a function of time for limestone batches (10 g) in a fluidized bed at 850°C. The small amount of fresh limestone added to the bed minimized the thermal effects caused by calcination. Data relative to particles belonging to the size ranges—300–425 μm, 425–600 μm, and 600–850 μm—are given in the figure. Comparison between the curves suggests that the calcination times are only slightly dependent on particle size, at least within the size range investigated. About 90% of the calcium is converted into the oxide within 70–90 s after injection of the particles in the bed.

Apparent Kinetics of Sulfation. The apparent kinetics of sulfation has been characterized by a limited number of experiments carried out in conditions in which the reactor could be reasonably approximated as being differential with respect to SO_2. Figure 10 shows the degree of calcium oxide conversion to the sulfate as a function of time for different particle sizes. Conversion degrees of 15% were reached 2.9, 3.8, and 6.2 min after the injection of the samples into the bed for, respectively, particles with average sizes of 390, 570, and 760 μm. These figures are much smaller than those evaluated during the previously reported FGR experiments. This reflects the higher levels of the average SO_2 concentration in the bed under differential reactor operating conditions. The maximum degrees of sulfation are in any case smaller than

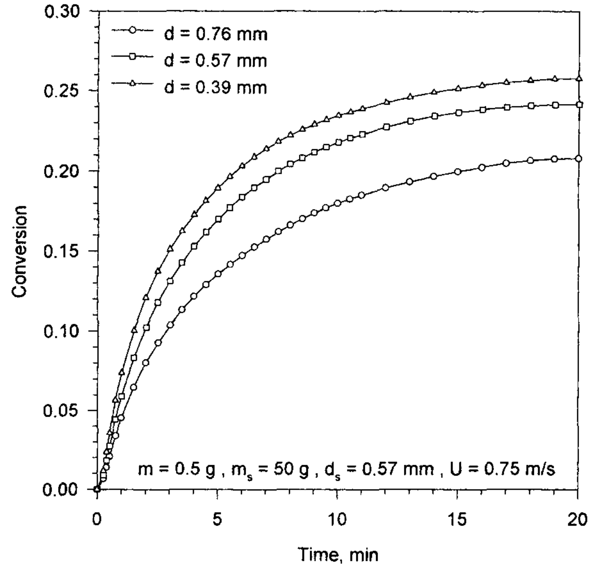

Figure 10. Conversion degree of calcium oxide into sulfate as a function of time for different limestone particle sizes sulfated in fluidized bed at 850°C in differential conditions with respect to SO_2.

30%: 21% for 600–850-μm; 24% for 425–600-μm; and 26% for 300–425-μm particles. It is worth noting that the maximum degree of sorbent sulfation decreases as the particle size increases. This is because the sorbent is utilized less effectively, because of intraparticle diffusional resistances as the particle size increases. The presence of a maximum degree of sorbent sulfation as particle size decreases, observed in Figure 6 and attributed to the increased elutriation of the finer particles, is not detected under differential operation of the reactor. This is probably because of the shorter time and exposure to attrition and elutriation required for complete sulfation of the particles under these conditions.

The smaller maximum degrees of conversion observed under differential reaction conditions compared with those found under integral reaction conditions (Figure 6) need to be explained. This might be because of the more limited extent of sintering to which the sorbent is exposed in the first case. Sintering results in an enlargement of the average particle pore size (Gullett and Bruce, 1987), and ultimately in an increase of the maximum degree of sulfation (Ulerich et al., 1978). This mechanism would also be consistent with the stronger sensitivity of the sulfation rate on particle size (related to stronger intraparticle diffusional resistances) observed under differential reaction conditions (Figure 10) compared to integral reaction conditions (Figure 6).

Influence of operative variables on comminution

This section focuses on the influence of the main operating variables of the bed on the fines generation rate during calcination or sulfation. The variables considered were the superficial gas velocity, the mass and average size of the sorbent in the bed, the relative amount of limestone and sand initially fed into the bed, and the average particle size of the sand.

As already discussed, attrition by abrasion is the dominant comminution mechanism under the conditions tested. It turns out to be a time- or a conversion-dependent phenomenon, depending on whether the key factor is particle round off or sorbent hardening due to sulfation. Whatever the controlling process, it has already been observed that the fines generation rate decays to a finite steady value E_∞ after rounding off and/or sulfation are over. In order to describe the influence of the bed operating variables on sorbent attrition, reference has been made to values of E_∞, which correspond to the steady mechanical and/or morphological properties of the particle.

Table 3 summarizes the steady-state fines generation rate E_∞ found after limestone calcination, sulfation, and simultaneous calcination and sulfation in a fluidized bed. Values correspond to the different initial amounts and particle sizes of the sorbent as well as to the different superficial gas velocities. Analysis of the data in Table 3 suggests the following dependencies:

1. E_∞ is directly proportional to the amount of sorbent, both after calcination and sulfation.
2. E_∞ is inversely proportional to the mean Sauter diametet of the sample, both after calcination and sulfation.
3. E_∞ is proportional to $(U-U_{mf})$. This relation has been experimentally investigated only after calcination.
4. As we have already seen, after simultaneous sulfation and calcination E_∞ is equal to that after sulfation of precalcined limestone, under comparable operating conditions.

The dependencies expressed under 1 to 3 agree with the results obtained by previous investigators using different materials (Merrick and Highley, 1974; Vaux and Shruben, 1983; Ray et al., 1987). These dependencies are lumped together by expressing E_∞ through the equation:

$$E_\infty = k_\infty (U-U_{mf}) m/d. \tag{1}$$

This equation was originally proposed to express the fines generation rate of carbon particles during combustion in fluidized bed (Chirone et al., 1991) and found theoretical grounds in Ray et al. (1987) and in Massimilla and Salatino (1987). In particular the ratio m/d is proportional to the external particle surface exposed to attrition by abrasion, and k_∞ is a constant that depends on the nature of the material.

Table 3. Steady-State Fines Generation Rate and Attrition Constant after Calcination and Sulfation in Fluidized Bed at 850°C for Selected Operative Conditions

Limestone Mass (g)	Limestone Mean Dia. (mm)	Sand Mass (g)	Sand Mean Dia. (mm)	Superficial Gas Vel. (m/s)	E_∞ (g/min)	k_∞ $*10^9$
Calcination						
20	0.57	150	0.57	0.75	0.045	68
15	0.57	150	0.57	0.75	0.032	65
10	0.57	150	0.57	0.75	0.022	64
20	0.39	150	0.57	0.75	0.065	66
20	0.76	150	0.57	0.75	0.033	65
20	0.57	150	0.57	0.57	0.032	65
20	0.57	150	0.57	0.66	0.04	71
20	0.57	150	0.57	0.84	0.048	70
20	0.57	150	0.57	1.00	0.051	63
20	0.57	150	0.57	1.24	0.061	64
20	0.57	150	0.57	1.45	0.075	71
Sulfation						
20	0.57	150	0.57	0.75	0.002	2.8
15	0.57	150	0.57	0.75	0.0018	2.7
10	0.57	150	0.57	0.75	0.0014	3
20	0.39	150	0.57	0.75	0.0027	2.6
20	0.76	150	0.57	0.75	0.0014	3
Simultaneous calcination and sulfation						
20	0.57	150	0.57	0.75	0.002	2.7

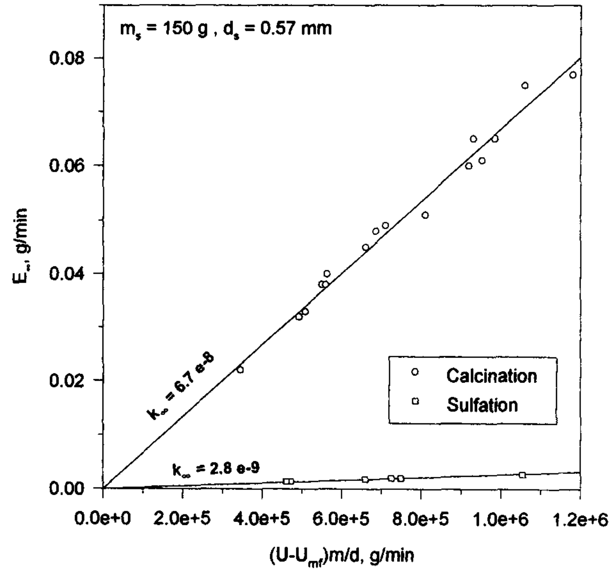

Figure 11. Steady-state fines generation rate as a function of $(U - U_{mf})m/d$ after calcination and sulfation in fluidized bed at 850°C.

In the context of the present work k_∞ depends only on whether limestone underwent calcination alone, or the entire path through calcination and sulfation. The soundness of the approach expressed by Eq. 1 is demonstrated in Figure 11, where the values of E_∞ that appear in Table 3 are plotted vs. the group $(U - U_{mf})m/d$. Best-fit straight lines through data points are also drawn in the figure. Their slope is $k_\infty = 6.7\ 10^{-8}$ and $2.8\ 10^{-9}$, respectively, for calcined sorbents and for the calcined and sulfated sorbents. Values of k_∞ are also given in Table 3 for each experimental condition investigated.

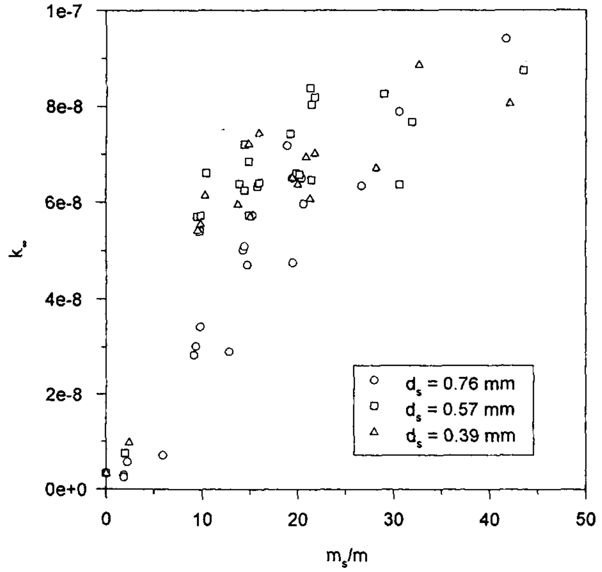

Figure 12. Influence of the relative amounts of sand and limestone and of the sand mean size on the steady-state attrition constant after calcination in fluidized bed at 850°C.

Figure 12 clarifies the influence of the relative amount of sorbent and of the inert material (silica sand) on the fines generation rate. In this figure, k_∞ for limestone calcined (but not sulfated) in beds using different relative inventories m_s and m of sand and limestone, respectively, have been plotted vs. the actual ratio m_s/m. The data points corresponding to $m_s/m = 0$ represent k_∞ obtained when the limestone is calcined in a bed of precalcined sorbent (without sand). The attrition constant increases by almost one order of magnitude as m_s/m increases from 0 to 40. This can be explained as a consequence of the larger abrasive capacity of sand when compared with that of the calcined limestone. Data points seem to indicate that k_∞ has an asymptotic value at large m_s/m. This condition would represent the case where each limestone particle is surrounded only by sand particles. Figure 12 also shows that the mean diameter of the sand particles barely affects the fines generation rate: as d_s decreases, k_∞ increases only slightly.

Notation

d_s = Sauter mean diameter of sand, m
k = attrition rate constant
m = mass of sorbent in the bed, kg
m_s = mass of sand in the bed, kg
t = time, s
U = superficial gas velocity, m/s

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