

Modeling of particle size distribution of limestone in sulfur capture in air and oxy-fuel circulating fluidized bed combustion

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Abstract: Measurements for partition of Ca-containing compounds in particles in air and oxy-fuel combustion are presented. A model for steady and unsteady state particle size distribution (PSD) of limestone including the effects of PSD of the feed, attrition, fly ash, and bottom ash removal is presented. By incorporating models for sulfation, a new model for distribution of Ca-containing compounds CaCO₃, CaO, and CaSO₄ in different particle sizes during sulfation is found. The model can be applied to study the effects of different factors on the PSD of limestone in the bed, to optimize the PSD in the bed, and to study reasons for the measured PSDs and distributions of Ca-containing compounds in different size fractions in the bed in sulfur capture in circulating fluidized bed combustion in air and oxy-fuel conditions.

Keywords: limestone, sulfur capture, circulating fluidized bed, population balance modeling, oxy-fuel

Introduction

The particle size distribution (PSD) is an important factor affecting the fluidization, heat transfer, combustion, and sulfur capture in fluidized bed combustion (FBC) and circulating fluidized bed combustion (CFBC). The solid material mainly consists of bed material, ash, limestone, and char. The particle size is reduced by attrition for ash and limestone and by reaction for char. PSD in the bed depends on the PSDs of the feed material and of the material outgoing as fly ash and bottom ash removal in addition to attrition and reaction.

Population balance models are widely applied in different fields of engineering sciences and biology. Kunii and Levenspiel¹ presented the general differential equation for the PSD in the bed without breakage. After this pioneering work, discretized equations have been applied to study PSD in fluidized and circulating fluidized beds, where PSD is changing due to surface reaction, attrition, or fragmentation. Population balance modeling has been applied in simulating PSD of char,^{2–16} limestone,^{17–25} ash in different solids or ash^{26–37} in FBC and CFBC and in other fluidized bed processes^{38,39} and gasification.^{40–42} The burn-off instead of particle size as the distributed variable has been used.⁴³ Most of the models are steady state, but dynamic evolution of the PSD has also been modeled.^{14,23,34,44,45} Coupling of PSDs and reactions described by shrinking core model have been discussed.^{46,47} The cyclone characteristics affect the PSD of the elutriated particles, which are returned to the reactor. The cyclone affects the demand of limestone.⁴⁸ The solid is divided into different materials such as char,

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ash, CaO, CaCO₃, CaSO₄ and make up sand and each of them is divided into different size fractions in a three-dimensional model for CFB.^{49,50} A balance is written for all of these size fractions. The partitioning of calcium and sulfur between bottom ash and fly ash in a CFB boiler has been studied.⁵¹

Oxy-firing is a promising technology leading to high concentration of CO₂ in flue gases allowing its effective separation for sequestration.^{52–59} There are some differences in sulfur capture in air-firing and oxy-firing as the gas atmosphere and temperature defines the sulfur capture mechanism. In air-firing and high temperature oxy-fuel conditions CaCO₃ is first calcined to CaO and then CaO reacts with SO₂ (and O₂) forming CaSO₄. This reaction path is called indirect sulfation. At a lower temperature (and high CO₂) conditions, CaCO₃ is not calcined due to high CO₂ partial pressure and CaCO₃ directly reacts with SO₂ (and O₂) forming CaSO₄. That reaction path is called direct sulfation. The sulfur capture is worse in direct sulfation region, but capture is enhanced by higher CO₂ partial pressure in direct sulfation region.^{60,61} The higher CO₂ content slows down the calcination reaction and improves the sulfur capture because the formation of dense CaSO₄ layer is prevented due to flow of CO₂ from calcination through the sulfation product layer.^{62,63} Scanning electron microscopy-energy dispersive X-ray spectroscopy micrographs of the particles reacted under indirect and direct sulfation conditions show differences in the sulfur distribution.⁶⁰

The dense CaSO₄ is the main reason for relatively low calcium utilization for sulfur capture in fluidized bed combustion applications. Normally, calcium conversion to CaSO₄ seldom exceeds 30%–40%. Sulfur capture by limestone particles in air-firing and oxy-firing conditions in fluidized beds has been studied.^{59,60} In addition there are some differences in the comminution behavior in air-firing and oxy-firing.^{23,64–67} In air-firing, the particles may undergo extensive primary fragmentation during calcination but in oxy-firing much less fragmentation takes place.^{23,67} During sulfation a product layer consisting of CaSO₄ is formed. The direct sulfation conditions in oxy-firing seem to enhance attrition. Attrition could effectively enhance particle sulfation under oxy-firing conditions by continuously disclosing unconverted calcium to the sulfur-bearing atmosphere.^{22,64,65}

This paper presents a new model for the calculation of the steady and unsteady state PSDs of limestone and distribution of different Ca-containing compounds in the PSD. Instead of a customary population balance model, the derivation of the model equations is based on Dirac's delta function and its properties. This gives a new two-dimensional approach, in

which the particle mass as function of size and compounds can be calculated.

Experimental

Steady state measurements

Experimental methods have been discussed earlier.⁶⁸ The continuously operated, traditional online analyzers of gaseous emissions include O₂, CO₂, CO, NO_x, and SO₂. In addition to the traditional online analyzers, emission measurements are usually complemented with the Fourier transform infrared spectroscopy gas analyzer (H₂O, CO₂, CO, NO, NO₂, N₂O, SO₂, SO₃, HCl, NH₃, HCN, CH₄, C₂H₂, C₂H₄, C₂H₆). The typical location of the Fourier transform infrared spectroscopy measurement point is at the flue gas line between the primary and secondary cyclone.

In addition to flue gas measurements, gas and solid material samples are taken from different levels of the riser during the steady state operation. These samples combined with pressure and temperature measurements describe the combustion profile in detail.

During the test campaign, many measurements are carried out and numerous material samples are collected for further analysis. A typical sampling and analysis procedure for fuel and ash samples is described in the following.

A comprehensive analysis of the prepared fuel is performed on one representative sample of each fuel, including proximate and ultimate analyses. For each test run, the fuel samples are combined to produce one representative fuel sample per test. A minimum of the following components are analyzed from the fuel samples of each test: moisture, ash content (815°C), and sulfur. A comprehensive analysis is performed from the prepared limestone sample, including at least the Ca, Mg, S, and C contents and moisture.

The ashes are sampled at regular intervals during each pilot test run. The ash samples include:

1. Bottom ash
2. Circulation material from the downcomer of the primary cyclone
3. Ash from the downcomer of the secondary cyclone
4. Ash from the gas cooler before the filter
5. Ash from the bag house (if the bag house is used).

All the ashes sampled and discharged during each test run are collected and weighed to define the ash balance and split. The circulation flow rate through the primary cyclone is also measured.

Three separate fly ash samples (3–5) can be analyzed as they are, or they can be mixed in the ratio of mass extracted

Table 1 Typical (minimum) list of chemical analyses for the solid material samples taken from the CFB pilot reactor

Total carbon, C_{tot}
Carbonate carbon, C_{carb}
Combustible carbon (as $C_{\text{tot}} - C_{\text{carb}}$), C_{comb}
Total sulfur, S_{tot}
Total calcium, Ca_{tot} (HCl-soluble calcium)

Abbreviation: CFB, circulating fluidized bed.

from the reactor at different sampling points to produce one fly ash sample per test. From the bottom ash, circulation material and fly ash sample(s) of each test at least components presented in Table 1 are analyzed.

Gas and solid material profiles along the furnace height can be measured with a gas–solid sampling probe (at least four points, Fourier transform infrared spectroscopy and O_2 analyzers) during the specified test runs. In addition to the fact that gas samples can be taken from different locations in the furnace, the temperature and pressure profiles along the riser are measured continuously during all the tests. As well as the analyses shown in Table 1, sieving can be applied to solid material samples to determine PSDs and produce fractional samples for the chemical analysis. Based on the chemical analysis shown in Table 1, concentrations of CaO, $CaCO_3$, $CaSO_4$, and combustible char can be produced with the following assumptions:

1. All carbonate carbon originates from $CaCO_3$;
2. All sulfur originates from $CaSO_4$;
3. The rest of the total calcium, which is not included ($CaCO_3$ and $CaSO_4$), originates from CaO;
4. Combustible char is determined as a difference between total carbon and carbonate carbon.

It is obvious that the assumptions shown above cause inaccuracy in the results, but the main elements can be analyzed with appropriate accuracy and efforts with this approach. The same chemical analyses as shown in Table 1 can also be applied to solid material samples taken during the profile measurements. If sieving is also applied, the fractional profiles for the main chemical components can be produced as a function of furnace height.

Results

The measured PSD of limestone feed and the particle size for the components CaO, $CaCO_3$, and $CaSO_4$ in air-firing and oxy-firing conditions are shown in Figures 1 and 2. The pilot scale CFBC has been described elsewhere.⁵⁵ The masses of different Ca-containing components are shown in Table 2 and other conditions in Table 3. The mass of $CaCO_3$ was much higher in oxy-firing and CaO much smaller as expected,

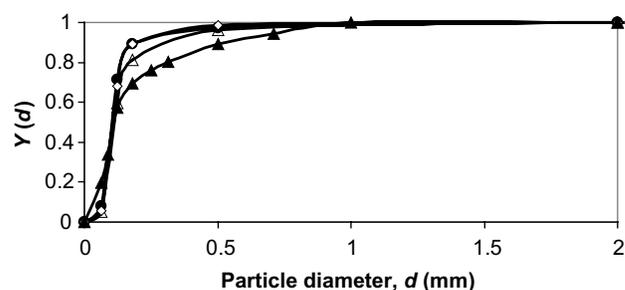


Figure 1 Cumulative PSDs for limestone feed (▲) and measured components CaO (◇), $CaCO_3$ (△), and $CaSO_4$ (●) in the bed in air-firing conditions.
Abbreviation: PSDs, particle size distributions.

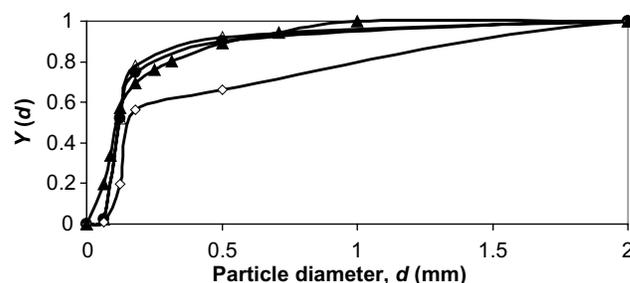


Figure 2 Cumulative PSDs for limestone feed (▲) and measured components CaO (◇), $CaCO_3$ (△), and $CaSO_4$ (●) in the bed in oxy-firing conditions.
Abbreviation: PSDs, particle size distributions.

Table 2 Mass (kg) of different components and Ca in the bed and feed mass flow rate of limestone (kg/s)

Mode	Feed, kg/s $CaCO_3$ (Ca)	Ca/S	Mass, kg $CaCO_3$ (Ca)	Mass, kg CaO (Ca)	Mass, kg $CaSO_4$ (Ca)	Mass, kg Total (Ca)
Air-firing	3.92×10^{-4} (1.57×10^{-4})	2.4	0.0904 (0.0362)	0.6029 (0.4309)	0.6602 (0.1944)	1.3535 (0.6615)
Oxy-firing	6.87×10^{-4} (2.75×10^{-4})	3.3	2.8038 (1.1228)	0.1016 (0.0761)	0.7072 (0.2082)	3.6226 (1.4131)

Table 3 Circulation rate, total bed mass, and ash removal rates by bottom ash and loop seal

Mode	Circulation rate (kg/s)	Total bed mass (kg)	Bottom ash flow (kg/s)	Loop seal ash flow removal (kg/s)
Air-firing	0.239	8.20	8.43×10^{-5}	7.62×10^{-4}
Oxy-firing	0.282	8.85	9.87×10^{-5}	9.17×10^{-4}

since negligible calcination takes place in these conditions. Some differences are seen in the partitioning of the different compounds in different sizes in air and oxy-fuel combustion.

It is also possible to calculate the PSD of Ca by summing its contents in different mass fractions by $m_{Ca} = M_{Ca} (m_{CaO} / M_{CaO} + m_{CaCO_3} / M_{CaCO_3} + m_{CaSO_4} / M_{CaSO_4})$ where m is mass and M is molar weight. For feed this is equal to the PSD of the limestone, since Ca is practically only the

compound CaCO_3 . The cumulative PSD is shown in Figure 3. In air combustion, the bed material containing Ca is smaller than in the feed or in oxy-fuel combustion, which is probably due to primary fragmentation in the calcination stage.

The conversion of particles in different size classes presented in Figure 4 is found as the ratio of mass of Ca in compound CaSO_4 to total mass of Ca in all compounds. It is seen that the conversion in air-firing is higher than in oxy-firing, which is partly due to lower Ca/S ratio in the feed. The shapes of the curves also differ. In air-firing, a minimum conversion is obtained at the diameter ~ 0.25 mm, whereas in oxy-firing the curve is rather flat or there is a slight minimum at size 0.15 mm.

The reason for the minimum observed in air-firing may be due to the method of ash removal. The rate of bottom ash removal is low and most of the material is removed after the cyclone, where there are fewer large particles. The larger particles have a longer time to be sulfated in the bottom area of the bed before entrainment; the smallest size are more rapidly reacted with higher final degree of conversion X_{\max} especially in air combustion before pore plugging. Then the minimum is probably due to loop seal ash removal, where part of particles large enough to be entrained is removed and their average residence time in the reactor becomes shorter.

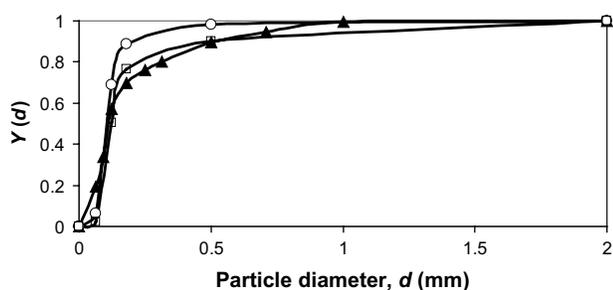


Figure 3 Cumulative PSD for Ca in limestone feed (▲), Ca in air combustion (O), and Ca in oxy-fuel combustion (□).

Abbreviation: PSD, particle size distribution.

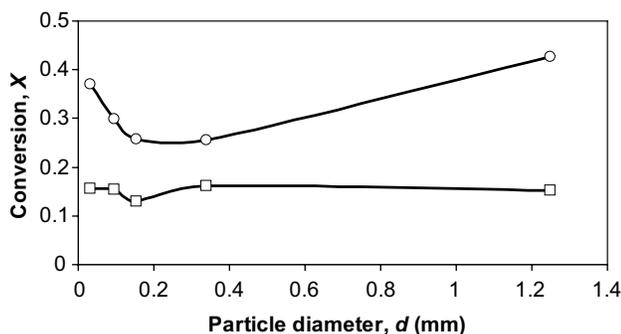


Figure 4 Measured conversion of particles in the bed in air-firing (O) and in oxy-firing (□).

Model

PSDs of different material in CFBC can be simulated by using population balance modeling. In the present paper another approach is taken, which gives the possibility to describe the partitioning of different compounds in different size fractions. The model is based on the application of Dirac's delta function and its properties. First, an analytical solution for the PSD in the bed as function of time with mono-sized feed is derived. Then, the PSD for a general PSD can be found by summing different mono-sized fractions. This treatment also makes it possible to include sulfation in the model, which would otherwise require a complicated two-dimensional population model (particle size and degree of conversion).

In oxy-firing conditions the calcination step does not take place leading to low primary fragmentation, whereas in air-firing conditions particles may undergo extensive primary fragmentation during calcination.^{23,64–67} In the model, the subsequent PSD after primary fragmentation is used as the effective PSD of the feed and attrition is the only comminution mechanism affecting the subsequent PSD. It is also assumed that the attrition products are so small that they are rapidly escaping from the reactor.

Time constant for bed material removal

There are several correlations of the type $dm/dt = -Km$ (m is mass, t is time and K is a coefficient) to estimate the rate of entrainment or elutriation of particles of a size class from the bed.¹ The propensity for entrainment of a particle from the bed increases with increasing difference between the gas velocity and the free settling velocity of the particle as shown by equations presented in the literature.^{69,70}

Later, more sophisticated models for the hydrodynamics of CFBC have been presented. The residence time of particles in the riser has been discussed.⁷¹ In the present paper, the circulation time τ_p is based on measurements, but literature correlations of computational fluid dynamics calculation for estimating the average residence time of a particle size class in the bed ($=1/K$) could also be applied. The time constant for circulation of a particle size was estimated by the relation $\tau_p = m / \dot{m}_p$, where m is the mass of that size fraction in the bed and \dot{m}_p is the measured circulation mass flow rate of the size. Average value (based on total mass and mass flow rate) calculated with measured values presented in Table 2 is shown in Table 4. Figure 5 shows that the time constant increases with increasing particle size, since it takes a longer time for large particles to escape the bed and rise up. This figure only applies for this reactor in these conditions. The measured circulation time is applied to avoid the error caused from literature correlations in this illus-

Table 4 Average time constant for circulation τ_p , ratio of material removal rate from loop seal to circulation rate k , average time constant for bottom ash removal τ_b and average residence time for Ca in the bed τ_{Ca} (mass of Ca in the bed divided by mass flow rate of Ca into the bed)

Mode	τ_p (s)	k	τ_b (s)	$\tau_{Ca} = m_{Ca} / \dot{m}_{Ca,0}$ (s)
Air-firing	34.3	3.19×10^{-4}	97,300	4,213
Oxy-firing	31.4	3.25×10^{-4}	89,700	5,139

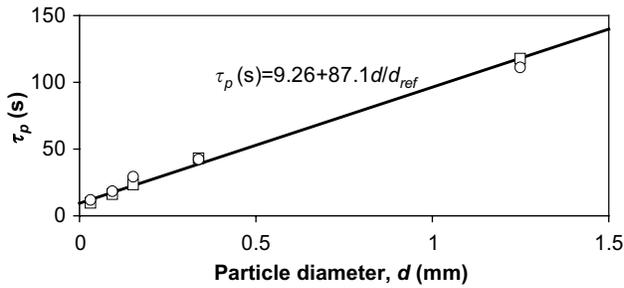


Figure 5 Dependence of circulation time constant on particle size in air-firing (O) and oxy-firing (□) experiments. Reference diameter (d_{ref}) = 1 mm.

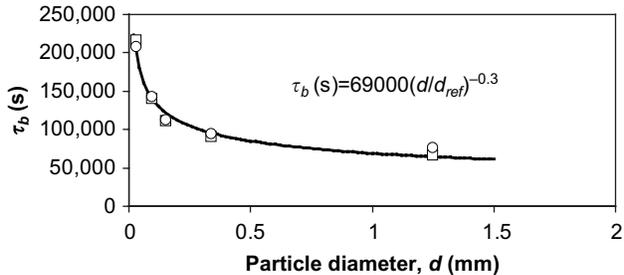


Figure 6 Dependence time constant of bottom ash removal on particle size in air-firing (O) and oxy-firing (□) experiments. Reference diameter (d_{ref}) = 1 mm.

tration, since the emphasis in this paper is in the understanding of the formation of PSD and not in hydrodynamics. However, the method is also applicable to other reactors or operational conditions by applying theoretically or experimentally found correlations for circulation time or mass flow through cyclone³⁴ using methods presented in the literature for hydrodynamics and particle flow. The average time constant for bottom ash removal, $\tau_b = m / \dot{m}_b$, is shown in Table 4. Depending on the removal location τ_b can be dependent on the particle diameter as τ_p or it may be constant if average bed material is removed. If bed material is removed at the bottom, coarse particles are more frequent due to segregation. The dependence of τ_b on particle diameter can be found by experiments (see Figure 6).

Evolution of mass after feeding a mono-sized batch of particles

A batch of material (bed material, ash from coal, Ca) with particle size d_0 is fed into the reactor. The subsequent mass of the batch will decrease due to reduction of particle diameter by attrition and due to loss of particles in fly ash and bottom ash,⁷²

$$m / m_0 = [f(t)]^3 g(t) \tag{1}$$

m_0 is mass of Ca, ash or char introduced to the reactor. Functions $f(t) = d/d_0$ and $g(t) = n/n_0$ describe the change of particle diameter and number of particles in the fluidized bed as function of time.

The particle size reduces due to attrition described by $dd/dt = -Kd^n$ where d is particle diameter, t is time, n is constant and K is a coefficient. There seems to be no systematic study on the effect of particle size on the rate of attrition. Attrition depends on the reactor type and the other bed material. The conditions of the experimental reactors may be different from that of full-scale boilers, where the particles can be moving between fuel-rich and fuel-lean zones. This affects the attrition rate due to different chemical reactions at the surface of particles. If the mass loss by attrition from a particle is assumed to be proportional to the surface area, the value of the exponent is $n=0$. Small particles follow the gas flow better than large ones. Then, large heavier particles may more frequently and with higher impact collide with reactor surfaces and other particles resulting in experimental exponent $n > 0$. The effect of particle size on attrition of limestone has been discussed.⁷³ In a bed of 100% limestone particles, the total attrition rate was independent of particle size, when excess gas velocity exceeding minimum fluidization velocity was constant.⁷³ This indicates value $n=1$. However, the minimum velocity depends also on n . The surface attrition rate of limestone proportional to the particle size ($n=1$) has been used in the modeling.¹⁸ Different values presented in the literature have been discussed.^{20,21} The calculated steady state PSD agreed with the measured one in a pressurized fluidized bed reactor with exponent $n=2$.^{21,24} It is possible to determine the attrition rate with no hypothesis about the functional form for the dependence on the particle size (such as $\sim d^n$) assuming no primary fragmentation, if the steady state PSD in the bed, PSD of the feed, the mass of the bed and the inlet mass flow rate of the material are measured.^{14,24}

In the case of char combustion, the form for particle size reduction is different.^{14,34} This gives the functions $f(t)$ for different n presented in Table 5. The attrition time constant is $\tau_a = d_0^{1-n} / K$. The efficiency of the cyclone is $\eta(d) = 1 / [1 + (d_{ref} / d)^{3.7}]$, where $d_{ref} = 0.0078$ mm.

Table 5 Function $f(t)$, its derivative $f'(t)$, and inverse function $t=u(f)$

n	$f(t)$	$f'(t)$	$t=u(f)$	$f'[u(f)]$
0	$1 - t/\tau_a$	$-1/\tau_a$	$\tau_a(1-f)$	$-1/\tau_a$
1	$\exp(-t/\tau_a)$	$-\exp(-t/\tau_a)/\tau_a$	$-\tau_a \ln f$	$-f/\tau_a$
2	$(1+t/\tau_a)^{-1}$	$-(1+t/\tau_a)^{-2}/\tau_a$	$\tau_a(f^{-1})-1$	$-f^2/\tau_a$
$n \neq 1$	$[1 + (n-1)t/\tau_a]^{1/(1-n)}$	$-[1 + (n-1)t/\tau_a]^{n/(1-n)}/\tau_a$	$\tau_a(f^{1-n})-1/(n-1)$	$-f^n/\tau_a$

Part of the bed material can be taken away from the loop seal. The decay function $g(t)$ for number of particles in this case is derived for a batch of particles fed into the reactor. The number flow of particles (\dot{N}) in a CFBC is shown in Figure 7. The balance for the number (N) of particles in the bed is,

$$-\frac{dN}{dt} = \dot{N}_p - (\eta\dot{N}_p - \dot{N}_s) + \dot{N}_b \quad (2)$$

The term on the left-hand side describes the reduction of the number of particles in the bed, the first term on the right-hand side is due to particles flowing to the cyclone, the second term is the particle flow back to the bed from the loop and the last is due to bottom ash removal. We use the time constants $\tau_p = N / \dot{N}_p$, $\tau_b = N / \dot{N}_b$ and cyclone time constant $\tau_c = \tau_p / (1 - \eta + \kappa)$, where a parameter κ has been added to the previous expression^{33,71} to include the possible removal of

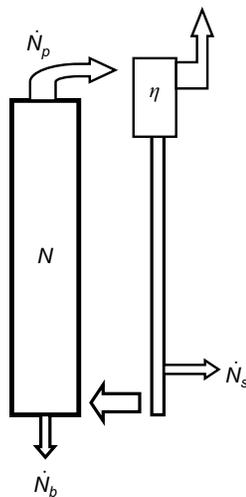


Figure 7 Particle circulation and removal in a CFBC. **Abbreviations:** CFBC, circulating fluidized bed combustion; N , number of particles; \dot{N} , flow rate of particles; b , bottom ash or bed; p , particle circulation; s , removal after cyclone.

material directly after the cyclone. Then the total time constant for material removal is $\tau_t = 1 / [(1 - \eta + \kappa) / \tau_p + 1 / \tau_b]$, where the ratio $\kappa = \dot{N}_s / \dot{N}_p$. We get,

$$-\frac{dN}{dt} = N / \tau_t \quad (3)$$

The particle size d of the initial particles may change with time due to attrition and τ_t then becomes a function of time, since it depends on particle size d . Then the solution of Equation 3 gives for the particle number decay function,

$$N / N_0 = g(t) = \exp\left(-\int_0^t (1 / \tau_t) dt\right) \quad (4)$$

where τ_t is the combined time constant for total material removal, $1 / \tau_t = 1 / \tau_c + 1 / \tau_b$. Function $g(t)$ can readily be calculated, when the change of particle size with time $d/d_0 = f(t)$ and the dependence of the total time constant τ_t on particle diameter are known.

The different time constants are presented in Figure 8A. If no material is removed in the loop seal after cyclone, the cyclone time constant would be much higher as shown in Figure 8B. Then, in practice the removal of bottom ash should be higher (time constant τ_b lower) in order to maintain the same level of bed mass.

In the conditions of direct sulfation, we can also consider the different components in CaCO_3 and CaSO_4 in the limestone (or CaO in air-firing conditions). Then the total mass of the limestone depends on its degree of conversion in the bed X_b ,

$$\frac{m}{m_{0,\text{Ca}}} = \left(\frac{M_{\text{CaCO}_3}}{M_{\text{Ca}}} (1 - X_b) + \frac{M_{\text{CaSO}_4}}{M_{\text{Ca}}} X_b \right) f^3(t) g(t). \quad (5)$$

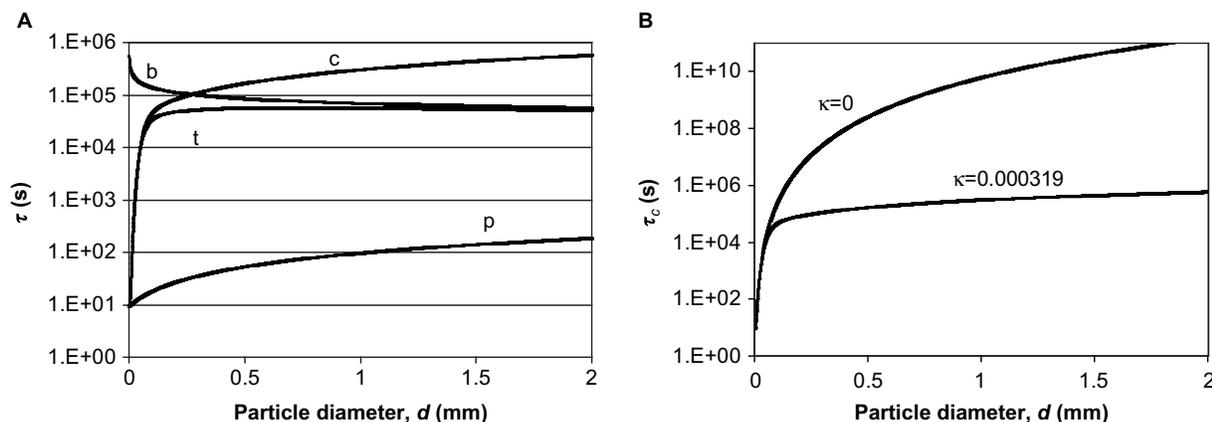


Figure 8 Time constants in CFBC. **Notes:** (A) Dependence of circulation (p), bottom ash (b), cyclone (c), and total (t) time constants on particle size with loop seal ash removal. (B) Comparison of cyclone time constants with and without loop seal ash removal. **Abbreviation:** CFBC, circulating fluidized bed combustion.

Note the misprint (missing X_b) in a previous publication.⁷² The first term in the brackets is due to CaCO_3 and the second one is due to CaSO_4 . In air-firing conditions the M_{CaCO_3} is replaced by M_{CaO} .

Evolution of mass with continuous feeding of mono-sized particles

We consider a continuous feed of material (ash, char, or Ca) into the fluidized bed. The feed rate $\dot{m}_0(t)$ may depend on time. The mass of this material in the bed at present time can be found by summing up differential batches fed, Equation 1, in the reactor in the past,

$$m = \int_0^t \dot{m}_0(t) f^3(t) g(t) dt \quad (6)$$

where t is time from the present ($t=0$) to the past. For limestone in direct sulfation in oxy-firing conditions,

$$m = \int_0^t \dot{m}_{0,\text{Ca}}(t) \left(\frac{M_{\text{CaCO}_3}}{M_{\text{Ca}}} (1 - X_b) + \frac{M_{\text{CaSO}_4}}{M_{\text{Ca}}} X_b \right) f^3(t) g(t) dt. \quad (7)$$

On one hand, the mass of the batch is reduced due to attrition and loss of material in fly and bottom ash flows and on the other hand, it is increased due to sulfation. In steady state ($t=\infty$) and constant inlet mass flow rate, the mass of inert material and limestone in the bed become

$$m = \dot{m}_0 \int_0^\infty f^3(t) g(t) dt \quad (8)$$

where t is time from present to the past. For limestone,

$$m = \dot{m}_{0,\text{Ca}} \int_0^\infty \left(\frac{M_{\text{CaCO}_3}}{M_{\text{Ca}}} (1 - X_b) + \frac{M_{\text{CaSO}_4}}{M_{\text{Ca}}} X_b \right) f^3(t) g(t) dt. \quad (9)$$

Evolution of PSD and partitioning of compounds in the PSD

At first we consider feed material with single particle size d_0 and later extend the results to a general PSD. The PSD of a single size can be described by the Dirac delta function $p_0(d) = \delta(d - d_0)$. The decreasing particle size in the reactor remains mono-sized, when the material is assumed to be homogeneous with no particle-to-particle differences in reaction or attrition rate. In reality, attrition is a stochastic process and using some distribution for attrition rate would be more accurate. The PSD as function of time is then $p(d) = \delta[d - d(t)]$. The PSD, $P(d)$, after a batch is fed can be expressed as,

$$P(d) = mp(d) = m_0 f^3(t) g(t) \delta[d - d_0 f(t)] \quad (10)$$

PSDs of different components of Ca in the bed,

$$P(d) = m_{0,\text{Ca}} \left(\frac{M_{\text{CaCO}_3}}{M_{\text{Ca}}} [1 - X_b(t)] + \frac{M_{\text{CaSO}_4}}{M_{\text{Ca}}} X_b(t) \right) f^3(t) g(t) \delta[d - d_0 f(t)] \quad (11)$$

where the first term in the brackets is due to CaCO_3 (or CaO) and the second due to CaSO_4 . The PSD due to continuous time dependent feed can be found by summing up (integrating) responses to differential batch feeds,

$$P(d) = \int_0^t \dot{m}_0(t) f^3(t) g(t) \delta[d - d_0 f(t)] dt \quad (12)$$

and for different components of Ca,

$$P(d) = \int_0^t \dot{m}_{0,\text{Ca}}(t) \left(\frac{M_{\text{CaCO}_3}}{M_{\text{Ca}}} [1 - X_b(t)] + \frac{M_{\text{CaSO}_4}}{M_{\text{Ca}}} X_b(t) \right) f^3(t) g(t) \delta[d - d_0 f(t)] dt. \quad (13)$$

In steady state the inlet mass flow rates are constant, $\dot{m}_0(t) = \dot{m}_0$, $\dot{m}_{0,\text{Ca}}(t) = \dot{m}_{0,\text{Ca}}$ and the upper integration limit $t=\infty$.

In order to evaluate the integrals, we recall the properties of the Dirac delta function,

$$\delta(at) = \delta(t) / |a|, \int_a^b f(t) \delta(t - c) dt = f(c) \quad (14)$$

when $a \leq c \leq b$. Function $d/d_0 = f(t)$ is continuous and monotonously decreasing. The relation between time and particle size is $t = f^{-1}(d/d_0) = h(d/d_0)$, where h is the inverse function of f . This gives the result for mono-sized feed,

$$P(d) = -\dot{m}_0 (d/d_0)^3 \frac{g[u(d/d_0)]}{d_0 f' [u(d/d_0)]} \quad (15)$$

where $\dot{m}_0 = \dot{m}_0 [u(d/d_0)]$ is constant in steady state. For limestone we have two components,

$$P(d) = -\dot{m}_{0,\text{Ca}} \left(\frac{M_{\text{CaCO}_3}}{M_{\text{Ca}}} \{1 - X_b[u(d/d_0)]\} + \frac{M_{\text{CaSO}_4}}{M_{\text{Ca}}} X_b[u(d/d_0)] \right) \frac{d^3 g[u(d/d_0)]}{d_0^4 f' [u(d/d_0)]} \quad (16)$$

For a general inlet PSD $p_0(d_0)$,

$$P(d) = - \int_0^{d_{\max}} \dot{m}_0 \frac{d^3}{d_0^4} \frac{g[u(d/d_0)]}{f'[u(d/d_0)]} p_0(d_0) dd_0 \quad (17)$$

An expression for the PSD for the components of limestone is found in a similar way from Equation 16.

It should be noted that this analysis requires attrition to take place, since the integration of Equations 12 and 13 involving the Dirac delta function, requires the relation between time and particle size $d/d_0=f(t)$. If no attrition takes place, $f(t)=1$, that is, the mono-sized feed with size d_0 remain in this size. For this case, an alternative form for the PSD with a general inlet PSD can be found by applying Equation 12,

$$P(d) = \int_0^{d_{\max}} \int_0^t \dot{m}_0(t) f^3(t) g(t) \delta[d - d_0 f(t)] p_0(d_0) dt dd_0 \quad (18)$$

which can be integrated,

$$P(d) = \int_0^t \dot{m}_0(t) f^2(t) g(t) p_0[d / f(t)] dt \quad (19)$$

In steady state, when the mass flow rate is constant,

$$P(d) = \dot{m}_0 \int_0^{\infty} f^2(t) g(t) p_0[d / f(t)] dt \quad (20)$$

For the case with no attrition $f(t)=1$ and we get,

$$P(d) / \dot{m}_0 = p_0(d) \int_0^{\infty} g(t) dt = p_0(d) \tau_i \quad (21)$$

where τ_i is also function of diameter d . The bed mass in this case becomes,

$$m / \dot{m}_0 = \int_0^{\infty} p_0(d) \tau_i dd \quad (22)$$

which could also be found directly by integrating from a response to a batch feed,

$$\frac{m}{m_0} = \int_0^{\infty} p_0(d) g(t) dd \quad (23)$$

The PSD of the limestone is presented in fractional form. It is assumed that the cumulative PSD is linear in the range between sieve sizes (points in Figures 1 and 2). Then the PSD $p_0(d)=p_i$ inside a fraction i between sizes $d_{i,\min} \dots d_{i,\max}$ is approximated as constant, $p_i = (m_i / m_{tot}) / (d_{i,\max} - d_{i,\min})$. Equation 17 gives the approximate result for a size fraction

$$P_i(d) / \dot{m}_0 = -(m_i / m_i) \{ H(d_{i,\min}) + 2H[\frac{1}{2}(d_{i,\min} + d_{i,\max})] + H(d_{i,\max}) \} / 4 \quad (24)$$

where

$$H(d_0) = \frac{d^3}{d_0^4} \frac{g[u(d/d_0)]}{f'[u(d/d_0)]} \quad (25)$$

A more accurate result is obtained by dividing the fraction into several subfractions. The total response of the PSD in the bed is obtained by summing up the contribution of all size fractions.

Model for sulfation

In air-firing condition, the sulfation is described by the simple model,⁷²

$$\frac{dX}{dt} = k(X_{\max} - X) \text{ or } X = X_{\max} (1 - e^{-kt}) \quad (26)$$

where t is time, k is reaction rate constant and X_{\max} is final degree of conversion. The direct sulfation taking place in oxy-firing is assumed to take place according to the shrinking core model,²⁴

$$\frac{dX}{dt} = \left(\frac{\tau_c}{3} (1 - X)^{-2/3} + 2\tau_D [(1 - X)^{-1/3} - 1 / f(t)] \right)^{-1} \quad (27)$$

where the first term in the brackets is due to chemical kinetics and the second is due to diffusion of SO_2 through the product layer. τ_D and τ_c are complete conversion times under control of diffusion and chemical kinetics, respectively. Attrition reduces the thickness of the product layer. The conversion is related to the location of the reaction front $X = 1 - (d_c / d)^3$. This equation gives,

$$t = \tau_c [1 - (1 - X)^{1/3}] + \tau_D [1 + 2(1 - X) - 3(1 - X)^{2/3}] - 2\tau_D \int_0^X [1 / f(t) - 1] dX \quad (28)$$

Discussion

Simple analytical solutions

It is possible to derive simple analytical solutions for simplified problems starting from the population balance modeling²⁰ or by the present approach. For example for mono-sized particle feed, when $d / d_0 = f(t) = \exp(-t / \tau_a)$, we get from Equation 18,

$$P(d) = -\tau_a \dot{m}_0 [-\tau_a \ln(d / d_0)] g[-\tau_a \ln(d / d_0)] d^2 / d_0^3 \quad (29)$$

Table 6 Particle size distribution and mass of bed when τ_t is constant (ie, does not depend on d)

n	$P(d)d_0 / (\tau_a \dot{m}_0)$	m / \dot{m}_0
0	$(d / d_0)^3 \exp[(d / d_0 - 1)\tau_a / \tau_t]$	$(\tau_t / \tau_a) \{ \tau_a - \tau_t (1 - e^{-\tau_a / \tau_t}) \}$
1	$(d / d_0)^{2+\tau_a / \tau_t}$	$\tau_a / (3 + \tau_a / \tau_t)$
2	$(d / d_0) \exp[(1 - d_0 / d)\tau_a / \tau_t]$	$\tau_a \exp(\tau_a / \tau_t) E_3(\tau_a / \tau_t)$
$n \neq 1$	$(d / d_0)^{3-n} \exp\{[1 - (d / d_0)^{1-n}](\tau_a / \tau_t) / (n-1)\}$	Integrating $P(d)$ numerically

Note: $*E_n(z) = \int_0^\infty t^{-n} e^{-zt} dt$.

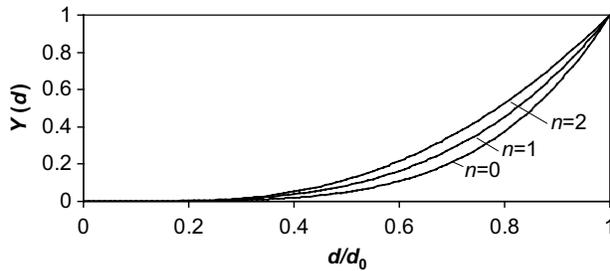


Figure 9 Effect of attrition exponent n on the shape of the steady state cumulative PSD.

Abbreviation: PSD, particle size distribution.

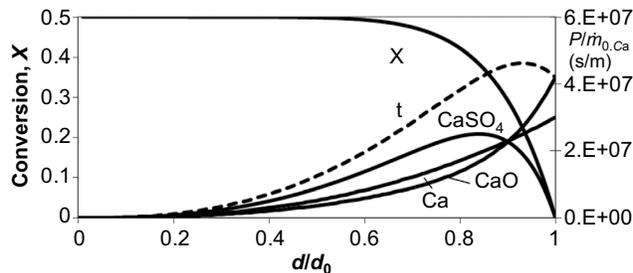


Figure 10 Calculated conversion X and mass PSD of Ca divided by mass flow rate of Ca into the reactor $P/\dot{m}_{0,Ca}$ (in compounds, right hand side axis), CaO, CaSO₄ and total (CaO, CaSO₄, t) in the bed resulting from mono-sized limestone feed ($d_0=1$ mm), when attrition time constant $\tau_a=30000$ s and reaction time constant $\tau_r=1/k=3600$ s ($X_{max}=0.5$).

Abbreviation: PSD, particle size distribution.

If \dot{m}_0 is constant and we approximate τ_t as constant, $g(t) = \exp(-t / \tau_t)$. This is exactly valid, if no attrition takes place, and we get the results presented in Table 6.

Calculations for mono-sized feed

The total time constant used in the calculations that includes the effect of cyclone, circulation time, and ash-removal is shown in Figure 8A. The effect of n on the shape of the steady state PSD calculated with Equation 17 is shown in Figure 9.

It is possible to find the exponent n , for example, by comparing measured steady state PSD Equation 17 with the calculated one. If particles are not removed from the reactor $g(t)=1$, then the measured $P(d)$ in steady state directly gives the function $f'[u(d / d_0)]$ and information of the attrition type. Function f can be found more directly by applying

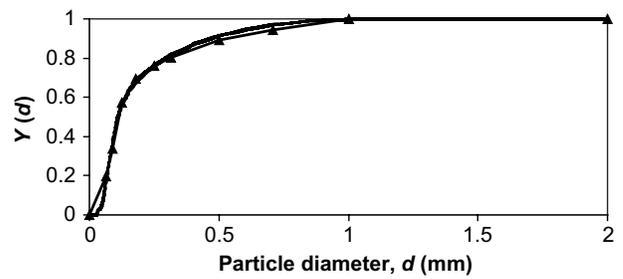


Figure 11 Calculated normalized cumulative PSD of Ca in the bed (no symbols) and PSD of limestone feed (\blacktriangle).

Abbreviation: PSD, particle size distribution.

Equation 1 for the mass of a batch or Equation 4 for the development of the mass with a continuing feed.

An example of the calculated distribution of Ca-containing compounds in air-firing is presented in Figure 10. The conversion of those particles originated from the 1 mm particles reaches a high degree as their size is reduced. However, their mass in the bed decreases due to smaller size and number. Thus, the mass of the particles with high CaCO₄ content has a maximum at a certain size. The mass average conversion (mass of Ca in CaSO₄/total mass of Ca) is 0.351 in this case.

Calculations for feed with a PSD

The PSDs and the location of different Ca-containing compounds (CaO, CaCO₃, CaSO₄) in different size fractions was measured as shown in Figures 1–3. Simulating the results by the model requires the knowledge of primary fragmentation, attrition, and reaction rate behavior and their model parameters. It was not in the scope to measure these parameters for the limestone used. The following calculation is so far presented as an illustration. The PSD (of Ca) is calculated with Equation 27. We do not have the information about the primary fragmentation, so the feed PSD is assumed to be that of the original limestone (see Figures 1–3). Since all other time constants are known except the attrition time constant, it was varied to reach the measured mass of Ca in the bed. The calculated mass of Ca in air-firing (Table 2, 0.66 kg) is obtained, if attrition time constant $\tau_a=17,600$ seconds ($n=1$) is chosen. The calculated mass of Ca in oxy-firing becomes the measured one (1.41 kg) with the choice of attrition time constant $\tau_a=22,400$ seconds. The resulting calculated PSD in the bed is shown in Figure 11. It is seen that it is rather close to the measured one in oxy-firing conditions in Figure 3. The measured and calculated (in the brackets) cumulative mass fractions were 0.24 (0.15), 0.50 (0.55), 0.76 (0.67), 0.90 (0.90), and 1.00 (1.00) for sieve sizes 0.063, 0.125, 0.18, 0.5, and 2 mm, respectively. The differences can be due to some inaccuracies in the model parameters (time constants),

due to some mild primary fragmentation or by the sampling method of material from the bed, material wearing in the subsequent sieving, and the basic PSD measurement method. The calculation of PSD of compounds containing Ca was earlier illustrated for mono-sized feed (Figure 10). In a similar way, it is possible to use the method for arbitrary feed PSD.

Conclusion

Experiments in air-firing and oxy-firing conditions in a pilot scale CFBC were carried out. The PSDs of the limestone and different calcium containing compounds were determined by sampling the bed material and analyzing. Major compounds in air-firing were CaO and CaSO₄ and in oxy-firing CaCO₃ and CaSO₄ as expected. The degree of conversion in air-firing in the bed limestone exhibited a minimum at a certain particle size, while the degree of conversion in oxy-firing was rather even regardless of the particle size.

Methods to calculate the PSD and mass of inert material and limestone in CFBC and FBC are presented. A new model for predicting PSDs for different Ca-containing compounds in different particle sizes was developed for steady and unsteady state. The model can be applied to study the effects of PSD of limestone feed, attrition, cyclone efficiency, circulation rate, bottom ash and other material removal (removal from loop seal), and reactivity of limestone. The model can also be used in optimizing the PSD in the bed by choosing proper cyclone and bottom ash or other ash removal method. This new model, that is, Equation 18 was validated by comparing the curve ($n=1$) in Figure 11 with results obtained by solving numerically the population balance model.²⁴ All the time constants have clear physical meaning. Attrition time constant describes the characteristic time for particle size reduction. Cyclone time constant describes the characteristic time for a particle to escape as fly ash through the cyclone. This depends on the combination of cyclone efficiency and the average circulation time interval for a particle to enter the cyclone. Bottom ash time constant describes the rate of particle removal by the operator from the dense bed. The reaction time constant describes reactivity of the limestone used. The total behavior of the system is determined by the combination of these time constants.

However, the application of the model to simulate the observations in the CFBC requires that information about the primary fragmentation behavior of the limestone used is known to estimate the effective PSD of the feed. Furthermore, the experimental bench scale information about the attrition and reactivity behavior of the limestone is required to simulate processes in the CFBC.

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Disclosure

The authors report no conflicts of interest in this work.

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