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DEPENDENCE OF SULPHUR CAPTURE PERFORMANCE ON AIR STAGING IN A 12 MW CIRCULATING FLUIDISED BED BOILER

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ABSTRACT

Three cases of air staging were examined in a 12 MW circulating fluidised bed boiler: *i)* no staging, *ii)* normal staging and *iii)* intensified staging. The conditions inside the combustion chamber were investigated by zirconia cell measurements of the oxygen partial pressure, 0.35, 0.65 and 8 m above the bottom air distributor plate. A significant effect of the degree of staging was seen in the two lower locations: At 0.65 m height the fraction of time under substoichiometric conditions was low in the no-staging case (2—35%), at normal staging it was 70—90%, whereas at intensified staging it was 100%. At 0.35 m height, *i.e.* in the dense bed, a similar effect was seen, although the fraction of time under reducing conditions was lower. The fraction of time under reducing conditions was low in the top of the combustion chamber in all three cases.

The increase in the fraction of time under reducing conditions with a higher degree of staging is associated with a decrease in sulphur capture. It is assumed that a release of SO_2 from $CaSO_4$ takes place during the transitions between oxidising and reducing conditions. Thus, the rapid alternations between oxidising and reducing conditions, as seen with the zirconia cell, offer an explanation of the reductive decomposition and, accordingly, of the dependence of sulphur capture on temperature and on the extent of staging.

INTRODUCTION

Fluidised bed combustion provides a possibility of abatement of sulphur dioxide emissions from solid fuels. The temperature in the combustion chamber of a fluidised bed boiler (FBB), 800—900°C, is sufficient to allow for calcination of a sorbent, *e.g.* limestone, $CaCO_3$. Yet the temperature is low enough to prevent sintering of the resulting porous calcine, CaO, which reacts with SO_2 in the presence of oxygen according to

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \qquad (1)$$

The average sorbent residence time in a commercial FBB is in the order of 10 h (Lyngfelt & Leckner, 1992) and typical sorbent conversions, *i.e.* molar ratio of $CaSO_4$ to total Ca, are 40–50% (Mjörnell *et al.*, 1991).

Despite extensive laboratory research on limestone behaviour, as well as a large number of studies showing global measurements of sulphur retention in commercial scale FBBs, there is still no satisfactory understanding of the parameters which limit the sulphur capture performance in FBBs. The limiting factors for efficient sulphur capture include:

1) Sorbent residence time.
2) Sorbent reactivity.
3) Reducing conditions.

The present investigation is related to the last of these three items, *i.e.* the limitation of conversion owing to the reductive decomposition of the reaction product. The net sulphur retention is the result of competition between sulphur capture, reaction (1), and reductive decomposition, *i.e.* the release of sulphur previously retained by calcium, represented by the overall reaction (2).

$$CaSO_4 + CO \rightarrow CaO + CO_2 + SO_2 \qquad (2)$$

The adverse effect of reductive decomposition on sulphur capture has been studied in laboratory scale combustors (Khan & Gibbs, 1991), pilot scale combustors (Bramer *et al.*, 1988) and in a 16 MW stationary (bubbling) FBB (Lyngfelt & Leckner, 1989*a*). In the 16 MW FBB, conclusive evidence of reaction (2) was obtained by raising the bed temperature above 890°C, where reaction (2) was faster than reaction (1), resulting in a net release of sulphur from the partially sulphated sorbent accumulated in the boiler. At the highest temperature, 940°C, the emission of sulphur was 2.5 times greater than the amount of sulphur introduced into the boiler with the fuel. Zirconia cell measurements showed that reducing conditions prevailed in the bed of the boiler (Cooper & Ljungström, 1987). These measurements were made in 14 locations at approximately half bed height and showed highly reducing conditions, *i.e.* a partial pressure of O_2, $P_{O_2} < 10^{-10}$ bar, for 80–90% of the time, although no air staging was used and the excess air ratio was high, 1.4.

Under constant reducing conditions the fuel sulphur can be expected to react with CaO to CaS. Under conditions changing between oxidising and reducing, however, an intermediate region is passed, see Fig. 1, where neither CaS nor $CaSO_4$, but CaO is stable. Thus, the captured sulphur is released during the shifts between oxidising and reducing conditions. A comprehensive study of the release of sulphur under such transitions between oxidising and reducing conditions was made by Hansen (1991; Hansen *et al.*, 1993). Hansen's study was performed in a fixed-bed reactor containing the sorbent, through which a gas flow containing 1500 ppm SO_2 and 10% CO_2 was led. The gas flow contained alternatingly 4% CO or 4% O_2. A typical result for a rather low conversion (about 10%) is shown in Fig. 2. The peaks in SO_2 during the shifts from reducing to oxidising conditions, caused by the oxidation of CaS, exceed the inlet concentration of SO_2 thus resulting in a net release in

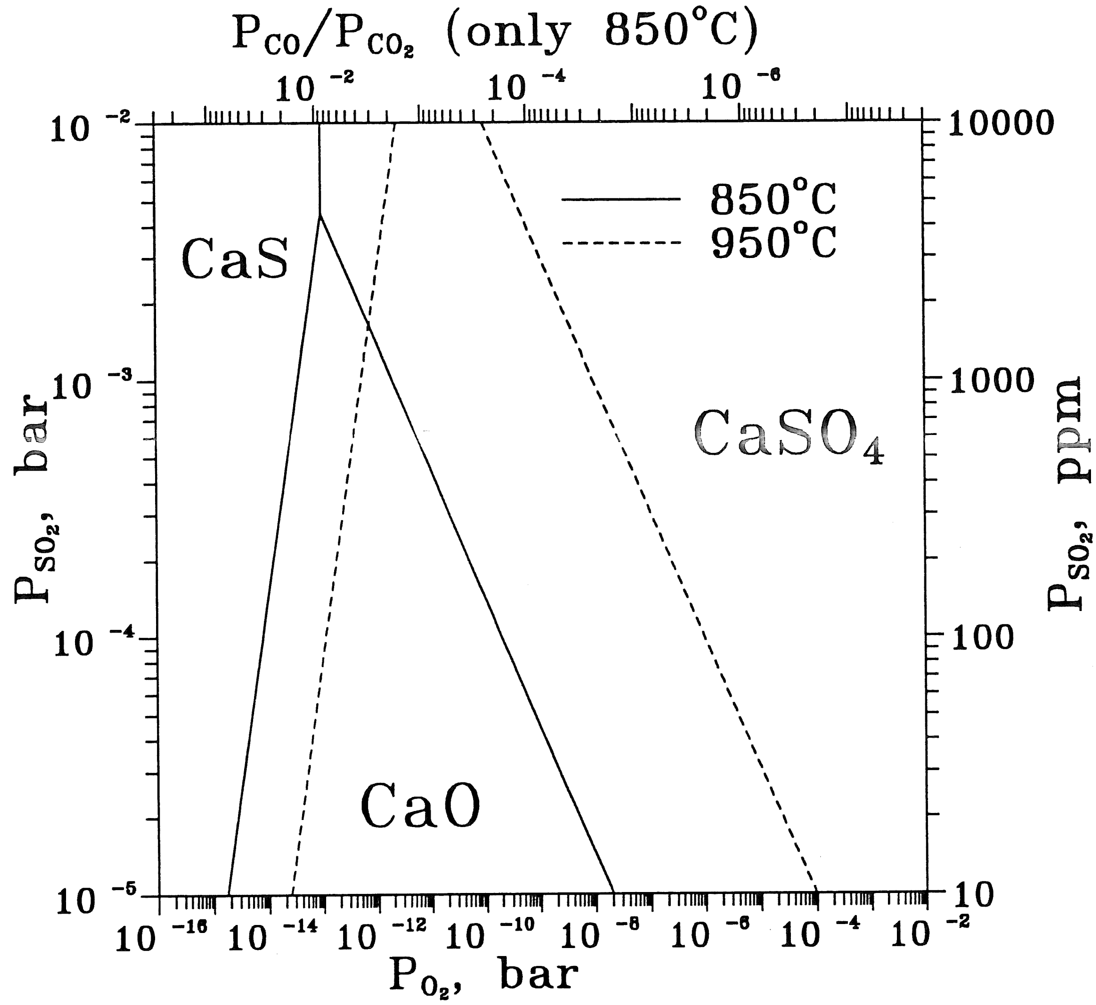

FIGURE 1. Phase equilibrium diagram for the system CaO, CaS, $CaSO_4$, SO_2 and O_2. Total pressure 1 bar.

SO_2. In the second shift from oxidising to reducing conditions, the SO_2 peak supersedes the inlet SO_2 concentration indicating a net release due to the reductive decomposition of $CaSO_4$. In general the SO_2 peaks caused by oxidation of CaS decrease with increased conversion, while the SO_2 peaks caused by reductive decomposition increase with increased conversion but shift to decrease at high conversions. There were, however, important differences between the various sorbents investigated and also depending on experimental conditions, for instance particle size.

The reducing conditions noted in the stationary FBB is an effect of the gas flow pattern in the bed and the consequence is a net sulphur release at increased temperature, but also a less efficient sulphur capture at normal operating conditions (Lyngfelt & Leckner, 1989*b*). A model of the release and capture of SO_2 suggests that the adverse effect of reducing conditions on sulphur capture is more or less present at all temperatures (Lyngfelt & Leckner, 1993*b*).

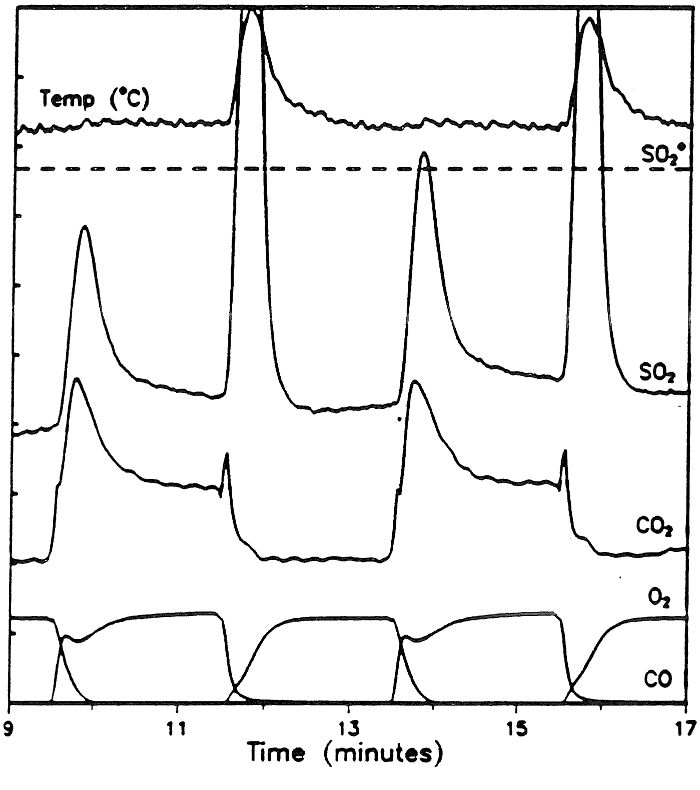

Fig. 2. Example showing temperature, SO_2, CO_2, O_2 and CO versus time under conditions alternating between oxidising and reducing (Hansen, 1991). SO_2° indicates inlet SO_2 concentration. Range of ordinate axis: temperature 780→880°C; SO_2 −150→2000 ppm; CO_2 9→14%; O_2 0→30%; CO 0→35%.

The information regarding the distribution and effect of reducing conditions in *circulating* FBB's is, however, incomplete and therefore tests were performed in the 12 MW circulating FBB at Chalmers University of Technology. The purpose was to examine the presence of reducing conditions in the combustion chamber for three cases of air staging, and to relate these to the sulphur capture efficiency. The object is to provide information about the conditions to which the sorbent is exposed, including where and how decomposition takes place. Increased understanding of how operating parameters, such as air staging, affect these conditions is valuable for minimising sorbent costs and SO_2 emissions. This is all the more important in view of the desire to reduce NO and N_2O emissions, since a measure implemented to reduce one emission often increases others.

Additional results from these tests, regarding the effect of air staging and temperature on SO_2 as well as N_2O and NO emissions, are previously published (Lyngfelt & Leckner, 1993*a*).

EXPERIMENTAL CONDITIONS

The tests involved variation of the degrees of air staging. Air staging is defined as the process by which a part of the combustion air, called secondary air, is added at a later stage in the combustion chamber. Thus, a primary combustion zone with a reduced air supply is formed. The extent of staging can be varied either by altering the ratio of secondary air to total air or by altering the position where secondary air is introduced.

Three cases of air staging were studied with limestone addition at a bed temperature of 850°C, see Table 1. Test conditions are shown in Table 2. The overall excess air ratio was held constant at about 1.2 in all three cases.

In order to obtain supplementary data from the lower part of the combustion chamber, a second test series was made with the same coal and under otherwise similar conditions. Operational parameters such as load, excess air, primary/secondary air ratio, and bed heights were close to identical, see Table 2. The only difference was that a dolomite was used instead of a limestone. The same Ca/S ratio, 3, was used which means a higher mass flow of dolomite.

TABLE 1.
The three cases of staging.

Normal staging	Reference case with approximately 55% primary air and 35% secondary air, which was introduced at level 1/2 about 2 m above the air-distributor plate. (The remaining 10% air was introduced elsewhere, *e.g.* in the particle cooler.)
No staging	No secondary air.
Intensified staging	Approximately 40% primary air and 50% secondary air which was introduced at a high level (level 4, at 5.5 m height).

TABLE 2.
Average values of operation parameters and gas measurements.

Degree of staging	No	Normal	Intensified
Bed temperature, °C	851	850	850
Top temperature, °C	858	857	867
Pressure drop, bed, kPa	3.7	4.9	5.8
Pressure drop, total, kPa	5.8	6.2	6.9
Total air flow, kg/s	3.5	3.4	3.5
Primary air flow, kg/s	3.1	1.9	1.3
Secondary air flow, kg/s	0	1.3	1.8
O_2, %, flue gas	3.7	3.8	3.9
CO (6% O_2), ppm, flue gas	114	117	151
SO_2 (6% O_2), ppm, flue gas	35	45	231
O_2, %, top of furnace, H11	3.3	3.0	7.4
CO, ppm, top of furnace, H11	660	866	1038
<u>Second test series:</u>			
Bed temperature, °C	848	853	851
Top temperature, °C	847	851	859
Pressure drop, bed, kPa	3.0	4.8	5.8
Pressure drop, total, kPa	5.4	6.3	6.7
Total air flow, kg/s	3.6	3.5	3.5
Primary air flow, kg/s	3.0	1.8	1.3
Secondary air flow, kg/s	0	1.3	1.7
O_2, %, flue gas	3.3	3.5	3.9
CO (6% O_2), ppm, flue gas	196	127	158
SO_2 (6% O_2), ppm, flue gas	28	40	184
O_2, %, below sec. air, H4	10.7	2.1	1.1
CO, ppm, below sec. air, H4	5400	5800	>10,000

The boiler

The 12 MW circulating FBB used for the experiments has the features of a commercial boiler, but was built for the purpose of research. The boiler is equipped for special measurements and has facilities that make it possible to vary parameters independently and in a wider range than is possible in a commercial boiler. It is also possible to run the boiler under extreme conditions inappropriate to commercial boilers.

The boiler is shown in Fig. 3. The height of the combustion chamber is 13.5 m and the square cross-section is about 2.5 m^2. Fuel is fed to the bottom of the combustion chamber through a fuel chute (3). Primary air is introduced through nozzles in the bottom plate (2) and secondary air can be injected through several nozzle registers located horizontally at both sides of the combustion chamber, as indicated by the arrows in Fig. 3. Entrained

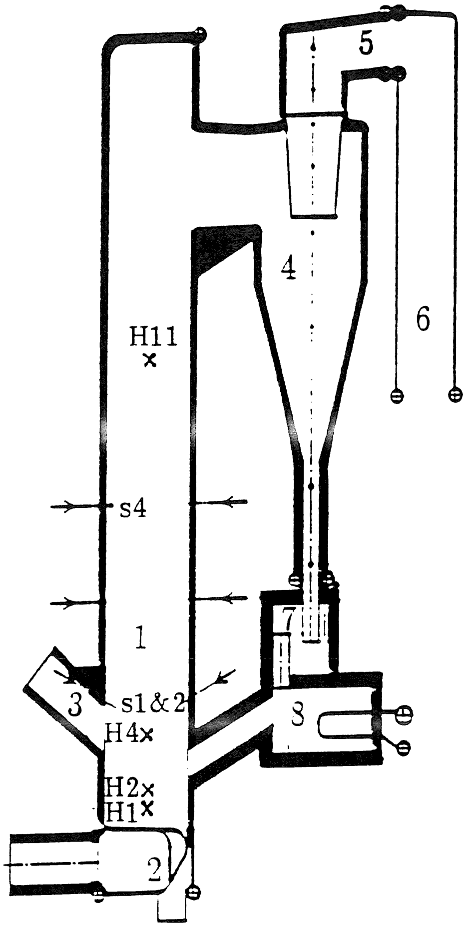

FIGURE 3. The Chalmers boiler. 1 combustion chamber, 2 air plenum and start-up combustion chamber, 3 fuel feed chute, 4 cyclone, 5 exit duct, 6 convection cooling section, 7 particle seal, 8 particle cooler; → secondary air nozzle registers (s1&2 and s4); x holes (H1, H2, H4 and H11).

bed material is captured in the hot, refractory-lined cyclone (4) and returned to the combustion chamber through the return leg and particle seal (7).

Figure 3 does not show the flue-gas recycling system, which supplies flue gas to the combustion chamber. This system is used for fine tuning of the bed temperature. Large, intentional changes in bed temperature can be made using the external, adjustable particle cooler (8).

The fuel and the sorbent

The fuel was a bituminous coal with low sulphur content and the sorbents were Ignaberga limestone (main test series) and a dolomite called Myanit (second test series). Sorbent and fuel data are shown in Table 3.

TABLE 3.
Fuel and limestone (daf=dry, ash–free).

	Mass fraction	Particle size
Fuel, bitum. coal		<16 mm, 50% < 3 mm
moisture	0.15	
ash	0.05	
volatiles, daf	0.39	
carbon, daf	0.88	
hydrogen, daf	0.06	
nitrogen, daf	0.01	
oxygen, daf	0.04, calculated	
sulphur, daf	0.008	
Sorbent, Ignaberga		0.2–2 mm, 50% < 0.6 mm
$CaCO_3$	0.90	
Sorbent, Myanit		0.1–1 mm, 50% < 0.4 mm
$CaCO_3$	0.525	
$MgCO_3$	0.439	

Measurements

Regularly calibrated on-line gas analysers were used for continuous monitoring of O_2, SO_2 and CO after the bag-house filter. In addition, gases were sampled from the centre of the combustion chamber with a suction probe in hole H11, at 8 m height. In the second test series the suction probe instead sampled in hole H4, at 1.6 m height, also in the centre.

Two zirconia cell oxygen probes were inserted into the combustion chamber through the side walls in hole H2, 0.65 m above the bottom, and hole H11, 8 m above the bottom, see Fig. 3. Hole H2 was in the splash zone of the bed and well below the secondary air inlet. On each level three measurements were made: one in the centre, *i.e.* halfway between the side walls, one halfway between the centre position and the side wall and finally the centre position was repeated. In the second test series the two probes were inserted at two levels: at 0.35 m height, H1, and at 0.65 m height, H2, and two measurements were made on each level: one in the centre position and one halfway between the centre and the side wall. Hole H1 is in the dense bottom bed.

In each measurement data from the oxygen probes were sampled every 0.05 s (20 Hz) during 30 minutes. The choice of sampling frequency was based on previous experimental experience, which shows that higher frequencies do not significantly improve the resolution. This is an effect of the response time of the probes.

One of the probes was water-cooled and the other was air-cooled. The water-cooled probe was inserted in hole H2 in the first test series and in hole H1 in the second. Thus, measurement data from hole H2 were obtained from both probes.

Both probes have Bosch zirconia cells, protected from larger particles by a shield with slits. The water-cooled probe is described by Ljungström (1985). The air-cooled probe cell is mounted on a lance, which is water—cooled except for the 10 cm nearest to the cell. Inside the lance, which has a rectangular cross section, and fitted to two sides is a cylindrical tube. Cooling water is introduced into one of the two channels surrounding this tube and returned, via a tube deformation, in the other. The cylindrical tube contains the electric circuits and two tubes through which cooling air is introduced.

The voltage signal from the zirconia cell measurements was somewhat off-set. The off-set was small for the air-cooled probe and larger for the water-cooled probe. The values have been corrected for this effect. The reason for the off-set seems to be related to the cooling flow, *i.e.* to the temperature gradients over the cell. Except for this off-set, the probes are reliable and their function has been checked in a number of ways, including comparitive tests which show that the probes react likewise to similar conditions. The amplitude and the character of the signal affirm that the probes worked properly.

The use of zirconia cell oxygen probes for measurements inside fluidised bed combustors is established (*e.g.* Cooke et al., 1972; Saari & Davini, 1982; Rocazella 1983; Stubington & Chan 1990).

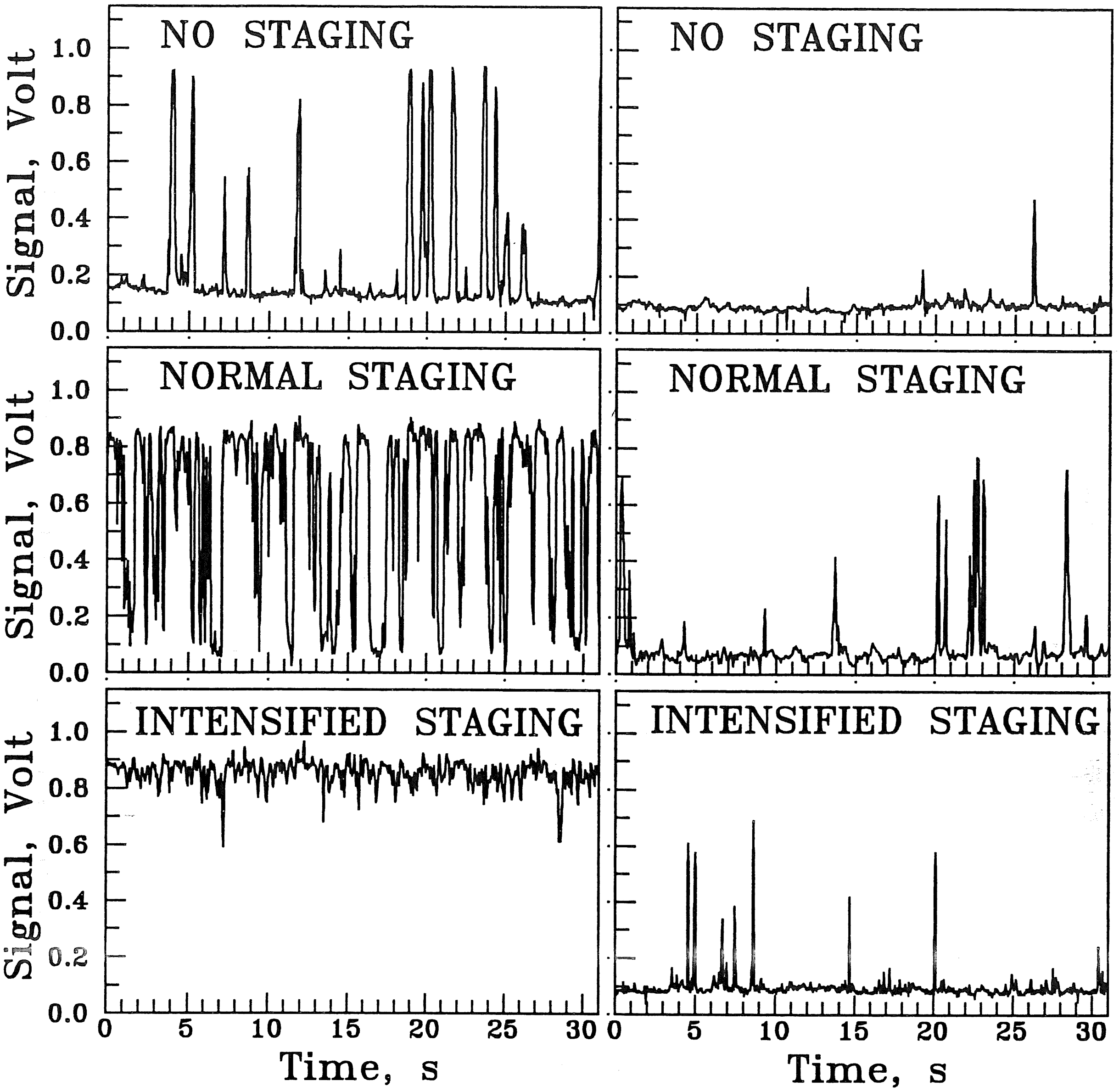

FIGURE 4. Examples of oxygen probe measurements.
To the left, at 0.65 m height (H2); to the right at 8 m height (H11).
From top to bottom: no staging; normal staging; intensified staging.

RESULTS

Zirconia cell measurements

The three diagrams to the left in Fig. 4 show typical examples of the signal measured with the zirconia cell in hole H2, in the splash zone 0.65 m above the distributor plate, for the three cases of staging. The low voltage level corresponds to oxidising conditions and the higher level to reducing (substoichiometric) conditions. In the no-staging case, oxidising conditions dominate with detours to reducing conditions. Under normal staging the pattern is reversed with reducing conditions dominating, but with frequent detours to oxidising conditions. In the case of intensified staging, reducing conditions predominate and occasional detours towards oxidising conditions are not successful.

The corresponding diagrams to the right in Fig. 4 show the zirconia cell signal measured in hole H11, 8 m above the distributor plate. In all three cases of staging oxidising conditions prevail with occasional detours towards reducing conditions.

In the following, a level of 0.3 V is chosen to differentiate between oxidising and reducing conditions. This is the point of stoichiometry, *cf.* Appendix A, which corresponds to an equilibrium oxygen partial pressure of $3 \cdot 10^{-7}$ bar and a P_{CO}/P_{CO_2} ratio of $4 \cdot 10^{-6}$. With this choice of voltage level the fraction of time under reducing conditions, f_{red}, can be calculated and the results are shown in Fig. 5.

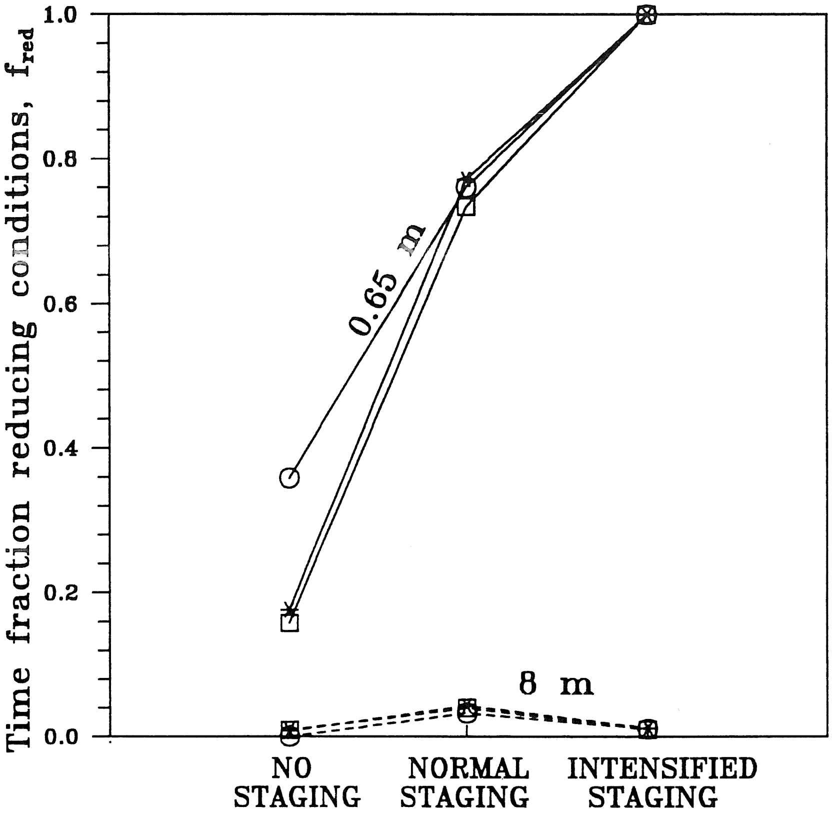

FIGURE 5. Fraction of time under reducing conditions at 0.65 m height (solid lines) and 8 m height (dashed lines): □, × centre; o halfway to wall

The signal character from the second test series was similar to that of the first test series. The time fraction under reducing conditions, f_{red}, is shown in Fig. 6. The data obtained in hole H2, at 0.65 m, are similar to the first test series, with the exception that the fraction of time under reducing conditions is lower in the no-staging case. The reason for this is not known. The fraction of time under reducing conditions measured in hole H1, at 0.35 m and in the dense bed, shows the same dependence on air staging, but the values of f_{red} are lower than in the measurements in H2 in the splash zone. The rather low fraction of time under reducing conditions in the dense bed for normal staging, about 30%, indicates that the dense particle phase is not predominantly reducing, which suggests a good gas-solids mixing.

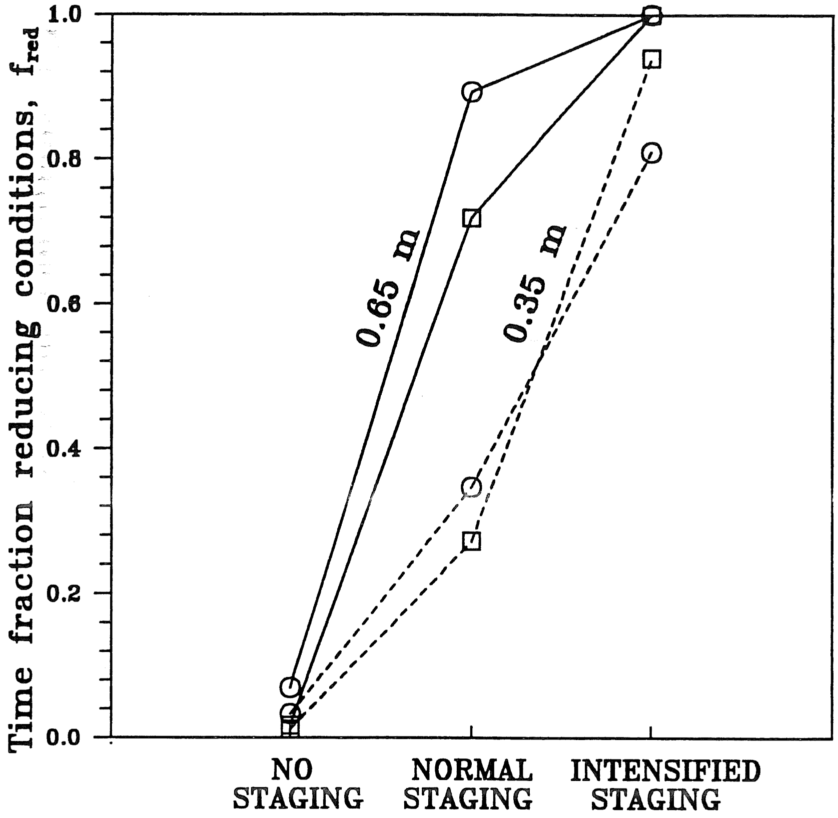

FIGURE 6. Fraction of time under reducing conditions in second test series at 0.65 m, H2, (full lines) and 0.35 m, H1, (dashed lines): □ centre; ○ halfway to wall.

Bed ash analysis

The results of the oxygen probe measurements can be compared with the amount of fuel in the bottom part of the furnace. This is done in Table 4 as follows: the amount of combustible solids is estimated from analysis of bed material samples, and the bed mass is determined from the pressure drop in the bottom part of the furnace. The fraction of reducing time is assumed to correspond to the probability of the probe of being in the fuel-rich plumes from burning or devolatilising particles in accordance with the simplified model derived in Appendix B:

$$f_{red} = 1-\exp(-c_1 m_{comb}/\dot{m}_{prim.\,air}) \qquad (3)$$

With the values for the normal staging case, f_{red} = 0.75 and $m_{comb}/\dot{m}_{prim\cdot air}$ = 32.6, c_1 can be computed and with this value of c_1, f_{red} for the two other cases of staging can be estimated, see Table 4. The good agreement with the measured values in Fig. 5, is probably partly co-incidental: the mass fractions of combustibles in the bed samples are somewhat uncertain, nor does the simple model account for differences in fluidising conditions caused by different bed heights and fluidising velocities. Also, the relationship between the amount of combustibles and volatiles release, char combustion and gasification, is not as simple as assumed in eqn. (3). Still, it appears that eqn. (3) can be used to relate f_{red} to changes in the $m_{comb}/\dot{m}_{prim.\,air}$ ratio caused by variation in the degree of air staging.

TABLE 4.
Calculation of the ratio of mass of combustibles to mass flow of air in the bottom part of the furnace and f_{red} according to eqn. (3).

Degree of staging	No	Normal	Intensified
Fraction combustibles, (-)	0.022	0.045	0.099
Pressure drop, kPa	3.80	4.50	5.85
Bed mass, kg	1120	1330	1730
Mass combustibles, m_{comb}, kg	24.8	60.4	170
Primary air flow, $\dot{m}_{prim.\,air}$, kg/s	3.10	1.85	1.30
$m_{comb}/\dot{m}_{prim.\,air}$	8.01	32.6	131
f_{red} eqn(3) with c_1=0.0425	0.29	0.75	0.996

Combustion chamber suction probe measurements

Average values from suction probe gas measurements made at 8 m height in the centre of the combustion chamber are shown in Table 2 for the three cases of staging. The O_2 concentration varied with an amplitude of approximately 1%, and the measured CO peaks did not exceed 4000 ppm. The reducing periods were not detected in these measurements because of the longer response time.

The most important observation in relation to the oxygen probe measurements is the much higher oxygen level in the case of intensified staging. This may explain the lower fraction of time under reducing conditions, f_{red}, in the top, see Fig. 5, as compared with normal staging. Since the load and the excess air ratio were constant, the difference between the three cases of staging should, in principle, only relate to the lower half of the combustion chamber. In reality, the conditions in the top were affected in several ways. The extent of secondary air penetration affects the O_2 concentration profile over the cross-section. In addition, an increased degree of air staging results in a higher concentration of solid combustibles which may involve an increased oxygen consumption in the cyclone, *i.e.* a higher O_2 concentration in the upper part of the furnace since the exit O_2 is held constant. A possible explanation for the measured oxygen levels is:

- Shift from no staging to normal staging: The secondary air does not penetrate in full and results in lower O_2 concentration in the centre.
- Shift from normal to intensified staging: The high degree of staging increases the concentration of combustible solids and thus the cyclone oxygen consumption. (The increased combustion in the cyclone can be seen from the smaller temperature fall over the cyclone for the case of intensified staging.)

In the second test series, the suction probe samples gas from hole H4, at 1.6 m height, well below the secondary air inlets. As expected, these measurements show an increase in CO and a significant decrease in O_2 with higher degree of staging, *cf.* Table 2.

The effect of staging on sulphur capture

The effect of air staging on sulphur capture performance is shown in Fig. 7. The effect of staging in a high temperature case, 930°C, is also included in the figure. The horizontal dashed line shows the "zero level", 414 ppm, *i.e.* the sulphur emission with a sand bed prior to the start of limestone addition. In the case of no staging, there was a decrease in sulphur capture efficiency from 90 to 60% when the temperature was increased to 930°C. This is attributed to the fact that reducing conditions are present, even in the case of no staging. For normal staging the sulphur capture efficiency was somewhat lower than in the case of no staging at 850°C (Lyngfelt & Leckner, 1993*a*). A large increase in SO_2 emission is seen at the high temperature where the sulphur capture has decreased from 90 to −20%. The latter, negative value indicates a net sulphur release from sulphur previously captured in the form of $CaSO_4$. (Of course, negative sulphur capture is not possible at steady state: the negative values are averages for time periods of 2—3 hours following a temperature increase.) A very pronounced effect on sulphur capture is seen in the case of intensified staging: here the sulphur capture efficiency already is reduced to 40% at 850°C and at the high temperature the net release of sulphur is large, with a sulphur capture efficiency of less than −100%.

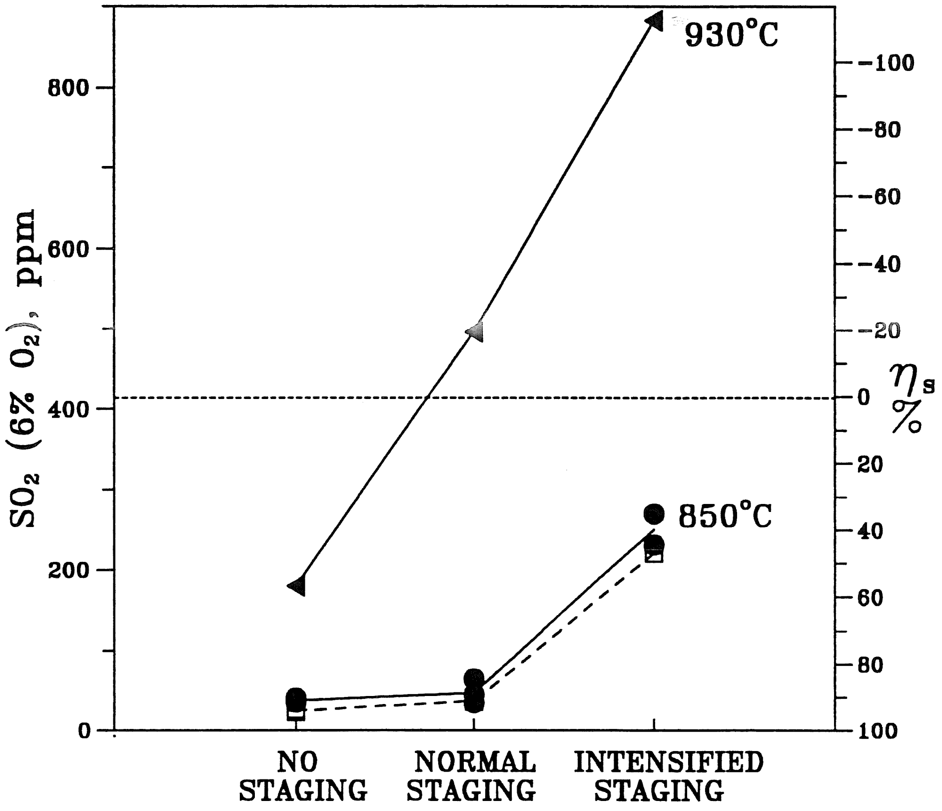

FIGURE 7. SO_2 (6% O_2) and sulphur capture efficiency, η_S, for three cases of staging: ● 850°C; ▲ 930°C. Ca/S = 3. Second test series: □, dashed line.

DISCUSSION

The oxygen probe measurements verify that the effect of a higher degree of staging is to increase the extent of substoichiometric conditions in the bottom part of the boiler. The fraction of time under reducing conditions in the top of the boiler was only a few per cent.

The bed height varied in the different cases of staging. For the measurements in H2, at 0.65 m height, the probe was in the splash zone, but the distance from the probe to the dense bottom bed decreased with increasing staging. The measurements in H1, at 0.35 m were, at least for the normal and intensified staging cases, made in the dense bottom bed. The strong effect of staging on the fraction of reducing conditions was seen at both levels, *i.e.* both in and above the dense bottom bed.

The combustion rate (mass of combustibles burnt per time unit divided by total mass of combustibles present) is inversely proportional to the mass of combustibles since the load, *i.e.* the mass of combustibles burnt per time unit, is constant. Increased staging results in a decreased combustion rate which is evident from the increase in the mass of combustibles, *cf.* Table 4. This decrease in combustion rate with increased staging is, of course, explained by the oxygen deficiency and is thus consistent with both the effects on sulphur capture and the oxygen probe data.

The average frequency of the shifts between oxidising and reducing conditions was in the order of 1 Hz. An important fraction of the number of shifts had a period length not much longer than the response time of the probe. It is not improbable that the resolution prevents detection of shifts with shorter duration.

It should be pointed out that the conditions experienced by small freely-moving sorbent particles may differ significantly from measurements with a 20 mm probe made in a few fixed positions.

Comparison of laboratory and boiler data

Although Hansen (1991; Hansen *et al.*, 1993) noted a net release of SO_2 during the transitions between oxidising and reducing conditions, he found no significant effect of the shifts on the degree of sulphation, except at high temperatures, 950°C. In the present measurements a significant effect of staging can already be seen at 850°C. This is probably explained by some important differences between the laboratory tests and the boiler measurements:

i) Time period length. The periods of sorbent exposure to oxidising or reducing conditions were 30 s each in Hansen's study, whereas they may be in the order of 1 s in the fluidised bed. Hansen showed that SO_2 is released during the transitions, and the expected effect of the much higher frequency of the shifts in the boiler is a higher rate of reductive decomposition.

ii) Fraction of time under reducing conditions. The sulphur capture is good at entirely reducing or oxidising conditions. In between these extremes, the sulphur capture should be at a minimum for a certain value of f_{red}. This "worst case" value of f_{red} may be significantly higher than that used in Hansen's study, 0.5. Experiments by Hansen (1991) indicate that the conversion of the sorbent is decreased when f_{red} is increased. No experimental data to determine a "worst case" value of f_{red} are available, however.

iii) Reducing agent. Hansen also studied the influence of H_2 and found a more pronounced effect than with CO. H_2 is found in volatile plumes in the combustion chamber.

Thus, the strong effect of reducing conditions in the case of intensified staging at 850°C as opposed to the small overall effect seen in laboratory tests may be explained by 1) higher frequency of shifts, 2) higher fraction of reducing conditions and, 3) presence of a more reactive reducing agent, H_2. At present it is not possible to safely conclude which of these is most important.

<u>The effect of alternations on SO_2 release</u>

It is not evident where and how SO_2 is released from the sorbent. The following discussion will point to some possibilities, based on the intensified staging case. In this case f_{red} was 1.0 in the splash zone at 0.65 m (below called reducing bottom zone), 0.8–0.9 at lower levels in the bed, at 0.35 m (lowest bottom zone), and about 0.01 at 8 m height. This indicates that sorbent particles in the top of the boiler as well as in the cyclone will experience predominantly oxidising conditions, while particles in the lower part of the combustion chamber will experience either conditions changing between reducing and oxidising (lowest bottom zone) or constant reducing conditions (reducing bottom zone). Thus, some general mechanisms for SO_2 release can be outlined: movement of sorbent particles to a reducing zone involving SO_2 release from $CaSO_4$ (items 1–3 and 8, below), movement to an oxidising zone involving SO_2 release from CaS (items 4–6), and local shifts (items 7 and 9):

1) Particles move into the reducing bottom zone after falling down from the oxidising zone higher up in the combustion chamber.

2) Particles enter the reducing bottom zone after being recycled via the cyclone.

3) Particles enter the reducing bottom zone after having experienced some degree of oxidising conditions in the lowest bottom zone.

4) Particles are thrown up from the reducing bottom zone into the oxidising zone above the secondary air inlets.

5) Particles are entrained from the reducing bottom zone through the combustion chamber to the cyclone.

6) Particles move from the reducing bottom zone to the lowest bottom zone where there are partly oxidising conditions.

7) Particles in the lowest bottom zone are subject to shifts without moving. (In fact, this may also be the case in the reducing bottom zone if the measured value of $f_{red} = 1.0$ is partly an effect of response time and probe size. The size of the probe, 20 mm, prevents the detection of smaller oxidising zones and the probe response time prevents detection of oxidising periods shorter than appr. 0.05 s.)

8) In addition, it cannot be excluded that recycled material is subjected to reducing conditions in the return leg.

9) Sorbent particles may also be exposed to reducing conditions in the upper part of the combustion chamber. This is probably not an important mechanism. If Figs. 5 and 7 are compared it is seen that the poor sulphur capture in the case of intensified staging is not associated with a high f_{red} at 8 m, instead it is significantly lower than in the normal staging case.

Several mechanisms are available to explain the release of sulphur involving movement of sorbent particles in and out of reducing zones as well as shifting conditions in one specific location. It is not possible at present to determine to what degree the various mechanisms contribute to the loss in sulphur capture efficiency.

Undesired parameter variations

A circulating FBB is a complex system which is difficult to run under otherwise constant conditions when individual parameters are intentionally varied. Unintentional variations in parameters are inevitable, but most parameters in the present study have remained reasonably constant, and the quantitave effect of undesired parameter variations is judged to be minor, see Lyngfelt & Leckner (1993*a*).

CONCLUSIONS

The fraction of time under reducing conditions was measured in the dense bed, in the splash zone and in the top of the combustion chamber. Increasing the degree of air staging from no staging to intensified staging significantly increased the fraction of time under reducing conditions in the lower part of the combustion chamber. The effect in the top of the combustion chamber was minor, which is also expected since the variation in air staging mainly affected the lower part of the furnace, while load, overall excess—air ratio etc., were constant. The fraction of time under reducing conditions as measured by the oxygen probe in the lower part of the combustion chamber appears to be related to the ratio of mass of combustibles and primary air flow.

The more substoichiometric conditions in the bottom zone following increased staging are also related to a reduction in sulphur capture. This can be explained by the reductive decomposition of $CaSO_4$ during the frequent transitions between oxidising and reducing conditions.

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APPENDIX A. POINT OF STOICHIMETRY.

The gas mixture is considered to be stoichiometric, *i.e.* excess oxygen = 0, when the partial pressure of O_2 is balanced by CO (for simplicity assumed to be the only oxygen consuming gas present), *i.e.*

$$P_{O_2} = \tfrac{1}{2}P_{CO} \qquad \text{(A1)}$$

At equilibrium the concentrations of CO and O_2 are given by

$$K_{eq} = P_{CO_2}/P_{CO}P_{O_2}^{\frac{1}{2}} \qquad \text{(A2)}$$

where K_{eq} is the equilibrium constant, $4 \cdot 10^8$ bar$^{-1/2}$. Assuming $P_{CO_2} = 0.15$ bar, and combining eqns A1 and A2 yields an equilibrium O_2 partial pressure of $3 \cdot 10^{-7}$ bar for a stoichiometric mixture at 850°C. This value may be inserted in the Nernst equation, which relates oxygen partial pressure to voltage signal, U, from a zirconia cell probe

$$U = \frac{RT}{4F}\ln(P_{O_2,\mathrm{ref}}/P_{O_2}) \qquad \text{(A3)}$$

where R is the universal gas constant, 8.31 J/mol,K, T is the absolute temperature, K, and F is the Faraday constant, 96487 As/mol. With a reference oxygen partial pressure, $P_{O_2,\mathrm{ref}}$, of 0.21 this yields a voltage signal of 0.3 V for a stoichiometric mixture at 850°C.

APPENDIX B. CONNECTION BETWEEN f_{red} AND MASS OF COMBUSTIBLES

Assume that the gas has a uniform flow rate and that a burning/devolatilising particle causes an understoichiometric gas plume. The probability that an oxygen measuring probe of infinitesimal size located at a higher level will be in this plume is A_p/A_{cs}, where A_p and A_{cs} are the cross–section areas of the plume and of the combustor. Assuming that the bed contains n such particles with plumes of cross–section areas of A_p yields the following probability for not being in a plume:

$$P_{ox} = (1 - A_p/A_{cs})^n \tag{B1}$$

and the probability for being in a plume

$$P_{red} = 1 - P_{ox} = 1 - (1 - A_p/A_{cs})^n = 1 - \exp(n \cdot \ln(1 - A_p/A_{cs})) \tag{B2}$$

which, since $(1 - A_p/A_{cs}) \simeq 1$, can be reduced to

$$P_{red} = 1 - \exp(-n \cdot A_p/A_{cs}) \tag{B3}$$

Here n is proportional to the mass of combustible particles, m_{comb}, and, assuming that the volume flow of reducing gas from a particle is independent of the gas flow rate, A_p is inversely proportional to the gas flow rate, $\dot{m}_{prim.air}$, which yields

$$P_{red} = 1 - \exp(-c_1 m_{comb}/\dot{m}_{prim.air}) \tag{B4}$$

where c_1 is a constant.

It should be pointed out that the model is a simplification and does not take into account, for example, the complicated gas flow pattern in a fluidised bed.