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# High-Temperature Release of SO$_2$ from Calcined Cement Raw Materials

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**ABSTRACT:** During combustion of alternative fuels in the material inlet end of cement rotary kilns, local reducing conditions may occur and cause reductive decomposition of sulfates from calcined cement raw materials. Decomposition of sulfates is problematic because it increases the gas-phase SO$_2$ concentration, which may cause deposit formation in the kiln system. In this study, the release of sulfur from calcined cement raw materials under both oxidizing and reducing conditions is investigated. The investigations include thermodynamic equilibrium calculations in the temperature interval of 800−1500 °C and experiments in a tube furnace reactor in the temperature interval of 900−1100 °C. The investigated conditions resemble actual conditions in the material inlet end of cement rotary kilns. It was found that the sulfates CaSO$_4$, K$_2$SO$_4$, and Na$_2$SO$_4$ were all stable under oxidizing conditions but began to decompose under reducing conditions. Particularly, CaSO$_4$ was sensitive to reducing conditions. The sulfur release was most significant if the gas atmosphere frequently shifted between oxidizing and reducing conditions. An increasing temperature from 900 to 1100 °C under alternating oxidizing and reducing conditions was also observed to increase the sulfur release from the calcined raw materials by a factor of 3, from 14 to 48%.

## ■ INTRODUCTION

Cement production is energy-intensive, with an energy usage of approximately 3 MJ/kg of cement clinker produced.[1] With an annual global cement production of 2.83 billion tons of cement, the cement industry is responsible for approximately 2% of the world's primary energy consumption.[2,3]

Fuel consumption accounts for about 30−40% of the total cement clinker production costs.[4] Traditionally, cement production has mainly depended upon the fossil fuels coal, oil, and natural gas. Because of fierce competition in the cement market, increasing fossil fuel prices, and environmental concerns, cement producers have increased the use of alternative fuels as a substitute for fossil fuels to achieve the most economic fuel mix. In this context, "alternative fuels" cover all nonfossil fuels and waste from other industries. Popular alternative fuels in the cement industry are tire-derived fuels, biomass residues, and different commercial and industrial wastes.

It is attractive to use coarse, solid alternative fuels in the material inlet end of cement rotary kilns to save expenses for shredding of the fuels to smaller particles and to increase fuel flexibility of the system. High temperatures in the rotary kiln and material retention times of several minutes provide good conditions for fuel burnout.

Figure 1 shows a simplified flow diagram and main sulfur reactions of a rotary kiln and calciner. Preheated cement raw materials are admitted to the calciner from the preheater (the preheater above the calciner is not shown). Because the raw materials have been preheated to around 800 °C, only inorganic-bound sulfur is present in the raw materials, mainly in the form of sulfates. Besides sulfur input from the cement raw materals, sulfur may also be introduced with the fuels in either calciner or rotary kiln. Sulfur from the fuel may be either organic- or inorganic-bound, and in Figure 1, sulfur input via the fuels is indicated by a S in parentheses.

The calciner acts as a fluidized-bed reactor where good contact between hot gas from the rotary kiln or tertiary air duct and raw materials from the preheater provide optimal conditions for gas−solid heat transfer and fuel combustion that drives the endothermic calcination of limestone.

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g) \qquad (1)$$
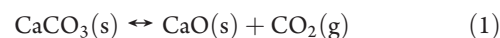
Besides calcination of limestone, the conditions in the calciner with temperatures in the range of 800−900 °C, good gas−solid mixing, and excessive amounts of CaO also favor the SO$_2$ capture reaction.[5]

$$CaO(s) + SO_2(g) + \frac{1}{2}O_2(g) \leftrightarrow CaSO_4(s) \qquad (2)$$
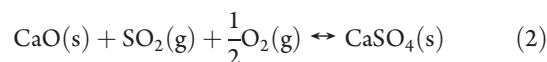
Because of the efficient SO$_2$ capture by CaO in the calciner, SO$_2$ emissions because of sulfur oxidation in the rotary kiln are negligible at modern cement plants equipped with a calciner. SO$_2$ emissions from cement plants are mainly due to oxidation of pyrite, Fe$_2$S, from the cement raw materials in the early stages of the preheater.[6] An exception, however, are cement plants operating with a bypass, where a fraction of the kiln gases are released to the atmosphere without being transported through the calciner. This may result in increased SO$_2$ emissions.

The partially calcined raw materials from the calciner are admitted to the material inlet end of the rotary kiln, where the calcination reaction is completed. In this paper, fully or partly calcined cement raw materials will be denoted calcined raw meal.

Sulfur present in the calcined raw meal is mainly bound as CaSO$_4$ or as alkali sulfates. The calcined raw meal is then
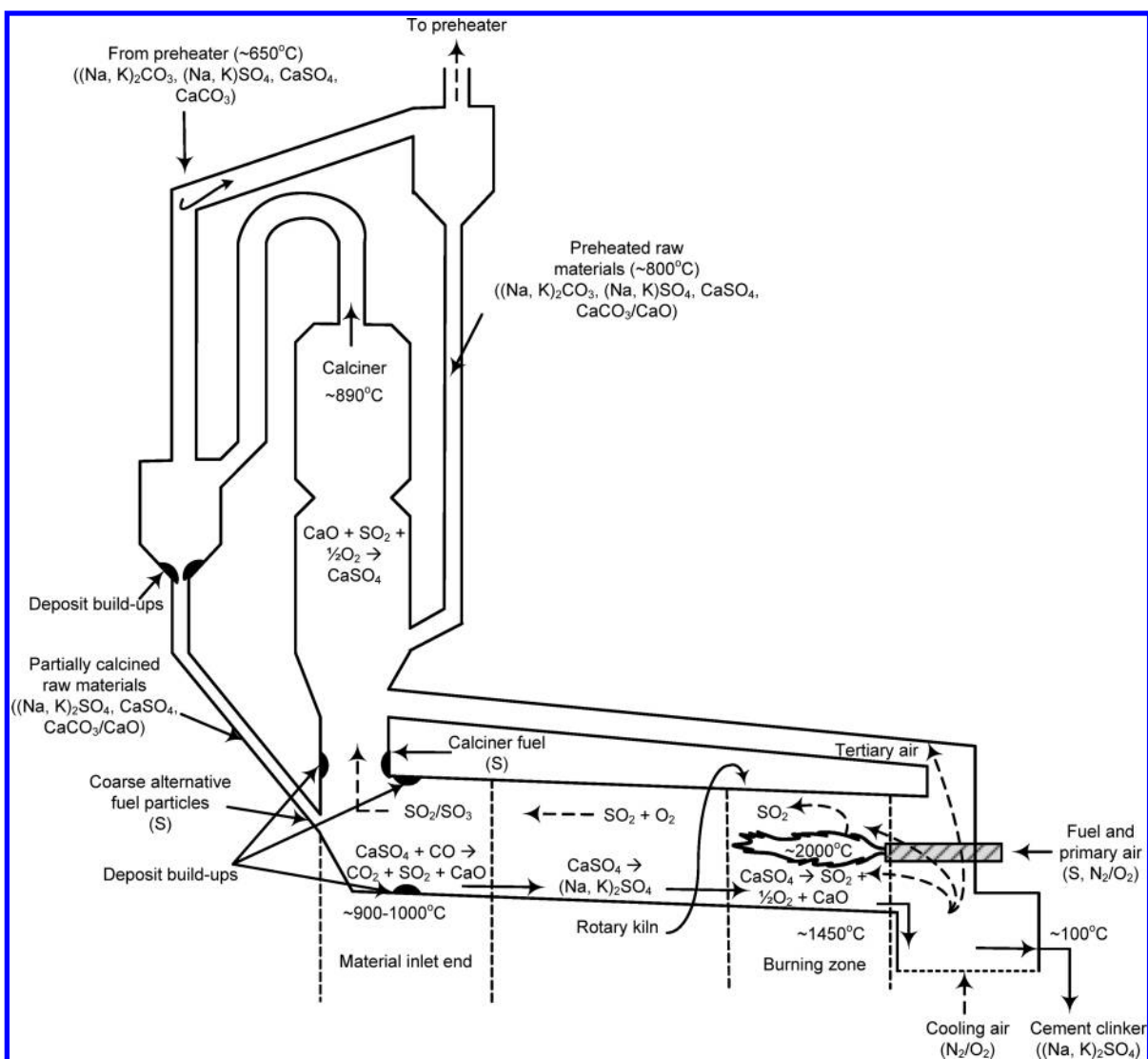
**Figure 1.** Simplified flow diagram of a rotary kiln, calciner, and material flows from a preheater, showing sulfur balances. Arrows indicate the flow direction, and the principal reactions are shown.

transported by the rotational movement and slight inclination of the rotary kiln toward the hot burning zone, where flame temperatures are in the range of 2000 °C and material temperatures are around 1450 °C. The clinker reactions take place during the gradual heating of the calcined raw meal as it is transported through the rotary kiln. During the gradual heating of the calcined raw meal, a sulfate melt is formed, which facilitates the formation of alkali sulfates, $Na_2SO_4$ and $K_2SO_4$, which are more thermodynamically stable than $CaSO_4$.[7] $CaSO_4$ will decompose at the high temperatures present in the burning zone and form $SO_2$.

$$CaSO_4(s) \leftrightarrow SO_2(g) + \frac{1}{2}O_2(g) + CaO(s) \qquad (3)$$
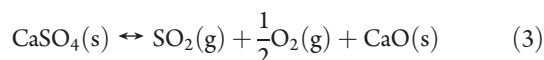
The fraction of $CaSO_4$ that decomposes in the burning zone depends upon parameters such as retention time, clinker and gas temperatures, gas composition, and clinker nodule size. High $SO_2$ concentrations in the gas phase suppress dissociation of $CaSO_4$ to CaO and $SO_2$ in the calcined raw meal.[7,8]

$SO_2$ formed in the rotary kiln is transported with the kiln gases to the calciner, where the previously described sulfur capture on

CaO takes place. Thus, an internal sulfur cycle in the rotary kiln and calciner is established. The fraction of sulfur released as $SO_2$ depends upon the sulfur/alkali ratio in the rotary kiln. High levels of alkali metals will favor the formation of alkali sulfates rather than the formation of free $SO_2$.[9]

After the rotary kiln, the cement clinker is quench-cooled by ambient air as cooling air. Sulfur in the cement clinker is mainly bound as $Na_2SO_4$, $K_2SO_4$, or $3K_2SO_4 \cdot Na_2SO_4$. However, it may also be present as $CaSO_4$.[10]

The main challenge with respect to alternative fuel use in the material inlet end of rotary kilns is that the solid fuel particles will be in physical contact with the calcined raw meal. During the fuel devolatilization, reducing agents, such as CO, $H_2$, and/or hydrocarbons, are formed. These reducing agents may react with minor elements in the calcined raw meal before they are oxidized to their ultimate combustion products, $H_2O$ and $CO_2$. In addition, if the fuel particles are fully or partly covered by calcined raw meal, mass transfer of oxygen to the fuel char will be hindered. Sub-stoichiometric amounts of oxygen will lead to incomplete oxidation of the fuel char, forming reducing agents in form of CO, $H_2$, and/or hydrocarbons.

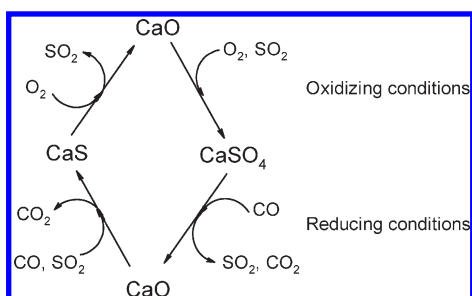**Figure 2.** Sulfur transformation during periodically changing oxidizing and reducing conditions.[17]

| calcined raw meal | wt % | mol/kg of clinker |
|---|---|---|
| $SiO_2$ | 18.00 | 3.000 |
| $Al_2O_3$ | 4.76 | 0.467 |
| $Fe_2O_3$ | 2.30 | 0.144 |
| CaO | 56.80 | 10.128 |
| $K_2O$ | 2.50 | 0.266 |
| $Na_2O$ | 0.20 | 0.032 |
| S total | 2.66 | 0.829 |
| Cl | 1.17 | 0.330 |

It is widely accepted that Portland cement should be burnt under oxidizing combustion conditions.[11] The reason is that the existence of local reducing conditions in the calcined raw meal charge may affect the product quality and process stability of the kiln system. The product quality can be influenced by calcined raw meal components, such as $Fe^{III}$, being reduced to $Fe^{II}$. $Fe^{II}$ catalyzes alite $(3CaO \cdot SiO_2)$ decomposition, the main strength-giving component in cement.[11] The process stability is affected by the increased release of sulfur from the calcined raw meal, mainly by reductive decomposition of $CaSO_4$.

$$CaSO_4(s) + CO(g) \leftrightarrow CaO(s) + CO_2(g) + SO_2(g) \quad (4)$$
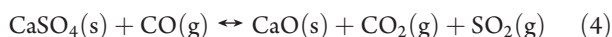
This reaction is shown in the material inlet end of the rotary kiln (see Figure 1). Increasing amounts of $SO_2$ in the cement kiln system are problematic because $SO_2$ promotes the formation of sulfospurrite $[2(2CaO \cdot SiO_2) \cdot CaSO_4]$ and calcium sulfoaluminate $(3CaO \cdot 3Al_2O_3 \cdot CaSO_4)$, some of the principal constituents of deposit buildups found in rotary kilns and kiln riser ducts[12] (see Figure 1). These sulfur-containing deposit buildups can lead to blockages that need to be removed, sometimes by a temporary plant shutdown.

With respect to local reducing conditions caused by alternative fuel combustion in the material inlet end of cement kilns, the most important challenge is assumed to be process stability because of sulfur release from the calcined raw materials and to a lesser degree product quality. Product quality is mainly affected by local reducing conditions in the kiln burning zone, which is a different situation.

The aim of this work is to obtain quantitative data on the release of $SO_2$ from calcined cement raw materials under conditions that resemble those in the material inlet end of rotary kilns. The purpose is to document the impact of variations in the local stoichiometry on the sulfur release. This type of information is useful in the prediction of effects on sulfur release during use of solid alternative fuels in the material inlet end of cement rotary kilns. The work includes both thermodynamic calculations on phase equilibria and experiments in a high-temperature tube furnace reactor. As described in the next section, most related knowledge is obtained under fluidized-bed conditions, where both temperatures and Ca/S ratios are typically lower than in the material inlet end of cement rotary kilns.

## ■ HIGH-TEMPERATURE REACTIONS BETWEEN $SO_2$ AND LIMESTONE

Absorption of $SO_2$ on limestone under fluidized-bed conditions has been studied extensively during the last few decades.[6,13−18] Even though these investigations are not directly applicable to describe the conditions in the material inlet end of cement rotary kilns, they

do include relevant descriptions of mechanisms for sulfur release and capture by limestone at temperatures up to 1200 °C and under oxidizing as well as reducing atmospheres. An important point to note however is that these investigations only include reactions between limestone and sulfur species, whereas a full investigation of the reactions taken place in cement rotary kilns should also include other major components present in the calcined cement raw materials because they may affect the sulfur chemistry. In addition, the Ca/S molar ratio studied under fluidized-bed conditions was typically in the range of 1:1−4:1 which differs from the conditions in cement rotary kilns, where there is a massive excess of Ca relative to sulfur. The Ca/S molar ratio in the calcined raw meal that enters the rotary kiln is typically higher than 10:1.[19]

The following reaction mechanism for reductive decomposition of $CaSO_4$ has been proposed:[17]

$$CaSO_4(s) + CO(g) \leftrightarrow CaSO_3(s) + CO_2(g) \quad (5)$$

$$CaSO_3(s) \leftrightarrow CaO(s) + SO_2(g) \quad (6)$$
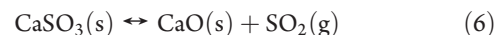
CO is believed to react directly on $CaSO_4$, giving $CaSO_3$ and $CO_2$. $CO_2$ is rapidly desorbed, while $CaSO_3$ disproportionates and forms CaO and $SO_2$. $CaSO_3$ is believed to be an important reaction intermediate. The formed CaO is subsequently sulfidized to CaS according to

$$CaO(s) + SO_2(g) + 3CO(g) \leftrightarrow CaS(s) + 3CO_2(g) \quad (7)$$
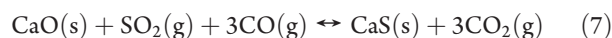
Returning to oxidizing conditions, CaS is oxidized to CaO by the reaction

$$CaS(s) + 1.5O_2(g) \leftrightarrow CaO(s) + SO_2(g) \quad (8)$$

The CaS oxidation is a rapid and very exothermal reaction, which may lead to a temperature increase.[20] The final step is the formation of $CaSO_4$ by the reaction of CaO, $SO_2$, and $O_2$, which is also an exothermal reaction[20]

$$CaO(s) + SO_2(g) + \frac{1}{2}O_2(g) \leftrightarrow CaSO_4(s) \quad (9)$$
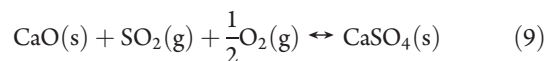
Hansen et al.[16,17] studied phase equilibria for the $SO_2$−CaO−$CaSO_4$−CaS−CO−$CO_2$ system. They performed experiments in an electrically heated laboratory-scale fixed-bed reactor developed to simulate the changing oxidizing and reducing conditions similar to the conditions that particles will experience in a fluidized-bed reactor. They found that any transformation between $CaSO_4$ and CaS takes place via CaO. This transformation cycle is shown in Figure 2, which also illustrates the competition between sulfur capture and sulfur release. This competition depends upon parameters such as partial pressures of $SO_2$, CO, and $CO_2$ (see the phase
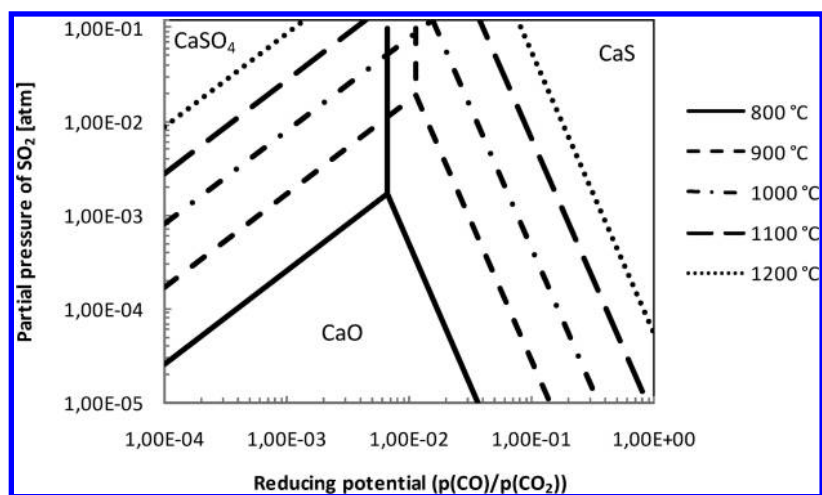
**Figure 3.** Phase diagram for the $SO_2-CaO-CaSO_4-CaS-CO-CO_2$ system (on the basis of thermochemical data from Barin).[21]

diagram in Figure 3). The temperature is a very important parameter. An increase in the temperature in the interval of 800−1200 °C will shift the equilibrium toward CaO and release more $SO_2$.[16]

During devolatilization and combustion of alternative fuels in an oxygen-lean environment, several reducing agents may be formed: CO, $H_2$, $CH_4$, as well as other hydrocarbons. It is well-documented that reducing agents, such as CO and $H_2$, can promote reductive decomposition of $CaSO_4$.[16,17,22] Hansen et al.[17] studied the rate of reductive decomposition with three reducing agents, CO, $H_2$, and $CH_4$. It was observed that the rate of decomposition was fastest with $H_2$ as a reducing agent. This is in agreement with earlier findings, which showed that the rate was increased by a factor 2 or 3 when the reducing agent was $H_2$ instead of CO.[23] Also, Diaz-Bossio et al. reported that the rate of reductive decomposition was fastest with $H_2$ relative to CO.[23] Hansen et al. did not detect any reductive decomposition of $CaSO_4$ with $CH_4$ as a reducing agent, even though the reaction is thermodynamically feasible.[17] It was assumed to be because reductive decomposition of $CaSO_4$ with $CH_4$ is a very slow process that did not have sufficient time to proceed during the 30 s intervals used in the experiments.

Turkdogan and Vinters also showed that elemental carbon could be used as a reducing agent.[24] The conversion rate of $CaSO_4$ to $SO_2$ and/or CaS was reported to be determined by the rate of oxidation of carbon to CO, which then rapidly reduced $CaSO_4$.

## THERMODYNAMIC EQUILIBRIUM CALCULATIONS

To provide the basis for a better understanding of the inorganic chemistry in the rotary kiln material inlet, thermodynamic equilibrium calculations were performed using the commercially available software FactSage 6.0. This program uses the principle of minimization of the total Gibbs free energy to calculate the equilibrium composition of a chemical system with known total elemental composition, temperature, and pressure.

**Input Data.** The equilibrium calculations are based on the composition of calcined cement raw meal and the flue gas leaving the rotary kiln. These compositions are shown in Tables 1 and 2. It should be noted that the calcined raw meal used in the calculations contains a relatively high amount of chlorine and sulfur, relative to the guidelines for a stable kiln operation.

The following input data were used: (1) Chemical compositions of calcined raw meal and flue gas are as specified in Tables 1

**Table 2. Flue Gas Compositions Used in the Equilibrium Calculations**

| oxidizing conditions ($\lambda = 1.3$) | vol % | mol/kg of clinker | reducing conditions ($\lambda = 0.9$) | vol % | mol/kg of clinker |
|---|---|---|---|---|---|
| $CO_2$ | 25.00 | 5.580 | $CO_2$ | 25.00 | 5.580 |
| $H_2O$ | 5.00 | 1.116 | $H_2O$ | 5.00 | 1.116 |
| $O_2$ | 5.00 | 1.116 | $O_2$ | 0.00 | 0.000 |
| CO | 0.10 | 0.022 | CO | 2.00 | 0.446 |
| $SO_2$ | 0.05 | 0.011 | $SO_2$ | 0.05 | 0.011 |
| $N_2$ | 64.85 | 14.475 | $N_2$ | 67.95 | 15.167 |
| total | 100.00 | | total | 100.00 | |

and 2. All elements are inserted as mol/kg of clinker. (2) It is assumed that there is 1 kg of calcined raw meal and 0.5 N m³ flue gas for each kilogram of clinker produced. (3) The following elements were included: C, H, N, O, S, Cl, K, Na, Ca, Si, Fe, and Al. (4) The flue gas is either oxidizing ($\lambda = 1.3$) or reducing ($\lambda = 0.9$). (5) Temperature = 800−1500 °C, with a step size of 25 °C. (6) Pressure = 1 atm.

For the equilibrium calculations, ideal gas-phase compounds, solid-phase compounds, and liquid-phase compounds were included from the FactSage 6.0 compound database.

**Limitations.** The equilibrium model has the following limitations, which should be considered when comparing the results to actual conditions: (1) The model does not consider mass-transfer and kinetic limitations. In an industrial rotary kiln, the residence time may be too short for the species to come in contact with each other and for reactions to take place. Furthermore, the residence time may be too short for the transformation or decomposition of some compounds. Therefore, the predicted formation of compounds may exceed that occurring in reality. (2) The model does not take into account in which form the elements are initially present in the calcined raw meal and flue gas. In reality, the elements may be bound in different minerals and be released at different temperatures. This may affect the distribution of the element between the solid, liquid, and gas phase. It may also affect the compounds formed and the phase distribution of other elements.

Because of these limitations, the results of the equilibrium calculations cannot be used for a quantitative comparison to
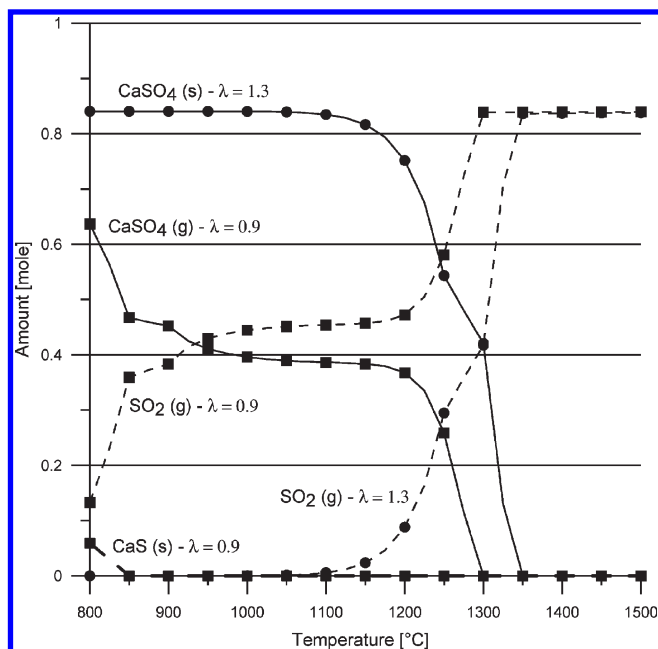
**Figure 4.** Equilibrium calculations for S distribution in calcined raw meal. The gas atmosphere is either oxidizing with 5 vol % $O_2$ ($\lambda$ = 1.3) or reducing with 2 vol % CO ($\lambda$ = 0.9).



**Figure 5.** Sulfur retention in calcined raw meal as a function of the temperature and gas atmosphere. Note the cutted y axis.

experimental data but only to determine which species are likely to be formed under different gas atmospheres.

**Influence of Reducing Conditions.** To investigate the effect of changing the atmosphere from oxidizing to reducing, the calcined raw meal is exposed to (a) an atmosphere with 5 vol % oxygen and (b) an atmosphere with 0 vol % oxygen and 2 vol % CO. The exact composition of calcined raw meal and flue gas is given in Tables 1 and 2.

The equilibria for oxidizing and reducing conditions are shown in Figure 4. Only the main sulfur-containing compounds are included for clarity. The figure shows the sulfur distribution between $CaSO_4$, CaS, and $SO_2$ at various temperatures and under either oxidizing or reducing atmosphere. It is noted that no alkali sulfates are formed in the studied case, because the formation of alkali chlorides is thermodynamically favored.

The most important observation from Figure 4 is that the decomposition of $CaSO_4$ to CaO and $SO_2$ takes place at lower temperatures when reducing conditions are prevailing. Under oxidizing conditions, $CaSO_4$ is stable until approximately 1100 °C. At temperatures between 1100 and 1350 °C, $CaSO_4$ is gradually decomposed, forming CaO and $SO_2$. Above 1350 °C, $CaSO_4$ is not thermodynamically stable and all sulfur is released as $SO_2$. The situation is very different under reducing conditions, where $CaSO_4$ is observed to be partly reductively decomposed already at temperatures below 800 °C. The reductive decomposition continues until approximately 1300 °C. At higher temperatures, all sulfur is present as $SO_2$. The reductive decomposition of $CaSO_4$ takes place because sulfates can be used as an oxygen donor under reducing conditions. It should also be noted that a fraction of the sulfur is present as CaS under reducing conditions. However, CaS is only stable at temperatures below 850 °C, and the sulfur is released as $SO_2$ at higher temperatures. This is in correspondence with the $CaSO_4$–CaS–CaO–$SO_2$–$O_2$–CO phase diagram in Figure 3.

Through the equilibrium calculations, it was also found that the phase distribution of Cl-containing compounds, such as HCl, NaCl,
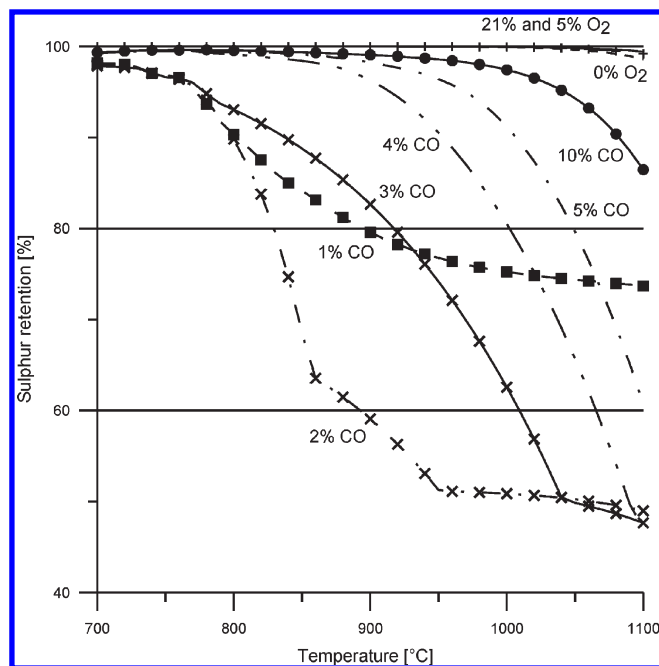
and KCl, is not affected by the change in the gas atmosphere. It is identical whether the atmosphere is oxidizing or reducing. This result was also expected because Cl is known to be much more sensitive to the temperature than to the gas atmosphere.[25]

The sulfur retention in the calcined cement raw materials will depend upon the specific degree of reducing atmosphere. The sulfur retention under different atmospheres and in the temperature interval of 700–1100 °C is shown in Figure 5. This temperature interval is representative for the conditions in the material inlet end of cement rotary kilns, where fully or partly calcined raw materials enter the rotary kiln with a temperature of approximately 900 °C and where the kiln flue gas leaves the rotary kiln with a temperature of approximately 1000–1100 °C. It is observed that all sulfur is retained in the calcined raw meal under oxidizing conditions with 5–21% $O_2$. These two curves are identical and at 100% sulfur retention in the temperature interval. Also, under inert conditions with 0% $O_2$, the sulfur retention is observed to be 100%, except above 1050 °C, where a minor sulfur release is observed.

The sulfur release increases significantly when reducing conditions prevail. The sulfur release does not increase with an increasing concentration of the reducing agent CO. Instead, the situation can be divided into mildly reducing conditions with 1–3% CO and strongly reducing conditions with 4–10% CO. The sulfur release is observed to be most significant under mildly reducing conditions, where it accelerates at temperatures above 780 °C. At 1% CO, a fraction of the sulfur is released because of reductive decomposition of $CaSO_4$. However, most of the sulfur is still retained in the calcined raw meal. The thermodynamic calculations suggest that the sulfur is stabilized as $K_2SO_4$ and $K_2Ca_2(SO_4)_3$ at 1% CO. The 2% CO is observed to lead to a high sulfur release, reaching 50% at 950 °C. This is because the compound $K_2Ca_2(SO_4)_3$ is not stable under this reducing atmosphere, but at the same time, the reducing atmosphere is not strong enough to stabilize sulfur as CaS. Thus, phase equilibria are shifted toward free $SO_2$.
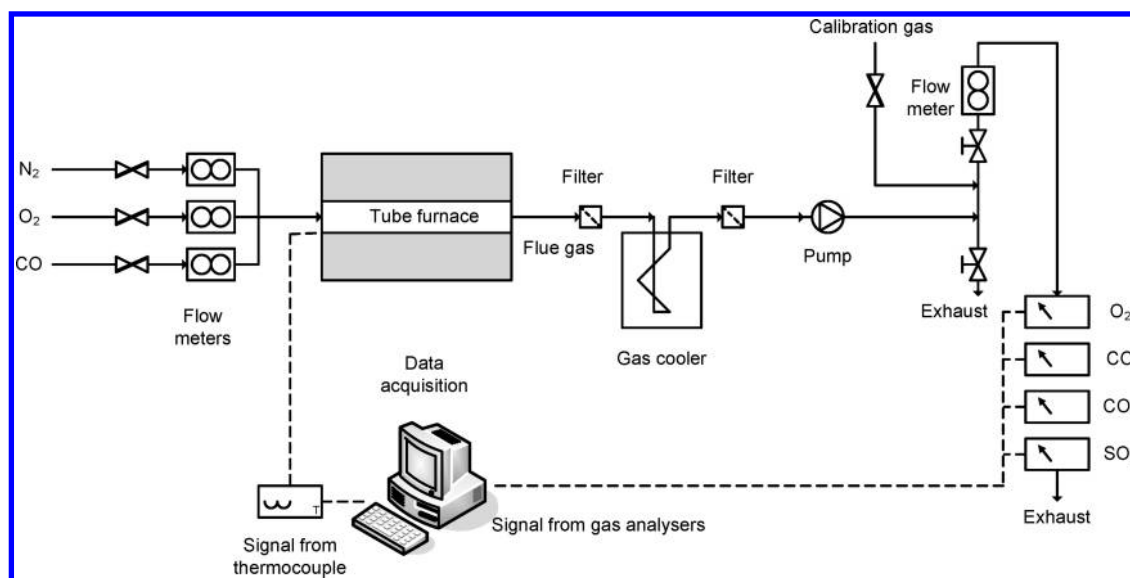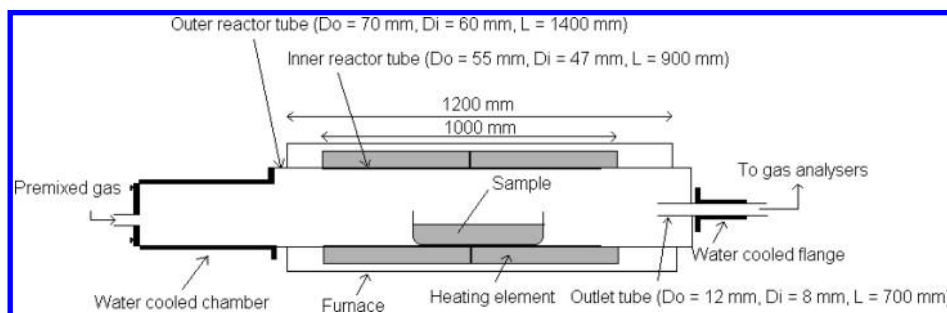
**Figure 6.** Experimental setup.



**Figure 7.** Sketch of the tube furnace reactor with size specifications of the reactor tubes ($D_o$, outer diameter; $D_i$, inner diameter; and $L$, length).

**Table 3. Composition of Calcined Raw Meal Used for the Experiments**

| component | amount (wt %) |
|---|---|
| CaO | 67 |
| $SiO_2$ | 20 |
| $Al_2O_3$ | 5 |
| $Fe_2O_3$ | 3 |
| $CaSO_4$ | 5 |

The sulfur release is lower at 3% CO because this stronger reducing atmosphere favors the formation of CaS. However, the thermal stability of CaS decreases as the temperature increases; therefore, at 1050 °C, the sulfur release reaches the same level as for 2% CO.

At strongly reducing conditions, 4–10% CO, the sulfur release is observed to be lower than under mild reducing conditions. This is again because sulfur is retained in the calcined raw meal as CaS. However, as the temperature increases and approaches 1100 °C, the sulfur release increases rapidly because of the thermal instability of CaS. These observations are in good correspondence with the phase diagram shown in Figure 3, which indicates that sulfur may be stabilized as either $CaSO_4$ at a low reducing potential or CaS at a high reducing potential.

**Relative Stability of Sulfates toward Reducing Conditions.** Sulfur introduced to the kiln system with the fully or partly

calcined raw materials will mainly be in the form of sulfates, $CaSO_4$, $Na_2SO_4$, and $K_2SO_4$. The distribution is dependent upon parameters such as concentrations of these individual elements, level of chlorine available to react with the alkali metals, temperature, etc. Because it is clear that the stability of sulfates is affected by the gas atmosphere, the relative stability of the sulfates has been studied through equilibrium calculations.

On the basis of these equilibrium studies of the three dominating sulfates present in the kiln system, it is clear that reducing conditions generally shift the equilibrium toward more $SO_2$ in the gas phase. The sulfates are used as an oxygen donor in the oxidation of CO to $CO_2$.

An interesting observation was that the relative stability of the sulfates was $Na_2SO_4 > K_2SO_4 \gg CaSO_4$, an observation that was later confirmed experimentally. $CaSO_4$ is thus less stable and more critical than the alkali sulfates. This observation may indicate that it is desirable to bind as much sulfur as possible as alkali sulfates, to keep the sulfur evaporation in the kiln system as low as possible.

## ■ EXPERIMENTAL SECTION

The release of sulfur from cement raw materials as a function of the gas atmosphere was quantified in the temperature interval of 900–1100 °C. Different gas atmospheres was tested, but most of the experiments were conducted with 5 vol % $O_2$ in $N_2$ to represent an oxidizing atmosphere and 2 vol % CO in $N_2$ to represent a reducing atmosphere. The temperature interval and gas atmospheres resemble realistic temperatures and atmospheres in the material inlet end of cement rotary kilns. The used cement raw materials
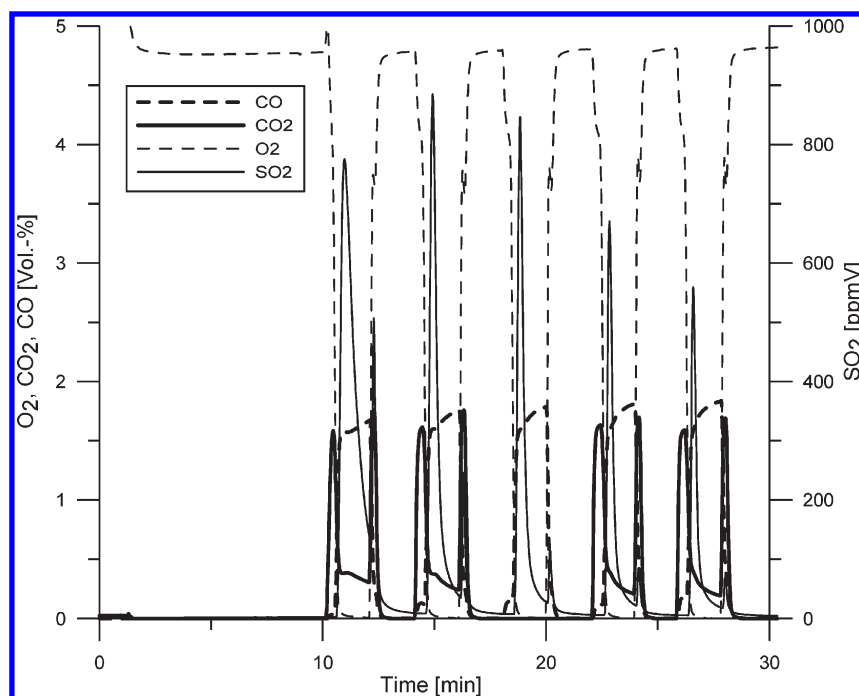
**Figure 8.** Concentrations of $SO_2$, $O_2$, CO, and $CO_2$ during an experiment with calcined raw meal under alternating oxidizing and reducing conditions at 1100 °C and gas flow = 10 NL/min.

were based on a synthetic mixture of pure chemicals of CaO, $SiO_2$, $Fe_2O_3$, $Al_2O_3$, and a sulfate, such as $CaSO_4$, $Na_2SO_4$, or $K_2SO_4$. These chemicals were mixed in the right proportions to simulate a simplified calcined raw meal, with a well-known content of sulfur. The compounds are also representative for the form that the elements have when they enter the rotary kiln.

**Laboratory-Scale Tube Reactor Setup.** A laboratory-scale tube reactor setup was used for the experiments (see Figure 6). It consists of a gas mixing panel to mix the gases in the desired concentration and flow, the electrically heated reactor in which the sample is placed, filters to remove particles and moisture, a pump, and the analysers that measure the gas concentration. Measured gas concentrations and temperatures are collected in a computer.

The reactor depicted in Figure 7 is a two-zone electrically heated tube furnace in which a horizontal alumina tube is mounted, having water-cooled flanges at both ends. The tube furnace has a maximum operating temperature of 1150 °C. The internal diameter of the inner tube is 47 mm, and it has a heated length of 900 mm. The sample is placed in a platinum/rhodium holder (95% Pt). The dimensions of the sample holder are $H \times W \times L = 2 \times 3 \times 10$ cm, corresponding to a volume of approximately 60 mL. During an experiment, the sample holder is placed in the center of the tube furnace and the tube furnace is sealed with a stainless-steel plate, which contains an opening for gas inlet. The gas composition exiting the reactor is monitored on the computer. The sample will be heated from room temperature to the desired temperature by conduction, convection, and radiation from the tube walls and gas.

To test whether the reactor setup are producing stable and sufficient gas temperatures, center-line temperature profiles in the tube reactor were established. It is concluded that, at the position of the sample holder, the measured temperature is within $\pm 5$ °C of the reactor set point temperature. The mass flow controllers were calibrated prior to the experiments. The actual gas flows were found to be within $\pm 4\%$ of the set point values on the mass flow controllers. The uncertainty on the $O_2$, CO, and $CO_2$ analysers is $\pm 2\%$ of the total span range of each species, while it is $\pm 5\%$ on the $SO_2$ measurement.

**Method.** The composition of used calcined cement raw meal is shown in Table 3. Only the main components as well as a sulfur-

containing component are included. The sulfur-containing component is $CaSO_4$, which is believed to be the dominant sulfur-containing component in calcined raw meal entering cement rotary kilns, because of the excessive amounts of calcium relative to alkaline metals. It should be noted that the sulfur content in the calcined raw meal is relatively high (1.17 wt %) but not unrealistic. Prior to the experiments, the synthetic calcined raw meal was stored under an inert atmosphere to prevent CaO from reacting with moisture or atmospheric $CO_2$.

The following procedure is followed during each experiment: A total of 5 g of the calcined raw meal sample is placed in a well-distributed layer in the sample container. The sample amount is chosen to have a suitable amount of sulfur in the experiments to detect sulfur releases in the parts per million (ppm) range of 0−1000 ppm. The sample container is then placed in the tube furnace at the desired temperature. A thermocouple is placed in the center of the sample container to continuously log the temperature. The tube furnace is sealed, and the sample is heated for 10 min in an oxidizing atmosphere of 5% $O_2$ in $N_2$. Practically no $SO_2$ release was observed under the 10 min heating time. After 10 min, the gas atmosphere can be changed to the desired atmosphere, whereby the experiment begins. The gas flow is kept at 10 NL/min at all times. The gas composition is logged with 1 s intervals for subsequent evaluation of the sulfur release. In all experiments, the sulfur release was measured by integrating the $SO_2$ signal over time. The experiments always lasted 20 min, not including the 10 min heating time. The $SO_2$ concentration was measured in parts per million by volume (ppmV), while $O_2$, $CO_2$, and CO concentrations were measured in volume percentages (vol %).

In addition to the fixed gas atmosphere, experiments were also conducted with an alternating gas atmosphere between oxidizing and reducing. In these experiments, 2 min intervals were used: 2 min with reducing conditions (2 vol % of the reducing agent in nitrogen), followed by 2 min with oxidizing conditions (5 vol % $O_2$ in $N_2$). This procedure was repeated over 20 min, which gave time for five reducing intervals and five oxidizing intervals.

**Assumptions and Uncertainties.** This section discusses important assumptions and uncertainties that may influence the obtained results. (1) It has been experimentally determined that the sample is
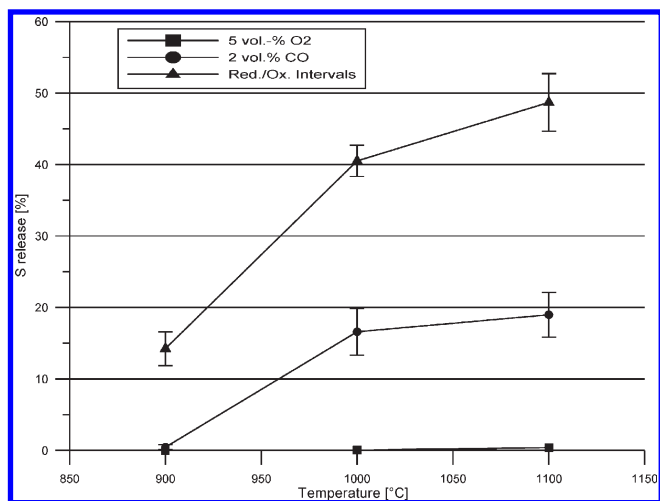
**Figure 9.** Effect of the gas atmosphere on the sulfur release from calcined raw meal. Sulfur release was evaluated after 20 min of reaction time.

heated for approximately 2−5 min in the tube furnace before the sample reaches the same temperature as the tube furnace. The exact heating time depends upon the sample size and temperature to be reached; a 5 g sample, which is the sample size used in the experiments, uses approximately 2 min to reach 900 °C. To ensure sufficient time for sample heat up, the sample will stay 10 min in the furnace under oxidizing conditions before an experiment is started. (2) The gas passing through the reactor will be pure $N_2/O_2/CO/H_2/CH_4$ in different compositions. Under industrial-scale conditions, the gas will also contain $H_2O$, $CO_2$, $NO_x$, $SO_x$, and various volatile species, such as alkaline metals or trace metals. It is assumed that the simplified gas composition used in the experiments contains the most important components and that the influence of the other components on the results can be neglected. (3) It is assumed that all sulfur released from the sample will form $SO_2$ before leaving the reactor. This assumption has been confirmed by two mass balances over two different calcined raw meal samples. After an experiment, the residual sulfur content of the sample was determined by chemical analysis and compared to the sulfur amount that was found in the flue gas as $SO_2$. In the first case, the sulfur mass balance was found to be 93%, and in the second case, 95% of the sulfur was found in either the sample or the flue gas as $SO_2$. Considering the uncertainties with sample composition, precision of analysers and mass flow controllers, as well as accuracy of the chemical analysis procedure, it is fairly safe to assume that nearly all released sulfur will be in the form of $SO_2$. This assumption is also confirmed by equilibrium calculations with the thermodynamic software FactSage, which calculates that nearly all sulfur is present as $SO_2$ under the studied conditions. (4) It is known from earlier experiments that the physical shape of the sample holder and sample mass will cause diffusion limitation of gas components, such as CO, to the sample. However, because all experiments are made with similar sample masses and procedures, it is assumed that results will be comparable. (5) The flue gas composition will not change significantly in the distance between the reactor and the analysers. To minimize this uncertainty and prevent, e.g., $SO_2$ absorption in filters and condensers, these parts were regularly cleaned or replaced to minimize the presence of compounds able to absorb $SO_2$. A gas with a known content of $SO_2$ was also regularly sent through the system to test if any $SO_2$ was absorbed before reaching the analysers. (6) The calcined raw meal to be used in the experiments is representative for calcined raw meal from an industrial plant. However, an industrial calcined raw meal will contain many minor components, which could have an effect on results.

## RESULTS AND DISCUSSION

Figure 8 shows an example of the measured concentrations during an experiment with alternating oxidizing and reducing conditions at 1100 °C. The first 10 min is the heating period under oxidizing conditions, initially atmospheric air with 21 vol % $O_2$, followed by 4.75 vol % $O_2$ in $N_2$ when the tube reactor is sealed. During the heating under oxidizing conditions, no $SO_2$ is observed. After 10 min, the gas concentration is changed to 2 vol % CO in $N_2$. Because the change is rapid, some oxygen will be left in the reactor and will react with CO, forming $CO_2$. Thus, the $CO_2$ concentration is observed to increase to approximately 1.5 vol %. After the last $O_2$ in the reactor is consumed, the CO concentration increases to approximately 1.8 vol %. At the same time, a dramatic increase in the $SO_2$ concentration is observed from 0 to 800 ppm. The formed $CO_2$ is also observed at a level of around 0.2 vol %. The $SO_2$ level drops relatively fast. When the atmosphere is again changed to oxidizing (4.75 vol % $O_2$), a new, smaller $SO_2$ peak is observed. The sulfur release cycle is observed to be repeated for each of the following reducing/oxidizing intervals, with a slight decrease in $SO_2$ each time, because the sulfur content in the sample gradually decreases. The experiment is stopped after 30 min when the fifth oxidizing interval is finished and the $SO_2$ concentration has dropped to values close to 0 ppm. However, it should be noted that more sulfur would be released from the sample if the cycles were repeated. This was tried out, and it can be concluded that the measured $SO_2$ level gradually decreases with time but that it takes more than 2 h before all sulfur has been released from the sample.

It is interesting to note from Figure 8 that the first $SO_2$ peak during the reductive decomposition of $CaSO_4$ only reaches 780 ppm, while the next $SO_2$ peak reaches 890 ppm. The first $SO_2$ peak is also wider than subsequent $SO_2$ peaks. This tendency was observed in all experiments with alternating reducing and oxidizing conditions. The same tendency has also been reported by other researchers.[16,23,26] The reductive decomposition of $CaSO_4$ is initiated by an induction period, which has been explained by the slow desorption of $SO_2$ and slow rate of nucleation of CaO. Ghardashkhani et al. reported that shifting from reducing to oxidizing and back to reducing conditions during reductive decomposition of $CaSO_4$ did not give rise to a new induction period.[26] This is in agreement with the experimental observations, where the second $SO_2$ peak reaches larger values than the first $SO_2$ peak.

The characteristic $SO_2$ peaks observed from Figure 8 during alternating reducing and oxidizing conditions can be explained by the existence of phase equilibria between different sulfur species. Under oxidizing conditions, sulfur is stabilized in the form of $CaSO_4$, and under reducing conditions, sulfur is stabilized as CaS. When the gas atmosphere changes, sulfur may be released to the gas phase as $SO_2$, as illustrated in Figure 2.

**Release Quantification.** The release of sulfur during the experiments is calculated by integration of the gas concentration of $SO_2$ over the relevant time interval

$$n_{\text{sulfur found}} = \int_0^t y_{SO_2} dt \times 10^{-6} \times \frac{PV}{RT} \tag{10}$$

where $y_{SO_2}$ is in ppmV and $V$ is the gas flow in L/s. It should be noted that, because of diffusion limitation of gas components, such as CO, only experiments made with similar sample masses can be compared. The sum of sulfur found as $SO_2$ is divided by
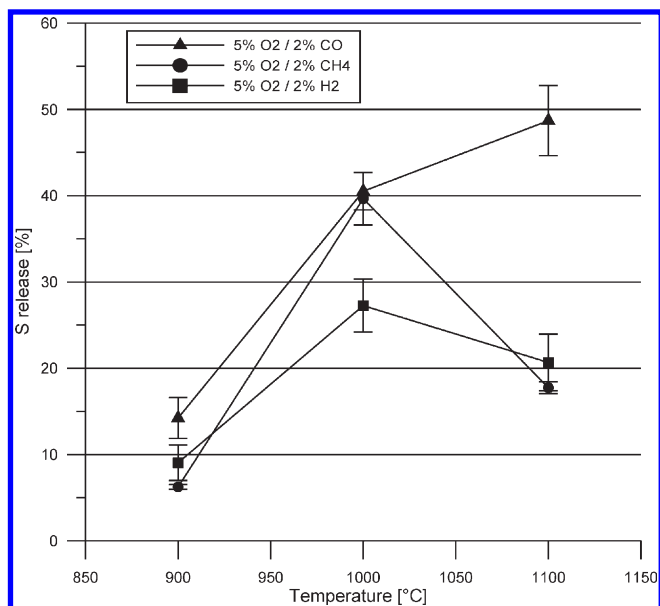
**Figure 10.** Effect of the reducing agent on sulfur release from calcined raw meal under alternating oxidizing and reducing conditions. Sulfur release was evaluated after 20 min of reaction time.

the total sulfur amount in the sample

$$\text{S release} = \frac{n_{\text{sulfur found}}}{n_{\text{sulfur in sample}}} \times 100\% \qquad (11)$$

**Effect of the Reducing Atmosphere with CO.** The sulfur release from calcined raw meal has been studied at the temperatures of 900, 1000, and 1100 °C. Two different atmospheres with 5% $O_2$ and 2% CO (pure nitrogen is the balance in both cases) as well as alternating reducing and oxidizing conditions have been studied. The results are shown in Figure 9. Under oxidizing conditions with 5% oxygen, the S release is approximately 0% in the studied temperature interval. This result has been found to be valid at all oxygen concentrations from 1 to 21%, indicating that $CaSO_4$ is generally stable under oxidizing conditions and temperatures below 1100 °C. This finding is in agreement with the thermodynamic equilibrium calculations, which did not show any decomposition of $CaSO_4$ below 1150 °C.

Under reducing conditions with 2% CO, the sulfur release was still approximately 0% at 900 °C but increased to 17% at 1000 °C and 19% at 1100 °C. This significant increase in sulfur release under reducing conditions may be explained by the formation of CaS from $CaSO_4$, in which CaO and free $SO_2$ are reaction intermediates. Each experiment was repeated 3 times, and the standard deviation were found to be ±2%.

Under shifting oxidizing and reducing intervals with 2 min of 2% CO, followed by 2 min of 5% $O_2$ continuously repeated 2 × 5 times, the sulfur release is observed to be significantly higher than under constant reducing or oxidizing conditions: 14% at 900 °C, 40% at 1000 °C, and 48% at 1100 °C. Each experiment has been repeated 3 times, and the standard deviation was found to be ±3%. This strong effect of alternating oxidizing and reducing conditions is in correspondence with the sulfur transformation cycle shown in Figure 2. Under oxidizing conditions, sulfur is stabilized as $CaSO_4$, and under reducing conditions, sulfur is stabilized as CaS. Every shift in atmosphere leads to the formation

of CaO and free $SO_2$. The formation of free $SO_2$ is particularly large at higher temperatures, whereas the lowest temperature of 900 °C can limit the sulfur release even under alternating oxidizing and reducing conditions.

The results are in correspondence with previous work, where sulfur release and capture has been studied under alternating oxidizing and reducing conditions. Lyngfelt and Leckner reported a decrease in the sulfur capture ability of limestone at temperatures above 880 °C and reducing conditions, because of reductive decomposition of $CaSO_4$.[5] Hansen et al. found that the competition between sulfur capture and sulfur release under alternating oxidizing and reducing conditions was shifted toward more sulfur release when the temperature increased.[17] Tarelho et al. found a maximal sulfur capture efficiency of limestone at around 825 °C. Higher temperatures reduced the sulfur capture efficiency, particularly under reducing conditions.[18]

**Effect of Other Reducing Agents.** Most investigations of reductive decomposition of $CaSO_4$ reported in the literature use either CO or $H_2$ as the reducing agent. Because combustion of alternative fuels in cement kilns may lead to the formation of significant amounts of CO, $H_2$, and hydrocarbons, such as $CH_4$, under substoichiometric conditions, these three reducing agents have been investigated with respect to sulfur release from calcined raw meal in the temperature interval of 900−1100 °C. The results are shown in Figure 10. The experimental conditions were shifting oxidizing and reducing intervals with 2 min of the reducing agent (2% of either CO, $H_2$, or $CH_4$), followed by 2 min of 5% $O_2$. The 2 min intervals were continuously repeated 2 × 5 times, thus 20 min of total reaction time. All experiments were repeated 3 times with a standard deviation in the order of 3%. Under these reaction conditions, the sulfur release when CO was used was 15, 40, and 48% at 900, 1000, and 1100 °C, respectively. When $CH_4$ was used, the sulfur release was 6, 40, and 17% at 900, 1000, and 1100 °C, respectively. Finally, when $H_2$ was used, the sulfur release was 8, 27, and 20% at 900, 1000, and 1100 °C, respectively.

While the results with CO are observed to lead to increased sulfur release as a function of the temperature, the results with $H_2$ and $CH_4$ are more surprising. The sulfur release increases from 900 to 1000 °C but then decreases again at 1100 °C. This was unexpected because it was assumed that the sulfur release would increase with the temperature, regardless of the reducing agent. It was also expected that $H_2$ would lead to a higher sulfur release than CO and $CH_4$ would lead to a much lower sulfur release than CO, according to Hansen's findings. Hansen found that the rate of reductive decomposition of $CaSO_4$ increased when $H_2$ was used instead of CO and that $CH_4$ gave no reductive decomposition at all.[17] However, the reaction conditions used in Hansen's experiments were quite different from the ones used in this investigation, because he used relatively short time intervals of 30 s/30 s and only studied the effect of the reducing agent at 850 °C. In this experiment, longer time intervals of 2 min/2 min were used and the temperature interval was 900−1100 °C. This may explain why $CH_4$ is found to be of comparable efficiency as $H_2$ and CO in this investigation, while Hansen reported it to be less efficient because of slower reaction kinetics.

With regard the lower sulfur release at 1100 °C relative to 1000 °C when $H_2$ and $CH_4$ were used as reducing agents, similar results have been reported by Kamphuis et al. At temperatures above 950 °C, a fraction of $SO_2$ was observed to be converted to $H_2S$, which was not detected by the analysis system, when the flue gas contained $H_2$.[27] On the basis of a series of tests with known $SO_2$ concentrations in a $H_2/N_2$ gas mixture passing

through the reactor without a sample, Kamphuis et al. established a correction factor to correlate for the formed $H_2S$. It is likely that the same phenomenon took place in the present experiments with $H_2$ and $CH_4$ because $H_2S$ can be formed from both reducing agents. This will explain why the found sulfur release is lower at 1100 °C relative to 1000 °C. Prior to the experiments, thermodynamic equilibrium calculations had been made for the calcined raw meal exposed to the reducing agents $H_2$ and $CH_4$. These thermodynamic calculations indicated that practically all released sulfur would be present as $SO_2$ under the experimental conditions. However, the thermodynamic calculations may be misleading because they do not consider reaction kinetics. $H_2S$ may be formed as an intermediate species, which leaves the reactor before the formation of $SO_2$ occurred. A sulfur mass balance should be performed to determine whether some sulfur has escaped from the system as $H_2S$ or not. Because a sulfur mass balance has not been conducted for the experiments with $H_2$ and $CH_4$, it is not directly possible to quantify the effect on sulfur release as a function of the reducing agent. However, the results do indicate that all three reducing agents, CO, $CH_4$, and $H_2$, have an effect on the sulfur release in the studied temperature interval.

## CONCLUSION

The release of sulfur from cement raw materials under both oxidizing and reducing conditions was investigated. The investigations included thermodynamic equilibrium calculations in the temperature interval of 800−1500 °C and experiments in a tube furnace reactor in the temperature interval of 900−1100 °C. The investigated conditions resemble actual conditions in the material inlet end of cement rotary kilns, where local reducing conditions may occur during combustion of solid, alternative fuel particles and where solid/gas temperatures are usually between 900 and 1100 °C. The following results were obtained: (1) The thermodynamic equilibrium calculations showed that the stability of sulfates present in calcined cement raw meal is strongly affected by the gas atmosphere. Especially, $CaSO_4$ tends to decompose at much lower temperatures under a reducing atmosphere. $K_2SO_4$ and $Na_2SO_4$ are also affected by a reducing atmosphere but not as significant as $CaSO_4$. (2) Experimentally, a clear tendency for increasing sulfur release was observed when the gas atmosphere shifted from oxidizing to reducing. No sulfur release was observed under oxidizing conditions (5 vol % $O_2$), whereas the sulfur release increased to 19% under reducing conditions (2 vol % CO) at 1100 °C. The sulfur release was particularly significant if the calcined raw meal was exposed to alternating oxidizing and reducing conditions, which led to a sulfur release of 48% at 1100 °C. (3) The sulfur release from calcined raw meal was observed to be dependent upon the temperature. Under alternating oxidizing and reducing conditions, the sulfur release was observed to be 14% at 900 °C and 48% at 1100 °C. (4) Sulfur release from calcined raw meal was shown to take place in the presence of any of the reducing agents CO, $H_2$, and $CH_4$. However, it was not possible to directly quantify the sulfur release as a function of the reducing agent, because part of the released sulfur from the experiments with $H_2$ and $CH_4$ presumably formed $H_2S$, which could not be detected by the analysis system.

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