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Published in:
Energy & Fuels

Link to article, DOI:
[10.1021/ef502746f](https://doi.org/10.1021/ef502746f)

Publication date:
2015

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Cortada Mut, M. D. M., Nørskov, L. K., Glarborg, P., & Dam-Johansen, K. (2015). SO₂ Release as a Consequence of Alternative Fuel Combustion in Cement Rotary Kiln Inlets. *Energy & Fuels*, 29(4), 2729-2737. DOI: 10.1021/ef502746f

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SO₂ release as consequence of alternative fuels combustion in cement rotary kiln inlets

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KEYWORDS: SO₂ release, calcium sulfate, combustion, alternative fuels, cement rotary kiln, reducing agents.

ABSTRACT :

The combustion of alternative fuels in direct contact with the bed material of the rotary kiln may cause local reducing conditions and subsequently decomposition of sulfates from cement raw materials, increasing the SO₂ concentration in the gas phase. The decomposition of sulfates

increases the sulfur circulation and may be problematic because high sulfur circulation can cause sticky material build-ups, affecting the process operation of the cement kiln system. The SO₂ release from cement raw materials during combustion of pine wood and tire rubber has been studied experimentally in a high temperature rotary drum, focusing on the influence of fuel particle size and volatile content. The SO₂ release increased with decreasing fuel particle size and with increasing fuel volatile content. Furthermore, CO, H₂ and CH₄, which are the main reducing gases released during fuel devolatilization, were introduced in different concentrations under the bed material. A threshold concentration for each reducing gas, below which no SO₂ release occurs, was found. Introduction of the same molar amount of gas in different concentrations during different time periods showed that a higher reducing gas concentration during a short period (representing fuel devolatilization) released a higher total SO₂ amount compared to a lower concentration during a long period (representing fuel char oxidation).

Introduction

Cement production is an energy intensive process, with an energy usage of approximately 3 MJ per kg cement clinker produced¹. The fuel consumption accounts typically for 30-40% of the total cement clinker production costs². During the last decades, an interest in replacing fossil fuels with selected waste, biomass, and by-products with recoverable calorific value, defined as alternative fuels, has arisen in order to lower production cost and due to environmental concerns². A wide range of alternative fuels is of interest, such as industrial and municipal waste, tire-derived fuels, plastic and wood waste. These fuels typically consist of relatively large particles, with different chemical and physical properties.

Alternative fuels are often directly fired in the calciner and/or to the main burner in the rotary kiln as coarse, large particles, because this requires a minimum of investments. Thereby,

partially converted or unburned solid fuels may drop into the material charge of the rotary kiln and affect the process stability. The solid fuels can end up in the bed material in the rotary kiln in four different ways depending on whether the fuels are fired in the calciner, main burner or directly into the material inlet of the kiln³. These scenarios are illustrated in Figure 1 and outlined briefly below:

1. Large solid fuel particles with a considerable weight, which are fed into the calciner and cannot be carried upwards with the gas flow, may drop through the riser duct, and into the rotary kiln.
2. Large solid fuel particles fed through the kiln burners may not be completely combusted in the flame of the main burner, and fall into the bed material.
3. Small and unconverted solid fuel particles, which are light enough to be carried upwards with the gas flow through the calciner and transported into the cyclones, can fall into the kiln inlet with the calcined raw material.
4. Coarse solid fuels may be fired directly into the rotary kiln material inlet end.

The combustion of alternative fuels in direct physical contact with the cement raw materials in the rotary kiln may cause local reducing conditions in the bed and facilitate an increase of the internal circulation of S, Cl, Na, and K, known as the volatile elements. The enhanced recirculation may lead to modifications of the process conditions (i.e., change of kiln temperatures and oxygen concentration) and may affect the clinker quality and the process operation, causing build-ups, blockages and/or corrosion.

Local reducing conditions may lead to release of SO₂ from the cement raw materials^{3,4}, enhancing the internal sulfur circulation in the cement plant. Sulfur can be introduced to cement

rotary kilns by the cement raw materials and/or by the fuels. Biomass fuels, such as wood waste and straw, contain from 0 to 0.2 wt. % sulfur, significantly less than typical fossil fuels (0.7-2.2 wt. % S in anthracite coal⁵ and 2.9-7.4 wt. % S in petcoke⁶). In the burning zone, where the bed material reaches its maximum temperature of around 1450°C, evaporation of S takes place forming SO₂, K₂SO₄ and Na₂SO₄ in the gas phase⁷. The gaseous SO₂, coming from the fuel fired in the main burner of the rotary kiln and from thermal decomposition of raw materials in the rotary kiln, flows to the calciner where good gas-solid mixing and a temperature of about 900°C favor nearly 100% capture of the sulfur by CaO^{8,9}. This reaction forms CaSO₄ that re-enters into the rotary kiln with the solid material. Thus, an internal sulfur cycle is established in the rotary kiln and the calciner. Moreover, calcium sulfate, being less thermally stable than alkali sulfates, can react with volatiles released by the fuels and release SO₂. The intensity of the sulfur cycle in the kiln system consequently is increased when fuel spillage occurs in the kiln inlet^{7,10}. The SO₂ in the hot gases of the rotary kiln can also interact with the dust in the gas, which is rich in CaO and alkali sulfates (Na₂SO₄ and K₂SO₄), and these may further react forming intermediate species that may lead to material build-ups at cooler temperatures.

Sulfur release from the cement raw materials during combustion of solid fuels has been studied only scarcely. The effect of oxygen, temperature, and fuel surface area on sulfur release during the combustion of tire rubber, pine wood, petcoke, sewage sludge and polypropylene was studied experimentally in a rotary drum by Nielsen et al.³ The SO₂ release from the raw materials was observed to increase with temperature from 700 to 1000°C and decrease with oxygen concentrations of 5 to 21%. Saw dust and tire granulates released more SO₂ in comparison with wood cubes of 10 mm thickness and tire rubber cylinders with 9 mm diameter. The effect of particle size for a specific fuel was not investigated.

The aim of the present work is to clarify the effect of particle size on sulfur release (using the same fuel and energy input) and to investigate the effect of fuel volatiles and char, respectively, on SO₂ release. Experiments are conducted in a bench-scale rotary drum similar to that of Nielsen et al.³ with fresh fuel, partly converted fuel, and char, as well as with different gaseous reducing gases (representing volatiles). In addition, the effect of temperature, oxygen and time of exposure is studied. Even though the conditions and mixing behavior in the bench-scale unit are different from those of a real rotary kiln, the findings have important implications for the industrial process.

Experimental Part

The experiments were performed in a high temperature rotary drum reactor³, which was able to simulate in a batch mode the process conditions at the material inlet end of an industrial rotary kiln and to introduce solid fuels at these conditions. In the kiln inlet of an industrial rotary kiln, the gas temperature is around 1200°C and the bed is characterized to be at 900°C with a rolling bed mode motion. The equipment is illustrated in Figure 2. It consisted of an electrically heated chamber furnace with a steel rotating drum inside. The atmosphere in the rotary drum could be controlled by introduction of different gases. The gas was admitted into the furnace through a hole of 25.5 mm in the roof and transported through the drum by an externally gas pump placed down-stream the rotary drum. Before passing the pump, the flue gas was cooled in a heat exchanger and soot particles were captured in a filter. After passing the pump, the flue gas was sent either directly to the stack or to the gas analyzers for measurements of O₂, CO, CO₂, SO₂ and NO. The fraction of the flue gas that was transported to the analyzers passed through a filter and a gas cooler for condensation of water. The chamber furnace door was equipped with a

window for visual inspection, two holes for thermocouples, and a centrally placed water-cooled tube for introduction of solid fuel. The solid fuels were placed in a sample container, which could be pushed into the hot rotary drum or pulled out to the water-cooled tube.

A mixture of quartz sand, with a particle size from 0.4 to 0.8 mm, and 2 wt. % CaSO₄ was used as synthetic raw material in order to have a controlled and homogenous bed to ensure repeatability. A volumetric bed fill degree of 5 % was used in all experiments.

The set-up was operated at 900°C, consistent with the conditions in the kiln inlet of an industrial cement kiln, with 6 rotations per minute to keep the raw material in a continuous rolling motion. A constant flow of 100 NL/min of gas with 5 or 10% O₂ in N₂ was transported through the rotary drum and passed over the raw materials. (All concentrations are volume based unless otherwise noted.) The gas was preheated to the same temperature as the raw materials in order to obtain a uniform temperature at all positions. The temperature and the gas composition were continuously logged for subsequent evaluation of the sulfur release.

The sulfur release was quantified by integrating the time dependent SO₂-signal:

$$n_{S_{release}} = \int_0^t y_{SO_2} dt \cdot 10^{-6} \cdot \frac{P \cdot V}{R \cdot T} \quad (1)$$

where y_{SO_2} [ppm] is the SO₂ concentration, R the gas ideal constant, P [Pa] the atmospheric pressure, T [K] the flue gas temperature, and V[m³/s] the volumetric gas flow.

The fuel analysis of pine wood and tire rubber cylinders is presented in Table 1. Three different particle sizes of pine wood and tire rubber were applied. The energy input was kept constant for each experiment when using different dimensions in order to enable a direct comparison of results. The pine wood cylinders had a length of 25 mm and diameters of 19, 13 and 8 mm. Due to the higher energy input of tire rubber, it was not possible to use tire rubber

particles with the same dimensions as the pine wood, while keeping both the number of particles and the total energy input constant. The tire cylinders had a length of 12 mm and diameters of 12, 9, and approx. 2 mm. For both fuels, the degree of fuel conversion, X, was calculated, assuming that the fuel conversion is proportional to the carbon conversion, by integration of the concentrations profiles of CO₂ and CO (equation 2). Figure 3 exemplifies the normalized carbon conversion of a 19 mm pine wood cylinder and indicates how the devolatilization and the oxidation is determined. The devolatilization period ends when the slope of the conversion curve decreases significantly, indicating the start of the slower char oxidation period. This definition was also used by Nielsen et al.³

$$X(t) = \frac{\int_0^t y_{CO} + y_{CO_2} dt}{\int_0^\infty y_{CO} + y_{CO_2} dt} \quad (2)$$

The effect of the degree of devolatilization was studied with the wood char. The char was made by introducing the wood cylinders into a horizontal tube reactor in a nitrogen atmosphere for 20 minutes at 300, 500 and 700°C. The degree of devolatilization was calculated on the basis of the content of volatiles before and after pyrolysis. Essentially all volatiles were released at 500°C. The average calculated degree of devolatilization was 24.5% for the wood char made at 300°C, 99.9% at 500°C, and 100 % at 700 °C.

Results and discussion

Effect of particle size

The influence of particle size on sulfur release from the synthetic raw materials at conditions corresponding to the kiln inlet is illustrated in [Figure Figure-4](#) and [Figure Figure-5](#) for tire rubber and pine wood, respectively. All experiments used an identical energy input of 55 kJ. The mass

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of the wood cylinders and the mass of tire rubber, respectively, were kept constant, e.g. five cylinders of 8 mm diameter, two cylinders of 13 mm diameter and one cylinder of 19 mm are used for wood, while for the tire rubber, a single cylinder of 13 mm diameter, two cylinders of 9 mm diameter and around 100 particles of tire granulate of 2 mm diameter were used.

When combusting tire particles, the fuel sulfur was released as S-volatiles and SO₂. The SO₂ release both from the fuel, quantified by measuring SO₂ from combustion in a bed consisting of quartz sand without CaSO₄, and from the SO₂ from the thermal decomposition of CaSO₄ were subtracted from the total emission in order to quantify the SO₂ release from the raw materials. During and in between experiments, decomposition of CaSO₄ took place due to the high operational temperature of the rotary drum. Table 2 summarizes the intervals of the SO₂ concentration measured in the analyzers when no reducing gas or fuel was introduced at different conditions. The thermal decomposition increases with temperature and decreases with increasing oxygen concentration, with temperature having the most pronounced effect. The SO₂ concentration from the thermal decomposition was subtracted to the previous results. This concentration only contributes significant when the sulfur release by reducing agent is low at 1000°C. Thermal decomposition of CaSO₄ is studied in more detail by Nielsen et al.⁴

The total SO₂ release increased with decreasing particle size of tire rubber and pine wood. This can be explained in terms of the smallest particles being heated faster than the bigger particles. This leads to a faster release of volatiles, which causes stronger local reducing conditions and thereby more SO₂ is released. The impact of the volatile concentration is investigated in the next section. The magnitude of SO₂ concentration peak measured was higher for the smallest particles than for the larger particles. For example, at 900°C and 5% O₂, the SO₂ concentration peak

reached a maximum of 1413 ppm for the 8 mm diameter pine wood particles, while 213 and 198 ppm SO₂ were measured for wood particles of 13 and 19 mm diameter, respectively. Apparently, the SO₂ release in the cement kiln inlet can be minimized by avoiding small particles to be in contact with the kiln bed material.

It was observed that the combustion behavior of the two fuels was quite different. Wood followed an unreacted shrinking core conversion while tire rubber rapidly cracked into several small fragments after the devolatilization. This is in good agreement with the previous observations by Nielsen et al.³ The tire rubber particles caused, especially for the larger particles, more SO₂ release from the synthetic raw materials in comparison with the pine wood particles. We attribute this to the fragmentation of the tire rubber. Thereby both the volatile release and the total conversion time, defined as the time required to complete the combustion of the particles, was much faster for tire rubber than for pine wood, as indicated in Table 3. As discussed below, a faster volatile release promotes sulfur release from the raw meal.

Effect of degree of devolatilization

Pine wood cylinders were pre-pyrolized at temperatures of 300, 500 and 700°C for 20 min in order to obtain wood char with different contents of volatiles. Identical energy input, 55 kJ, of the virgin wood was used to prepare the wood chars. Figure 6 shows the average fuel devolatilization time as a function of pre-treatment temperature. The devolatilization time was shortened when the temperature of pre-treatment was increased, as a consequence of the reduced content of volatiles.

Figure 7 shows the total SO₂ release from the virgin wood and wood chars with different contents of volatiles. It illustrates that the release of SO₂ occurs only during devolatilization.

Combustion of pre-pyrolized char at temperatures up to 700°C lead to reduced SO₂ release, presumably because CO is released in lower concentrations. As discussed below, concentrations of CO below a certain threshold value are not effective in reducing CaSO₄. The results indicate that SO₂ release in the cement kiln inlet can be reduced if the fuel devolatilization does not take place in contact with the kiln bed, only allowing char oxidation to occur on the material bed.

Effect of Reducing Gases

Reducing gases, i.e., volatile components capable of oxidizing sulfate to sulfur dioxide, are formed during devolatilization and have a significant impact on the SO₂ release from the raw meal. During combustion experiments with the solid fuels, mixing of the fuel with the bed material, heating up of the fuel particles, release of volatiles, char combustion, reaction of reducing agents with CaSO₄, and release of SO₂ all occurred simultaneously. It was not possible to control all of these steps and we could not identify and quantify all of the reducing agents released from the fuel during devolatilization and char oxidation. For this reason, the effect on the sulfur release of introducing reducing gases in controlled concentrations into the rolling bed in the high temperature rotary drum was investigated. An L-shape steel tube was used to introduce reducing gases at a distance of 0.5 cm from the bottom of the bed to establish local reducing conditions in the bed material, maintaining an oxidizing freeboard atmosphere.

The main volatiles released during devolatilization of fuels such as wood, plastic and agricultural biomass are CO, CH₄ and H₂^{11,12, 13, 14} and these components were selected for the experiments. The gases were supplied by pressurized 50 L gas bottles with a purity of 99.97 % CO, 99.5 % CH₄ and 50 mol. % H₂ in N₂, respectively. The reducing agents were mixed with nitrogen with a purity of 99.999 % in order to vary their concentration from 5% to 20% in the mixture which was introduced in the bed at a flow of 1 NL/min.

In the literature it is has been reported that competing reactions between these gases and CaSO_4 exist, i.e. netto reactions (3) and (4) for CO ^{15, 16, 17}, (5) and (6) for H_2 ^{17, 18}, and (7) and (8) for CH_4 ^{19, 20}, yielding CaO and SO_2 or CaS . However, CaS formed by reactions (4), (6) and (8) is likely to be transformed to CaO and SO_2 in accordance with reaction (9) when CaS is in contact with oxygen entraining into the bed from the freeboard.

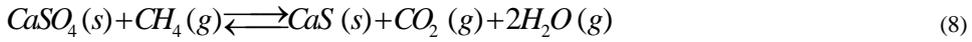
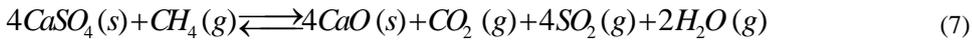
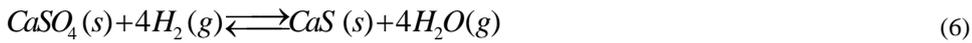
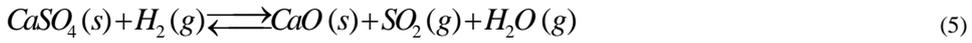
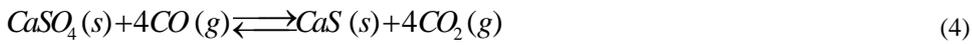
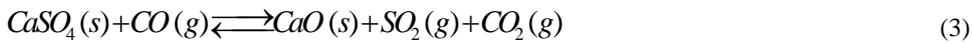


Figure 8 shows an equilibrium phase diagram for the system of CaSO_4 , CaO and CaS in the presence of CO . It is seen that the stable phases and any transformation depend on the temperature and the partial pressures of SO_2 , CO and CO_2 . Figure 9 shows a similar equilibrium phase diagram for CaSO_4 , CaO and CaS as a function of temperature and partial pressures of SO_2 , H_2 and H_2O . These diagrams help explaining the results of Figure 10 and Figure 11, discussed below.

- *Experiments with CO , H_2 and CH_4 concentrations varying O_2 content*

The effect of introduction of different concentrations of reducing gases, from 5 to 20% into the bed, on the SO₂ release was investigated at 900°C and at 5-0% O₂ in the freeboard atmosphere. The reducing gas was introduced during a period of 4 or 5 min in order to establish steady-state conditions with a constant SO₂ concentration in the gas phase. The averages of the steady-state SO₂ concentrations, when different CO, CH₄ and H₂ concentrations were introduced, are presented in Figure 10.

The concentration of SO₂ is highly dependent on the concentration and type of reducing gas. The SO₂ release increases with increasing CO, CH₄ and H₂ concentrations because the bed experiences higher local reducing conditions. Increasing the reducing potential, the phase diagrams (Figure 8 and Figure 9) showed that CaS is more stable. The oxidation product of CaS is CaO and SO₂ (reaction 9). CO and CH₄ concentrations lower than 5% with 5% O₂ in the freeboard gas and H₂ concentrations lower than 15% with 10% O₂ in the freeboard gas did not cause significant SO₂ release. The few ppm observed were insignificant in comparison with the subtracted SO₂ concentration from the thermal decomposition of CaSO₄ of 20-30 ppm SO₂ at 900°C and 10% O₂. The results indicate the existence of a threshold concentration below which SO₂ release does not occur. This threshold concentration can be explained through the equilibrium phase diagrams, which show that for a low CO concentration (i.e., a low reducing potential), the stable product is CaSO₄ even for low SO₂ concentrations, and very little SO₂ release would be expected. Therefore, the threshold concentration may vary with temperature and reducing agent.

The O₂ concentration in the freeboard is another factor that influences the release of SO₂. An increase of the O₂ concentration from 5 to 10% resulted in a considerable decrease in the SO₂ concentration for all reducing gases. This is in agreement with Tian et al.²² who stated that the

presence of oxygen (10 to 21%) in the system inhibited the decomposition of CaSO_4 . This effect was also observed for the experiments using tire rubber and pine wood, when the particles were placed on top of the bed during devolatilization and the gases released were oxidized in the proximity of the particle by oxygen because the gas-phase reaction often is faster than a gas-solid reaction. Hence, the oxygen concentration influences the SO_2 release both when the gases are released into the bed, and in the proximity of the bed. The oxygen may diffuse into the bed, oxidizing the reducing agent and consequently reducing the SO_2 release.

The effect of the O_2 concentrations is most prominent for high concentrations of reducing gases and each type of gas responds differently to a change in the O_2 concentration. The order of sensitivity of the gases towards the O_2 is $\text{H}_2 > \text{CO} > \text{CH}_4$, consistent with the order of reactivity of these components towards oxygen. It has been reported that the autoignition temperature, which is defined as minimum temperature required igniting a gas/vapor in air without a spark or flame being present, of these gases follows the same order: 500°C for H_2 , 609°C for CO and 580°C for CH_4 ²³. This may suggest that when the gas reaches the autoignition temperature, the oxidation reaction is favored instead of reacting with CaSO_4 and therefore, less SO_2 is released.

- *Experiments with CO, H₂ and CH₄ concentrations varying temperature*

Figure 11 shows the effect of the temperature in the interval $900\text{-}1000^\circ\text{C}$ and concentration of CO , CH_4 and H_2 , respectively, on the SO_2 release. The effect of temperature depends on the reducing agent. The SO_2 release increases with temperature for CH_4 and CO , with the effect of CH_4 being most sensitive towards the temperature, whereas it decreases for H_2 . The reason may be that H_2 at elevated temperatures reacts faster with oxygen present in the bed (gas-phase reaction) than with CaSO_4 (gas-solid reaction).

The temperature is one of three factors, which affects the chemical stability of $\text{CaSO}_4/\text{CaS}/\text{CaO}$ species, the others being the reductive potential of the gas phase and the SO_2 partial pressure¹⁷. The equilibrium phase diagram shows that an increase in temperature shifts the phase limits upwards in SO_2 concentration, where the stability regions of CaSO_4 and CaS decrease and the stability region of CaO increases. Studies of the solid products have shown that reaction (3) is thermodynamically favored at a high temperatures and a low reductive potential ($P_{\text{CO}}/P_{\text{CO}_2}$) of the gas phase. The yield of CaO decreases due to the formation of CaS , when the CO concentration increases, because reaction (4) becomes predominant at 800-1000°C¹⁷. At 900°C and 10% CO in N_2 , no CaO or CaSO_4 were detected; the only reduction product was CaS and there was no SO_2 in the flue gas^{18,24}, whereas the amount of CaO in the residue product increased when the reaction temperature was above 950°C¹⁸.

The reaction rate of CH_4 increases with increasing temperature. This is consistent with the findings of Song et al.¹⁹ who studied the decomposition of CaSO_4 with pure CH_4 in a fixed bed reactor, varying sample mass, particle size, flow rate and reaction temperature.

For H_2 , less SO_2 was released at 1000°C, in comparison with the same experiment at 900°C. This is contradictory to the observations of Shen et al.¹⁸. They studied the rate of CaSO_4 reduction with 5% H_2 and 95% N_2 in the temperature range 870- 970 °C by thermo gravimetric analysis, characterizing the products by Fourier transform infrared spectroscopy and X-ray diffractometry. They found that the rate of CaSO_4 reduction increased remarkably with the temperature. We attribute the apparent discrepancy to the difference in equipment and availability of oxygen.

- *Effect of exposure time*

The effect of varying the concentration and the injection time for the same total amount of reducing gas was investigated. A total molar amount of 0.4 L of reducing gas was introduced into the bed in concentrations of 5 to 20% at 900°C. The time required to introduce a total of 0.4 L of reducing agent at 5, 7, 10, 15 and 20% was 480, 343, 240, 160, and 120 seconds, respectively.

Figure 12 shows the SO₂ concentrations when CO was introduced into the bed in different concentrations. Similar experiments were performed using CH₄ and H₂ and the total SO₂ release, obtained for the three reducing gases, are summarized in Figure 13. The highest release was obtained using CO concentrations of 15 and 20%, followed by H₂, while CH₄ and H₂ seem to give higher total SO₂ release than CO at low concentrations.

The results of the investigation regarding the effect of exposure time are consistent with the results on the effect of different degrees of devolatilization. The volatile gases from a fuel particle are released in high concentrations during a short period, while char oxidation or devolatilization of large particles yield lower concentrations, but for an extended time. Keeping the total amount of reducing agent introduced constant, showed that the highest concentration introduced during 2 minutes (representing devolatilization) released a higher total SO₂ release compared to lowest concentration during 8 minutes (representing char combustion or devolatilization of large fuel particles). Thus, the concentration of the reducing agent and the time of exposure are of high importance for SO₂ release.

The results indicate that a threshold fuel flow for the kiln inlet may exist giving no sulfur release, since no SO₂ release takes place below a threshold concentration of reducing agent. However, each kiln may have its own threshold fuel flow in the kiln inlet, depending on the kiln characteristics and raw materials and fuels used.

- *Effect of binary mixtures*

Several different volatile gases are released simultaneously during devolatilization. In order to study the interactions between the gases, binary mixtures with different concentrations of CO, from 0 to 20%, combined with H₂ and CH₄ concentrations in 80% N₂ were investigated. The SO₂ concentrations measured for the different mixture combinations are shown in Figure 14. The SO₂ release increased nearly linearly with the CO content in the CO/CH₄ mixture, whereas the SO₂ release decreased with increasing CO content in the mixture CO/H₂ but increased when 20% CO was introduced. The CO/H₂ mixtures yielded more SO₂ release than the CO/CH₄ mixtures.

Figure 15 shows results for similar experiments with binary mixtures of CH₄ and CO or H₂, respectively, in 80% N₂. The SO₂ release decreases with increasing CH₄ content in the mixture CH₄/CO, initially very rapidly. The SO₂ release is very similar, regardless of whether CH₄ is mixed with CO or with H₂,

The obtained experimental data illustrate that interactions between the reducing gases occur and the SO₂ release cannot be predicted by addition of the single contributions from the individual reducing gases; this would lead to overestimation of the SO₂ release.

Conclusions

The SO₂ release from cement raw materials during combustion of tire rubber and pine wood has been studied experimentally using three different particle sizes ranging from 19 to 2 mm at identical energy inputs. The smallest particles, pine wood cylinder with a diameter of 8 mm and tire granulate, caused more SO₂ release than the bigger particles. The release of volatile gases is related to the heating up of the particle. Small particles, which have larger surface area, are heated faster than big particles and higher concentrations of volatiles are released during a

shorter period for smaller particles, yielding higher concentrations of SO₂ release and total SO₂ release.

The effect of wood cylinders with different degrees of volatiles showed that the SO₂ release mainly took place during devolatilization, corresponding to the cases with virgin wood and wood chars made at 300 and 500°C. The SO₂ release decreased with decreasing content of volatiles in wood.

A modification of the experimental setup allowed introduction of reducing gases under the bed material. The effect of different concentrations of CO, H₂, and CH₄ on SO₂ release has been investigated experimentally at different temperatures, oxygen contents and time of exposure. A large increase in the measured SO₂ concentration is obtained for H₂ followed by CO and CH₄, with decreasing O₂ concentration and increasing the reducing gas concentration. The SO₂ release increased significantly for CH₄ and followed by CO with increasing temperature, except when H₂ was injected under the bed material. Short pulses with high concentrations of reducing gas yielded higher concentrations of SO₂ and higher total SO₂ release compared to long pulses with low concentrations of reducing gas. The experiments with different concentrations of reducing agent indicated that a threshold concentration, below which SO₂ release does not occur, exists. This observation is in good agreement with the equilibrium phase diagrams.

The experimental results of binary mixtures containing CO showed that SO₂ increases with increasing CO concentration in the mixture. Similar SO₂ release was obtained for the mixtures of CH₄ and H₂.

From the experimental results of this articles it can be concluded that the particle size and the fuel flow are key parameters to ensure a proper combustion in the calciner before the particles reach the bed material in the kiln inlet causing sulfur release. High sulfur release may take place

if the combustion of small particles in large amounts is not completed in the calciner and thereby occurs in the kiln inlet. The sulfur release may decrease when operating the kiln with an oxygen concentration above 5%. The sulfur release in the inlet of the rotary kiln can be avoided when the volatile gases from fuels are not released in contact with the bed material, thereby, only allowing fuel char to be in contact with the kiln bed material.

Acknowledgments

This project is established within the framework of the advanced technology platform 'New Cement Production Technology' founded by the Danish National Advanced Technology Foundation, FLSmidth A/S, and the Technical University of Denmark.

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Table 1: Pine wood and tire rubber proximate and ultimate analyses and lower heating values (LHV). No drying of the fuels occurred prior to the analysis. Notes: ¹ Volatile matter, ² Fixed carbon.

Fuel	Proximate analysis [wt. %]			Ultimate analysis [wt. %]					LHV [MJ/kg]
	VM ¹	FC ²	Ash	C	H	N	S	O	
Pine Wood	76.8	11.3	0.5	44.7	5.54	0.04	0	49.72	15.97
Tire rubber	64.4	32.6	2.8	87.4	7.1	0.3	1.2	4.0	36.9

Table 2: SO₂ concentration from thermal decomposition of CaSO₄ changing temperature and O₂ content. Note: ^A Experiments performed at 5% O₂, ^B Experiments performed at 900°C.

	Temperature ^A [°C]		O ₂ conc. ^B [vol.%]	
	900	1000	5	10
SO₂ concentration [ppm]	40-50	100-130	40-50	20-30

Table 3: Average time of total conversion for the different cylinder sizes of tire rubber and pine wood at 900°C and 10% O₂.

Tire rubber	Pine wood
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	$\phi 13$ mm	$\phi 9$ mm	$\phi 2$ mm	$\phi 19$ mm	$\phi 13$ mm	$\phi 8$ mm
Time of total conversion [s]	152	150	145	1030	640	470

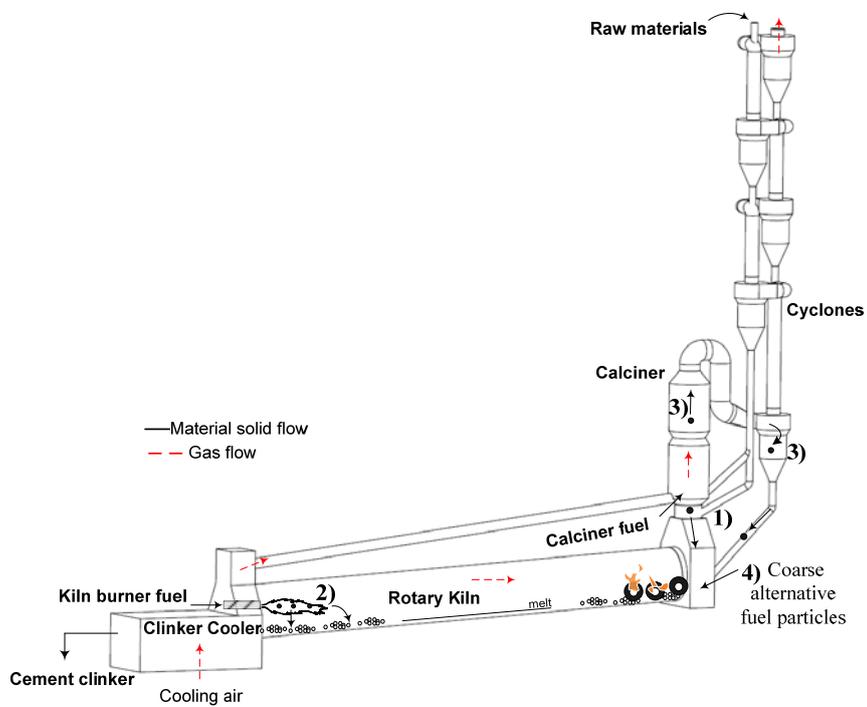


Figure 1: Illustrative scheme of the four scenarios, whereby solid fuels can drop into the bed material in the rotary kiln. The numbers from 1 to 4 refer to the scenarios described in the text.

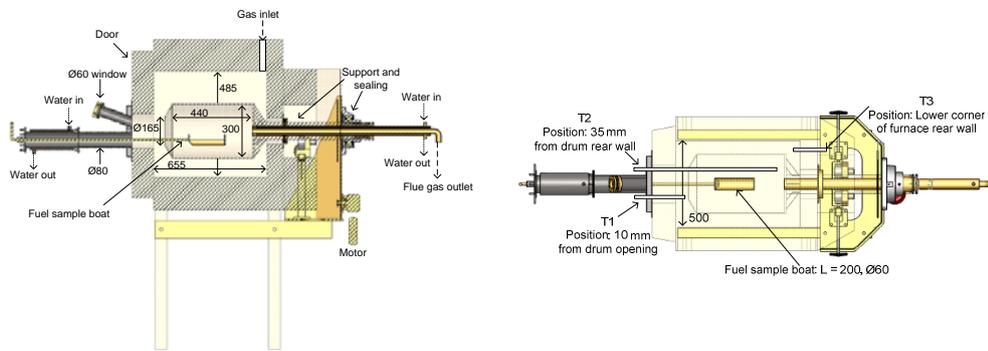


Figure 2: High temperature rotary drum. Left: Side view. Right: Top view.³ Note: T1, T2 and T3 refer to thermocouples, L refers to length, and ϕ to diameter in mm.

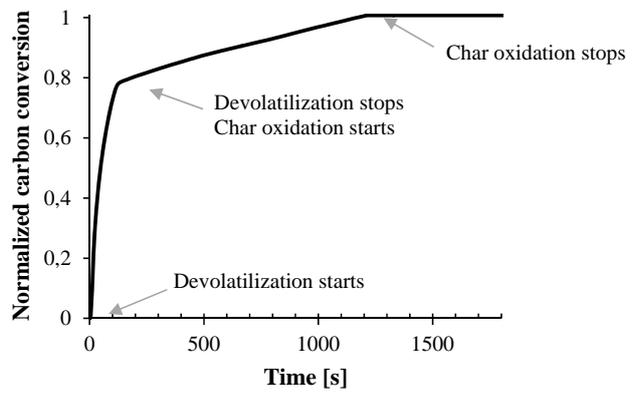


Figure 3: Normalized carbon conversion for \varnothing 19 mm pine wood cylinder. Experimental conditions: 900°C, 5 % fill degree, 2 wt. % CaSO₄, 100 NL/min, 5% O₂ in N₂, 6 rpm.

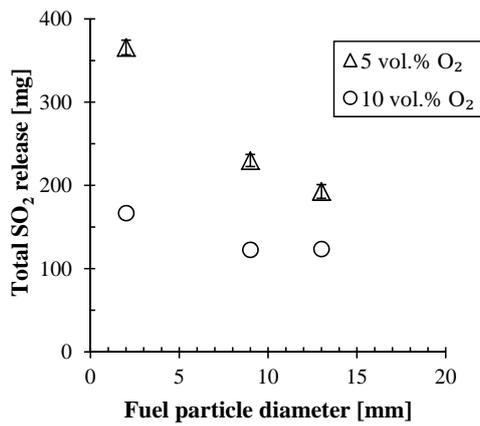


Figure 4: Effect of particle diameter of tire rubber cylinders on sulfur release from the raw materials due to combustion. Experimental conditions: 900°C, 5% fill degree, 2 wt. % CaSO₄, 100 NL/min, 6 rpm.

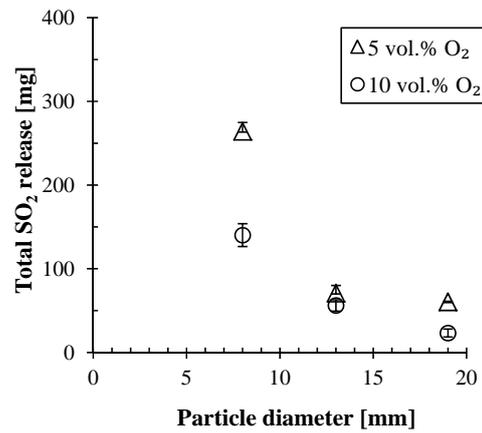


Figure 5: Effect of particle diameter of pine wood cylinders on sulfur release from the raw materials due to combustion. Experimental conditions: 900°C, 5% fill degree, 2 wt. % CaSO₄, 100 NL/min, 6 rpm.

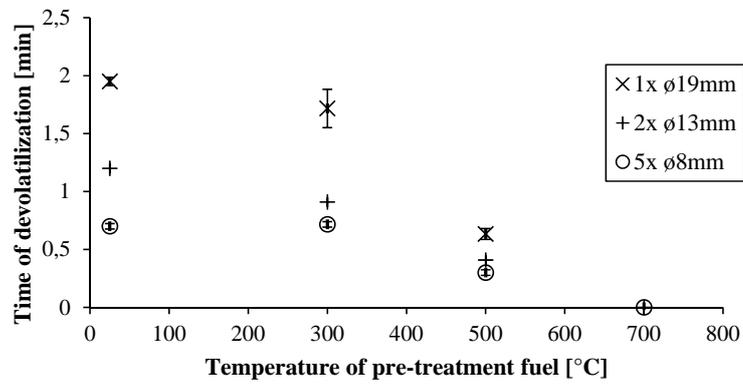


Figure 6: Devolatilization time of virgin wood and wood char made at 300, 500 and 700 °C for particle size of 8, 13 and 19 mm. Experimental conditions: 900 °C, 5 % fill degree, 2 wt. % CaSO₄, 10% O₂ in N₂, 100 NL/min, 6 rpm.

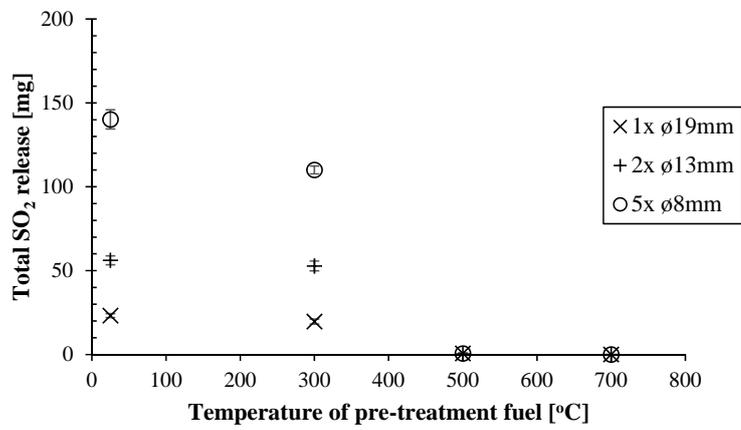


Figure 7: Sulfur release from the synthetic cement raw materials due to combustion of the virgin wood and wood char made at 300, 500 and 700°C for particle size of 8, 13 and 19 mm. Experimental conditions: 900°C, 5 % fill degree, 2 wt. % CaSO₄, 10% O₂ in N₂, 100 NL/min, 6 rpm.

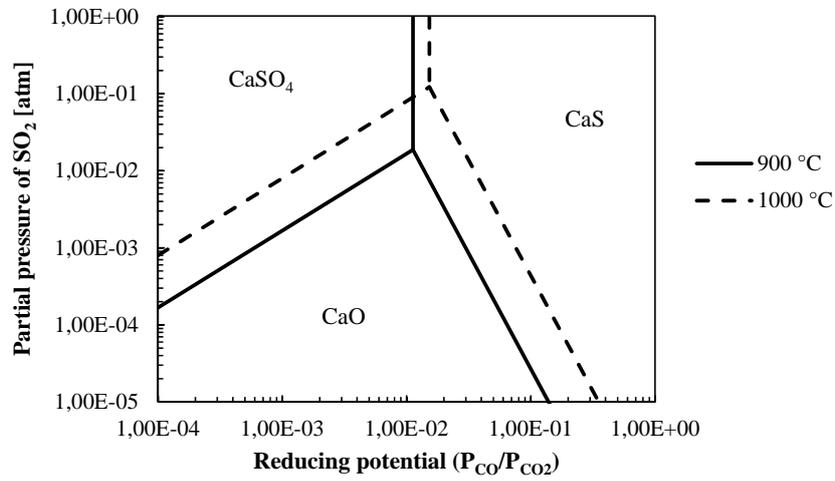


Figure 8: Equilibrium phase diagram for the $\text{SO}_2\text{-CaO-CaSO}_4\text{-CaS-CO-CO}_2$ system at 900 and 1000°C. Thermodynamic data from ²¹.

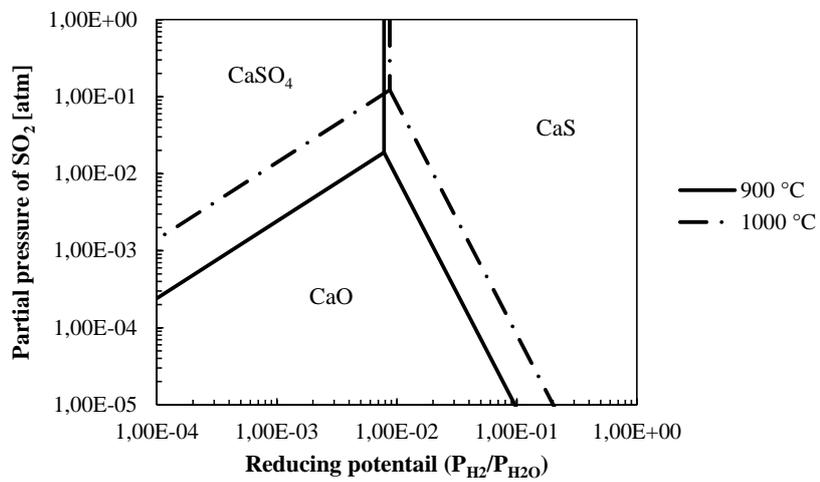


Figure 9: Equilibrium phase diagram for the SO_2 -CaO-CaSO₄-CaS-H₂-H₂O system at 900 and 1000°C. Thermodynamic data from ²¹.

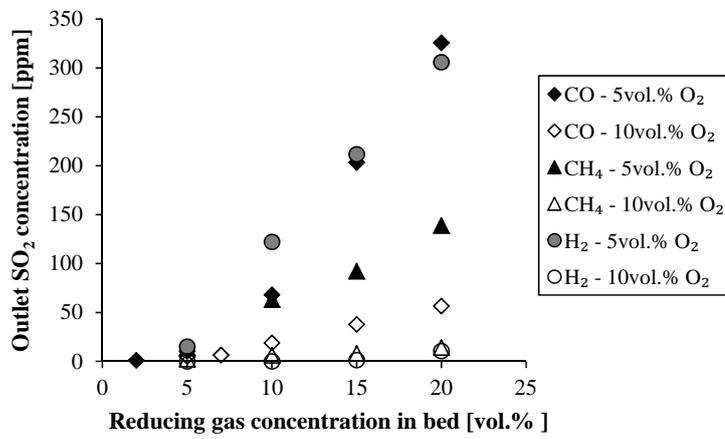


Figure 10: Effect of different CO, CH₄ and H₂ concentrations introduced under the bed material on SO₂ concentration in the total gas flow with 5 and 10% O₂. Experimental conditions: 900 °C, 5 % fill degree, 2 wt. % CaSO₄, 100 NL/min, 6 rpm.

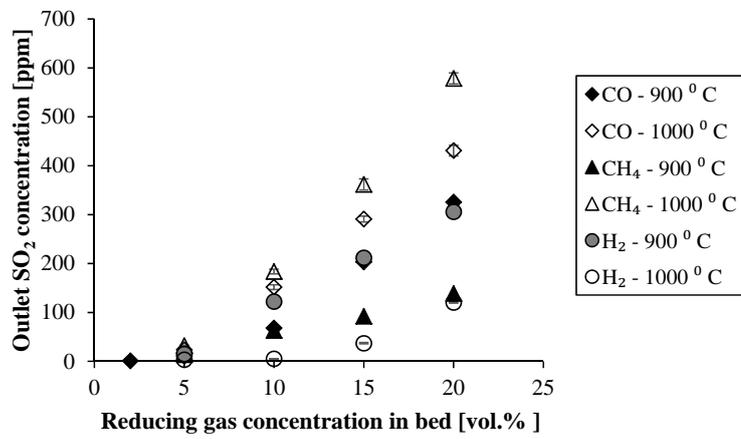
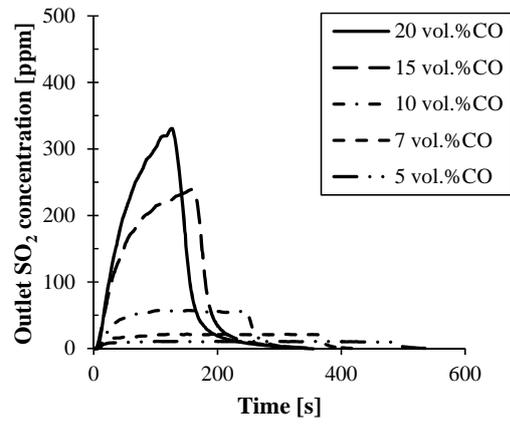


Figure 11: Effect of different CO, CH₄ and H₂ concentrations introduced under the bed material on SO₂ concentration at 900 and 1000 °C. Experimental conditions: 5 % fill degree, 2 wt. % CaSO₄, 5% O₂, 100 NL/min, 6 rpm.



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Figure 12: SO₂ concentrations when a total of 0.4 L of CO was introduced under the bed material with 5, 10, 15 and 20% CO. Experimental conditions: 900 °C, 5 % fill degree, 2 wt. % CaSO₄, 5% O₂, 100 NL/min, 6 rpm.

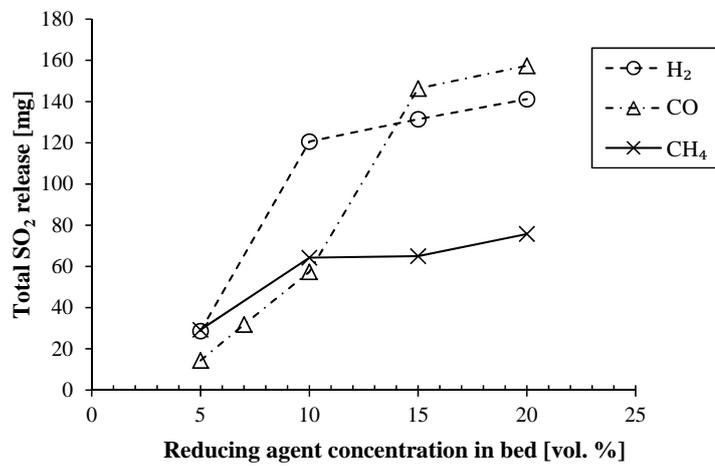


Figure 13: Total SO₂ release when a total of 0.4 L of H₂, CO and CH₄ were introduced under the bed material varying the concentration up to 20%. Experimental conditions: 900 °C, 5 % fill degree, 2 wt. % CaSO₄, 5% O₂, 100 NL/min, 6 rpm.

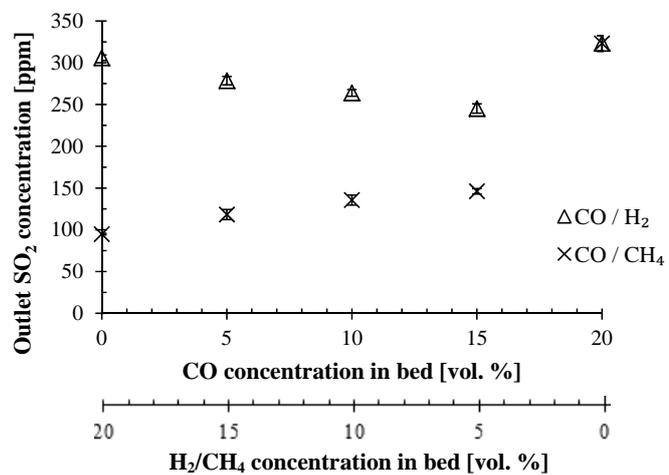


Figure 14: SO₂ concentrations when mixtures of CO/H₂ and CO/CH₄ were introduced under the bed material. Experimental conditions: 900 °C, 5 % fill degree, 2 wt. % CaSO₄, 5% O₂, 100 NL/min, 6 rpm.

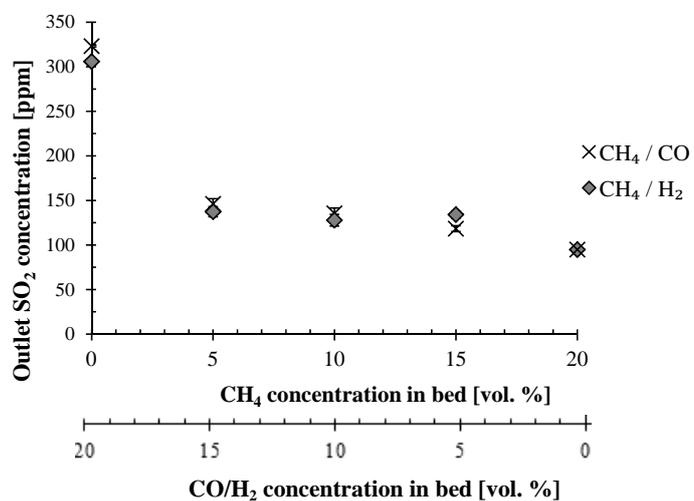


Figure 15: SO₂ concentrations when mixtures of CH₄/CO and CH₄/H₂ were introduced under the bed material. Experimental conditions: 900 °C, 5 % fill degree, 2 wt. % CaSO₄, 5% O₂, 100 NL/min, 6 rpm.