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Citation for the original published paper (version of record):

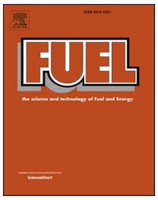
Vigoureux, M., Leffler, T., Knutsson, P. et al (2022). Sulfur capture and release by ilmenite used as oxygen carrier in biomass combustor. Fuel, 309. http://dx.doi.org/10.1016/j.fuel.2021.121978

Fuel 309 (2022) 121978

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Sulfur capture and release by ilmenite used as oxygen carrier in biomass combustor

Mariane Vigoureux [a,b,*], Tomas Leffler [b], Pavleta Knutsson [b], Fredrik Lind [a]

[a] Department of Space, Earth and Environment, Chalmers University of Technology, Göteborg 412 96, Sweden
[b] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Göteborg 412 96, Sweden

ARTICLE INFO

Keywords:
Circulating Fluidized Bed
Oxygen-Carrier-Aided Combustion
Ilmenite
Sulfur
Biomass
Ash

ABSTRACT

Oxygen-Carrier-Aided Combustion (OCAC) is a promising technology for the combustion of solid heterogeneous fuels such as biomass and waste. However, a frequently encountered problem with biomass and waste is their high alkali contents, which can lead to the build-up of deposits on heat transfer surfaces, leading to corrosion and increased maintenance costs.

The addition of elementary S is one of the options used in combustion processes to mitigate corrosion. Sulfation of KCl reduces the severity of corrosion on heat transfer surfaces due to the transformation of KCl into K_2SO_4, which is considered to be less corrosive. Even though many studies have been performed on the influence of sulfur on the corrosion process, there is to date little knowledge about the interaction of S with ilmenite used as an oxygen carrier (OC). Therefore, there is a need to understand the influence of S on both the properties of the ilmenite used as an OC and the morphologic development of the ilmenite particles. This study investigates the interactions between S and ilmenite as bed material, with the focus on the roles of ash layers in the capture and release of the added S under different combustion conditions.

The present study focuses on bed material that was exposed in the Chalmers 12-MW_{th} Circulating Fluidized Bed (CFB) combustor run with biomass as fuel and with the addition of elemental S. Calcined ilmenite without ash elements was used as a reference material and the collected bed material samples were tested for their abilities to capture S in a laboratory fluidized bed batch reactor run at 950 °C. Controlled SO_2 exposures in an oxidizing environment were carried out, and the reversibility of the mechanisms for uptake and release of S was tested. Understanding the uptake and release of S components by ilmenite is of importance not only for the handling of bed materials, but also for developing new protocols for corrosion prevention in OCAC.

In the present study, the ilmenite-sulfur interactions were followed using gas analysis, solid material characterization (SEM-EDX), and thermodynamic calculations (FactSage). The results suggest that SO_2 is captured under oxidative conditions, preferentially by bed materials with developed ash layers, and released under reducing conditions. Mixed-sulfate-phase $K_2Ca_2(SO_4)_3$, K_2SO_4 and $CaSO_4$ are found to be the main formed phases that can participate in S uptake and release.

1. Introduction

According to the International Energy Agency (IEA), almost one-third of the global anthropogenic greenhouse gas emissions originate from the electricity and heat sector [1], where fossil fuels such as coal, natural gas and oil account for 81% of the total energy supply [2]. To decrease the impact of the heat and power generation sector on the levels of CO_2 released to the atmosphere, the use of more sustainable energy resources with smaller carbon-footprints is needed. Biomass, which is considered to be a fuel with a small carbon-footprint, could contribute to decreasing the CO_2 impact on the heat and power sector [3]. Circulating Fluidized Bed (CFB) combustion is regarded as an effective technology for biomass conversion. Even though it allows for good mixing in the bed, this technology can still suffer from uneven oxygen distribution within the gaseous phase in the furnace, especially when heterogeneous fuels, such as biomass, are combusted. This can result in locally high temperatures both temporally and spatially in the furnace, leading to ash melts and the formation of deposits, with the consequence of corrosive attacks on the heat-transferring surfaces. To further improve the oxygen distribution within the furnace, the Oxygen-

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[*] Corresponding author at: Department of Space, Earth and Environment, Chalmers University of Technology, Göteborg 412 96, Sweden.
E-mail address: marvigo@chalmers.se (M. Vigoureux).

https://doi.org/10.1016/j.fuel.2021.121978
Received 17 May 2021; Received in revised form 8 September 2021; Accepted 9 September 2021

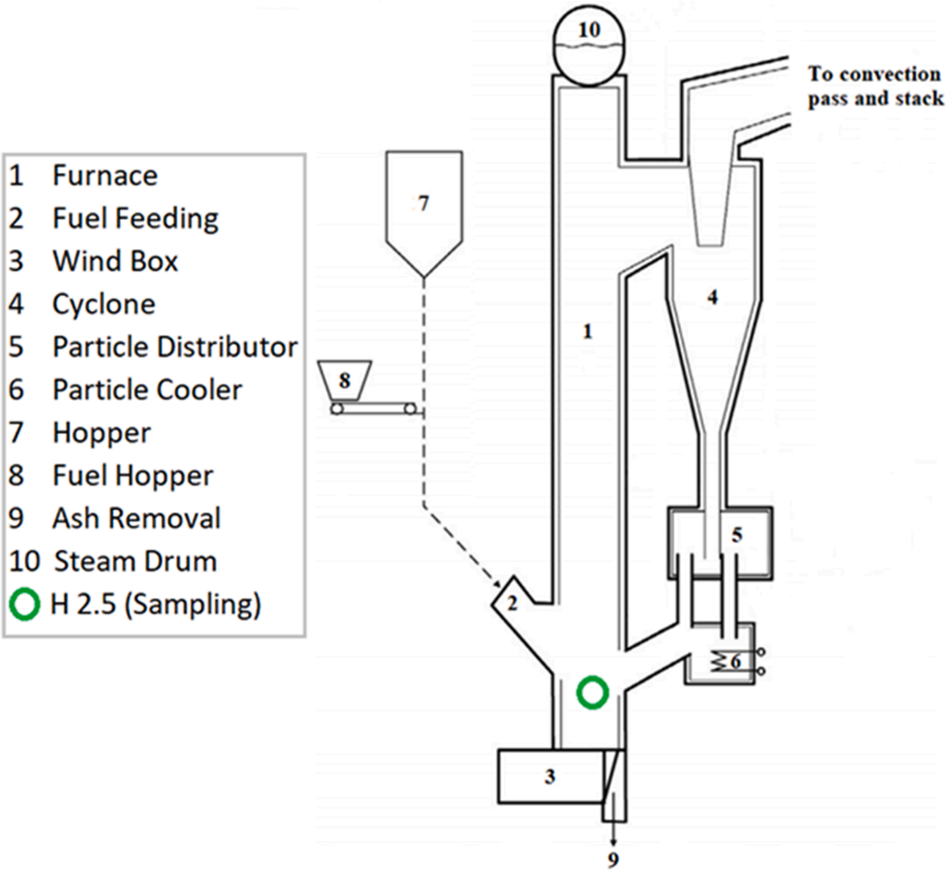

Fig. 1. Schematic of the 12-MW_{th} CFB boiler. The particle extraction port is indicated as H 2.5.

Carrier-Aided Combustion (OCAC) concept was developed in 2013 by Thunman *et al.* [4], in which an oxygen carrier (OC) bed material replaces the conventionally used silica sand. The OC is commonly a metal-oxide (MeO) that can take up oxygen under oxidizing conditions and release it under reducing conditions, thereby increasing the oxygen supply to the fuel. Different types of OC materials have been tested [5–7]. Ilmenite is the material that has shown the most-promising results, providing a combination of sufficient reactivity, good oxygen transport capacity, and strong resistance to mechanical, chemical and thermal stresses [8,9]. Moreover, ilmenite is not harmful to the environment and is readily available at a relatively low cost [10,11].

Ilmenite, as an OC, has been the subject of multiple studies in which the focus has been on its interactions with ash components [9,12–16]. No signs of inhibition of the oxygen-transferring ability by the ash components during the investigated residence time in the combustor have been reported [12,17]. Previous investigations have shown that of the studied major ash compounds, K migrates into the ilmenite particle core and Ca is enriched in the ash layer formed around the particles [13].

The ashes from biomass combustion are challenging to handle because they are rich in alkali compounds and have a low sulfur (S) content, which can lead to corrosive attacks on the heat transfer surfaces and to an increased need for S additives. In conventional coal-fired CFB combustors, it has been observed that, through sulfation of the released alkali with an S-containing additive, less-corrosive alkali sulfates are formed that can prevent the development of corrosion. However, sulfation and its effects on biomass-fueled units and under conditions of OCAC have not been elucidated. In a previous study, it was observed that S was captured by ilmenite and was essentially bound to the main ash elements Ca and K [13]. It was also observed that S was accumulated in the bed material over time and that it could be released in the form of SO_2 [18].

The purpose of this study was to understand how and under what conditions S is captured and released by ilmenite particles and how this uptake and release are regulated. The investigations have been designed to determine the conditions that trigger S capture and release and to define whether this is a reversible phenomenon. The influence that ashes have on S capture and release have also been investigated.

Understanding the mechanism of S uptake and release, and the conditions that influence these processes, can facilitate the optimization of S additions under OCAC conditions to mitigate corrosive attacks on heat transfer surfaces. Ilmenite could thereby be regarded as an S carrier as a result of the alkali and S reactions that occur in and on the particles. The acquired knowledge is also important for optimizing the amount of added S additive, while keeping the level of waste material handling as low as possible.

2. Material and methods

2.1. Chalmers 12-MW_{th} CFB boiler

The current study was performed in a 12-MW_{th} CFB boiler used for research purposes, as well as for the heating of the Chalmers campus in Gothenburg, Sweden. A schematic of the CFB boiler is shown in Fig. 1. The unit height is 13.6 m and the cross-sectional area of the combustion chamber is 2.25 m^2. The unit has been described in detail by Thunman *et al.*[3]. During the experimental campaign described in the present study, the bed temperature in the combustion chamber was maintained at 870 °C ± 10 °C. The bed material was sampled over time using a water-cooled suction probe that was inserted through the boiler wall (*via* extraction port H 2.5 green circle in Fig. 1) into the fluidized bed. For each sample, approximately 1 kg was taken out of the 3 tons of ilmenite

Table 1
Composition of the wood chips (based on fuel as received).

Characteristic	wt%
Moisture	38.50–45.30
Volatiles	43.80–50.10
Ca,	0.11
K	0.06
S	<0.02
Ash	0.40–0.60

Lower Heating Value dry ash-free of 18.29 MJ/kg.

Table 2
Elemental composition of ilmenite in its non-oxidized form (in wt%), as provided by Titania AS.

Element	wt%
Fe	34.20
Ti	27.90
Mn	0.48
Mg	0.44
Al	0.19
Si	0.15
K	0.07
Ca	0.06
Na	0.04
P	0.01
S	<0.02

Table 3
Notation of the tested ilmenite samples, and their S exposure time in the boiler.

Sample notation	Average residence time in the boiler (h)	Sulfur exposure time in the boiler (h)
Calcined	None	None
I 48H	49	48
II 0H	78	None

in the boiler.

2.2. Materials

Softwood chips (from spruce and pine trees) were used as fuel in the experiment. The composition of the used chips is presented in Table 1. The fuel was fed into the boiler at a rate of ~2 t/h. Elementary S in granular form was added into the furnace at a rate of 1.5 kg/h. This was done by a separate feeding system (not shown in Fig. 1) *via* the return leg of the particle distributer (5).

The ilmenite used in this study, comes originally from Norway and commonly referred to as “rock ilmenite”, was supplied by Titania AS. The ilmenite composition is listed in Table 2.

The main components of the used ilmenite are Fe_2O_3 (45.5 wt%) and TiO_2 (36.1 wt%). The particle size distribution of the used bed material was 100–300 μm. Due to attrition, a portion of the bed material was lost to the fly ash during operation of the unit. To maintain the differential pressure over the bed, fresh ilmenite was introduced into the combustion chamber. Due to this addition of fresh bed material, part of the bed had a shorter residence time in the boiler. Table 3 shows the sample notation used in the present study, the bed material total residence times, and the duration of S exposure in the boiler. Two samples were extracted from the boiler: 1) Sample I 48H, had a residence time of 2 days in the boiler with S addition, and as a result developed an ash layer containing S; and 2) Sample II 0H, which corresponded to fresh ilmenite with a residence time of 3 days in the boiler without S addition and had, therefore, developed an ash layer without S.

The exposure time to S is noted in the name of the sample. To determine the levels of released and recaptured S, the samples collected from the combustor were further tested in the laboratory setup described below. Calcined ilmenite was used as a reference sample because it does not have a developed ash layer. The reference sample was obtained by the calcination of ilmenite at 950 °C for 24 h in air [19].

2.3. Batch reactor test

The levels of S capture and release were investigated in a laboratory-scale fluidized bed batch reactor, hereinafter referred as ‘the reactor’. The system has previously been used for chemical looping combustion and is described in Fig. 2. More detailed information about the reactor system can be found elsewhere [8,20,21]. The reactor comprises a tube of quartz glass with a height of 82 cm and a diameter of 2.2 cm. To allow the gas flow through the bed material, a porous quartz plate is used upon which the 15 g of bed sample is placed, and which is situated 37 cm from the bottom of the reactor. The gas is distributed from the bottom of the reactor and allows fluidization of the bed material.

The outlet flue gas (at the top of the reactor) passes through a cooler, where the condensate is removed. It is important to note that a part of the SO_2 outlet can be dissolved in liquid water during the condensation of the outlet gas. It can, therefore, be suspected that the true amount of SO_2 released is much higher than that detected. However, the trends observed during the experiment seem to be correct [22]. The remaining dry flue gas was then analyzed in a Rosemount NGA 2000 instrument and was released thereafter to the ventilation. O_2 was measured with a paramagnetic technique, CO and CO_2 are measured with a non-dispersive infrared technique, and SO_2 was measured with a non-dispersive ultraviolet technique. Two thermocouples were used to measure the temperature in the bed and below the porous plate. The differential pressure over the bed was measured continuously to ensure constant fluidization of the bed material.

The reactor was heated in a furnace to 950 °C. Under oxidizing conditions, a gas mixture of 5% O_2 in N_2 was used. Thereafter, the bed material was exposed to cyclic reducing and oxidizing conditions. Between each phase, inert gas (N_2) was flushed through the bed, to remove any residual gas components from previous phases. The conditions of the redox cycles are presented in Table 4. During the experiment, the measured parameters (temperature, pressure, and the concentration of the gases) were recorded every seconds.

2.4. Characterization methods

The total elemental contents of the samples from the 12-MW_{th} CFB boiler and from the laboratory-scale reactor were determined after total digestion of the sample in HNO_3/HCl/HF, using inductively coupled plasma sector field mass spectroscopy (ICP-SFMS). This analysis was carried out by ALS Scandinavia AB using the standard ISO/IEC 17,025 with a measurement uncertainty of 5%. It is of importance to report that working with a large-scale CFB boiler induce possible errors due to that only a fraction of the total bed material is analyzed. 15 g of sample has been tested out of 3 tons of bed material, representing 5.10^{-6} % of the bed.

To follow the distribution of elements within the ilmenite particles, Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM-EDX) analysis was used. The scanning electron microscope used for this analysis was Quanta 200FEG equipped with Oxford EDX system. Samples were mounted in epoxy and subsequently ground and polished to provide a flat cross-section of the bed particles. Representative particles were chosen based on shape and composition.

To predict which components would be most likely to be formed from a thermodynamic equilibrium point of view under the defined experimental conditions, thermodynamic equilibrium calculations were performed using the integrated database computing system, FactSage 7.2® [23]. The FToxid, FTsalt, FTdemo and FactIPS databases were used in the calculations. The Base-Phase considered in the calculation was

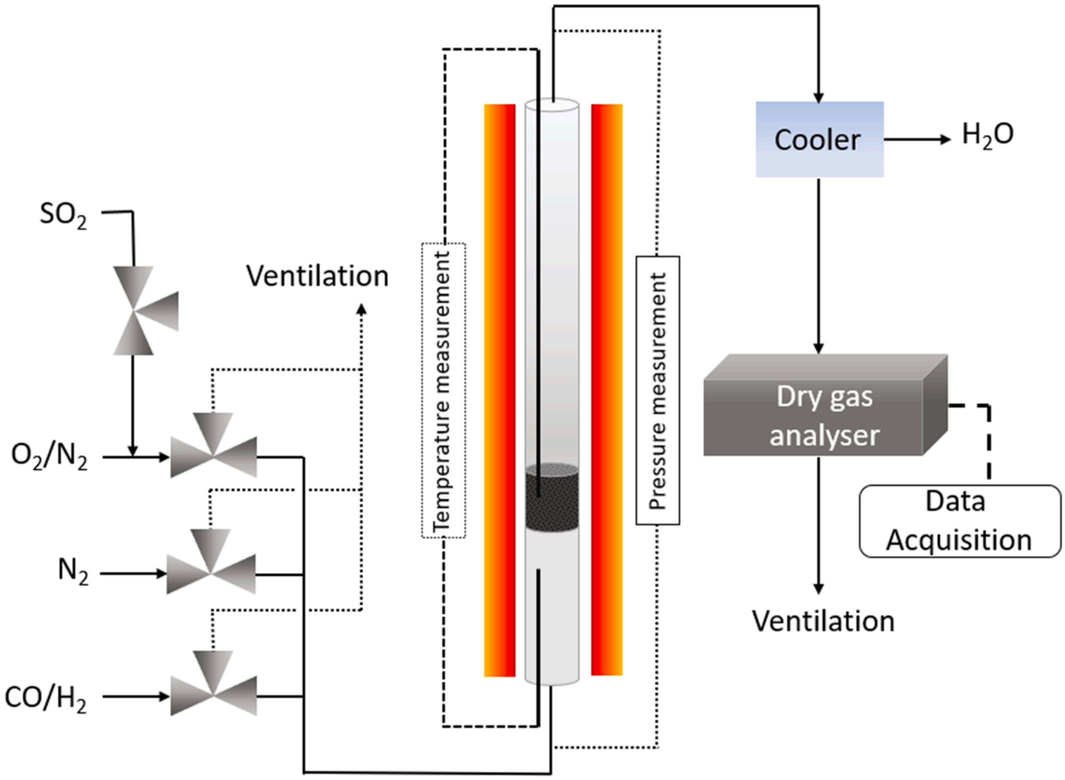

Fig. 2. Schematic of the laboratory-scale fluidized bed batch reactor system used in the experiment with the selected bed material. The gas analyzer has a detection limit of <2%.

Table 4
Experimental parameters used for testing the bed material samples in the laboratory-scale fluidized bed batch reactor.

Phase	Gas Mixture (mole %)	Gas flow (ml$_N$/Tmin)	Temperature (°C)	Time (s)
Oxidizing	O_2/N_2 (5/95)	1000	950	600
Inert	100 % N_2	1000	950	180
Reducing	CO/H_2 (50/50)	900	950	20
Inert	100% N_2	1000	950	180
Oxidizing with SO_2	$SO_2/O_2/N_2$ (1/5/94)	1000	950	1200

Table 5
S contents (in g/kg) of selected samples before and after SO_2 release. The results are obtained by ICP-SFMS.

Sample	Fresh ilmenite	Calcined ilmenite	I 48H	II 0H	I 48H after SO_2 release	II 0H after SO_2 release
S content (g/kg)	0.46	0.18	2.91	0.84	<0.1	<0.1

As no SO_2 release was detected during further exposures to reducing conditions in the reactor and S could no longer be detected in the samples, it can be hypothesized that all of the S contained in the samples was released in the form of SO_2 during the experiment.

FToxid-ILMEA. The modules *Equilib* and *Predom* were used in this study. Oxidizing and reducing conditions were simulated. The main elements of the bed within this study (Fe, Ti, Ca, K, S) and O_2 and SO_2 as gaseous atmosphere were used for the calculations. The concentrations of O_2 and SO_2 were the variables used in the calculations.

3. Results and discussion

The results of the analyses are described in the following subsections and focus lies on the processes of S release and capture, the conditions under which they occur, and the influences of the ash elements on these mechanisms.

3.1. S release

It has been previously observed that S, naturally present in fresh ilmenite, is released in the form of SO_2 under OCAC conditions [18]. The total elemental ICP-SFMS analysis results confirm that fresh ilmenite contains more than twice as much S as calcinated ilmenite (Table 5). S uptake and release were, therefore, followed based on SO_2 release and uptake and through experiments conducted in the laboratory-scale reactor (Fig. 2). The levels of SO_2 released from the three selected samples in the reactor are shown in Fig. 3.

It is clear that for all the samples the majority of the SO_2 is released during the reducing cycles. In Fig. 3, a brief increase in SO_2 is apparent during the first oxidizing phases. This can be attributed to the residual SO_2 present in the reactor before the introduction of other gases. This observation has been confirmed by testing with an empty reactor, i.e., where no bed material was used. Thus, the SO_2 release with bed material present in the system was observed exclusively under the reducing condition, i.e., during the redox cycles. The described SO_2 release was detected during the subsequent cycles until S was not detected anymore, suggesting that all the S content of the samples was released.

To confirm and quantify the release of S from the bed material, a total elemental analysis with ICP-SFMS was performed on the samples before and after the SO_2 release during redox cycles. The results are presented in Table 5. The total elemental analysis reveals that the S was released from the particles. No S was detected in the samples after the redox cycles, due to either a lack of S in the samples (total release of sulfur throughout the experiments) or the fact that the S concentration

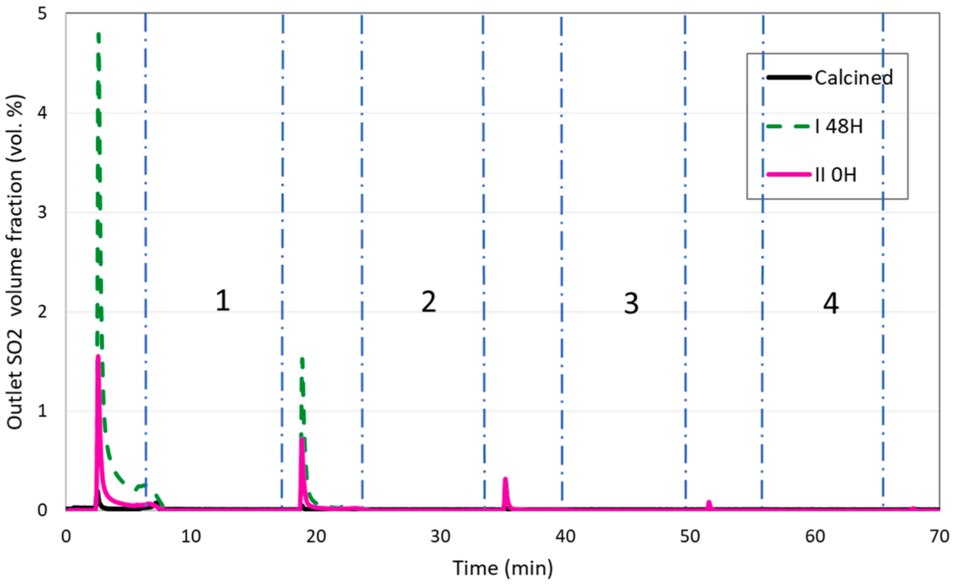

Fig. 3. SO_2 release during reducing cycles for the three selected samples. Four redox cycles are represented. Zones 1 to 4 delimit the oxidizing phases.

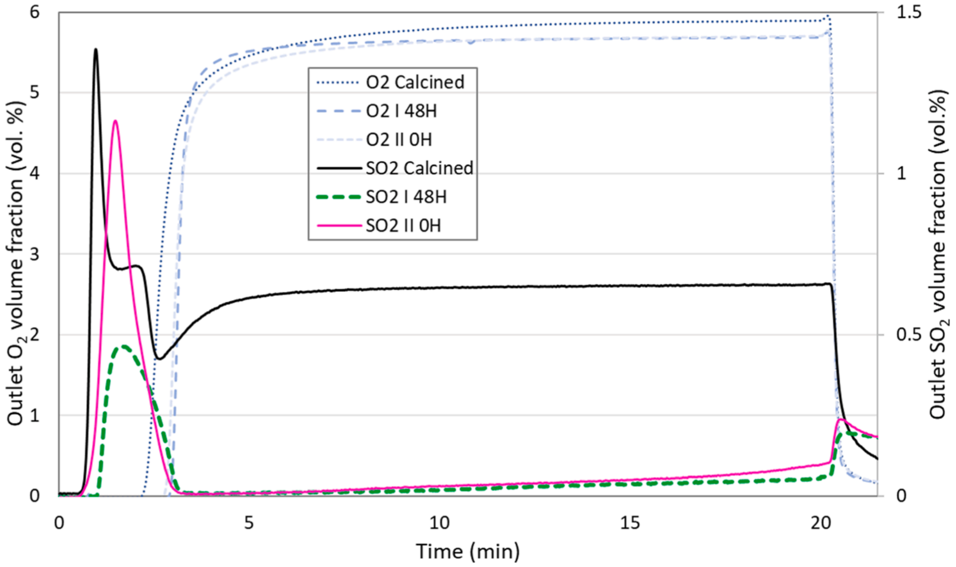

Fig. 4. Concentration of SO_2 during recapture under oxidizing conditions for the three selected samples. The recapture proceeds over 20 min. The O_2 concentrations of the 3 samples are also displayed.

in the samples is below the detection limit of the assay.

3.2. S capture

To evaluate the ability of the ilmenite to reuptake SO_2 after release of SO_2, the samples in which SO_2 was no longer detectable were exposed to a new series of cycles with SO_2 being added under oxidizing conditions. New samples of the three described ilmenite samples (Table 3) were exposed for 20 min to SO_2 under oxidative conditions. Differences in the SO_2 uptake patterns are observed for the three samples in Fig. 4. In the case of calcined ilmenite, a plateau (saturation) is reached after about 6 min, whereas for the other two samples SO_2 uptake continues throughout the experiment, with signs of saturation after 15–20 min of exposure (noted as an increase in the level of detected SO_2). As the differences between the three samples are the exposure times in the combustion reactor (to S as additive and to fuel) and, therewith, the accumulated coating layers of the ash components, the effects of ash components and previous S exposure on the SO_2 uptake will be discussed below. The results presented in Fig. 5 show that after SO_2 exposure, Sample I 48H contains 3-times more S than it held previously and Sample II 0H contains 10-times more S than it did before the SO_2 exposure. Calcined ilmenite does not show any enrichment of S, as it contains similar amounts of S before and after its exposure to SO_2 (Table 6). This observation confirms that, unlike the samples that contain an ash layer, the calcined ilmenite is not efficient regarding SO_2 capture due to its lack of ash elements.

An example of redox cycles for SO_2 capture is given in Fig. 6 for Sample I 48H, where 50 minutes of SO_2 exposure under oxidizing conditions is represented. After SO_2 capture, the sample undergoes reduction conditions, such that the SO_2 is released. As can be seen in the figure, the concentration of SO_2 in the flue gas starts to increase after about 20 minutes, suggesting that at that point the SO_2 capture reaches saturation.

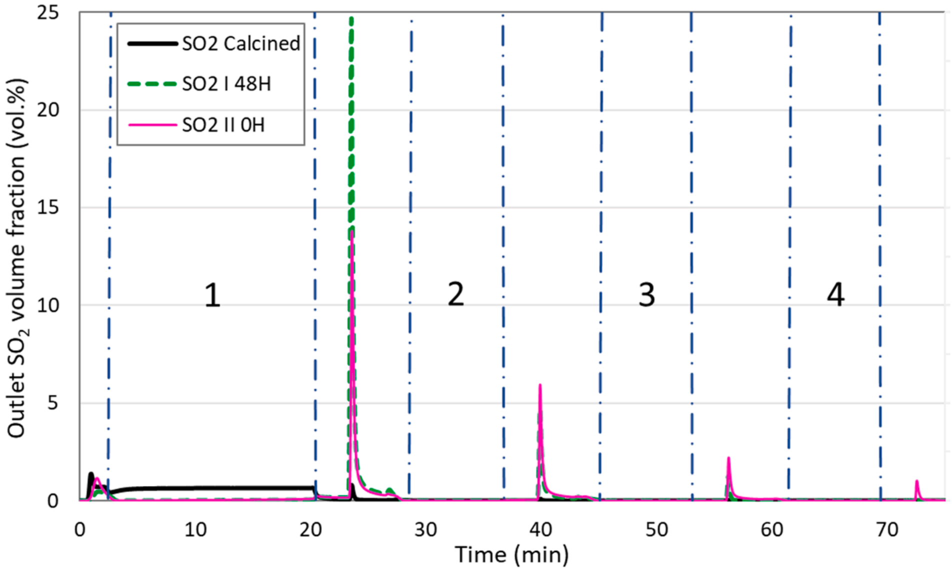

Fig. 5. Levels of SO_2 released from the three selected samples after SO_2 capture. The SO_2 capture at the beginning of the cycle is shown in greater detail in Fig. 4. Zones 1 to 4 represent the oxidizing phases with 5% O_2 in N_2. Between each numbered area, reduction take place where SO2 release is visible.

Table 6

Sulfur contents, as detected by ICP-SFMS in bed materials before and after SO_2 exposure for the three selected samples.

Sample	Calcined	I 48H	II 0H	Calcined after SO_2 exposure	I 48H after SO_2 exposure	II 0H after SO_2 exposure
S content (g/kg)	0.18	2.91	0.84	0.20	9.08	8.55

3.3. *Reversibility*

Based on the observed release and uptake of S in the form of SO_2, it can be expected that S uptake and release by ilmenite is a reversible phenomenon. In order to test this hypothesis, the ilmenite samples were first depleted of sulfur during several reducing cycles. When SO_2 was no longer detected in the released gases, the samples were exposed to SO_2 under oxidizing conditions. A similar pattern to that described for the first SO_2 capture and release was observed for all three samples. Thus, it can be concluded that the SO_2 capture is a reversible phenomenon. S analysis of the bed samples was carried out to confirm this reversibility. The results are shown in Table 6. The maximum number of cycles of uptake and release that the material can withstand remains to be investigated. In the present study, the repeatability of SO_2 capture and release was tested and confirmed through four cycles.

3.4. *Influences of the ash components*

As discussed in the previous section, the effects on S uptake of ash compounds accumulated throughout the exposure in the combustion reactor were analyzed. In previous studies, it has been shown that Ca and K are the major contributors to the formed ash layers. Therefore, the possible effects of Ca and K on the capacity for S capture were further investigated.

Ash influence. The initial concentrations of the main ash elements (Ca and K) for each of the three samples used in the previous steps were determined by ICP-SFMS. The results are presented in Fig. 7. As expected, samples from the Chalmers 12-MW$_{th}$ CFB boiler (samples I 48H and II 0H) contained up to 6-times more Ca and K (between 15 and 22 mg/kg) than the fresh ilmenite (up to 3.5 mg/kg). The participation of

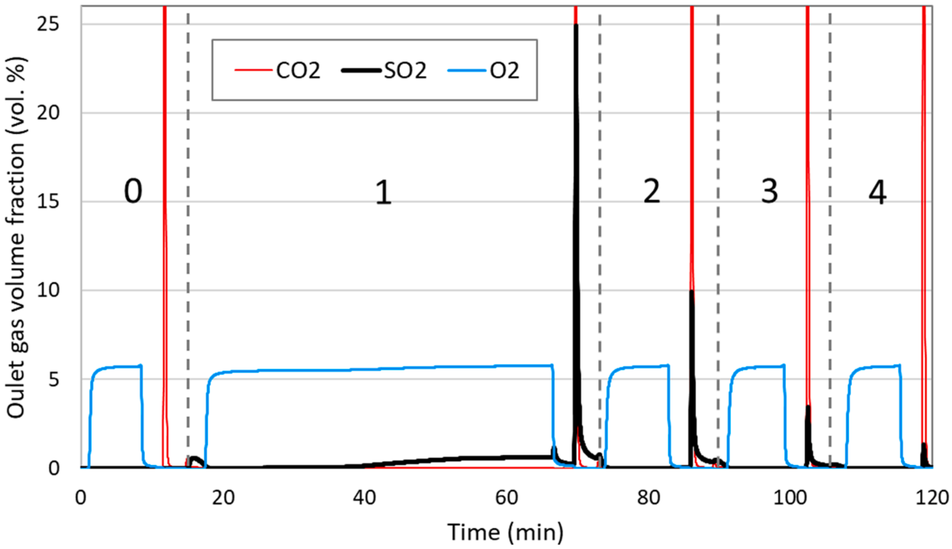

Fig. 6. SO_2 was fed for 50 min under the oxidizing condition, followed by reduction phase with SO_2 release (1) and three other redox cycles (2–4) in the reactor for the sample with S addition and ash layer build-up (I 48H). Note that five complete cycles are illustrated in the figure for the oxidative phase. A reduction phase is visible with the CO_2 peak. During the first redox cycle (0), SO_2 is no longer detected. The second oxidizing cycle (1) contains 1% SO_2 and 5% O_2 in N_2 and has a duration of 50 min, while the three subsequent cycles contain only 5% O_2 in N_2.

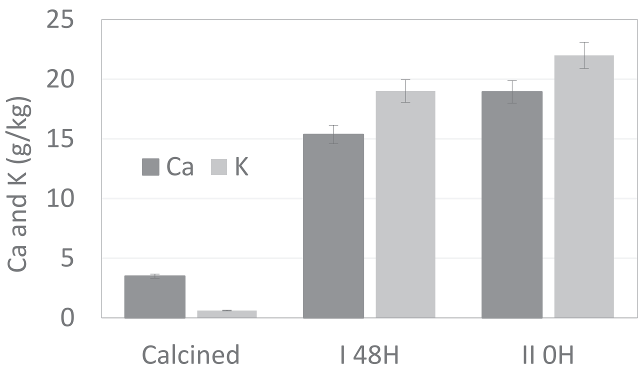

Fig. 7. Ash components of the three selected samples before the laboratory-scale reactor experiment. The results were obtained using total elemental analysis by ICP-SFMS method (in g/kg).

Ca and K in the formed ash layer has previously been reported in various studies [13,14]. With comparison with Table 6 it is clear that the increase in S uptake follows the increases in Ca and K concentrations. To follow the elemental distribution of the S captured by ilmenite, SEM-EDX analysis of the sample cross-section was performed. Fig. 8 shows the result of EDX mapping of Samples I 48H and II 0H after S capture. From the EDX maps it is clear that Ti and Fe are present throughout the particle, while Ca and K are located predominantly on the surface of the particle and only partly in the core of the particle. This was as expected, given that Ca tends to form a layer around the particle and K tends to penetrate the particle during combustion, as previously shown by Corcoran et al. [14]. When it comes to S, it is found predominantly around the particle, mainly in the same location as the K and Ca. S is also present in the core of the particle. These observations confirm that the main ash compounds are linked to S and that the interactions of Ca and K with the ilmenite particle have an impact on S capture. It should be noted that calcined ilmenite was not analyzed, as it did not contain a level of S sufficient to be detected by the microscope and, therefore, it is not shown here.

To evaluate the thermodynamically stable phases that can be formed between K, Ca and S under the studied conditions, a thermodynamic equilibrium calculation using the FactSage Predom software were made. A simulation based on the Ca and K ratio obtained from the bed samples of calcined ilmenite and samples with formed ash layer were used for the calculations (Fig. 9). A calcium-potassium-sulfate mixture, $K_2Ca_2(SO_4)_3$, was found to be the dominating phase in both cases under oxidative conditions with SO_2. $CaSO_4$ was detected in the calcined ilmenite, while K_2SO_4 was found in the ash-containing ilmenite and calcined ilmenite when SO_2 was in a lower concentration.

Furthermore, it was found that S binds first to K, then Ca, under both oxidative and reducing conditions. When the oxygen is in excess, mixed-sulfate-phase $K_2Ca_2(SO_4)_3$ is formed, as well as K_2SO_4 in the presence of ash elements (or $CaSO_4$ in the case of calcined ilmenite). Furthermore, it was observed from the thermodynamic calculations that lowering the SO_2 concentration leads to an increase in the level of CaO, while S remains bound to K in the form of K_2SO_4. Furthermore, when SO_2 is present at a low concentration, K is transformed into K_2O in a process that is dependent upon the availability of oxygen in the reactor.

Further calculations using the FactSage Equilib software revealed that S seems to bind preferentially to Ca when it encounters calcined ilmenite, whereas S will bind to K, thereby forming potassium sulfate, when it interacts with bed material that has accumulated ashelements (Table 7). In the case of calcined ilmenite, S can also bind to K, as it appears to form center87085700center456120500$K_2Ca_2(SO_2)_3$.

Those results are also confirmed by previous researchers [24–27] where $CaSO_4$ was found to form in oxidizing conditions and CaO in reducing condition, explaining the release of SO_2 by the following reactions (Reaction R(1) and R(2)):

Oxidizing:

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \tag{R1}$$

Reducing:

$$\begin{gathered} CaSO_4 + CO/H_2 \rightarrow CaO + \ SO_2 + CO_2/H_2 \\ \# \end{gathered} \tag{R2}$$

It has also been observed that above 900 °C, CaS could react with $CaSO_4$ thus releasing SO_2 (Reaction R(3)) [28]:

$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2 \tag{R3}$$

Previous study also showed the SO_2 release during the shift between oxidizing and reducing condition in lab study with coal as fuel. The study also reveals that a high concentration of CO and H_2 provides a stronger reducing condition for $CaSO_4$ to CaS, confirming the results given by FactSage (Fig. 9)[29].

Concerning K, the formation of arcanite (K_2SO_4) and syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) has been observed by Kępys [17], but its presence was found in the fly ashes. The same study also confirms that in the case of bottom ash, the application of S to limit corrosion did not have a negative impact on its chemical properties and consequently does not

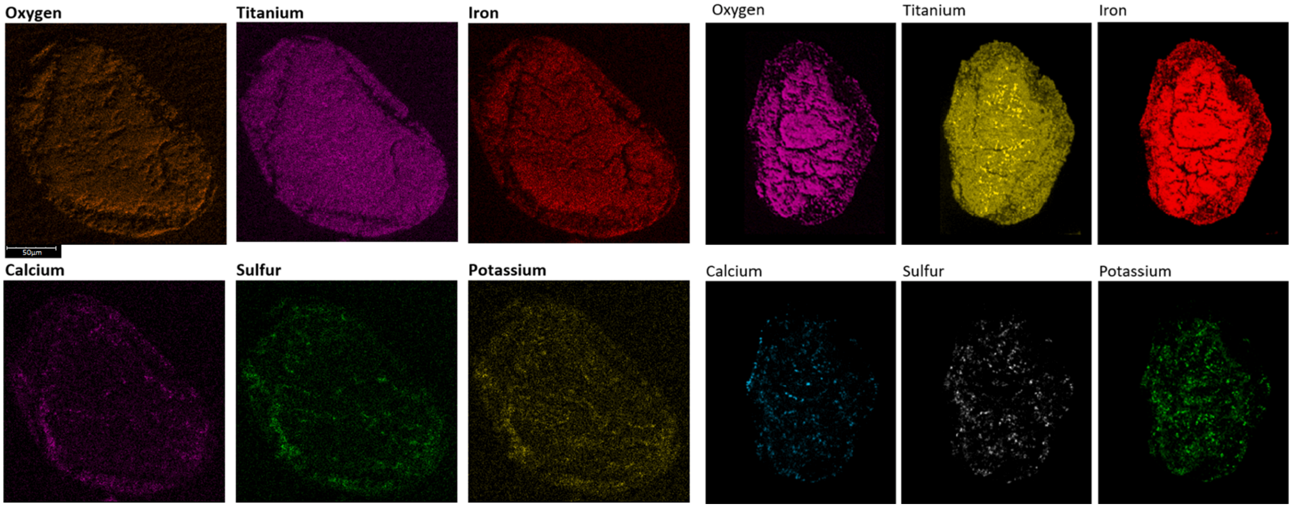

Fig. 8. SEM-EDX intensity maps showing the distributions of O, Ti, Fe, Ca, K and S in the cross-sections of ilmenite particles from Sample I 48H (left) and Sample II 0H (right) after the SO_2 capture experiment in the laboratory-scale reactor.

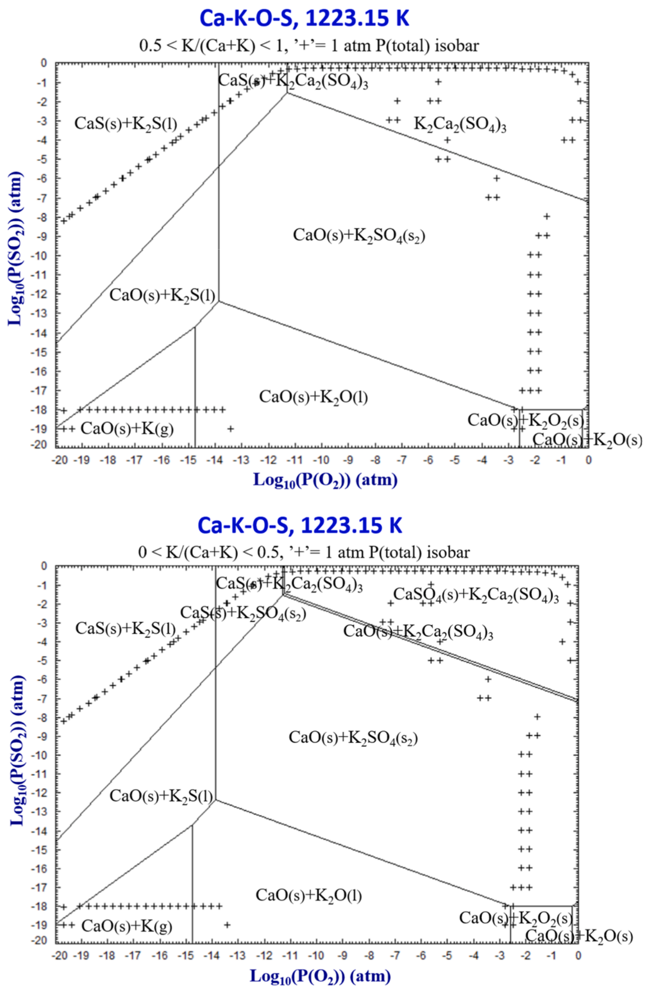

Fig. 9. Phase diagram showing Ca, K and S depending on the O_2 and SO_2 availability and the types of samples. The top panel represents the calcined ilmenite composition, while the bottom panel represents the ilmenite with ash composition. The diagram was generated with the FactSage Predom program.

Table 7
Main components of the ilmenite forms given by thermodynamic equilibrium calculations from FactSage ver. 7.2, at 950 °C and 1 atm.

Sample	Composition	
Calcined	Fe_2O_3	Hematite
	TiO_2	Rutile
	$CaSO_4$	Anhydrite
	$K_2Ca_2(SO_4)3$	Calciolangbeinite
II 0H	Fe_2O_3	Hematite
	TiO_2	Rutile
	CaTiO3	Perovskite
	K2SO4	Arcanite

limit its use.

3.5. Summary

Based on the performed analysis, a representation of SO_2 capture and release as a function of the presence of an ash layer is proposed. The schematic (Fig. 10) of an ilmenite particle shows a possible mechanism development during SO_2 exposure under oxidative conditions and SO_2 release under reducing conditions. In Fig. 10, the top row represents a calcined ilmenite particle (i.e., without an established ash layer), while the bottom row represents a particle of ilmenite that has been exposed to the boiler conditions.

Owing to the calcination conditions, the surface of the calcined ilmenite becomes heterogeneous and porous. According to previous observations, the S that is naturally contained in fresh ilmenite is released at around 860 °C, and this leads to the formation of pores in the particles. Exposure of the ilmenite surface to SO_2 after its release leads to a low level of SO_2 capture under oxidizing conditions with $SO_{2.}$

If prior to S exposure the ilmenite is exposed to combustion conditions (fuel, oxidation environment) (Fig. 10, bottom row), pores and crack are created due to the physical and chemical constraints to which the particles are subjected. The main ash compounds are accumulated around the ilmenite particle as a coating layer. When exposed to S, the compounds in the ash layers interact with the SO_2 and form K_2SO_4, $K_2Ca_2(SO_4)_3$ and $CaSO_4$. After S is accumulated, the conditions become reducing and S is released from the coating in the form of SO_2. K is then found in the form of K_2O and Ca in the form of CaO. In both cases (with and without the ash layer), capture and release of SO_2 is a reversible phenomenon, whereby saturation with SO_2 is reached faster with calcined ilmenite, confirming that the presence of ash elements play a major role in S capture.

4. Conclusion

The purpose of this study was to understand the conditions and main mechanisms through which S is captured and released by ilmenite particles during OCAC. The focus of the investigation was to map the mechanisms for S capture and release by ilmenite and to determine whether the S interacts with the ilmenite phase and/or solely with the formed ash layer. Three bed samples were tested in a batch reactor at 950 °C:

- Calcined ilmenite was used as reference;
- Sample II 0H, which had a residence time of 3 days in a 12-MW_{th} CFB boiler and accumulated an ash layer during the measured period;
- Sample I 48H, which had a residence time of 2 days in a 12-MW_{th} CFB boiler fed with S, and pre-accumulated ash layer.

The findings of the present study show that: (1) S is released in the form of SO_2 during the redox cycles, with the highest content being released by ilmenite with the ash layer; (2) SO_2 is captured in the bed particles under oxidizing conditions and is released under reducing conditions; (3) ilmenite reaches saturation after exposure to SO_2 for 20 min; (4) the capture and release of SO_2 are part of a reversible phenomenon. This work also shows that S is found within the entire particle when ilmenite is exposed during OCAC, albeit predominantly in the ash layer region. The S is mainly found in the same location as the K and Ca. This study suggests that Ca and K from biomass ashes are good candidates for S capture, forming calcium-potassium-sulfate ($K_2Ca_2(SO_4)_3$) under oxidizing conditions. When ash elements are accumulated, K exhibits the highest affinity for S in forming K_2SO_4.

CRediT authorship contribution statement

Mariane Vigoureux: Writing - original draft, Investigation, Conceptualization. **Tomas Leffler:** Investigation, Writing - review & editing. **Pavleta Knutsson:** Conceptualization, Supervision, Writing - review & editing. **Fredrik Lind:** Funding acquisition, Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

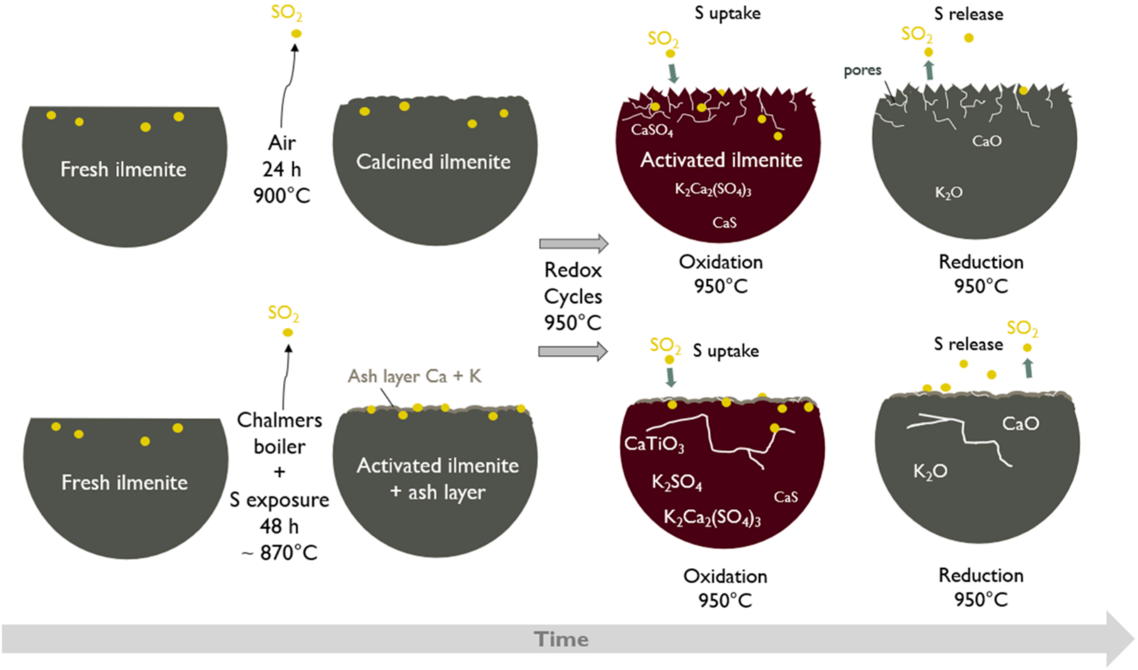

Fig. 10. Schematic representation of the different stages of SO_2 release and capture by ilmenite particles during redox cycles depending on the presence or absence of an ash layer. The top row represents calcined ilmenite without the ash element. The bottom row represents ilmenite that has undergone combustion and thereafter has developed a thick ash layer.

Acknowledgements

This research was financially supported by E.On, Improbed AB and the Swedish Energy Agency (46450-1 "Syrebärarstödd förbränning för effektivare bränsleomvandling i FB-pannor med samtidig återvinning av alkaliföreningar"). Special thanks are directed to Johannes Öhlin and Jessica Bohwalli for their assistance in the experimental work. The authors are grateful for all the support given by the staff of Akademiska Hus related to operating the Chalmers boiler during the campaign.

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