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Oxygen carrier aided combustion with copper smelter slag as bed material in a semi-commercial wood-fired circulating fluidized bed

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ABSTRACT

Fluidized bed combustion (FBC) is a well-established technology in Sweden for the conversion of biomass and waste-derived fuels. Recent research has shown that the process can be upgraded by using oxygen-carrying bed material, for example in the form of iron oxide-containing minerals and slags. The concept, called Oxygen Carrier Aided Combustion (OCAC), has demonstrated enhanced oxygen distribution and thermal efficiency in commercial boilers, using the iron-titanium ore ilmenite as oxygen carrier. This study demonstrates the first large-scale utilization of a commercial copper slag product (Järnsand) as oxygen carrier in a 12 MW_{th} circulating fluidized bed boiler. By exchanging between 21 and 100 % of the silica sand bed with Järnsand it was possible to successfully reduce the air-to-fuel ratio from 1.2 down to 1.08 with CO emissions remaining low, at concentrations of around 20 mg/nm³ at 6 % O₂. In contrast, an air-to-fuel ratio of 1.08 with silica sand bed gave a 5-min average CO concentration of 800 mg/nm³ at 6 % O₂. The NO emissions were also reduced by about 30 % with the introduction of Järnsand. For 3.5 days of the campaign, the boiler was operated with a 100 % Järnsand bed without any bed material regeneration. K was absorbed by Järnsand, and a K concentration of 3.5 wt.-% was reached. No agglomeration or increasing CO emissions were observed. K-saturation was not reached, and a longer lifetime than the studied 3.5 days is suggested. In conclusion, similar performance as ilmenite is suggested for Järnsand as an oxygen carrier in OCAC operation.

1. Background and aim

Sweden has a long history of using domestic, renewable energy sources in the form of solid biomass- and waste-derived fuels, for which fluidized bed combustion (FBC) is an efficient combustion technology. The bed provides thermal inertia, air and fuel become mixed efficiently, the bed can absorb volatile ash species, and co-combustion of different fuels is possible [1–4]. This has resulted in around 120 FBC boilers operating in Sweden, converting wood, forestry residues, waste-derived fuels or a combination of fuels. About 1/3 of those FBCs are circulating fluidized beds (CFB) and the rest are bubbling fluidized beds (BFB) [5].

FBC was originally developed for coal combustion and has later been adapted for other fuels [6]. Coal is still the most used solid fuel globally, and it's important to point out the differences between coal and solid biomass- and waste-derived fuels. Compared to coal, typically, biomass and waste-derived fuels have the following characteristics [6–8].

- The char is more reactive
- The total ash content is lower, but the ash contains alkali and other species that make it very reactive, and
- The fuel composition and moisture (especially for waste-derived fuels) can vary significantly during feeding.

These aspects are important to consider when designing the fuel conversion process. For example, the ability of the bed to absorb volatile ash species is important. Volatile alkali species contribute to slagging, fouling, and corrosion [8,9], but if absorbed by the bed material, they can be removed by bottom ash extraction, which prevents them from accumulating in the boiler. However, absorption of ash can also cause agglomeration of the bed by formation of sticky compounds. A high enough rate of bed regeneration must therefore be applied to avoid defluidization.

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⁻The moisture and volatile contents are higher

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1.1. Oxygen carrier Aided combustion

One of the main design challenges in combustion is to ensure the effective mixing of fuel and air to avoid emissions of unconverted fuel species. This can be especially challenging with fuels with high volatile content, like biomass. Devolatilization is fast, and the volatiles are released before the fuel has had time to disperse in the bed. This creates a volatile-rich zone close to the fuel-feeding location [10,11]. An air surplus is applied to compensate for the local oxygen deficiencies caused by the uneven distribution of volatiles. By running the boiler at a higher than stochiometric air-to-fuel ratio, large emissions of CO and hydrocarbons can be avoided. However, excess air introduces unavoidable thermal losses. The air-to-fuel ratio is represented by the lambda value, defined as the ratio between the supplied air flow and the air flow required for stoichiometric combustion. A lambda value higher than one means that there's a total oxygen surplus supplied to the boiler.

During the last 10 years, a concept called Oxygen Carrier Aided Combustion (OCAC) has been developed to enhance the oxygen distribution in the bed, to compensate for local oxygen deficiencies [5,12]. The technique is based on using an oxygen-carrying bed material in the form of solid metal oxide particles. The oxygen carrier can oxidize the gaseous fuel components, i.e. volatiles and gasification products. The oxygen carrier circulates in the boiler and is either oxidized by air or reduced by fuel, depending on the local oxygen partial pressure [13]. In this way, the fuel can be converted even where there's locally a shortage of gaseous oxygen.

OCAC has been examined in large-scale experiments and operated in commercial settings in Sweden for a few years. The concept was introduced in 2012 and demonstrated in Chalmers University's 12 MWth CFBtype research boiler with ilmenite as oxygen carrier, which is an iron titanium mineral used for producing TiO₂ [12]. Exchanging the bed partly with ilmenite was successful and it was possible to reduce the lambda value without increasing CO emissions [12]. Since the air supply is often the limiting factor for the boiler load, a reduced lambda value allows for increased thermal load in commercial boilers. In one 75 MW_{th} CFB boiler firing municipal solid waste, it was possible to decrease the air surplus by 25 % and increase the load by 13 %, when using ilmenite instead of silica sand as bed material [13]. In a 115 MWth wood-fired CFB boiler the load was increased by 7 % and the air surplus decreased by up to 30 % with ilmenite [14]. More examples of successful operation of commercial boilers are provided in Ref. [5]. The concept has been commercialized by the Swedish company Improbed AB, which is a subsidiary of the utility company E.ON. The current study investigates using a commercially available copper smelter slag product as oxygen carrier.

Effort have been made to explain the functionality of the oxygen carrier in the bed. Thunman et al. [12] found in their semi-commercial scale demonstration study with ilmenite that the concentrations of CO and total hydrocarbons were lower across the whole cross-section of the bed. This included the bottom bed and locations near the fuel feeding, where conditions are reducing, and CO concentrations are typically higher. This indicated that the ilmenite enhanced the distribution of the oxygen and supported the conversion of the gaseous fuel species. The redistribution of the fuel conversion was also supported by the temperature profile over the cyclone, showing that the fuel burnout in the cyclone was lower, i.e. that the fuel was to a larger extent converted inside the combustion chamber. On top of redistributing the oxygen in space inside the bed, dedicated fuel pulsing experiments in the semi-industrial scale boiler have also demonstrated that the oxygen carrier has an oxygen buffering effect in time [10]. This means that a sudden, short-term increased fuel load can be handled by oxygen stored in the bed by the oxygen carrier. This can be especially useful with fuels like municipal solid waste, which can vary in composition during feeding. The function of the oxygen carrier in OCAC operation has also been demonstrated in laboratory-scale fluidized bed experiments, e.g. in one experiment using methane as a fuel model component [15].

Methane is a quite stable fuel component and is typically converted mainly in the freeboard during CFB combustion. However, with ilmenite, more of the conversion was demonstrated to take place inside the bed than when an inert silica sand bed material was used. This demonstrated that the fuel was partly converted by interaction with the oxygen carrier, rather than only with the gaseous oxygen. An initial lab-scale study with copper smelter slag suggests a similar redistribution of fuel conversion from the freeboard towards the bottom bed [16]. Certain oxygen carriers have an oxygen uncoupling effect (referred to as Chemical-Looping Oxygen Uncoupling, CLOU), meaning that gaseous oxygen is released from the oxygen carrier at a low oxygen partial pressure [17]. This enables the oxygen carrier to participate in direct char combustion. This effect has been observed for Mn-, Cu, and Co-based oxygen carriers but is not expected with iron-based oxygen carriers that are the focus of this study.

A reduction in NO emissions was observed in the first large-scale experiment with ilmenite [12]. However, the underlying mechanism is not well understood, and it could not be determined whether the presence of ilmenite reduced the NO formation or if it facilitated its conversion to N2. Lab-scale OCAC experiments have demonstrated that even slightly reduced ilmenite can reduce NO to N₂ [18]. The fate of NO and ammonia with Ilmenite and steel converter slag (LD-slag) as oxygen carriers was further explored in Ref. [19]. A more even temperature distribution in the boiler was also observed with ilmenite, which in turn was suggested to contribute to reduced NO emissions [12]. It should be pointed out that since the initial large-scale experiment, consistent evidence of reduced NO emissions using ilmenite or other oxygen carriers has not been clearly demonstrated, to the best of the authors' knowledge. According to other published literature, enhanced oxygen distribution is more likely to increase NO emissions [20,21]. Regardless of the effect of the oxygen carrier directly, reducing the lambda value is in itself effective for reducing the NO formation [21]. Lower lambda values, and therefore lower concentrations of gaseous O2, limit the oxidation of fuel-N to NO. This trend is consistent in all previous studies with LD-slag, Mn-ore and ilmenite in the Chalmers boiler [12,22,23]. It's suggested that the presence of oxygen carriers would affect the NO formation mechanisms, but the mechanisms are not well described. Further, NO emissions are generally low in FBC, as the temperature is too low for thermal NO formation [18]. The NO emissions will therefore only be discussed briefly in this work.

OCAC is closely related to a technology called Chemical-Looping Combustion (CLC), where the oxidation of the oxygen carrier and the conversion of the fuel are separated into two interconnected reactors [24]. Several hundred different oxygen carriers, both naturally occurring minerals and synthetic particles, have been suggested and evaluated for CLC applications [25]. Some of these materials are also relevant in OCAC applications, although the conditions and requirements differ slightly. By separating the air from the fuel, CO₂ becomes inherently separated from the other flue gas components, making it a suitable technology to couple with Carbon Capture Utilization and Storage (CCUS). CCUS is identified as a key strategy for limiting global warming to 1.5 °C, according to the IPCC [26]. Further, as biomass is regarded as a CO2-neutral energy source, storing the CO2 produced from biomass combustion results in negative CO2 emissions. This concept is referred to as Bio-Energy Carbon Capture and Storage (BECCS) [27]. Even though OCAC itself is not directly a CCUS technology, it could act as an important intermediate step towards Bio-CLC. Large-scale deployment of OCAC involves developing knowledge about the manufacturing, logistics, and utilization of particulate oxygen carriers. On top of that, OCAC could potentially make biomass- and waste derived fuels more accessible for utilization, by upgrading the FBC technology. This further motivates the research into oxygen carriers.

1.2. Biomass ash interactions

Biomass- and waste-derived fuels contain challenging ash

compounds like alkali. Interactions between the ash and the bed material might result in problems like agglomeration, slagging, and fouling. Furthermore, volatile alkali present in the combustion can interfere with the conversion process and lead to incomplete fuel burnout in the gas phase [28–30]. Free K is also known to contribute to corrosion downstream, in the convection section [8].

Agglomeration of bed material has been studied extensively [2,3,31, 32], and the mechanisms depend both on the ash and the bed material compositions. Silica sand tends to agglomerate relatively quickly with alkali-rich fuels, as the interaction creates K-silicates with low melting temperatures [3,33]. On a positive note, the capacity of silica sand to absorb alkali results in an effective way to remove problematic ash species from the boiler. It is evident from previous studies that the ability of the bed material to capture K is important for fuel conversion: some previously evaluated oxygen carriers have a relatively poor ability to absorb alkali, which has been negative for the fuel conversion [22,23, 34]. Using LD-slag as bed material in an industrial-scale boiler [22,34] actually resulted in increased CO emissions compared to the reference case with silica sand, even though oxygen-carrying properties of LD-slag had been confirmed in lab-scale experiments [35,36]. A similar phenomenon was seen in an experimental campaign with Mn-ore [23]. In both cases, adding ammonium sulphate to the boiler solved the problem and lowered the CO emissions, as the available gas-phase K was captured as solid K₂SO₄. Ilmenite, on the other hand, has been found to capture K by forming stable K-titanates in the particle core. This is advantageous for the fuel conversion but also for the lifetime of the material, as the stable K-titanates don't induce agglomeration [37] like K-silicates do. This has resulted in a reduced bed material consumption with ilmenite compared to conventional silica sand bed material.

Another possible advantage of iron-containing oxygen carriers is that the material potentially has magnetic properties, meaning that it can be separated from non-magnetic ash particles and recirculated to the boiler. A belt separation unit has been used in industrial boilers to continuously separate large flows of ilmenite and ash. Results reported by Lind et al., 2020 [38] with a 75 MW and an 85 MW CFB burning municipal solid waste showed that the make-up rate could be reduced to around 3 or even 1 kg/MWh, while still documenting the positive oxygen-carrying effect in the boiler. Gyllén et al. [39] further studied the use of magnetic separation in the 12 MW_{th} Chalmers and the 115 MW_{th} Kraftringen boilers. For comparison, typical consumption rates for silica sand bed material in conventional FBC range between 3 and 6 kg/MWh, depending on the fuel and operation strategies [5].

1.3. Copper smelter slag as an oxygen carrier

Assuming that the harsh conditions in the boiler will require a large throughput of oxygen-carrying bed material, the following features, or a combination of them, should be fulfilled by the bed material to make is feasible for OCAC.

- The bed material can be obtained at a low cost, including both the cost of raw material and the processing to obtain particles in a suitable size range.
- The oxygen carrier can be separated from the ash particles, e.g. through magnetic separation
- The material is available in large quantities
- The material is preferably produced from non-virgin material
- The material has low toxicity and can be safely handled by operators

Sweden and neighboring countries Finland and Norway all have large metallurgical industries that handle huge amounts of ores and industrial by-products [40]. Ores and slags from smelting processes contain metal oxides (mainly iron oxide), potentially making them feasible as oxygen carriers. The potential for using slags and ores as bed material was discussed in Ref. [5].

Copper smelter slag is a major by-product generated in the copper

smelting process. The largest copper smelting company in Sweden is Boliden AB, which produces in total around 1.5 million tons/year of copper smelter slag across their sites in Sweden and Finland. The product used in this experimental campaign is a water-granulated slag. The water granulation process involves cooling the molten slag quickly, which results in glassy particles up to 4 mm in size. The watergranulated slag is sold on the Swedish market under the name Järnsand ("iron sand") and different size fractions are used as construction aggregate and abrasive media [5]. Out of the 1.5 million tons of copper slag produced annually by Boliden, only approximately 250 kton is currently granulated into Järnsand. The remaining copper smelter slag is air-cooled, for which there is currently limited utilization. Thus, the potential for scaling up production and utilization is substantial. For bed material purposes, a granulated material should be advantageous over air-cooled slag that would require more extensive crushing and sieving to produce particles at a suitable size range.

The main components of the slag are Fe- and Si-oxide. Since the water granulation process cools the slag quickly, the resulting material is amorphous. Upon calcining the material, crystalline Fe₂O₃, Fe₃O₄, and SiO₂ (cristobalite) appear [41]. Hematite (Fe₂O₃) and magnetite (Fe₃O₄) make up a suitable oxygen-carrying system. Fuel conversion and fluidization properties of Järnsand have been demonstrated previously by Purnomo et al. [41]. The ability of Järnsand to convert CH₄, CO, and pine forest residue char was confirmed. However, previous work with Järnsand has been focused mainly on applying it for gasification and has so far only been conducted in laboratory-scale experiments, with short timescales, and no relevant ash exposure. The fluidization and fuel conversion of Järnsand in the presence of model K-compounds has been studied in experimental work by the authors of this paper, concluding that K can be absorbed by Järnsand. A publication summarizing these findings is currently under review and available as a preprint [42].

1.4. Aim of the study

In summary, the OCAC concept is worth developing further for several reasons.

- The thermal efficiency can be increased compared to conventional FBC. By moving the air-to-fuel ratio closer towards a stochiometric process, both the fuel efficiency and the fuel load can be increased.
- Changing the bed material might influence the ash chemistry. Ilmenite, for example, is free from Si and has demonstrated a lower risk for agglomeration in the presence of alkali.
- Existing FBC boilers can be upgraded to OCAC boilers with limited effort. The operational procedures might have to be adapted to altered fluidization properties of the oxygen carrier and ash handling. However, in many instances, implementation has been possible without large efforts.

This study aims to examine the use of the copper smelter slag product Järnsand as an oxygen-carrying bed material in an industrial-scale CFB boiler. The following aspects were investigated.

- The general operability of Järnsand as bed material in CFB combustion of wood chips.
- Whether Järnsand could have an advantage over silica sand with respect to emissions, especially at low air-to-fuel ratios.
- How ageing of the bed material in the boiler affects its composition, morphology, and reactivity with fuel.

2. Materials and methods

An experimental campaign was conducted for 9 days over two consecutive weeks. During the first week, the bed consisted of mixtures of silica sand and Järnsand. The bed was then replaced and during the second week, the boiler was operated with 100 % Järnsand as bed material. During the main part of the experiment, the boiler was operated in a nominal mode to evaluate the operability of Järnsand and Järnsand-silica sand mixtures as bed material. Additionally, the boiler was operated periodically at lower than nominal lambda values to explore the oxygen-carrying ability of Järnsand.

2.1. Chalmers 12 MWth research boiler

The boiler used for the campaign is a CFB boiler located at the campus of Chalmers University of Technology in Gothenburg, Sweden. The boiler is operated commercially to produce heat for the local district-heating system during the colder months. It is designed for a maximum load of $12 \text{ MW}_{\text{th}}$ with coal as fuel. Currently, the main fuel is wood chips, for which the maximum load is around 8 MW_{th}.

A schematic representation of the boiler is presented in Fig. 1. The furnace (1) has a square cross-section of 2.25 m^2 and a height of 13.6m. The bed material is mainly located in the dense bed of the boiler but is also entrained with the fluidizing gas. A water-cooled cyclone (4) separates the entrained bed material from the flue gases. The separation is not perfect, and some fine bed material and fly ash particles need to be separated from the flue gas at a later stage. After the cyclone, the bed material particles enter the particle distributor (9) and are then directed back to the boiler either via an external particle cooler (10) or via the gasifier (11). The fuel is fed through a fuel chute to the top of the furnace bed (2). Optionally, 25 % of the fuel can instead be fed to the gasifier (11). During the experimental campaign, no fuel was fed to the gasifier and most of the time, the gasifier was disconnected from the boiler. However, for practical reasons not related to the campaign, a circulation of bed material through the gasifier was required during the last three days of operation. For this reason, the total bed inventory was then increased by 1700 kg, from about 2000 to 3700 kg. Bottom ash is extracted from the bottom of the bed (21) to remove ash species and regenerate the bed material. The fluidizing gas is supplied in the wind box (3) and is a mixture of combustion air and recirculated flue gas. The flue gas leaves the furnace via the cyclone and enters the convection

path (5), in which water is heated for district heating. The flue gas is cleaned from the remaining fly ash and entrained bed particles in a secondary cyclone (6) and finally in textile bag filters (7).

Bed material samples can be extracted from the bottom bed using a cooled probe. The measurement port used for the bed material extraction is H2.5, located between H2 and H3 in Fig. 1. The bed material silo, bottom ash container, and fly ash collection containers for the secondary cyclone and textile filter are mounted on scales and continuously weighted to determine the flow of solids in and out of the boiler.

The pressure and temperature at different locations, fuel feeding rate, primary and secondary air flows, and flue gas compositions, among other parameters, are measured and logged during operation. The CO and O_2 concentrations reported in this work are measured in the convection path (kh2). NO is measured in the stack. The gas concentration measurement techniques used are presented in Table 1. The data is collected with a timestep of 6 s or 1 min, where the average value over each timestep is logged.

Table 1

Gas concentration measurement techniques. NDIR = Non-Dispersive Infrared sensor, GC = Gas Chromatography, PMOD = Paramagnetic Oxygen Detector, CL = Chemiluminescence, FID = Flame Ionization Detector.

Gas component	Measuring method
Methane	Nondispersive infrared detector (NDIR), Gas chromatography
	(GC)
Carbon monoxide	NDIR, GC
Oxygen	PMOD, GC
Hydrogen	GC
Nitrogen	GC
Nitric oxide	CL
Nitric dioxide	CL
Dinitrogen oxide	GC
Total	FID
hydrocarbons	



Fig. 1. A schematic representation of the Chalmers 12 $\ensuremath{\text{MW}_{\text{th}}}$ research boiler/gasifier.

2.2. Bed material

The oxygen carrier bed material used in the campaign was derived from the commercial product Järnsand 0/2 from Boliden. The size distribution of Järnsand 0/2 is presented in Fig. 2. The material was first dried by UVR-FIA in Germany. The material was then crushed and sieved by Comminution Reimagined Sweden AB (CRS) and 16 tons of bed material was delivered to Chalmers. The resulting size distribution as reported by CRS is also presented in Fig. 2, along with the size distribution of the silica sand B28, which is commonly used in the boiler. The production process was to some extent trial and error, and in hindsight, the drying step might not have been necessary with the selected crushing and sieving method.

There were about 5 wt.-% fines smaller than 0.09 mm in the delivered material. According to CRS, this fine fraction could be removed by wind sieving, with only small amounts of extra time and effort. However, this was not done since no equipment was available at the time. The product yield from the crushing and sieving was reportedly about 80 %. The bulk density of the fresh material was measured at 1.66 g/ $\rm cm^3$.

The composition of the Järnsand bed material is shown in Table 2. The composition was determined by a standard method of dissolution in LiBO₂-melt or HNO/HCl/HF solution and ICP-MS analysis. The standard bed material used in the boiler is silica sand Baskarp B28. This is also what is used during the reference period and for mixing with järnsand during the first week. The composition of B28, according to product specifications, is presented in Table 2.

2.3. Fuel

The fuel used during the experimental campaign was wood chips. The fuel is a commercial product consisting mainly of stem wood from pine and spruce and is delivered in trucks to open storage at the site. Thus, the properties, and especially moisture content, of the fuel vary somewhat over time. Fuel samples were taken each day from the fuel feeding line. The moisture content, presented in Table 3, varied between 40 and 49 wt%.

2.4. Campaign overview

An overview of the two weeks of experiments is presented in Table 4. Day 1, the bed consisted of 100 % B28 silica sand. The first day of the experiment was used to generate reference data to be compared to the operation with Järnsand. The boiler had been operating continuously for a few weeks leading up to the experiment. Thus, some ash had accumulated already at the start of the experiment. On the morning day 1, 100 kg of bottom ash was removed and replaced with fresh silica sand. In



Fig. 2. Size distribution of the product feed Järnsand 0/2 and of the bed material after processing. B28 (the commonly used silica sand bed material in this CFB boiler) is included for reference.

the afternoon on day 1, about 250 kg of bed material was further regenerated to empty the bed material silo of silica sand before loading it with 100 % Järnsand (regeneration is here defined as the removal of bottom ash and addition of fresh bed material). During the following days of the first week (day 2–5), the Järnsand content was increased gradually each morning by extracting bottom ash and adding Järnsand. Approximate amounts of regenerated bed material are given in Table 4. The resulting Järnsand content was estimated afterwards based on a total elemental analysis of bed samples.

After day 5, the boiler was shut down, emptied of bed material, and subsequentially filled up with 100 % Järnsand. The boiler was restarted on Tuesday morning (day 6). For the remaining time (day 6-day 9), there was no extraction of bottom ash. On the afternoon of day 6, around 1700 kg of material was added to allow for a circulation through the gasifier (this was required for technical reasons and not related to the experimental campaign). On the morning of day 8, around 70 kg bed material was added to adjust the pressure drop and compensate for bed material lost in the form of fly ash. Apart from that, no renewal of the bed was done during the second week, with the intended goal of studying the ageing of Järnsand and its capability to absorb ash species. Samples of bed material were extracted at least twice per day: in the morning directly the after regeneration of bed material and the afternoon.

2.5. Operation at reduced air-to-fuel ratios

Operating the boiler at a lower than nominal lambda value is a convenient method to explore the ability of the oxygen carrier to facilitate fuel conversion and act as an oxygen buffer. Lambda experiments were conducted according to the following procedure.

- The total airflow was fixed at 2.3 kg/s. The distribution between primary and secondary air was fixed.
- The fuel feeding rate was adjusted so that the outlet oxygen concentration was 4.0 % measured in the wet gas. The exact fuel feeding rate depends mainly on the moisture content of the fuel but is typically around 1800–2100 kg/h. This corresponds to between 5 and 6.5 MW_{th}, depending on the fuel moisture content.
- The lambda value was lowered in several steps. In practice, this means manually increasing the fuel feeding rate by 20–60 kg/h at a time. For each lambda value reached, the fuel feeding rate was kept constant for 20–30 min before either increasing it further or terminating the experiment and returning to nominal load, in the case that CO emissions became unacceptable (consistently higher than a few hundred ppm). By this method, the lambda values were not predetermined, but a similar range was explored during the experiments.

The bottom bed temperature was a set point controlled automatically by the recirculation of flue gas. Thus, an increase in heat production from increased fuel feeding or reduced moisture content was automatically handled by an increased flue gas recirculation rate. 850 °C was used as bottom bed temperature most of the time, except for during the operation at reduced lambda values on the last day with 100 % Järnsand operation, where the bottom bed temperature was instead kept at 875 °C. Nevertheless, the recirculated flue gas is only a small part of the total gas flow, and the superficial gas velocity in the boiler was always between 2.5 and 3.1 m/s (most of the time in a narrower range just below 3 m/s).

The CO and NO flue gas concentrations were evaluated as a function of the lambda value (λ). The average value for at least 5 min of operation was used for CO-, NO- and O₂ concentrations. The resulting average COand NO concentrations were plotted against the calculated average lambda-value, as defined according to Equation (1) where *l* is the actual, total air flow to the boiler and *l*_{o,t} is the theoretic air flow required for stoichiometric combustion. The lambda value was estimated according

Table 2

Compositions, in wt.-%, of the bed materials used in the experiments. For Järnsand: The analysis method is the one presented in 2.6, balance is mainly oxygen. For B28: Composition according to product specification.

[wt%]	Fe	Si	Al	Ca	Zn	Mg	Cu	Na	К	S	Mn	Cr
Järnsand	34.6	18.6	2.9	2.4	1.0	1.0	0.6	0.5	0.5	0.4	0.3	0.2
		Fe ₂ O ₃		SiO ₂			Al ₂ O ₃		K ₂ O			Na ₂ O
B28		0.4–0.7		88–92			4.5–6.6		0.9–2	.7		1.9–1.4

Table 3

Moisture content in wood chips samples.

	en empe emp								
Date dd/mm	20/11	21/11	22/11	23/11	24/11	28/11	29/11	30/11	01/12
Moisture [wt %]	42.6	43.0	42.3	40.6	42.0	46.5	48.8	49.2	48.6

to Equation (2), where $c_{O_2,dry}$ is the oxygen concentration measured in the dry flue gas.

$\lambda = \frac{l}{l_{o,t}}$	Equation (1)
$\lambda = \frac{0.21}{0.21 - c_{O_2, dry}}$	Equation (2)

2.6. Material analysis of bed samples

The physical and chemical development of the bed material during the experiment was examined through material analysis of representative samples of bed material. The particle size distribution was evaluated using sieves with mesh sizes 1 mm, and 710, 500, 355, 250, 180, 90 and 45 μ m. Larger chunks of char and rocks were removed before sieving the samples. Approximately 70–80g of material from each sample was sieved. A shift in size distribution was expected since particles can undergo fragmentation, elutriation, agglomeration, swelling, and ash layer build-up. The Brunauer-Emmett-Teller (BET) surface area was measured in a Micromeritics TriStar 3000 by the method of gas adsorption. The bulk density was measured with a standard funnel method (ISO 3923–1:2008). The total elemental composition was analyzed by ALS Scandinavia AB with a standard method of dissolution in LiBO₂- melt (ASTM D3682:2013) or HNO/HCl/HF solution (SS-EN 13656:2003) and subsequent ICP-MS analysis (ISO 17294–2:2023).

Particles were subject to scanning electron microscopy (SEM, FEI ESEM Quanta 200) and energy dispersive X-ray spectroscopy (EDS). Particle cross-sections were prepared with two different methods. The first method was done by embedding several grams of particles in epoxy resin which was subsequently ground and polished to obtain a smooth surface that could be analyzed with SEM. However, this mechanical grinding method is insufficient when recording higher-resolution cross-sections. To do so, a small number of particles were glued between two Si wafers which were first mechanically ground but a smoother surface was created by subsequently using a broad ion beam (BIB, Leica EM TIC 3X) [43].

2.7. Lab-scale fuel conversion experiments

Dedicated fuel conversion experiments were conducted to examine whether the reactivity of the oxygen carrier with fuel gases changed with ageing in the boiler. 20g of oxygen carrier sampled during the campaign was placed in a stainless-steel fluidized bed reactor with an inner diameter of 26 mm. The reactor was placed in a furnace and connected to a gas supply and gas analysis equipment measuring the concentrations of CH_4 , CO_2 , CO, H_2 , and O_2 of the exiting flue gas. Details about the equipment and the surrounding infrastructure can be found elsewhere [44,45].

The bed was alternatingly fluidized with air and fuel, to simulate the

movement of the oxygen carrier between oxidizing and reducing location in the combustion chamber. The fuel conversion function of the oxygen carrier was studied during fluidization with a fuel gas. CH₄ or syngas (50/50 CO and H₂) were used as fuel model components. The details of the gas flows and compositions are presented in Table 5. Nitrogen was used as fluidizing gas in between the air and the fuel periods, to purge the reactor and avoid mixing. During each experiment, 3–5 cycles with methane as fuel were followed by 3–5 cycles with syngas as fuel, to study the conversion of each fuel component. The fuel conversion was evaluated from the concentrations of CO₂, CO, CH₄, and H₂. A high CO₂ concentration would be related to a high fuel conversion, and a low fuel conversion would be related to high concentrations of CH₄ and CO (with methane as fuel model component). The experiments were conducted at 850 °C.

3. Results

3.1. Operability

The general operability of the bed material was good. No unexpected problems occurred during crushing, sieving, logistics, loading to the silo, feeding to the boiler or during continuous operation. Further, no visual signs of agglomeration were observed, albeit this is a qualitative assessment based on findings during particle sampling and emptying of the boiler. The material had good mechanical integrity, but some bed material was lost during operation in the form of fly ash. A more detailed discussion regarding fly ash production will be presented below.

In one instance, it was found that the CO emissions increased significantly during the night. This was between day 2 and day 3, i.e. the night with 21 % Järnsand in the bed. In the morning on day 3, the 1-min average CO concentration was around 250 mg/nm³ at 6 % O₂, which was deemed high. The CO concentrations went back to normal when some bed material was regenerated with Järnsand in the morning, and it was therefore assumed that this experience had to do with the alkali levels in the boiler. This will be discussed in more detail below. A similar, but much less pronounced, trend was observed also for the following nights with Järnsand and B28-mixtures, where the CO concentrations increased during the night and were around 50 mg/nm³ at 6 % O₂ in the mornings. No such trend was seen in the following week with 100 % Järnsand.

3.2. Operation at reduced air-to-fuel ratio

As expected, the O_2 concentrations decreased when the fuel load increased. An oxygen-carrying effect of the Järnsand was immediately noticed since its presence caused a considerable delay between increased fuel feeding and decreasing outlet O_2 concentrations. Also, longer timesteps were required for reaching a steady state. This is in line with the theory of oxygen buffering ability of the oxygen carrier, the assumption being that the change in fuel load is initially partly handled

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by solid-gas interactions rather than a decreased concentration of gaseous oxygen.

3.2.1. CO-emissions

The graphs in Fig. 3 show the CO emissions as a function of lambda during the operation at reduced lambda values. The left graph shows the results for the first week with mixtures of Järnsand and B28, while the right graph shows data for the second week with 100 % Järnsand. The reference case with 100 % B28 is included in both graphs. The lambda experiment on the last day (100 % Järnsand day 9) was done with a higher bottom bed temperature of 875 °C.

During the experiment with 80 % Järnsand in the bed, the fuel moisture changed very suddenly due to switching to a new batch of fuel, and this resulted in difficulty in achieving stable data. However, as seen from the graph, this did not significantly affect the relation between CO concentrations and lambda value. Somewhat higher CO concentrations at low lambda can be seen during day 9 compared to day 7. The CO concentrations were in general higher during day 8 and day 9, and not only during the lambda experiments. This likely has to do with the ageing of the bed material inside the boiler, which will be discussed in more detail below.

The following conclusions can be drawn.

- With Järnsand in the bed, the CO emissions were lower at any lambda value, compared to the reference case. This includes the first point at nominal operation (with lambda about 1.2). This was likely an effect of the oxygen-carrying ability of Järnsand.
- There is no significant difference between the different cases: a bed with 21 % Järnsand performed just as well as a 100 % substituted bed.
- For any amount of Järnsand in the bed, a lambda value of around 1.08 could be reached with essentially no increase in CO emissions. As a comparison, the same operation conditions with 100 % B28 gave a 5-min average CO concentration of about 800 mg/nm³ at 6 % O₂.
- With the Järnsand mixtures, lambda values of around 1.06 were possible with a maximum 5-min average CO concentration of around 100–200 mg/nm³ at 6 % O₂. A lambda value of 1.06 corresponds to a flue gas oxygen concentration of around 1.2 %, measured in the dry gas.

3.2.2. NO-emissions

Fig. 4 shows the NO emissions during the operation at reduced lambda values. The left graph shows the results for the first week with mixtures of Järnsand and B28. The right graph shows data for the second week with 100 % Järnsand, and both figures have the reference case included. The experiments with Järnsand in the bed resulted in about 30 % less NO than with 100 % B28, at any given lambda value and any amount of Järnsand in the bed. The ageing of the bed seemingly didn't

affect the NO emissions, as day 7 and day 9 gave similar results. As was discussed in the introduction, the mechanisms for NO formation and the effects of the oxygen carrier are not well understood. A decreasing NO concentration with reduced lambda value is anyway consistent with the results from previous studies [22,23].

3.3. Bed material ageing

The results in this section concern mainly boiler samples from the second week with 100 % Järnsand bed. Apart from the large material addition after around 6 h of operation, no regeneration of bed material was done during the second week. Thus, it is possible to follow the development of the Järnsand particles over time. The samples from the second week are referred to by their age in the boiler. For example, 31h (day 7) was sampled from the boiler 31h after the boiler was re-started with 100 % Järnsand, which took place during the 7th day of the campaign. The samples are listed in Table 4.

3.3.1. Morphology and composition of aged bed material

The particle size distributions of the fresh materials and boiler samples are presented in Fig. 5. For B28, shown in the left graph, the boiler sample had clearly larger particles than the fresh material. Much of the material was over 1 mm. This was expected since the B28 bed had been in operation for quite some time, with fractions >500 μ m formed through agglomeration and ash layer buildup. Some fine particles may also have been lost as fly ash through elutriation.

In contrast, during the second week with 100 % Järnsand, no buildup of larger particles was established. Loss of fine particles resulted in a general increase in particle size when reported as wt.-%, and a slight shift of particles from the 250–355 μ m to the 355–500 μ m fraction was also observed.

The particle size distribution changed during the first few hours but was then stable, as the sieving showed very similar size distributions for the 6h, 31h, and 79h samples. The change was probably mainly related to the elutriation of fines. The fly ash emissions and the material balance of bed material will be discussed in more detail in section 3.4, but in general, the elutriation of particles smaller than 180 μ m happens soon after the bed material has been added to the boiler. Other mechanisms affecting the particle size might be.

- (i) Agglomeration,
- (ii) Formation of ash layers,
- (iii) Swelling of the particles

Regarding (i) agglomeration, the particle sizes were not so large that agglomeration is suggested, since that would at least double the particle size, and far more material would be found in the $>500 \ \mu m$ fraction. Further, no agglomerates were identified in the SEM analysis, or from visual observation of the samples. However, the SEM analysis did



Fig. 3. CO concentrations in the flue gas as a function of the air-to-fuel ratio (lambda). The left graphs show the results from the first week with initially 100 % B28 in the bed and mixtures of up to around 80 % Järnsand in the bed (day 1–5). The right graph shows the reference together with the 100 % Järnsand days (day 7 and day 9).



Fig. 4. NO concentrations as a function of lambda during the oxygen staging experiments. Left: B28 reference and B28-Järnsand mixtures. Right: B28 reference and 100 % Järnsand.

Table 4

Overview of the 2 weeks of experiments in the boiler. The regeneration was done in sequence, i.e. some material was removed before adding new material, and the process was then repeated 1 or 2 times. All the regeneration was done in the morning, if not stated otherwise. * = approximate numbers.

Date dd/mm	Reference	Regeneration*	λ experiment	
	(samples analyzed)	Removal (kg)	Addition (kg)	
Mon 20/11	100 % B28, day 1	100 250	100 (morning) 280 (afternoon)	Yes
Tue 21/11	21 % Järnsand, day 2	120+190	230+100	Yes
Wed 22/11	52 % Järnsand, day 3	190+190	200+350	Yes
Thu 23/11	69 % Järnsand, day 4	100+60+60	200+200+200	Yes
Fri 24/11	80 % Järnsand, day 5	200+250	320+340	Yes
Sat 25/11	2			
Sun 26/11	Shut off, emp	tied, loaded with	100 % Järnsand	
Mon 27/11				
Tue 28/11	100 % Järnsand, day 6 (6h)	0	1700 (afternoon)	No
Wed 29/11	100 % Järnsand, day 7 (31h)	0	0	Yes
Thu 30/11	100 % Järnsand, day 8 (48h, 56h)	0	70 (morning)	No
Fri 1/12	100 % Järnsand, day 9 (79h)	0	0	Yes
Sat 2/12 Sun 3/12				

confirm the formation of ash layers (ii) – particles in the 79h sample particles had ash layers with a thickness of around 15 $\mu m.$ SEM micrographs of the fresh Järnsand and 6h and 79h samples are presented in Fig. 6.

Particle cross-sections showing the elemental distribution of K, P, Ca, and Mg in the 79h sample are presented in Fig. 7. The elemental maps show that the formed layers contained mainly Mg, P, and Ca, while K had migrated into the bulk of the particle. Most of the Ca in the layer likely originated from the fuel ash. It has also been observed in a previous, unpublished study that Ca inherent to Järnsand migrates towards the particle surface during thermal treatment. The presence of P and Mg

Table 5

Gas flows used in the fluidized bed reactor experin	nents.
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Period	Gas flow (NmL/min)	Gas composition	Time
Heating	620 NmL/min 780 NmL/min	Air N ₂	
Inert	1260 NmL/min	N ₂	180 s
Start of exper Reduction	imental cycles 700 NmLmin 700 NmL/min	CH4 or syngas N2	40 s
Inert	1260 NmL/min	N ₂	180 s
Oxidation	620 NmL/min 780	Air N ₂	Until fully oxidized ^a
Inert	1260 NmL/min	N ₂	180 s (approx.)

^a The oxygen carrier was assumed to be fully oxidized when the measured concentration of O_2 was the same as the inlet (9.3 %).

in the layer nevertheless suggests that the layer had mainly formed through ash deposition on the particle surface. It can be assumed that the formation of ash layers is a slow, continuous process (compare the 6h and 79h samples in Fig. 6), but the registered change in size distribution was sudden. Therefore, the ash layer development is not assumed to contribute strongly to the altered measured particle size distribution.

There are no clear signs of swelling of the particles (iii), as this would be related to a decrease in density, and likely morphological changes such as visible cracks in the material and increased porosity. The BET surface area and density are presented in Table 6. While the BET surface area did increase from 0.068 m²/g in the fresh material to 0.149 m²/g (79h, day 9), note that both numbers reflect very low BET surface areas. Essentially, neither fresh nor used particles were rough or highly porous.

The bulk density increased slightly, and much of the increase happened already during the first 6 h. The bulk density for the fresh material was 1.66 g/cm^3 and the increase, in %, is indicated in the table. The increase was considered modest and could possibly be attributed to reduced roughness, causing the material to pack more densely. The SEM image in Fig. 6 shows that the fresh material had a layer of Fe-oxide on its surface that is not visible in the 79h sample and is partly removed in the 6h sample. It's possible that the removal of this outer layer, from mechanical stress and attrition in the boiler, contributed to the densification of the material. In general, the bulk density measurements suggest that the particles were relatively durable and mechanically stable.

The elemental composition of bed samples is presented in Fig. 8. As expected, the Fe and Cu concentrations increased while the Si decreased during the first week, as the silica sand was gradually replaced by Järnsand. The concentrations of the ash species K and P decreased slightly during this period, which can be expected since the bed regeneration rate was high for the purpose of increasing the Järnsand content



Fig. 5. Particle size distributions of fresh and used bed material. Left: 100 % B28 (reference). Right: 100 % Järnsand.



Fig. 6. SEM micrographs. The upper row shows the top-view (surfaces), and the lower row shows cross-section of some particles. The fresh material and the 6h sample cross-sections were prepared by grinding. The 79h sample cross-section was prepared by BIB to study the ash layers in more detail.



Fig. 7. SEM-EDS intensity maps on the cross-section of particles from the 79h (day 9) sample. The elemental distributions of K, P, Ca, and Mg are presented.

in the bed. Ca and Mg remained constant or increased slightly, as they originated from both the fuel ash and the fresh bed material.

During the second week with 100 % Järnsand and no regeneration, the Fe and Si concentrations decreased slightly over time, as the bed was

enriched in Ca, K, and small amounts of P originating from the fuel. The Fe/Si ratio was quite constant, and this ratio was used as the basis for calculating the Järnsand concentrations in the bed during the first week. The 6h (day 6) sample composition agreed well with the composition of

Table 6

BET surface area and bulk density of bed material samples taken after 6, 31, 48, 56, and 79 h of operation.

Sample extraction time	BET surface area (m ² /g)	Bulk density (g/cm ³)
(Fresh, sampled from silo)	0.068	1.66
6h (day 6)	0.108	1.74 (+5 %)
31h (day 7)	0.094	1.79 (+8 %)
48h (day 8)	0.107	
56h (day 8)	0.113	1.82 (+10 %)
79h (day 9)	0.149	1.82 (+10 %)

the fresh Järnsand, i.e. the composition didn't change much during the first few hours of operation.

As seen from the elemental distribution of K in Fig. 7, K was absorbed into the particles, rather than forming a layer. The elemental composition of the sample showed that the K concentration increased linearly with time, and it is not suggested that the material would have become saturated during four days of exposure in the boiler. The elemental distribution shows a less saturated core compared to the outer areas of the particle, further suggesting that the particles were not saturated throughout.

3.3.2. Reactivity with gaseous fuels

The reactivity with methane and syngas was explored for the 2h, 6h, and 79h boiler samples in the lab-scale fluidized bed reactor. The outlet concentrations of CO_2 , CO, and CH_4 during fluidization with methane are presented in Fig. 9. Each sample is represented by one color in the graph. As seen in the graphs, the CO_2 concentrations (solid line) were slightly higher with the 79h and 6h samples, as compared to the 2h sample. The CH_4 concentrations (dashed line) were similar in all three experiments, but the CO concentrations (dotted line) differed slightly, showing a less complete fuel conversion for the 2h and 6h samples.

Fig. 10presents the CO₂, CO, and H₂ concentrations measured during the conversion of syngas. Little variation is seen between the 2h and 6h samples. As with methane, the aged sample converts the fuel to a larger extent, resulting in higher concentrations of CO₂ and lower concentrations of CO and H₂. The ageing effect was more pronounced with syngas than with methane. Some fresh materials, like ilmenite, require several oxidation and reduction cycles before the reactivity stabilizes, a process often referred to as activation [44,46], so these results are expected. Most importantly, this concludes that Järnsand has a fuel conversion ability, i.e. oxygen carrying properties. Further, there are no signs of the material becoming deactivated during the time in the boiler, even though some ash layer formation was observed (see Fig. 6).

3.4. Bed material balance and fly ash production

Fly ash contains fuel ash particles and fine bed material particles that follow the flue gas to the cyclone. Fine bed material particles can be either present already in the fresh material, or form from fragmentation or attrition in the boiler. Making a detailed mass balance over the boiler is not straightforward, but some general trends and conclusions can be



Fig. 9. The CO_2 , CO, and CH_4 concentrations recorded during the reduction of the oxygen carrier with methane as the fuel model component. Note that the CH_4 concentrations are presented on the right y-axis.



Fig. 10. The CO_2 , CO, and H_2 concentrations recorded during reduction of the oxygen carrier with syngas as fuel model component.



Fig. 8. Total elemental composition of samples from the bed with 100 % Järnsand (day 6–9), results are in wt.-% and balance is mainly oxygen. Note the different y-axis for Cu, Mg, P.



Fig. 11. Fly ash accumulation (kg) and fly ash accumulation rate (kg/h) throughout the experiment.

observed.

The accumulated weight of fly ash collected during week 1 and week 2 is presented in Fig. 11. The accumulation rate is also expressed in kg/h. The days are indicated, defined as starting at 6:00 a.m. The soot blowing each morning is visible as a sudden increase in the accumulated ash. During the first week, bottom ash removal and addition of fresh bed material was done immediately after the soot blowing. Addition of new material was related to the elutriation of fines, and the peaks in accumulation rate are proportional to the amount of regenerated bed material, which was the lowest on the first day. This is in line with the observation from above, that fresh material below 180 μ m has a short residence time in the boiler.

During the second week, fines were emitted at the startup of the boiler (hour 0) and at around hour 8, when more material was added. These events are clearly visible in the graph. The accumulation rate levelled out after that but was continuously high throughout the following 2 days. Apart from the elutriation of fines, some initial attrition of fresh particles could be expected, since the fresh particles have rough edges and non-spherical shapes (compare the fresh and aged particles in Fig. 8). Another effect could be that there is mechanical stress inside the particles causing them to break upon heating, which has been discussed for ilmenite in Ref. [47]. The fresh material is amorphous and crystal phases of Fe and Si-oxides appeared upon heating [41]. This phase transition, along with the continuous oxidation and reduction of the iron oxide, might induce some fragmentation.

Between hours 35 and 50, the fuel load was around 16-20 % higher than nominal due to a higher heating demand. The fly ash accumulation rate, however, increased by around 70 % (from 7 to 12 kg/h). Thus, increasing the load not only increased the fuel ash accordingly but also the elutriation of bed particles. This was likely an effect of reduced cyclone efficiency at increased flue gas flow rates. The gas velocity increased from around 2.7 to 3.1 m/s. The fly ash production during days 8 and 9 was again quite low.

A final qualitative verdict would be that the Chalmers research boiler has previously been operated with a range of bed materials, of which some have had poor mechanical properties. Based on this experience, together with the observations presented above regarding fly ash production and bed material analysis, Järnsand is not expected to be subject to problematically high attrition or fragmentation.

4. Discussion

When reducing the air-to-fuel ratio in the boiler, local oxygen deficiencies are expected to become more severe. With B28, CO emissions increased significantly at lambda values of around 1.1–1.12. In the experiments with Järnsand, on the other hand, reducing the lambda value to around 1.06, corresponding to 1.2 % O₂ in the dry flue gas, was possible without excessive increase in CO concentrations. The results suggest that Järnsand was involved in and facilitated the fuel conversion, most likely by making oxygen more available throughout the boiler and acting as an oxygen buffer. The interaction between Järnsand and fuel was further demonstrated in the lab-scale fluidized bed reactor with methane and syngas as fuel model components. The findings regarding

the enhanced fuel conversion at low lambda values is in line with previous studies showing the positive effects of changing from inert bed material to ilmenite.

It should be noted that CO emissions depend on many factors and can differ significantly over the season, depending on the cleanliness of the boiler and the fuel composition. Apart from oxygen availability, fuel conversion is also known to be affected by the concentration of volatile alkali [28–30]. The interference of alkali complicates the evaluation of the results. Especially during the first week, since not only was an oxygen carrier introduced, but the bed exchange was also high, meaning that accumulated ash was removed faster than new ash was supplied to the bed. Indeed, the K concentration in the bed decreased throughout the first week, from 7 down to around 4 wt.-% due to the high bed replacement. However, the lambda experiments during day 2, with 21 % Järnsand, showed significantly decreased CO concentrations compared to the reference case, even though the K concentrations were still high. Typically, extraction and replacement of bottom ash is done continuously in this boiler, to avoid the accumulation of ash species in the bed. However, bed material was only regenerated once per day during the experimental campaign. Accumulated alkali was likely the reason for the increased CO concentrations observed on the night between day 2 and day 3. The problem was relieved when some bed material was regenerated the following morning. During the second week, almost no material was regenerated during the last 3.5 days of operation. The K concentration in the bed samples of around 3.5 wt.-% was reached, and no trend towards increasing CO emissions was seen. Based on experience, it is believed that operating the boiler with B28 during this long time period without regeneration would likely have resulted in elevated CO emissions and possibly other problems. Typically, 300 kg of bed material is regenerated daily during normal operation.

The fate of K in the boiler can be discussed with a simple material balance.

- The fresh Järnsand sample contained around 0.5 wt.-% K, as seen in Table 2.
- According to a wood chips sample analysis, the ash content in the fuel is expected to on average be 0.5 wt.-%, and the K-concentration in the ash was 10 wt.-%.
- Assuming a fuel feeding rate of 2000 kg/h, 1 kg of K is added to the bed every hour.
- During an operation time of 79h, a total of 79 kg K is added to the bed.
- Assuming a bed inventory of 3000 kg, 79 kg corresponds to about 3 wt.-%.
- The total elemental analysis of the last bed sample showed a Kconcentration of 3.4 wt.- %. The analysis of samples taken throughout the week showed a linear increase in K concentration with time.

These are simplified calculations, not considering the K in the fly ash. Keeping in mind also that the elemental analysis was performed on a small sample size, the results anyway indicate that the K added with the fuel was mainly captured by the bed. In contrast, LD-slag particles

contained only about 1.4 wt.-% K after 65 h in the same boiler with similar operating conditions, and LD-slag has been shown to have a relatively poor ability to capture K [34,48]. What is further interesting is that there are no signs of agglomeration, even though Järnsand contains Si, which in the form of quartz in silica sand readily reacts with K to form low-melting K-silicate. Faust et al. [33] studied ash interactions with different Si-containing materials and concluded that the K interactions depended on the Si-structure in the material. Indeed, the presence of Fe and the other components of Järnsand might contribute to the material being more agglomeration resistant than Si-sand, but further studies are required. Longer experiments with complementary gas phase alkali measurements and more extensive material analysis could provide a better understanding of the absorption of K in Järnsand. As a comparison, an ilmenite bed has been operated for over 300h without bed regeneration, but with magnetic separation of ash [39]. No problems with increased CO emissions or agglomeration were observed during that study.

Regarding the durability of the material in the boiler, nothing in these findings suggests that the material should have a short lifetime. The conclusions regarding the material balance and mechanical lifetime would be more accurate if the fresh material contained less fine material initially (there were about 5 wt.-% fines smaller than 0.09 mm in the delivered material). Järnsand anyway seems to have suitable mechanical properties, absorbed alkali during the whole campaign, doesn't seem to agglomerate and doesn't lose its fuel conversion reactivity over time. The reactivity with methane and syngas observed in the lab-scale experiments actually increased somewhat with time in the boiler, which is in line with previous studies concluding that fresh oxygen carriers undergo activation [12,39]. The activation can be due to a combination of migration of Fe to the surface, and that the inclusion of ash compounds contributes to a catalytic effect on the fuel conversion [39]. Determining a detailed ash layer formation mechanism and discussing its catalytic effects are outside of the scope of this study.

It should not be overlooked that the bed material itself could have a catalytic effect on the conversion of the fuel. This has been demonstrated before. For instance, olivine has a catalytic effect on biomass gasification, attributed its content of Fe, Ca, and K [49,50]. However, in the present lab-scale experiments, fuel conversion and re-oxidation of the oxygen carrier was demonstrated in separated time intervals, simulating a chemical-looping process. It is therefore not possible that the fuel conversion observed in the lab-scale studies is attributed solely to a catalytic effect. The confirmed oxygen-carrying property of Järnsand indicates that the enhanced combustion observed in the campaign is in fact mainly due to enhanced oxygen distribution in the combustion chamber. Furthermore, an oxygen buffering effect in time was observed during the lambda experiment in the boiler campaign - with Järnsand in the bed, there was a considerable delay between increasing the fuel feeding and observing a drop in gaseous oxygen concentrations in the flue gas. This delay was small in the reference case and increased with the amount of oxygen carrier in the bed.

During the experiment, the NO emissions decreased by about 30 % for any given lambda value with Järnsand compared to the reference case. A similar effect was observed during the first OCAC campaign with ilmenite in the Chalmers boiler [12], where the NO concentration decreased with ilmenite compared to the reference silica sand operation. However, lowered NO emissions have not been reported in any subsequent large-scale experiments with ilmenite, or with any other oxygen carrier, as far as the authors are aware. In fact, a slight increase in NO emissions, as compared to reference silica sand operation, has been observed with LD-slag [22] and Mn-ore [23] oxygen carriers, and it was suggested that it was because the oxygen carrier increased the availability of oxygen required for NO formation. In conclusion, it's currently unknown how Järnsand contributed to reducing the NO emissions in the campaign, or if the observed effect is replicable in other settings. It is anyway evident that reducing the lambda value is positive with regards to NO emissions, which agrees with previous research findings [12,22,

23].

During normal combustion with B28 as bed material, the bottom ash is typically returned to the forest to prevent exhaustion of minerals in forest soil. According to the product safety information on Järnsand, the potentially toxic metals (mainly Cu and Zn) are stable in the material in the form of glass- or crystalline silicate compounds and can leach only to a low extent at a low pH. The waste from Järnsand can therefore be treated as inert material. However, the operation in the boiler might affect the leachability of certain elements as the material is subject to changes in the crystal structure. In this study, as a precaution, the bottom ash containing Järnsand was therefore instead taken care of by Hällesåker Slamsugning AB, who presumably treated it as ash from waste incineration. The cost for bottom ash disposal was somewhat higher than for B28 bottom ash, but not unreasonable for this instance. If the concept is to be upscaled, ash recycling, ash utilization and the environmental properties of ash need to be studied in detail. In the case that bottom ash containing Järnsand must be classified as hazardous waste, it would be recommended to consider the application of for example incineration of municipal solid waste, as the classification of the bottom ash will be determined by the contribution of the fuel minerals rather than the bed material itself. No other safety issues are reported for Järnsand when used for example as abrasive media or construction aggregate. When introducing a new bed material, changes in mechanical properties must be considered as density, shape, and hardness of the particles affect the erosion on the boiler walls [51]. The bulk density of Järnsand is 1.66 g/cm³, which is only slightly higher than for B28 (1.5 g/cm^3). While a detailed evaluation of the erosion is not suitable with in the current study, further research is recommended to investigate this aspect, as increased wear of boiler equipment induce increased costs for the boiler operator.

Since ilmenite has been used a lot for OCAC and there is a lot of previous experience, it could be seen as the benchmark oxygen carrier for this application. The first experiment with ilmenite in the Chalmers boiler [12] showed that lambda value could be decreased to around 1.04 before reaching too high CO concentrations. From the current study, it seems like Järnsand performed much like ilmenite when it comes to CO emissions, while being a secondary resource rather than a primary resource.

5. Conclusions

A commercial, granulated copper smelter slag (also referred to as copper slag) product was used as bed material in a semi-industrial scale circulating fluidized bed boiler with wood chips as fuel. The general operability and the oxygen carrying potential of the material was evaluated through a two weeklong campaign, that was followed-up with dedicated experimental activities and material analysis.

The following conclusions can be drawn from this study.

- Järnsand had a positive effect in fuel conversion. This was demonstrated by CO measurements and successful operation at reduced airto-fuel ratios. A lambda-value of 1.08 was reached without noticing any increase in CO-emissions. Corresponding conditions with the reference material silica sand resulted in severely increased COemissions.
- The substitution of only 20 % of the bed resulted in similar results as substituting 80 or even 100 % of the bed with Järnsand.
- A 100 % Järnsand bed was in operation for around 80 h, out of which around 70 h was without any replenishment of bed material.
- An uptake of K was concluded, based on bed material samples. A saturation of K was assumed not to have been reached and no agglomeration was observed.
- Reactivity with the fuel model components methane and syngas increased slightly over time in the boiler.
- The utilization of Järnsand as bed material is promising and could be advantageous over common silica sand. It could perform similar to

the well-studied oxygen carrier ilmenite and should therefore be examined further.

CRediT authorship contribution statement

Felicia Störner: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis. Robin Faust: Writing – review & editing, Writing – original draft, Visualization, Investigation. Pavleta Knutsson: Writing – review & editing, Supervision. Magnus Rydén: Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization.

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Data availability

Data will be made available on request.

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