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Review

Oxygen Carrier Aided Combustion in Fluidized Bed Boilers in Sweden—Review and Future Outlook with Respect to Affordable Bed Materials

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Abstract: Oxygen carriers are metal oxide particles that could potentially enhance both fuel conversion and heat distribution in fluidized bed combustion, resulting in e.g., lowered emissions of unconverted species and better possibilities to utilize low-grade fuels. A related technology based on fluidized beds with oxygen carriers can separate CO_2 without large energy penalties. These technologies are called oxygen carrier aided combustion (OCAC) and chemical-looping combustion (CLC), respectively. In the past few years, a large number of oxygen carriers have been suggested and evaluated for these purposes, many of which require complex production processes making them costly. Affordable metal oxide particles are, however, produced in large quantities as products and by-products in the metallurgical industries. Some of these materials have properties making them potentially suitable to use as oxygen carriers. Uniquely for Sweden, the use of oxygen carriers in combustion have been subject to commercialization. This paper reviews results from utilizing low-cost materials emerging from metallurgical industries for conversion of biomass and waste in semi-commercial and commercial fluidized bed boilers in Sweden. The paper further goes on to discuss practical aspect of utilizing oxygen carriers, such as production and transport within the unique conditions in Sweden, where biomass and waste combustion as well as metallurgical industries are of large scale. This study concludes that utilizing metal oxides in this way could be technically feasible and beneficial to both the boiler owners and the metallurgical industries.

Keywords: oxygen carrier aided combustion; chemical-looping combustion; oxygen carriers; fluidized bed combustion; slag utilization; Waste-to-Energy (WtE)

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1. Introduction

1.1. Fluidized Bed Combustion in Sweden

Biomass is an important source of energy and materials in the Nordic countries, especially in Sweden and Finland. The forestry industry, including the pulping industry, is of major importance in these countries. This has contributed to many decades of experience using biomass as fuel. When utilized in a sustainable manner, biomass can be considered a renewable energy source, making it a viable alternative to fossil fuels. According to Energiläget, the national energy status report published annually by the Swedish Energy Agency (Energimyndigheten), 105 TWh of the primary energy generated in Sweden 2018 was from wood fuels, most of which is produced in Sweden [1]. This corresponds to 19% of the total primary energy input to Sweden's energy system. Another large energy source in the Nordic countries is waste (Waste-to-Energy; WtE), which allows for simultaneous energy production and waste management. Waste is a broad term that includes both municipal solid waste (MSW) as well as other streams like recycled waste wood, and industrial wastes. Thus, it covers fuel fractions with very different chemical compositions, moisture, heating value, ash, etc., and can consist of both renewable and non-renewable materials. Also, when it comes to biomass fuels, the composition and fuel quality differ with biomass type.

During combustion, both wood fuels and waste fuels present considerable challenges related to ash chemistry in the boiler. Ash in woody biomasses contains mainly K, Ca, and Si. Forest residues have a higher ash content with similar elemental composition [2]. Ashes in fast-growing biomass like energy crops and agricultural wastes generally have a higher content of P, K, and Cl. K and Cl contribute the most to slagging, fouling, and severe corrosion during combustion, especially at high temperatures [2,3]. The discussion about waste ash composition becomes more complicated due to its large variations, but the same type of challenges can be expected [4].

To summarize, high ash reactivity, high moisture content, and potentially large feed composition variations are all challenging properties of waste and biomass fuels. Consequently, large-scale combustion of such fuels calls for specific boiler requirements. Fluidized bed combustion (FBC) is widely used in Sweden (and some other countries such as Finland) since it has several advantages that make it suitable specifically for this purpose. Some 120 industrial facilities in Sweden are currently using FBC, out of which 1/3 are circulating fluidized-bed boilers (CFB). The remaining 2/3 are bubbling fluidized bed boilers (BFB). Compared to other boiler types, like grate fired boilers and rotary kilns, FBC has the following advantages [4–7]

- High thermal inertia, i.e., good at handling sudden variations in fuel feed composition and heating value
- The bed material can adsorb volatile alkali components, which reduces the risk of high-temperature corrosion of heat transferring equipment.
- Relatively low temperature levels; possibly low NOx formation
- Co-combustion of different fuels is possible

Historically, FBC has also had the advantage over grate-fired boilers of also being efficient at relatively low air-to-fuel ratios. However, nowadays, the difference between FBC and modern grate-fired boilers is low due to sophisticated air feeding systems [4]. The main disadvantage with FBC is that fuel processing is sometimes required. Fuel processing might include crushing, milling, sorting out incombustible components, etc., and can amount to large costs and maintenance work. In the following sections, "bed material" is defined as actively added minerals such as silica sand, while "bed" includes also fuel minerals and fuel.

FBC was originally developed for coal combustion and has later been adapted for other fuels. Compared to biomass, coal contains more ash. Further, coal ash has typically larger concentrations of S, Al, and Fe, and lower concentrations of Si, K, and Cl [3]. The bed in coal FBC to a large extent consists of the coal ash and the coal itself. This, however, is not feasible for biomass- and WtE-FBC, where ash interactions with the bed material and the boiler walls play an important role. The ash content in these fuels might also be too low, or form particles of sizes not suitable for fluidization. Beyond causing corrosion and fouling, ash reactions also increase the risk of bed agglomeration. Agglomeration has been studied experimentally both on lab scale [8–10] and on industrial scale [6,11–13] to gain an understanding of the formation mechanisms and possible remedies. Agglomeration is mainly caused by the formation of K-components which melt and become sticky already at relatively low temperatures. The sticky components originate from the fuel or forms by interactions between the ash and the bed material. Thus, agglomeration is a function of bed material properties, ash composition, temperature, etc. Agglomeration negatively affects the bed by interfering with the fluidization, but alkali absorption in the bed can also reduce alkali-induced problems downstream of the boiler. This can be enhanced by adding alkali-capturing components to the bed. Certain minerals have shown to be resistant towards agglomeration, and this is used in a few plants by using Al-, Ca- or Mg-rich additives, like kaolin [3,5]. Another way to inhibit the harmful K-interactions is to add sulfur to the bed, which forms the stable compound K_2SO_4. This was done historically through co-combustion with coal or peat, but these fossil fuels are barely used any more in Sweden. Nowadays, elemental sulfur is sometimes used as additive.

However, the main measure taken to prevent defluidization is to have a high rate of replacement of the bed itself. Silica sand is the commonly used bed material in FBC. Silica sand (or quartz sand) is extracted at three locations in Sweden. It is a primary product that risks becoming scarce in the future. Silica sand and gravel deposits are furthermore important for ground-water production by removing impurities from the water through filtration. Therefore, protecting natural deposits of gravel is a subgoal of the Good-quality groundwater objective, which is one of Sweden's environmental objectives [14,15]. An evaluation in 2019 by the Geological Survey of Sweden found that the subgoal is not fulfilled and that approximately 10 Mton of natural gravel was still being extracted in the year 2016 [16,17]. The trend is that natural gravel is being replaced by crushed rock in many applications such as construction material, but this is: (a) not always technically feasible, which is the case with bed material sand in FBC and (b) risks shifting the problem over to exploiting another non-renewable resource (rock). The production of quartz sand in Sweden was between 579 and 783 kton during the years between 2008 and 2018 [18].

To put FBC in perspective, the silica sand consumption in FBC can be illustrated by some examples [19]: The bed material consumption in three wood-fired BFB plants with 30, 50 and 80 MW_{th} output was 0.4, 2–5, and 15–20 metric tons per day, respectively. This shows that the regeneration rate of bed material is not only high but also differs a lot between plants of similar type. The main reason for replacing bed material was stated to be to reduce the risk for bed agglomeration. Sand consumption and other practical aspects of agglomeration prevention in FBC will be discussed in greater detail in Section 3.2. One more negative aspect of using silica sand as bed material needs to be highlighted, which is that long-time exposure to silica sand can cause silicosis in workers, a lung disease that can lead to cancer [20].

Apart from the negative environmental effects of sand extraction, high sand consumption in the boiler is also a significant monetary cost. This cost can be divided into two parts: the cost of new bed material, and the cost of disposing of the replaced bed. Spent bed material ends up in both bottom- and fly ash. Bottom ash is mainly disposed of in landfills, but since landfilling is restricted in Sweden, different ways of utilization is currently being discussed. Bottom ash is used for minor construction purposes, mainly as construction material in the final covering of landfills [21,22]. A small amount is used in forestry to mitigate acidification. This way of handling bottom ashes is not sustainable; the number of landfills in Sweden in need of covering is declining. The bottom ash also contains nutrients from the fuel (like K and P), which should ideally be returned to the biosphere. Fly ash is typically classified as hazardous waste and is approximately 10 times more expensive to dispose of than bottom ash.

To summarize, FBC has many advantages when it comes to WtE and biomass combustion, but the current use of bed material is non-sustainable both when it comes to extraction and end-of-life handling. Silica sand is also subject to agglomeration and other technical issues that will be discussed in more detail below.

1.2. Oxygen Carriers as Bed Material in FBC

Due to rapidly increasing CO_2-concentration in the atmosphere, it has been suggested by the IPCC that carbon capture and storage (CCS), or some other form of carbon dioxide removal will be necessary to meet current climate targets [23]. CCS in combination with biomass combustion (Bio-Energy CCS; BECCS) could allow for net-negative emissions. Chemical-looping combustion (CLC) is an emerging combustion technology that could be very useful for CO_2 capture, since it has the advantage of inherent CO_2 separation [24]. In CLC, two interconnected reactors are used, one to which the air is supplied and one in which the fuel is converted. Instead of mixing the fuel and air, the conversion of fuel is made possible by providing oxygen via a solid oxygen carrier that circulates between the two reactors, as illustrated in Figures 1 and 2.

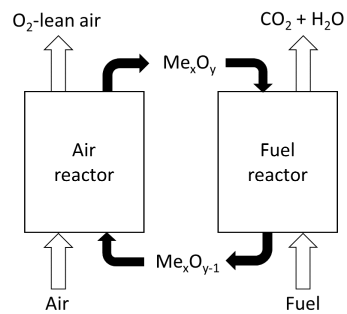


Figure 1. Schematic description of CLC.

Oxygen carriers are solid materials capable of providing oxygen for fuel conversion and becoming regenerated by oxidation under conditions typical for combustion. A set of desirable properties of the oxygen carrier have been established. Oxygen carriers should:

- Have sufficiently high reactivity with oxygen and fuel at relevant conditions
- Have sufficiently high oxygen transport capacity to be viable
- Be environmentally sustainable
- Be economically feasible
- Have sufficiently good mechanical properties to allow for use in fluidized beds

Failure to meet the minimum demands means that the material is unsuitable for large-scale application. There is, however, no fixed definition of the above properties, but rather they will vary for different applications. Oxides of Fe, Cu, Ni, and Mn, among other less studied materials, have been evaluated and a large number of oxygen carriers have been proposed for different applications [25,26]. Experimental evaluations of oxygen carriers specifically for solid fuel CLC has been reviewed by several researchers: [27–30]. Much of the early CLC research focuses on synthetic oxygen carriers. While synthetic materials potentially are well-performing and stable in sustained operation with clean fuels such as natural gas, they have yet to be proven to maintain their properties in the harsh chemical environment that is the reality for fuels with reactive ashes. In light of current knowledge about FBC, long oxygen carrier lifetime seems difficult to realize for such fuels. Thus, the high cost of synthetic materials makes them unlikely for applications where high regeneration rates are expected. For this reason, the interest in using mineral ores and similar affordable materials as oxygen carriers has increased lately [28,30].

CLC has yet to be developed into a practically viable technology. Instead, this study focuses on the use of oxygen carriers in the context of a related, and more readily available spinoff technology: Oxygen carrier aided combustion (OCAC). OCAC is a technology in which oxygen carrier particles are used as bed material in FBC. The oxygen carrier is used instead of, or in combination with, conventional bed material. Utilizing oxygen carriers in FBC changes the reaction paths in the bed which can provide many advantages. Increased efficiency and reduced emissions of CO and NO have been demonstrated. A discussion of the technology and practical aspects will be presented below. OCAC can be implemented in existing boilers with more or less no adaptation of the equipment, which was concluded in [31]. Further motivation for developing OCAC is that, even though it doesn't have the advantage of inherent CO_2-separation that CLC possesses, it could become a bridging technology between current conventional, large-scale biomass combustion and future facilities for CO_2-capture. Essentially, commercial deployment of OCAC contributes to creating experience with and acceptance for using oxygen carriers in combustion applications. The development from FBC to OCAC and finally to CLC is illustrated schematically in Figure 2. The figure shows that the development from FBC to OCAC requires few changes and results in better oxygen availability throughout the boiler and takes advantage of oxygen carrier—fuel interactions. Further development to CLC requires more significant changes in the equipment and relies solely on oxygen carrier—fuel interactions.

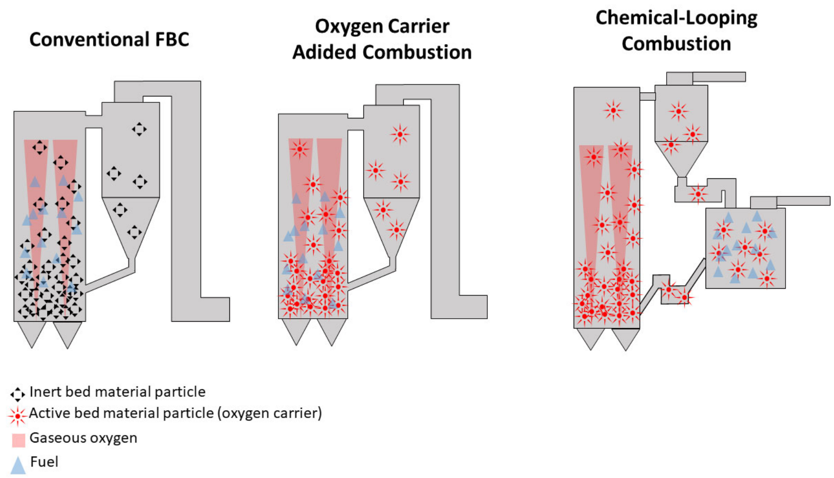


Figure 2. Schematic representation highlighting the main differences between conventional FBC (**left**), OCAC (**middle**) and CLC (**right**).

Even though applying OCAC can lead to immediate improvements in plant performance, it has yet to become a widespread technology. To date, OCAC is only used commercially in a few boilers in Sweden. One reason is that the oxygen carriers currently available are more expensive than conventional bed material. However, Sweden and also neighboring countries Finland and Norway have large metallurgical industries that handle huge amounts of ores and industrial by-products, many of which contain metal oxides (mainly iron oxide), potentially making them feasible as oxygen carriers [32]. Some of these products are inherently produced as particles and have properties that make them suitable to use more or less directly as bed materials. Cost aspects of oxygen carriers will be thoroughly discussed in Section 4.1, where it's made clear that there are significant costs associated with bed material preparation.

Concluding this introductory section: utilizing oxygen carriers in biomass combustion has been proven to reduce practical operational problems in the boiler and increase efficiency. It has also been shown that the concept can be implemented with no or little adaptation of the available equipment. However, costs and other practical issues to some extent hinder large-scale implementation.

1.3. Aim of This Study

The hypothesis behind this work is that the recent deployment of OCAC in Sweden provides unique insights into the practical application of oxygen carriers in biomass combustion technologies, which could serve as guidance for future developments. The specific aims of this study are to

- Provide an overview of recent use of oxygen carriers as bed material in industrial-scale facilities in Sweden, many of which have not previously been reported in the scientific literature. This includes commercial operation of OCAC and research performed at a semi-commercial scale e.g., in Chalmers University's Research Boiler/Gasifier.
- Briefly present what main conclusions can be drawn from this body of work concerning factors such as material handling, procurement, and logistics. These conclusions are of high relevance for biomass combustion in general, but also for the development

of future technologies such as CLC. Especially since hands-down experience of large-scale handling and logistics is difficult to provide in lab environment.
- Present an overview of current material flows for fluidized-bed boilers in Sweden and compare the demand for bed material with existing flows of potential oxygen carriers. This includes reviewing flows of intermediate products, by-products, and waste products generated in metallurgical industries in Sweden and neighboring countries. The goal is to provide input about what would be a realistic material choice for affordable and sustainable large-scale application of CLC and OCAC.

Ultimately, the overreaching goal is to provide guidance concerning the choice of bed material for future development of technologies such as OCAC and CLC.

1.4. Methods

The methods of this study can be divided into two parts. One part is to present and discuss the existing practical experience of obtaining and using large quantities of oxygen carriers for OCAC, including necessary preparation, transportation, and operation. This is presented in Section 2 mainly as first-hand anecdotal explanations and will be further discussed later in the article. The second part is to investigate the existing flows of potential oxygen carriers in major Swedish industries, in the form of raw material, products, and by-products. The aim is to identify available and more or less "ready-to-use" material flows. The availability of oxygen carriers is compared to the total amount of conventional bed material currently used, which also has been estimated in this study. This is done by reviewing reports from and personal communication with producing companies. This is presented in Section 3.

2. Oxygen Carrier-Aided Combustion (OCAC)

One of the main challenges in combustion is to ensure effective mixing of the fuel and the air, to avoid release of unconverted species. This is also the case for FBC, where uneven and incomplete combustion results in increased emissions, the need for high air-to-fuel ratio and temperature variations across the boiler. Fundamentally, what happens in the boiler when an oxygen carrier is introduced is that new types of reactions are allowed to take place—reactions between the fuel and the oxygen atoms available in the solid oxygen carrier, as well as between gaseous oxygen and reduced sites on the oxygen carrier. A laboratory-scale experimental study demonstrated that the conversion of methane to a larger extent takes place inside the bed when an oxygen carrier is used, compared to with inert silica sand. This shows that the heterogenous solid-gas reaction is significant [33]. The oxygen carrier is also acting as an oxygen buffer, meaning that the boiler could be better at handling a sudden increase in fuel feed. This is often relevant for WtE, due to the large variations in waste composition. The buffering ability also applies to spacious variations in oxygen availability, potentially reducing both hot and cold spots in the boiler. Figure 2 illustrates the difference in oxygen availability between conventional FBC and OCAC.

2.1. Review

OCAC has been examined in large-scale experiments and operated in commercial settings in Sweden for the past few years. The concept was first demonstrated in 2012 in Chalmers University's 12 MW_{th} CFB-type research boiler with the oxygen carrier ilmenite [34]. The concept has since been commercialized by the Swedish company Improbed AB, which is a subsidiary of the utility company E.ON. Table 1 shows an overview of activities performed in Sweden with oxygen carriers in industrial facilities. The methodology and results are described in detail in the respective reference, and a review of the findings are presented here.

Table 1. Overview of experimental campaigns referred to in this paper.

Oxygen Carrier	Facility	Description	References
Rock Ilmenite	Chalmers (12 MW_{th} CFB)	OCAC proof of concept study with wood chips as fuel and up to 40 wt.-% ilmenite in a bed otherwise consisting of silica sand.	[34,35]
Rock Ilmenite	Chalmers (12 MW_{th} CFB)	OCAC various research activities with wood chips fuel.	[36–42]
Australian sand ilmenite	Chalmers (12 MW_{th} CFB)	OCAC various research activities with wood chips fuel.	[40]
Rock Ilmenite	Chalmers (4 MW_{th} gasifier)	CLC/CLG large-scale proof of concept with wood pellets as fuel.	[43]
Rock Ilmenite	Händelö P14 (75 MW_{th} CFB)	OCAC of MSW in commercial boiler	[44,45]
Rock Ilmenite	Händelö P15 (85 MW_{th} CFB)	OCAC of MSW, test campaign of 3 weeks in commercial boiler	[45]
Rock Ilmenite	Örtofta (115 MW_{th} CFB)	OCAC of waste-derived wood and wood chips in a commercial boiler.	[31,42]
Rock Ilmenite	Eskilstuna (50 MW_{th} CFB)	OCAC of biomass in commercial boiler	NA
Rock Ilmenite	ÖrebroP5 (170 MW_{th} CFB)	OCAC of biomass in commercial boiler	NA
Rock Ilmenite	Sollefteå (19 MW_{th} BFB)	OCAC of biomass in commercial boiler	NA
Rock Ilmenite	Borås (20 MW_{th} BFB)	OCAC of MSW in commercial boiler	NA
LD-slag	Chalmers (12 MW_{th} CFB)	OCAC proof of concept with LD-slag. The campaign included operation with only LD-slag and different mixtures of LD-slag and silica sand.	[46–48]
LD-slag	Chalmers (4 MW_{th} gasifier)	CLC/CLG large-scale proof of concept with LD-slag.	[49]
LD-slag	Sävenäs HP2 (95 MW_{th} BFB)	OCAC BFB boiler and about 7 wt.-% LD-slag in the bed. A larger substitution was hindered due to problems related to pneumatic transport of the LD-slag.	NA
Sibelco Mn-ore	Chalmers (12 MW_{th} CFB)	OCAC proof of concept with a manganese ore and wood chips. The campaign included operation with only manganese ore as well as mixtures of manganese ore and sand.	[50,51]
Sibelco Mn-ore	Chalmers (4 MW_{th} gasifier)	CLC/CLG large-scale proof of concept with a manganese ore and wood pellets.	[43]
Elwaleed C Mn-ore	Chalmers (12 MW_{th} CFB)	OCAC campaign that lasted only one day due to extensive elutriation of bed material.	NA
Foundry slag	Lidköping Energi (13 MW_{th} BFB)	OCAC campaign during 4 days with MSW. The slag was continuously added to a bed of silica sand resulting in the bed consisting of an estimated amount of 18 wt.-% slag.	[52,53]

Eight boilers (six CFB- and two BFB-boilers) in the scale from 12 to 170 MW_{th} have been operated in OCAC mode with ilmenite as bed material. These large campaigns clearly show that the oxygen-carrying property of the ilmenite makes it possible to reduce the amount of excess air (here defined as the amount of air exceeding stoichiometric conditions) and still achieve adequate combustion of the fuel and low CO-emissions. As much as 25% reduction of excess air was demonstrated during the combustion of MSW in a 75 MW_{th} CFB boiler [44]. A 30% reduction of excess air was possible during combustion of mixed waste-derived wood and wood chips in a 115 MW_{th} CFB boiler [31]. Unpublished results from a three-week experiment in the 85 MW_{th} MSW fired CFB boiler P15 at Händelö showed that a 14% decrease in excess air was feasible with ilmenite. Similar observations were also made during operation with ilmenite in a BFB boiler. A six-week-long experiment (two weeks of reference operation using silica sand as bed material and four weeks of ilmenite operation, unpublished data) in a 19 MW_{th} biomass-fired BFB boiler showed a drastic reduction of the CO concentration in the flue gases by more than 50% during the first day of ilmenite operation.

Dedicated tests performed in Chalmers University's 12 MW_{th} CFB boiler [36] confirmed that the oxygen buffering properties of ilmenite could compensate for insufficient mixing in the gaseous phase in space and time of the furnace. The effect of a more even oxygen distribution was further investigated by measuring the carbon monoxide concentration profile in three positions close to the furnace tube membrane wall in the Chalmers University boiler. The investigation [37] details that the concentration of CO near the wall was drastically reduced when ilmenite was used as bed material. The difference in CO emissions was reported the be most prominent as the excess oxygen (here defined as the concentration of oxygen measured in the flue gas) was decreased from the normal of 3.5 vol.-% down to 1.6 vol.-%.

Several investigations further detail that higher thermal output was possible with ilmenite as bed material due to the improved oxygen distribution in the furnace. A reduced excess air flow results in a lower volume flow of flue gas, which in turn frees up space for increased fuel load without exceeding design values for flue gas velocities in the convection section of the boiler. Operating the boiler above design flue gas velocities increases the risk of erosion that leads to material losses on heat transferring equipment, unplanned stops, and higher maintenance costs. An increase in thermal output of 7% was reported in the tests at Örtofta [31] and as much as 13% in the tests at Händelö [44]. Previously unreported tests from the Örebro boiler and Eskilstuna boiler reveals an increase in thermal output of 3% and 8% respectively, both attributed to the effect of improved oxygen distribution in the furnace.

Regeneration of the bed material is necessary to avoid an accumulation of ash species that can create boiler operating issues, such as sintering or agglomeration of the bed material. An industry-wide accepted rule of thumb is that waste combustion consumes around 6 kg fresh sand/MWh produced heat whereas the same metrics for biomass combustion is around 3 kg fresh sand/MWh produced heat [54]. This is detailed further in Section 3. In the case of ilmenite, it has been reported that less addition of fresh bed material is needed compared to sand. The consumption of fresh ilmenite was as low as 0.72 kg/MWh at Örtofta (wood and waste wood-fired) [31], 3 kg/MWh in P14 at Händelö (MSW-fired) [44]. Unpublished results reveal that as low as 0.8 kg/MWh was possible in P14 at Händelö when a system for magnetic separation [45] and recycling of the ilmenite was introduced. Unpublished results from the tests in Eskilstuna (biomass-fired) show that the consumption of fresh ilmenite can be kept at around 1 kg/MWh. The lower risk for agglomeration of ilmenite also allows for higher possible boiler temperatures [31].

An experimental campaign with LD-slag as bed material and wood chips as fuel has been conducted in Chalmers University's 12 MW_{th} boiler [46]. Crushing and sieving was done by the steel producer SSAB to obtain suitable bed material particles. The resulting material was easy to handle and was pneumatically transported to the boiler and subsequently removed from the boiler by a bottom ash screw. It was more resistant towards sintering than silica sand. The mechanical integrity was decent even though the generation of fly ash increased significantly. The temperature profile of the furnace suggested that the fuel conversion was enhanced. However, the impact on emissions was not positive. When using 100% LD-slag the emissions of especially CO was much higher than what could have been expected with silica sand. The hypothesis presented was that the relatively poor ability of LD-slag to absorb alkali [47] could have contributed to inhibit full burnout in the cyclone. Recent studies have shown that potassium indeed can have this effect [54,55]. The high CO emissions could be addressed by adding small amounts of ammonium sulphate to vortex finder of the primary cyclone to reject alkali as sulphate, or by using a bed with a mixture of LD-slag and silica sand [46].

The campaign in Chalmers University's 12 MW_{th} boiler was followed by experiments in the commercial 95 MW_{th} BFB plant at Sävenäs. That campaign was not successfully concluded according to the original plan [56] and was aborted having reached about 7 wt.-% LD-slag in the bed. The reason was severe problems in the pneumatic transport of the LD-slag to the bed material silo. The bed material in this case was a commercial fraction of LD-slag normally used as feedstock for mineral wool production. It was not established why pneumatic transport did not work satisfactory, but it is believed to have been due to the high fraction of fine material in the batch. No significant effects were seen on the performance of the boiler with this low level of substitution.

Experiments in a 13 MW_{th} MSW-fired BFB showed that adding foundry slag into the bed lowered the CO-emissions by 80% and enabled approximately 15% increase in thermal output [53]. The slag content in the bed was continuously increased, reaching an estimated total amount of 18% foundry slag. The added foundry slag enabled as low as 3.8 vol.-% excess oxygen without reaching unacceptable levels of CO-emissions, while the limit with silica sand was determined to be 4.6 vol.-%. The risk for agglomeration was determined to be low and the experiment was carried out with no operational difficulties related to the slag [57]. The ash disposal could be handled in the same way as during normal operation with silica sand.

For some of the campaigns outlined in Table 1, no reports are found in the open literature. These refer to activities conducted by companies at commercial facilities. Also, the campaign with Elwaleed C manganese ore is unpublished. This is because the material had too low mechanical integrity for operation in CFB, i.e., it was elutriated from the bed as dust in just a few hours.

CLC has yet to be demonstrated and operated on a truly industrial scale. However, Chalmers University's 12 MW_{th} semi-commercial research boiler is integrated with a BFB gasifier. When using oxygen-carrying bed material and the gasifier this allows for operation with continuous reduction and oxidation of the bed material in what could be described as CLC/CLG mode. However, the setup is not specifically adapted to achieve high fuel conversion—the bed is rather shallow, fuel is top-fed and the temperature is limited to around 830 °C. Nevertheless, fuel conversion of 55–60% is typically achieved.

2.2. Procurement of Oxygen Carriers for OCAC-Experiments

For the activities outlined in Table 1, it has been required to procure large amounts of oxygen carrier particles. The procedure has been different for different kinds of materials. The basics are explained below:

- Rock ilmenite has been received predominantly from the company Titania A/S, which operates an open-pit mine located in Hauge in Norway. The ore is crushed to a small size on site and subject to mechanical beneficiation to enrich the ilmenite concentration to 85–90%. The facility produces about 850 kton of ilmenite concentrate per year. The process inherently produces particles low in dust in a range of different size fractions. Thus, extraction of a few dozens or hundreds of tons of particles can be done at a moderate cost. The product was sieved to provide particles at the size range required for OCAC. Once extracted from the process chain, the material was dried before transport and use.
- Sand ilmenite originating from Australia has been provided by the material trading company Sibelco. Ilmenite sands can be found in placer deposits of heavy minerals occurring for example in South Africa, Australia, North America, and Asia [58]. Sand ilmenite generally stems from weathered rock deposits. The weathering causes the iron content to decrease while increasing the concentration of TiO_2. Due to the natural iron oxidation and dissolution, hence also called altered ilmenite, the TiO_2 content can be as high as 90 wt.-%. In this case, the alteration product is called leucoxene [58].

The sand ilmenite was used as is in the OCAC experiments, without further processing. This material was found to be suitable but contains a fraction of fines which are elutriated immediately when the sand enters the boiler.

- LD-slag has been provided by the Swedish-Finish steel producer SSAB, via their subsidy SSAB Merox AB. LD-slag (sometimes referred to as steel-converter slag) is produced as large chunks in the ore-based steel production. Merox handled the whole preparation chain which included crushing LD-slag from an open-air storage site, drying in a diesel-fired furnace, grinding, and sieving. Similar equipment as is normally used for crushing and grinding to produce slag products were applied. The desired particle size of 100–400 μm was smaller than what is typical for slag-based products, which normally is in the size range of several mm or a few cm. Sieving was done with a horizontal shaker outfitted with a woven wire mesh sieve. This was likely not an optimal choice and sieving reportedly was very time-consuming, despite leaving <15 wt.-% material finer than 100 μm in the batch. The yield from large chunks to particles in the desired size range reportedly was only about 20–25%. The process involved significant elements of trial-and-error. It seems likely that a significantly higher yield and a reduced fraction of fines could be achieved with some procedural developments.
- Manganese ores have been procured from two different sources, namely Sibelco Nordic AB and Elwaleed. The Sibelco ore was provided as large heat-treated chunks. Elwaleed grade C is a low-grade ore provided as smaller chunks. Particles were produced from the ores by the company UVR-FIA GmbH in Germany. The Sibelco ore was first crushed into smaller fragments. This was apparently not needed for the Elwaleed C ore. The principal step for producing particles was multi-stage grinding, sieving, and dedusting. Final sieving reportedly was conducted by wind sifter rather than horizontal-type shake sieve. This resulted in batches principally free from fine material. The yield in the desired particle-size range 100–400 μm was 40–50%.
- Foundry slag from Sandvik SRP AB was used for the experiment in Lidköping. The slag is produced at the foundry as chunks that were crushed, dried, and sieved to obtain the desired size fraction. The processing was handled by Sibelco. The material contained some elemental metal which complicated the crushing. Crushing the material also led to approximately 50% loss due to fines. The sieving resulted in around 30–40% of the inserted bed material being smaller than 0.7 mm, which is approaching the minimum size for BFB [53,57]. A higher yield could be expected by developing the crushing and sieving process.

With some straightforward precautions, the logistics of oxygen carrier particles should not pose significant challenges. For all experiments outlined in Table 1 above, except for foundry slag, the bed material was transported by pressure discharge truck, which is the preferred method for transportation of silica sand to fluidized bed boilers in Sweden. The reason for using pressure discharge trucks is that once on site, the bed material is loaded into a bed material silo located at elevated height for easy bed material feeding into the boiler. Thus, pneumatic transport is applied. For the campaigns outlined in Table 1, pneumatic transport of bed materials has mostly worked well, but unexpected problems have arisen occasionally. During the campaign at Sävenäs HP2, 95 MW BFB boiler with LD-slag, significant problems with clogging were experienced. The reason for this is still not clear but the bed material for this campaign had some non-ideal characteristics. A commercial fraction referred to as LD-slag 0/2 intended for the production of mineral wool was used as bed material. This commercial fraction had a suitable size for use in BFB boilers but much more fine material than what the pneumatic transport system was adapted for [59]. Other campaigns with LD-slag have not resulted in similar problems. Foundry slag was transported to the site in bags and 90 L at a time was inserted into the boiler via pneumatic lines [53]. Some minor problems with the transport via the pneumatic line were experienced during the experiment, but it was not assumed to be related to the bed material.

Some material-specific precautions may be needed to avoid fouling and corrosion. Notably, the combination of materials such as LD-slag and blast furnace slag with significant moisture content and aluminum may result in unacceptably rapid corrosion. This is because the protective oxide film of aluminum is attacked and deactivated at alkaline conditions [60].

3. Materials and Production

3.1. Current Bed Material Consumption in Fluidized Bed Boiler

When considering the development of OCAC and CLC, it is of interest to begin with examining what large-scale FBC looks like presently. Current bed material handling and quantities can give an idea of how the transition to novel bed materials could look like. "Bed material" is here defined as actively added minerals such as silica sand, while "bed" includes also fuel minerals and fuel. The material balance of minerals over the boiler can be explained as follows. Minerals enter the boiler in two forms; as bed material, and as minerals present in the fuel. The minerals then leave the boiler either as fly ash following the flue gas, or as actively extracted bottom ash. Both the fly ash and the bottom ash contain minerals that originate from both the fuel and the bed material. The material balance looks different for coal and biomass/WtE, which is illustrated in Figure 3. The amount of minerals that enter the boiler with coal typically exceeds the amount of fly ash. Thus, bottom ash extraction is primarily performed to control bed growth. In biomass or waste combustion, on the other hand, the amount of fly ash typically exceeds the amount of minerals entering with the fuel. Thus, theoretically, the bed height would decrease without a continuous addition of bed material. In practice, however, bottom ash extraction is performed to avoid an accumulation of unwanted species in the bed and downstream in the boiler.

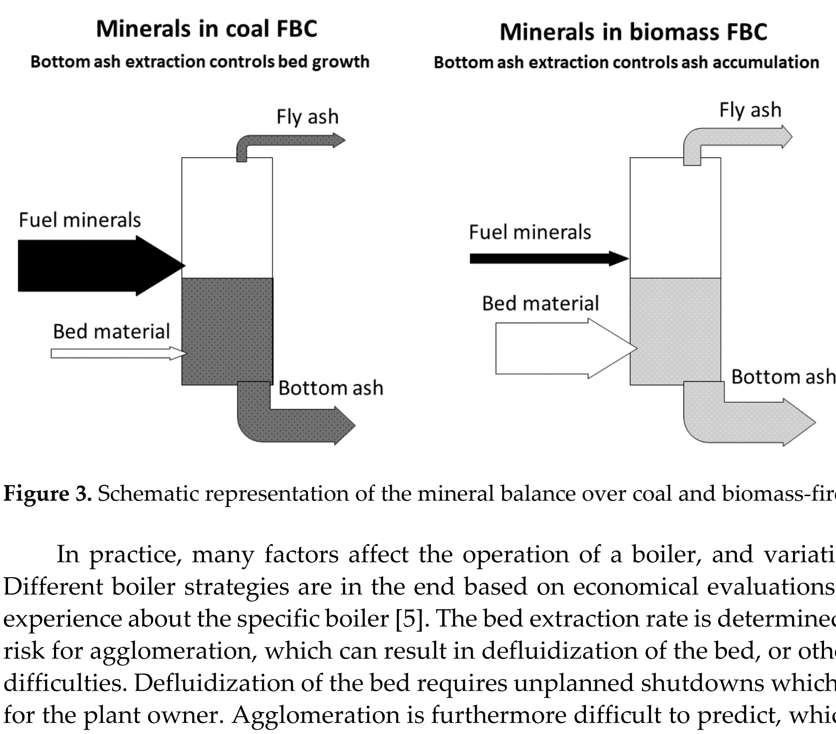


Figure 3. Schematic representation of the mineral balance over coal and biomass-fired FBC boilers.

In practice, many factors affect the operation of a boiler, and variations are large. Different boiler strategies are in the end based on economical evaluations and practical experience about the specific boiler [5]. The bed extraction rate is determined based on the risk for agglomeration, which can result in defluidization of the bed, or other operational difficulties. Defluidization of the bed requires unplanned shutdowns which is very costly for the plant owner. Agglomeration is furthermore difficult to predict, which is an incentive for plants to operate with large safety margins. A rule of thumb for describing continuous sand replacement is that 3 kg/MWh of sand is used in biomass combustion and 6 kg/MWh of sand is used in WtE [54]. However, three examples from wood-fired plants were provided in Section 1.1, and those correspond to approximately 0.5–10 kg/MWh.

The amount of sand currently consumed in FBC units in Sweden has been estimated as follows. The basis for the calculation is a collection of data on FBC units done in 2016, including their location, fuel type burned, and capacity (Electrical capacity, steam capacity, and heat capacity). The data is taken from the Chalmers Power Plant Database [61,62]. For the calculation, assumptions have been made regarding the annual operating hours (h/yr.), load, and replacement of bed material in the boilers. The assumptions used in the calculation are presented in Table 2 (for both CBF and BFB plants) and are discussed here.

- Autoproducers (such as pulp mills) and WtE plants are assumed to be operating as much as possible, leaving downtime only for unplanned and planned stops for maintenance and repairs.
- The utilization rate for biomass combustion plants producing primarily heat and power is more complicated to estimate. Biomass as fuel can be either cheap or expensive depending on the type, and the incentives for using it vary in different plants, due to several factors. The local energy mix varies throughout Sweden, resulting in a low or high threshold for including biomass in the active energy mix. Thus, three different assumptions of annual operating hours are used in the calculations.
- The bed inventory of the BFB plants was estimated by collecting data about the bed inventory of a few plants (data from [19,59,63]) and assuming a linear relationship between bed material inventory and steam capacity. The bed inventory of the CFB plants was assumed to be 50 tons, regardless of their steam capacity, due to the limited amount of data points.
- The sand replacement is assumed to be 3 kg/MWh for combustion of biomass and 6 kg/MWh for combustion of waste.

Table 2. Assumptions used for calculating the annual consumption of bed material in fluidized bed boilers in Sweden.

Plant Type	Fuel	Uptime (h/yr.)			kg Sand/MWh	Bed Material Replaced (times/yr.) *	Load (% of Capacity)
Autoproducer	Wood		8497 **		3	1	95
Biomass combustion	Wood	3380	4380	5380 ***	3	1.5	95
WtE plants	Waste		7884 ****		6	3	95
Other (peak load)	Peat or coal		1000		2	1	95

* The bed material is completely replaced after each stop, both planned and unplanned. ** Corresponding to 97% of the time, leaving 1.5 weeks/yr. for planned and unplanned stops, repairs, and maintenance. *** The first number corresponding to 1000 h/yr. less than 50% of the year, the second number corresponding to 50% of the year, the third number corresponding to 1000 h/yr. more than 50% of the year. **** Corresponding to 90% of the time, leaving the remaining 10% of the time for unplanned and planned stops, repairs, and maintenance.

The results from the calculations are presented in Figure 4, showing an estimated total of 160–180 kton of silica sand being consumed yearly as bed material in Sweden. Completely replacing the bed inventory a few times a year (for example during planned shut-downs) is contributing to the total amount of sand consumption by around 1–2%. CFB and BFB sand can be assumed to originate from the same sources, but their properties differ when it comes to particle size distribution. CFB and BFB sand are in the approximate size ranges 0.2–0.4 and 0.8–1.2 mm, respectively. These fractions are obtained by sieving natural sand.

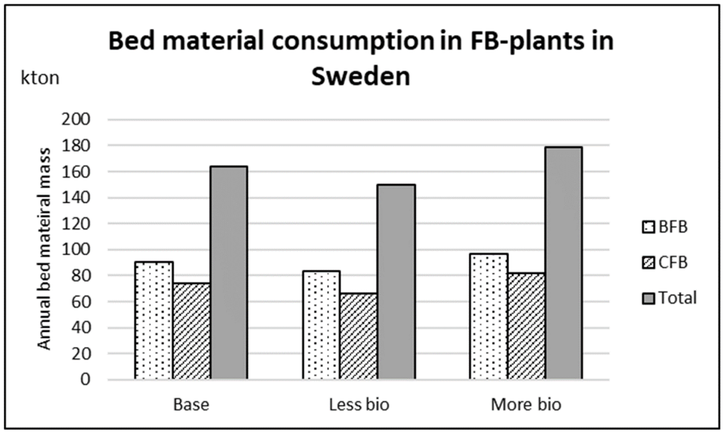


Figure 4. Estimated amounts of sand consumed annually as bed material in BFB and CFB boilers in Sweden for three different assumptions about biomass combustion.

3.2. Industrial Products and By-Products Suitable as Bed Material

Table 3 summarizes production volumes and other general information about the materials suggested in this study for replacing conventional bed material. The production volumes are presented in kton along with an indication of producing country. The table is not exhaustive when it comes to production in the Nordic countries. Some of the materials are available as commercial products, which are presented together with the producing company.

The main process steps required to utilize the materials are indicated, these include drying, crushing (and grinding), and sieving. In the case of sieving, it's indicated whether it's done to remove fines or to remove large particles/chunks, which might have an impact on the workload—removing chunks is typically less demanding. The cost of related activities is discussed in Section 4.1. Details regarding each material are provided in the following sections. The composition of the materials is presented in Table 4.

Table 3 includes olivine and blast furnace slag, even though they are not oxygen carriers. They have, however, been considered and evaluated as bed material in large scale FBC combustion and are used commercially in a few boilers. The table also includes ilmenite, which is mined for its titanium content. Ilmenite has become a type of standard oxygen carrier, both in lab-scale experiments and large-scale implementation in boilers. Production and experiments with ilmenite have been discussed in Section 2 and more information about production and bed material properties of ilmenite can be found in provided references.

The focus in this study is on the larger industries, where the production is distributed in few locations and is often handled by one company. Less focus will be on smaller, decentralized, producers of potential oxygen carriers such as foundries, rolling mills, and other downstream processes.

Table 3. Alternative bed materials originating from industrial production processes.

Material	Origin	Production (kton)	Properties as Bed Material	Commercial Products	Current Use (Main)	Status of Bed Material Development	Processing Required (Main)	Refs.
Iron ore	Mining	30,000 (SE), 5000 (NO)	Oxygen carrier	Sinter fines (MAF and MHF, LKAB)	Steel production	Untested as bed material (fines). Small scale (ore).	Sieving	-
Iron ore concentrator tailings	Ore beneficiation (by-product)	5000 (SE)	Oxygen carrier (Probable)	-	-	Untested as bed material	Sieving/wet classifying, drying	-
LD-slag	Steel production (by-product)	300 (SE), - (FI)	Oxygen carrier, aggl. resistant	LD-sten 0/2, LD-sten 0/7 (SSAB)	Mineral wool, steel, constructions	Proven at large scale	Crushing, sieving (fines), drying	(See Table 1) [64]
Foundry slag	Steel foundries (by-product)	20 (SE)	Oxygen carrier	-	-	Proven at large scale	Crushing, sieving (fines)	[52,53]
Iron mill scales	Steel production (by-product)	60 (SE)	Oxygen carrier	Glödskal A, Glödskal B (SSAB)	-	Potential, small scale tests.		[65]
Granulated copper smelter slag	Copper production (by-product)	250–270 (SE), - (FI)	Oxygen carrier	Järnsand (0.5/2) & (0.1/0.7) (Boliden)	Roads, construction	Untested as bed material	Sieving (large particles)	-
Rock ilmenite	Mining	600–700 (NO)	Oxygen carrier, alkali absorbent	Improbed (Improbed)	Titanium, pigment	Proven at large scale, commercial	Crushing, sieving, drying	(See Table 1)
Olivine *	Mining	3000 (NO)	Aggl. resistant, tar conversion	-	Steel production (fluxing agent)	Proven at large scale, commercial.	-	[66]
Blast furnace slag *	Steel production (by-product)	450 (SE)	Aggl. resistant	Hyttsand 0/4, Hyttsten 0/2, GR-Granule	Roads, construction	Proven at large scale, commercial.	Sieving, crushing	[67,68]

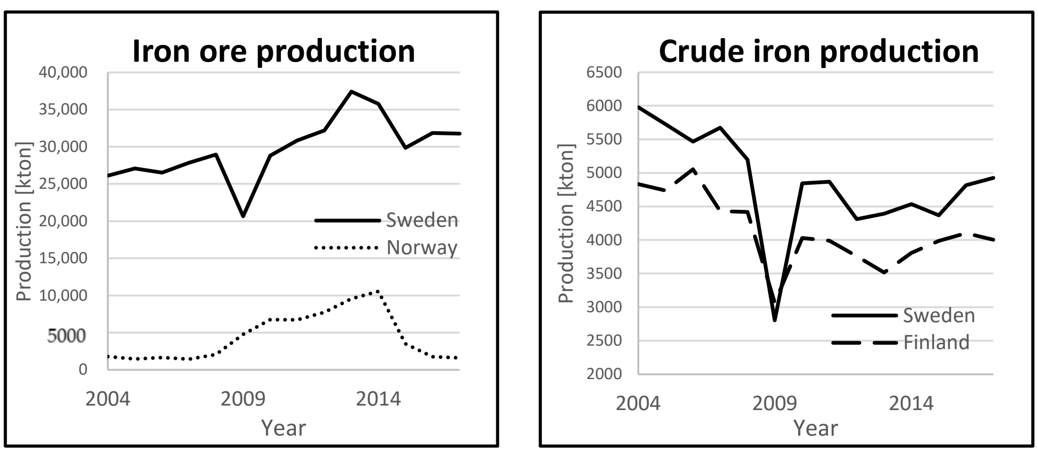
aggl. = agglomeration; SE = Production in Sweden; FI = Production in Finland; NO = Production in Norway; * = Not oxygen carriers; - = No data.

Table 4. Composition of representative samples of the materials. Note that some entries present composition as oxides, some as elements. Balance is mainly oxygen.

Material	Component	References
Iron ore sinter fines (MAF)	Fe(71) SiO_2(0.9) MgO(0.5) TiO_2(0.5) CaO(0.2)	LKAB
Iron ore concentrator tailings	SiO_2(44) CaO(10) Al_2O_3(9.9) Fe(9.1) MgO(8.3) K_2O(2.3) P(1.6) TiO_2(1.6)	LKAB
LD-slag	CaO(43) FeO(22) SiO_2(10) MgO(9) MnO(3) V(1.5) TiO_2(1.3) Al_2O_3(1.1)	Merox, product specification sheet
Foundry slag	Mn(18) Mg(14) Si(9.0) Ca(8.9) Fe(5.7) Al(2.7) Ti(1)	Elemental analysis Sandvik SRP [53]
Iron mill scales	Fe(102) Mn(0.45) Si(0.31) Al(0.16)	Elemental oxygen free analysis Glödskal B [69]
Copper smelter slag	FeO(43) SiO_2(36) Al_2O_3(2–5) CaO(2–5) MgO(1) Zn(1) S(0.6)	Boliden, product specification sheet Järnsand
Rock ilmenite	Fe(34) Ti(28) Mn(0.5) Mg(0.4) Al(0.2) Si(0.2)	Norwegian (Titania A/S) [40]
Sand ilmenite	Fe(33) Ti(24) Mg(1.8) Si(0.9) Al(0.3) Ca(0.3) Mn(0.1)	Australian (Sibelco) [40]
Olivine	MgO(50) SiO_2(42) Fe_2O_3(7.4) Al_2O_3(0.46) NiO(0.32) Cr_2O_3(0.31)	[66]
Blast furnace slag	SiO_2(34) CaO(31) MgO(17) Al_2O_3(13) TiO_2(2.3) S(1.3)	Merox, product specification sheet Hyttsand

3.2.1. Iron Ore and Steel Production

The iron ore- and steel industry is one of Sweden's largest industries. In 2019, the total amount of ore mined in Sweden was 47.5 Mton, being refined into 27.3 Mton ore-products [70]. A smaller amount of iron ore is also mined in Norway, where the amount has varied a lot historically due to the closing and reopening of mines [71]. Ore-production quantities for Sweden and Norway between 2004 and 2017 are presented in Figure 5a. Steel production in Sweden amounts to approximately 4.5–5 Mton crude steel, including both ore-based and scrap-based steel production. A similar amount of crude steel is produced in Finland.



(**a**) (**b**)

Figure 5. Iron ore and steel production between the years 2004–2017, in kton. (**a**): Iron ore production in Sweden and Norway. (**b**): Crude steel production in Sweden and Finland. Data from [72].

The crude steel production in Sweden and Finland between the years 2004 and 2017 is presented in Figure 5b. The large drop in production in 2009 was due to the financial crisis. Approximately 600 kton scrap-based steel is also produced in Norway (not included in the graph).

Swedish ore is produced by Luossavaara-Kiirunavaara Aktiebolag (LKAB) as pellets and fines. Pellets are the main product produced by LKAB by quantity (around 80–90% of the products are pellets). There is some flexibility in the production process, so that the ratio between pellets and fines production can adapt to the current demand. However, only a fraction of the raw ore has properties making it possible to turn into sinter fines, while the requirements for pellets production is less strict [73]. Figure 6 presents the production by type of products between the years 2014–2017. Due to their high iron content and a size interval of 0–2 mm, hematite and magnetite fines are of interest to use in OCAC. Iron ore from LKAB has not been a subject for OCAC or CLC experiments, but other samples of iron ores have shown good bed material properties in CLC experiments. Crushed iron ore has been used in experiments using coal and wood char as fuel (e.g., [74,75]). However, due to the high purity, the MAF-product produced by LKAB more closely resembles iron mill scales in composition [65].

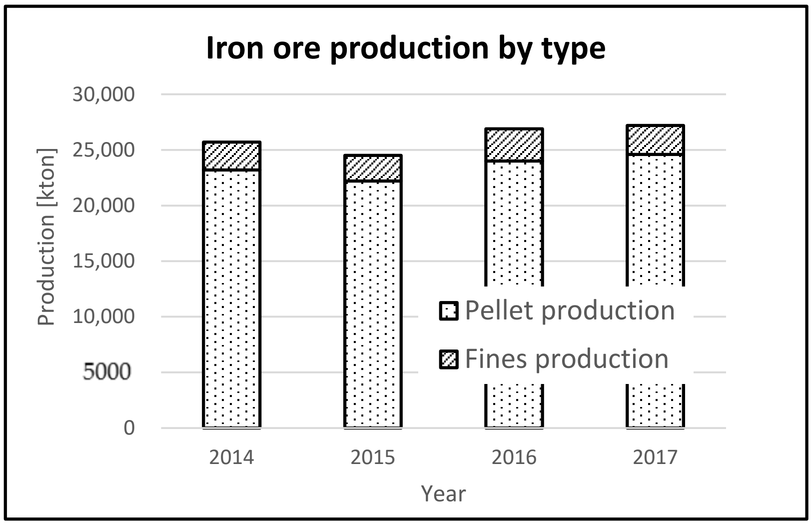


Figure 6. Iron ore production by type. Data from [70].

A major by-product emerging in the ore beneficiation process is concentrator tailings, which is essentially crushed silica rock with approximately 8% iron content. According to environmental reports from LKAB, the production of concentrator tailings in the year 2018 was in total around 5 Mton from the three mines [76–78]. Even though the iron content in this fraction is low, it could be expected to have some oxygen-carrying properties and it should be of interest to evaluate it as a bed material. The main advantage is that it is produced in large quantities and has no current applications, thus, it is practically a waste fraction. A challenge with concentrator tailings could be the relatively high concentration of phosphorous, which is known to potentially cause agglomeration when alkali is present in FBC. Preliminary inspection of concentrator tailings samples from LKAB suggested that it could have a large fraction of fine or fragile material. However, due to the good availability and the fact that it currently is regarded as end-of-life waste material, a large material loss can be accepted for the production of bed material from concentrator tailings.

Production of low-carbon steel generates LD-slag, which has been a subject for OCAC and CLC experiments. As seen in Table 4, LD-slag contains both iron and a few percent manganese, which gives it its oxygen-carrying properties. LD-slag is also naturally rich in CaO, which suggests that it could be resistant to agglomeration [3]. Indeed, Ca-phases in LD-slag have been seen to react with and capture alkali components without causing agglomeration in fixed bed experiments [79]. A lower agglomeration tendency than silica sand was also concluded by dedicated agglomeration tests in connection with the OCAC experiment at Chalmers University's CFB [46]. The yearly production of LD-slag in Sweden is approximately 200 and 100 kton in Luleå and

Oxelösund, respectively. The LD-slag production quantity is closely correlated with the ore-based steel production [32]. About half of the LD-slag can be recycled back to the steel production process. A small fraction of the remaining LD-slag is utilized in applications such as road construction and mineral wool production. The methods used for manufacturing the bed material for OCAC tests are discussed in Section 2, and based on experience, it is estimated that bed material yield could be somewhere around 40%. This means a total possible Swedish annual production of around 60–120 kton of LD-slag-based bed material, depending on how much is recirculated for steel production or utilized for other purposes.

Further, potentially suitable by-products are generated also in the final stages of steel production, like rolling and casting. Approximately 20,000 tons of foundry slag is produced annually in Sweden, half of which is estimated to be suitable as oxygen carriers [52,53]. Approximately 60 kton of iron mill scale is produced in rolling processes [32]. Iron mill scales have a high Fe-content but show some agglomeration tendencies and other mechanical issues in CLC experiments [65,79]. These materials are interesting options to consider as local sources of bed material. However, the production is comparably small and decentralized, making them difficult to include in a larger discussion.

3.2.2. Copper Smelting

Another large industry in Sweden is copper mining and smelting. Boliden minerals operates two large coppers smelters: one in Rönnskär in Sweden and one in Harjavalta in Finland. Copper production volumes during the years 2004–2017 are presented in Figure 7. A by-product of the copper smelting process is copper smelter slag. Approximately 1.5 Mton of slag is produced yearly by Boliden across Sweden and Finland, 1/3 of which is water granulated into amorphous particles [80]. 250–270 kton water granulated slag is produced in Rönnskär (Sweden) and sold under the name Järnsand ("iron sand"). According to Boliden, the production of water granulated slag could be increased if there was a growing interest on the market. The Swedish water-granulated slag is today used as an construction aggregate, abrasive media, and as an iron source in cement clinker and glass manufacturing.

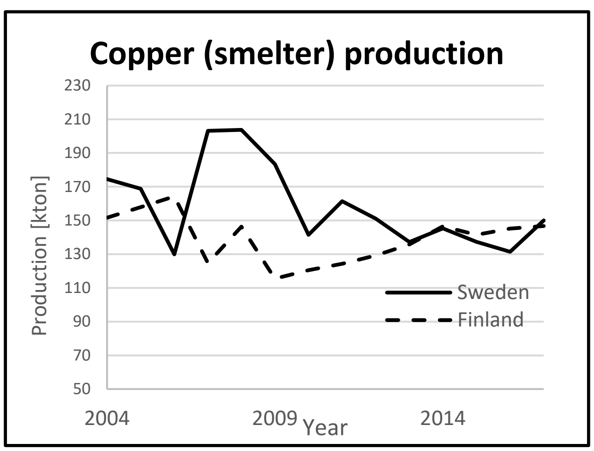


Figure 7. Copper production in Sweden and Finland between the years 2004–2017, in kton.

Copper smelter slag has an iron content of around 35 wt.-% [81] (or 43 wt.-% FeO according to the data in Table 4), bound in oxides and silica oxides, which suggests that it has oxygen-carrying properties. Another aspect that makes it especially interesting as a bed material is that the water granulated slag is produced directly as particles in the size range of 0–2 mm. This means that it could potentially be utilized as a bed material as-is, with no or little further preparations, aside from sieving.

3.3. Summary

According to the estimations, approximately 160–180 kton of silica sand is used each year in Sweden directly as bed material for FBC. Most of this silica sand is subsequently disposed of without being further utilized. This is a significant amount and corresponds to about 20% of the total Swedish silica sand production. It can be argued that this alone is a reason to start considering alternatives. Figure 8 presents the estimated potential for slag-based bed materials compared to current estimated silica sand consumption.

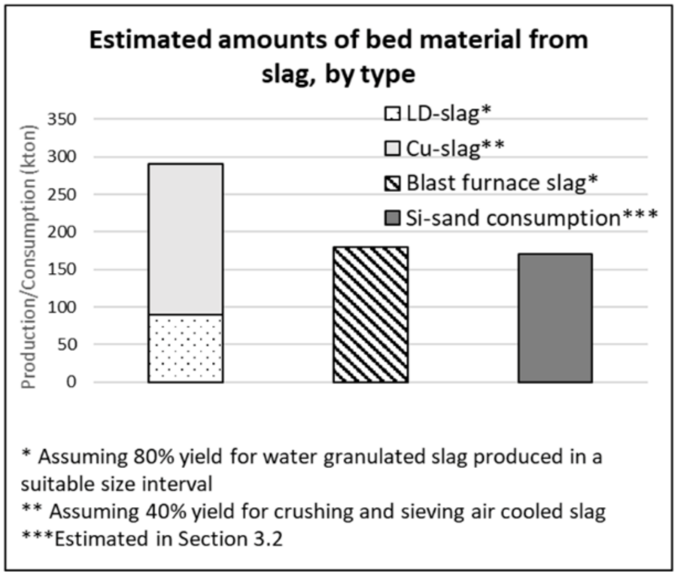


Figure 8. The estimated potential for slag-bed material production compared to estimated current silica sand-bed material consumption. Blast furnace slag is included but is not an oxygen carrier.

Iron ore could be an interesting alternative as bed material. There are two products (magnetite fines and hematite fines) produced today at a large scale, both of which could potentially be utilized as bed material with no or just minor further processing. Thus, even though the selling price for iron ore fines can be expected to be higher than the by-products discussed here, it is not necessarily so that the final cost for using the material is higher. The cost for material preparation is discussed in Section 4.1. Out of the by-products discussed, water granulated copper smelter slag (Järnsand) might have the largest potential when it comes to production volume and potential bed material yield. There is already a large production of granulated slag today, and apart from that, there is a significantly larger amount of air-cooled slag which is barely utilized at all. As far as the authors are aware, neither LKAB's iron ore fines nor Boliden's Järnsand, or similar materials, have been evaluated as bed material in small- or large-scale experiments. The next step should therefore be to conduct tests to determine their properties. Activity with oxygen and gaseous fuel can easily be determined in small-scale experiments. Mechanical properties such as agglomeration tendency and mechanical integrity can be determined in large-scale experiments or in lab-scale experiments simulating extreme conditions. Before that is done, not much more can be concluded about their suitability, but comparisons to similar materials can be done. Copper smelter slag contains a significant amount of iron, more than for example LD-slag which has proven to have sufficient oxygen-carrying capacity in OCAC. Apart from iron oxide, the main components of copper slag are Si-, Ca- and Al-oxide. Ca- and Al-oxides are known to reduce the propensity for agglomeration. Si-oxides are known to react with alkali and phosphorous from the fuel and make up the main part of available conventional bed materials. There is no apparent reason to believe that the main components of Järnsand should cause any direct problems in the boiler or when handling the bottom ash. The same can be said about iron ore fines.

Another by-product that shows good potential when it comes to volume is LD-slag. The main drawback for LD-slag might be the large amounts of fines produced when crushing the material, leading to the need for intensive sieving activities and a large material loss.

4. Discussion

Research and large campaigns in commercial boilers show that using an oxygen carrier as bed material in FBC can increase efficiency and reduce emissions. The technology can usually be implemented in existing industrial-scale boilers without any adaptation of the equipment. Comparing the data presented in Sections 3.2 and 3.3 it can further be concluded that, for the specific case Sweden, by-products from metallurgical industries could easily replace conventional bed material when it comes to quantity. A significant part of the by-products and intermediate products in metallurgical industries is furthermore produced as particles in a suitable size range for FBC. Those can potentially be utilized with only a few or no processing steps. Producers have expressed interest in increasing production of certain size-fractions if the market shows demand for it. It should also be mentioned that the bed material consumption in the boiler is potentially lower with novel bed materials than with silica sand. This is because they can be e.g., less prone to agglomerate.

Out of the by-products with oxygen carrying properties, slags (LD-slag and copper smelter slag) show great potential due to large production and low utilization. Only about 1/3 of the copper slag is granulated and the rest is air-cooled and disposed of, meaning that there is potential to increase the production of granulated copper slag. Boliden is planning to expand granulation within the next 10 years and is actively looking for market opportunities. When it comes to the concept of using slag-based bed materials, GR Granule can be presented as an example. GR Granule is a bed material produced from blast furnace slag and sold by the Finnish company Fescon Oy. GR Granule is used commercially in around 13 boilers in Finland for combustion of fuels with high alkali content. It is not an oxygen carrier but has shown other advantageous properties in FBC when it comes to avoiding agglomeration and related problems [68,82], properties which have been connected to the high Mg-content. According to the producer, the bed material consumption in boilers was seen to decrease by up to 80% by switching from conventional bed material to GR-Granule. The material is produced from both water-granulated slag and air-cooled slag, making the process relevant to compare with both copper- and LD-slag. No available data on yield, cost, or production methods are disclosed by Fescon. Bottom ash handling is not different with GR-Granule than with silica sand [68], which is an important feature for boiler operators.

Though there are seemingly many advantages, OCAC is to date only used in a few plants in Sweden. Power plant owners might argue that the concept is not yet well tested and that the risks connected to switching to a practically untested bed material outweigh the potential economic gain. A risk could be that the material causes corrosion or some other type of unexpected damage to the boiler. Another type of risk is that ash handling becomes significantly more expensive if the ash must be classified differently than with conventional bed material. Disposing of the bottom ashes already corresponds to a large part of the bed material cost. The boiler operators need to know how the material develops in the boiler to be able to plan all the aspects of material handling [54]. Gaining that kind of experience will take time. Another challenge can be the actual price per kg of a new bed material and how this is valued to the overall gains produced in a boiler when replacing the silica sand. That is, even though the cost per kg of bed material could be several times higher if using a mineral (e.g., ilmenite) than that for silica sand, it might still be economically favorable to change concerning the overall positive effects on boiler operation. Further, even though an oxygen carrying bed material can increase the overall efficiency of the plant it might be difficult to quantify how big this increase is in practice. Extensive reference operation with silica sand might be needed to evaluate this. In the same manner, positive effects in costs related to maintenance might be visible first after a couple of years of operation with the new bed material. It is not uncommon that the maintenance budget is separated from the operation budget, meaning that any potential long-term gains will be less visible for the person that is paying for the actual bed material. Apart from the technical considerations and the positive effects of decreased emissions, this study also highlights the positive environmental effects of reducing silica sand extraction. However, the idea that silica sand extraction is unsustainable is probably not widespread in the industry. It is not reflected in the sand market, since the availability of sand is high and the cost is quite low. Thus, from the view of the boiler operator, this is not a problem that needs fixing. Another reason for the quite few implementations might be simply a lack of knowledge about the advantages of using oxygen carriers or other alternative bed materials.

It should be in the interest of all concerned parties to get the most value out of their activities, and utilization of by-products is a much-discussed topic for several reasons. However, to create a market for a new product, there will have to be investments into building and operating refining facilities as well as organizing transportation of the materials. There are many different forms a possible oxygen carrier market could take and some different options can be mentioned:

- The material producer (i.e., LKAB, SSAB, or Boliden) creates a niche towards bed material production and invests in facilities in connection to existing industry.
- The boiler operator installs equipment for bed material refining and buys "raw" material from the metallurgical industry. An alternative to this is that contractors are hired to sieve and crush bed material on-site when required.
- A third party invests in building a dedicated bed material production facility, buys raw material from the steel industry, etc., and sells it to the boilers.
- A combination of points 1 and 3, where a third party trades the right size fraction from the material producer, handles the logistics from producer to user, and acts as the technical competence as well as trains the operating personnel for the shift to operation with oxygen carriers.

The first option has the advantage that the existing facilities and flows in e.g., a steel plant are so large that adding a facility like the one required would not be large in proportion to the main activities. There is also already to some extent infrastructure for and experience of processing by-products at the site, and this would in some cases be an adaptation of existing processes rather than building completely new facilities.

In the second option, the boiler owner produces the right particle sizes from the raw material. This might be less attractive from a boiler owner's perspective as it demands large free areas and extensive logistics. Free areas are commonly not available at the boiler site, as all open space usually is covered by fuel piles during boiler operation. Further, this option also produces a byproduct where the rejected material (particles of the wrong size) is to be handled and transported away from the site. There are examples where e.g., fuel contractors bring their equipment to boiler sites to produce woodchips from round wood and when the work is carried out, they leave the site together with their equipment. In this manner, the boiler owner does not have to invest or handle the operation and maintenance of any extra equipment, nor providing the staff for it. A similar setup might be a possible solution for handling the raw material to the right size fraction. However, as this operation will be carried out under limited periods of time, storing the material might be challenging as it again requires free area at the site. Somewhat large storage facilities would be required where the sieved bed material can be stored in dry conditions before it is used in the boiler. Dry bed material is needed as the internal boiler house bed material logistics in almost all cases includes some kind of pneumatic transport.

The third option could potentially offer an attractive path for both the boiler owner and the material producer. This option has several similarities to the existing and well-established model used for silica sand handling. In this case, a third party working as a subcontractor handles the trading and logistics with the raw material producer, establishes the desired size fraction in accordance with the boiler owner's demands, stores the dry bed material, and handles the logistics to the boiler site. In this model, the boiler owner simply orders the amount that accommodates their bed material silo. In this way, both the boiler owner and material producer are offered a comfortable arrangement where the risks related to the material handling and potential investments are handled by the subcontractor. However, from a business perspective, one can argue that this option leads to the material producer losing the opportunity to refine their by-product and thus loses a possible market opportunity. Further, it is likely far from obvious that the boiler owner will adapt to a new bed material on the basis of that it can be provided in an attractive manner.

The fourth option is a model that has many similarities to the ones used by e.g., Improbed™ and Fescon and this is based on a combination of the options discussed. In this case, the material producer takes the first part of the value chain by handling the sieving to produce particles of the demanded size that will constitute the bed material. A subcontractor owns or procures a service for intermediate storage of the dry bed material and all the logistic from the material producer to the storage and from the storage to the boiler site. Additionally, the subcontractor provides a feasibility study for implementing the concept in the boiler. If there is a decision for implementation of the new bed material the subcontractor provides the technical competence needed for introducing the bed material in the boiler and educates the boiler staff. In this manner, the boiler owner can benefit from the accumulated experience in the field and secure that the needed competence is available.

The discussion so far can be summarized to a few important reflections about the readiness of large-scale OCAC implementation. Not only is the technology proven with many hours of both dedicated experiments and commercial-scale operation, but practical solutions concerning aspects of bed material handling have also been developed and tested in some cases. The geographical proximity to large material sources in Sweden is furthermore positive from a transportation point of view, which can also be said of neighboring countries Finland and Norway, which have similar metallurgical industries. Thus, it seems likely that there are potentials for near-future implementation of OCAC with low-cost, available bed materials. This study is to some extent also relevant for future CLC implementation with biomass, since this technology can be assumed to have similar (high) regeneration of bed material. Low-cost oxygen carriers might be advantageous over synthetic ones when it comes to applications with high bed material regeneration.

4.1. Cost

The real (or perceived) cost of producing large amounts of oxygen carriers is often sensitive information that companies are not eager to disclose. In many circumstances, production costs are unknown and difficult to estimate, potentially leaving the selling price largely disconnected from the production cost. Instead, the selling price is determined by traditional price mechanisms, which means that it is an opaque function of supply, demand, and competition with alternative products. The answer one gets when inquiring also close collaboration partners about production costs and expected price of a potential product is that "the price will be what the customer is prepared to pay".

To be fair, in many instances it is likely true that the real production cost of oxygen carrier particles cannot be accurately calculated. LD-slag is a by-product for which there is limited demand, and can be used as an example; Should parts of the cost for building and operating the steel mill be attributed to the oxygen carrier cost? Or can excess LD-slag be assumed a waste material that can be obtained for free? Both options are reasonable but will result in quite different estimations for production cost. Particulate slag-based products (based on copper smelter slag and blast furnace slag) sell on the consumer market in Sweden for as little as 5–10 €/ton. Available products typically have too large particle sizes to use in CFB boilers and may contain unacceptable amounts of fine material. An already much costlier variant of this family of products (LD-slag 0/2 sieved to have particle size below 2 mm) was used for the BFB campaign at Sävenäs mentioned in Table 1. As has been explained above, this commercial fraction was difficult to pneumatically transport at the site, likely due to the high content of fines. While just an anecdotal observation, it seems reasonable to believe that even more extensive processing (e.g., sieving) would be required for use in boilers, which would inevitably affect the price.

The same would be true for extracting limited amounts of materials from other large industrial plants e.g., for processing of ilmenite described above. As long as only a small fraction of the production is extracted for use as an oxygen carrier it may be reasonable to neglect capital costs for equipment, assuming that the rest of the production carries these costs. But if one were to build a facility dedicated to the production of large amounts of oxygen carriers, the oxygen carriers would have to carry the capital costs on their own.

If mineral ores are considered as bed material, the raw material price varies greatly with quality and form, and also with the current demand for commodities. Surveying trading sites, one can conclude that the approximate raw material costs in autumn 2020 are 40–300 €/ton for iron ore, 100–400 €/ton for ilmenite concentrate, and 100–500 €/ton for manganese ore. This does not consider any treatment. If extensive processing of raw materials is needed, this is set to increase the ultimate sales price significantly. This can be compared with the cost for silica sand for Swedish boilers which is in the order of 50 €/ton.

Table 5 summarizes the offered price for the preparation of three large batches of oxygen carrier particles, two of which were ultimately ordered and received. Most of the cost items are likely to be significantly reduced for truly large-scale operations due to economics of scale. The numbers are interesting nonetheless, if only as indications for the cost of e.g., a large CLC demonstration unit. The data in Table 5, shows that the raw material cost is dwarfed by the processing costs. The high costs offered for drying and calcination are noteworthy. The cost per ton oxygen carrier received ultimately was in the order of 10–15 times higher than for ilmenite concentrate.

Table 5. Costs for large-scale preparation of oxygen-carrier particles. Note that these are costs for preparation of one large batch for experimental purposes. Economics of scale and learning curve are likely to reduce these costs significantly for a dedicated manufacturing process.

	Tierga (Iron Ore)	Sibelco (Mn-Ore)	Elwaleed C (Mn-Ore)
Raw material batch size (tons)	25	25	20
Raw material cost (€/ton)	310	850	200 *
Preparations etc. (€/batch)	-	-	4300
Calcination (€/ton)	1900	(pre-calcined)	-
Drying (€/ton)	750	-	-
Crushing from large chunks (€/ton)	-	450	-
Milling, sieving, dedusting, packaging (€/ton)	900	962.5	1080
Declaration of analysis for waste disposal (€/batch)	-	350	350
Disposal of residues (€/ton residues)	-	280	300
Amount 100–400 μm particles received (tons)	15 (estimated)	12.1	8.2
Yield in production (%)	60 (estimated)	48.4	41
Final cost (€/batch)	96,500	60,525	33,790
Final cost (€/ton particles)	6433	5002	4121

* Assumed representative price for low grade ore.

The data presented in Table 5 suggest that material flows that require few pre-processing steps would likely have a significant economic advantage over materials that require several steps of pre-treatment. Thus, identifying promising fractions within existing production processes, such as ilmenite concentrate, iron ore fines, and Järnsand described above, seems like an excellent approach. If fractions with suitable properties can be found within existing production chains and used with limited processing, the cost increase compared to silica sand will not necessarily be big. In this context, it shall be pointed out that bed material is not the major cost when operating a boiler. It shall also be acknowledged that costly minerals with high purity are not necessarily superior to cheaper ones when used as oxygen carriers for OCAC or CLC.

4.2. Circular Flows

Enhancing the efficiency of combustion as well as mitigating the use of silica sand by utilizing waste streams are in themselves ways to make FBC more sustainable and resource-efficient. A problem that remains unsolved, however, is how to treat the bottom ashes without relying on landfilling as an alternative. Due to the composition of the materials discussed here, there's no reason to believe that they are not possible to handle in the same way as conventional bed material. This type of end-of-life handling is, however, not desirable and should be considered unsustainable.

Bottom ash treatment and utilization possibilities will have to be evaluated from case to case, and research is ongoing on how to turn ashes into a resource rather than a waste. This includes both using it as construction material and using it as feedstock to extracting certain valuable components [83]. Some options are here presented which could be a part of a solution that does not involve landfilling. Further discussion about these options is out of the scope of this study.

- Bottom ash from OCAC with iron ore materials are recirculated to the steel industry for steel production
- Bottom ash from OCAC with LD-slag is used for soil amendment. LD-slag has been seen to absorb alkali and phosphorous in OCAC [47,79]. It has been approved to be used for soil amendment to counter forest and land acidification, although it is currently not used for this purpose. It's reasonable to believe that the absorption of nutrients in the boiler makes it even more suitable for this.
- Bottom ash from OCAC with LD-slag replaces fresh LD-slag as feedstock for current uses, such as mineral wool production.
- Valuable minerals like V and Zn are extracted from bottom ashes. The bed materials undergo changes in the boiler, potentially making certain valuable phases more available for extraction. A process for extracting Zn from fly ashes
- Bottom ash from OCAC with ilmenite is used to produce TiO_2.

5. Conclusions

This study has investigated and discussed the potentials for using products and by-products from metallurgical industries as oxygen carrying bed material in FBC. The study has been focusing on the situation in Sweden, which however is possible to extrapolate at least to neighboring countries Finland and Norway. The main findings are:

- Previous research and commercial activities show that the efficiency and capacity of existing fluidized bed boilers can be increased by using an oxygen carrier as bed material, so called Oxygen Carrier Aided Combustion (OCAC). OCAC can be implemented on an industrial scale with no or little adaptation of the equipment. The improvements have often been significant e.g., up to 15% increase in thermal output, up to 30% reduction of excess air, and significant reduction in bed material consumption.
- At least 20% of all the silica sand mined in Sweden (160–180 kton/year), is used directly as bed material in FBC. Natural silica sand is a resource that plays an important role in groundwater production. Protecting natural deposits and replacing primary silica sand in industrial applications is in line with the Swedish environmental goals.
- Steel- and other metallurgical industries produce large flows of by-products that are suitable as oxygen-carrying bed material. These flows could completely replace silica

sand consumption in existing FBC boilers, based on calculations done in this study. This could also be a way for metallurgical industries to monetize large amounts of by-products that currently is disposed of in landfill and be one step closer a circular use of materials.

- Some materials are produced directly as particles in existing processes and needs little in terms of additional processing. Notable such materials are granulated copper-smelter slag and iron ore fines.
- Other materials require significant mechanical processing (e.g., crushing and sieving) to produce particles that are suitable as bed material. This is likely to increases the price of the material, but also enables business opportunities. A notable such material is LD-slag.
- For researchers working with the development of CLC of biomass there might be things to learn from the commercialization of OCAC. While the strong focus on fuel conversion in CLC research is understandable, the OCAC experience shows that there is much more to a practically useful bed material than single parameters. Due to the influence of ash, the bed material consumption is likely to be larger than commonly anticipated. This makes factors such as good availability, low cost and acceptable end-of-life disposal very important.

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