IMPROVED COMBUSTION IN FLUIDIZED BED WITH MANGANESE ORE AS BED MATERIAL

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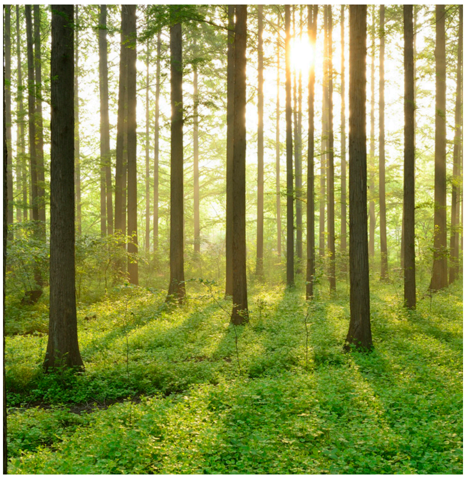

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Improved combustion in fluidized bed with manganese ore as bed material

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Förord

Denna rapport är slutrapportering av projekt A 38758 Miljövänligare och effektivare förbränning i fluidbädd med manganmalm som bäddmaterial med Energimyndighetens projektnummer P 38758. Projektet ingår i teknikområde anläggnings- och förbränningsteknik inom Samverkansprogrammet för bränslebaserad el- och värmeproduktion, SEBRA.

Projektet har följts av en referensgrupp bestående av Bengt-Åke Andersson (E.ON), David Eskilsson (Göteborg Energi), Håkan Kassman (Vattenfall), Kari Peltola (Amec Foster Wheeler) och Rikard Norling (Swerea KIMAB).

SEBRA, samverkansprogrammet för bränslebaserad el- och värmeproduktion, är efterföljaren till Värmeforsks Basprogram och startade som ett samarbetsprogram mellan Värmeforsk och Energimyndigheten 2013. All forskningsverksamhet som bedrevs inom Värmeforsk ingår sedan den 1 januari 2015 i Energiforsk. Därför ges denna rapport ut som en Energiforskrapport.

Programmets övergripande mål är att bidra till långsiktig utveckling av effektiva miljövänliga energisystemlösningar. Syftet är att medverka till framtagning av flexibla bränslebaserade anläggningar som kan anpassas till framtida behov och krav. Programmet är indelat i fyra teknikområden: anläggnings- och förbränningsteknik, processtyrning, material- och kemiteknik samt systemteknik.

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Sammanfattning

Omblandning av bränsle och syre från förbränningsluften är en av de viktigaste faktorerna som påverkar förbränningsresultatet i termiska kraftverk. Oxygen Carrier Aided Combustion (OCAC) är ett nytt förbränningskoncept med en intressant extra mekanism med potential att förbättra omblandningen mellan bränsle och syre rejält.

OCAC bygger på förbränning i fluidiserad bädd. Idén är att helt eller delvis ersätta det pulverformiga bäddmaterialet (vanligen kvartssand) som används i denna typ av anläggningar med ett kemiskt aktivt syrebärande material. I bränslerika delar av förbränningsrummet kommer det syrebärande materialet att reduceras av bränslet, medan det i syrerika delar kommer att oxideras. Genom att möjliggöra kemisk reaktion mellan bäddmaterialet och bränslet skapas en helt ny mekanism för omvandling av bränslet. Förfarandet medger också för transport av syre i inte bara i rumsdimensionen, utan också i tidsdimensionen.

Denna rapport beskriver OCAC med manganmalm som aktivt syrebärande bäddmaterial. Konceptet har undersökts i två experimentella studier. Den första beskriver beredning av och experiment med fem olika manganmalmer i en mindre labbreaktor, vilken nyttjar bäddmängder i storleksordningen 140-200 g. Bränslet var metan samt metan blandat med ammoniak (det sistnämnda för att undersöka effekt på NO_x-bildning). Den andra studien beskriver försök i en lite större cirkulerande fluidiserad bädd (CFB-panna). Till denna studie införskaffades en större mängd manganmalm (>12 ton). Bränslet var här träflis. Anläggningen kördes i 23 dagar med 10-100% manganmalm i bädden. Av dessa involverade 14 dagar forskningsverksamhet.

Bland annat kan följande slutsatser dras av projektet:

• OCAC-förbränning av biomassa med manganmalm som bäddmaterial uppvisar potential att kunna förbättra prestandan i befintliga fluidiserad bäddpannor.

• För låga lambda (<1.11) uppmättes beroende på inblandningsgrad av manganmalm mellan 5% ökning och 70% sänkning av CO, medan det för något högre lambda erhölls likvärdiga eller ökade CO-halter. Resultaten antyder att en betydande minskning av luft-bränsle-förhållandet för förbränning skulle vara möjlig, utan att mängden oförbränt ökar jämfört med referens.

- 100% manganmalm som bäddmaterial resulterade i kraftigt ökade emissioner av CO och NO jämfört med referensförsök. I kombination med sekundär åtgärd i form av tillsats av elementärt svavel kunde en minskning i CO-emissioner på 60-90% för låga lambda (<1.11) erhållas. Motivet bakom att dosera svavel var att tillföra en alternativ mekanism för att bortföra kalium, då manganmalmen i sig hade hög kaliumhalt och misstänks ha haft begränsad förmåga att adsorbera mer. Men då svaveltillsats vid förbränning i fluidbädd sig kan leda till sänkning av CO-emissioner är det oklart vilka slutsatser som kan dras.
- Efter en tids drift i CFB-pannan ökade emissionerna av CO och NO betydligt. Detta gällde också blandningar av manganmalm och sand. Vi tror att detta var relaterat till ackumulering av askkomponenter i bädden, i huvudsak kalium. Under aktuella försök regenererades bädden sparsamt och inte i samma utsträckning som vid körning med sand. Detta är en faktor som behöver undersökas närmare.

- Ur ett rent operativt perspektiv fungerade manganmalm utmärkt som bäddmaterial i fluidiserad bädd. Inga problem med agglomereringar, nötning eller förslitning noteras.
- Labbexperimenten visade att syrebärande partiklar kunde beredas ur olika malmer. Dessa hade dock mycket olika mekaniska egenskaper. Särskilt densiteten varierade betydligt vilket antyder att inte alla malmer är lämpliga som bäddmaterial utan något typ av förbehandling.

Summary

Mixing of fuel and oxygen from air is one of the most important aspects affecting the combustion performance in thermal power plants. Oxygen Carrier Aided Combustion (OCAC) is a new combustion concept that can be directly implemented in conventional Fluidized Bed boilers with a unique mechanism that potentially can facilitate mixing of fuel and oxygen greatly.

OCAC is realized by partial or complete substitution of the bed material used in Fluidized Bed boilers (usually silica sand) with a chemically active oxygen-carrying bed material. The active bed material will be reduced by fuel in fuel rich parts of the combustion chamber, while it will be oxidized in oxygen rich parts. This adds new possibilities for how fuel can be oxidized and how fuel and oxygen can become mixed. It also adds fundamentally new ways in which oxygen can be transported in the combustion chamber, both in the space dimension and in the time dimension.

In the project described in this report, OCAC using manganese ore as active bed material is examined in two separate experimental campaigns. Firstly, five different manganese ores were prepared and examined in a continuously operating laboratory reactor. The solids inventory in the combustor was 140-200 g and it was operated continuously using methane and methane mixed with ammonia (as NOx-precursor) as fuel. Secondly, one of the materials was chosen and procured in larger amounts (>12 tons) for evaluation in a semi-commercial Circulating Fluidized Bed (CFB) boiler. In total, the CFB boiler was operated for more than 23 days with 10-100% manganese ore as bed material, of which 14 days involved research activities. The following conclusions can be drawn:

- Oxygen Carrier Aided Combustion (OCAC) of biomass using manganese ore as bed material demonstrate potential to be able to improve performance of existing fluidized bed boilers.
- For low air to fuel ratios (<1.11) the measured effect on CO emissions varied from 70% reduction to 5% increase compared to a sand reference, depending on the degree of substitution with manganese ore. For higher air to fuel ratios the CO emissions were comparable or slightly higher. The results suggests that it should be possible to reduce the air to fuel ratio for combustion significantly, without increasing the amount of unburnt compared to reference.
- With 100% manganese ore as bed material the emissions of CO and NO increased substantially. In combination with secondary measure in form of sulphur feeding a reduction in CO-emissions of 60-90% could be achieved for low air-to-fuel-ratios (<1.11). The motivation for this measure was to add an alternate mechanism for removal of potassium, since the manganese ore has a high potassium content and thus could have had poor ability to adsorb more. However, since sulphur feeding in fluid bed combustion in itself can lead to a reduction in CO emissions it is unclear what conclusions can be drawn.
- During multi-day operation in the CFB boiler issues with respect to increasing CO and NO emissions manifested itself. This was true also for mixtures of manganese ore and sand. It is believed that this was related to accumulation of alkali containing compounds, mainly potassium. This could be expected since the bed material was not regenerated to the same extent as during normal operation with sand. This is a factor that needs to be studied further.

- From an operational point of view, manganese ore was shown to perform excellent as bed material in fluidized bed boilers.
- In the laboratory experiments several manganese ores were shown to be viable as oxygen carrier particles, but it was clear that different ores have very different mechanical properties. Especially bulk density varied in a wide range, suggesting that not all ores are suitable for OCAC without pre-treatment.

Glossary

General

CLC = Chemical-Looping Combustion

CLOU = Chemical-Looping with Oxygen Uncoupling

OCAC = Oxygen Carrier Aided Combustion

CFB = Circulating Fluidized Bed

CCS = Carbon Capture and Storage

ppm = Parts Per Million

wt% = Percentage by weight

vol% = Percentage by volume

l_n = Normal litres

λ = air-to-fuel-ratio during combustion

Manganese ores

NCH = Nchwaning

SF-AUS = Sinfin-Australia

SIB-MG = Sibelco-Mangagran

SIB-SF = Sibelco-SF

UMK = United Manganese of Kalahari

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1 Introduction

Mixing of fuel and air is likely the single most important aspect affecting the combustion performance in thermal power plants. Poor mixing between fuel and air results in insufficient rate of consumption of gaseous oxygen, and therefore emissions of carbon monoxide, unburnt hydrocarbons and char particles in the flue gases.

For solid fuel applications such as combustion of biomass very good mixing is not easy to achieve, the obvious reason being the multi-phase nature of the process. Therefore, in order to minimize unwanted emissions and residence time in the combustion part of the boiler, commercial combustion facilities are operated with a considerable excess of air added to the furnace, compared to what is needed for stoichiometric combustion. This is undesirable for several reasons:

1. The increased gas flow increases the dimensions of the combustion facility, which in turn increases its investment cost, capital cost and operational costs.
2. The excess air increases the heat loss associated with the hot flue gas leaving the chimney.
3. The excess air increases the power consumption of equipment such as fans, which in turn increases operational costs.

In practice, the effects of high air-to-fuel ratio includes decreased thermal efficiency, increased fuel consumption, increased environmental footprint and increased cost of generating heat and power. Because of this, it is highly desirable to lower the amount of excess air fed to thermal power plants, as long as emissions of unburnt are kept within acceptable levels.

Common measures include the optimization of burners, fuel feeding and air staging. But such measures will only take you so far, especially for combustion of solid fuels such as biomass and waste. Therefore novel technical solutions to enhance mixing of fuel and oxygen during combustion are of both academic and of commercial interest.

Fluidized bed boilers are very common and represent a commercially attractive technology for combustion of biomass, solid waste, lignite and hard coal. Interestingly, combustion in fluidized beds also offers a unique and very sparsely examined opportunity to apply one additional measure to facilitate the mixing of fuel and oxygen, compared to other combustion techniques.

In fluidized bed boilers the fuel is burnt in presence of fluidized solid particles. For combustion of biomass and waste the bed material consists mainly of almost inert material such as silica sand. For combustion of lignite and hard coal considerable amounts of limestone for sulfur capture and coal ash are also present in the bed. The bed material is important for heat transfer, as thermal flywheel to equalize temperature in space and time, for fluidization and hydrodynamic performance of the reactor and for the absorption of certain elements such as alkali metals. For biomass applications these properties are not necessarily strongly connected to the chemical nature of the bed material, suggesting that switching from sand to something else could be feasible. This insight opens a currently unexplored area of process development.

The fundamental idea behind the project covered in this report is to utilize a chemically active bed material in form of manganese ore that is capable of providing oxygen for the conversion of fuel. This will add a new option for how oxygen and fuel

can be mixed and react with each other in fluidized bed combustors. It will also add a fundamentally new way in which oxygen can be transported, both in the space dimension and in the time dimension. The general assumption underpinning the project is that these new mechanisms would have positive effects on the combustion performance, allowing reduction of the excess air fed to the boiler.

1.1 BACKGROUND

The concept of oxidizing fuels with oxygen provided by solid oxygen carrier materials, rather than with oxygen from air, have several potential applications. For example, it has been suggested and examined for generation of synthesis gas[1], hydrogen[2] and for tar reduction in biomass gasification[3]. In medium and long term the perhaps most interesting application and the one having received most attention is Chemical-Looping Combustion (CLC), which is a combustion technology that would enable carbon dioxide capture without significant costs for gas separation[4]. In CLC the fuel is completely oxidized exclusively with oxygen from a solid oxygen carrier material in particle form, exemplified below by oxidation of methane with manganese (II,III) oxide, see reaction (1).

$$CH_4(g) + 4Mn_3O_4(s) \rightarrow 12MnO(s) + CO_2(g) + 2H_2O(g) \quad \Delta H^o_{298} = 125 \text{ kJ/mol}_{CH4} \quad (1)$$

The products are carbon dioxide, steam and manganese (II) oxide, of which the latter is oxidized to its initial state with air in a separate reactor vessel, see reaction (2).

$$2O_2(g) + 12MnO(s) \rightarrow 4Mn_3O_4(s) \qquad \Delta H^o_{298} = -927 \text{ kJ/mol}_{CH4} \qquad (2)$$

The oxidized material can then be returned to the first reactor vessel and oxidize more fuel. With two reactors with a steady flow of oxygen carrier between them a continuous process can be achieved, see Figure 1.

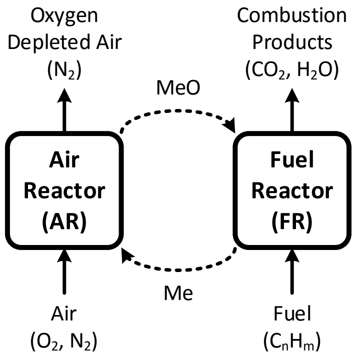

Figure 1. Schematic illustration of Chemical-Looping Combustion (CLC). MeO = oxidized oxygen carrier, Me = reduced oxygen carrier.

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[1] *Rydén M, Lyngfelt A, Mattisson T. Synthesis gas generation by chemical-looping reforming in a continuously operating laboratory reactor. Fuel 2006;85:1631-1641.*

[2] *Rydén M, Lyngfelt A. Using steam reforming to produce hydrogen with carbon dioxide capture by Chemical-Looping Combustion. International Journal of Hydrogen Energy 2006;31:1271-1283.*

[3] *Lind F, Seemann M, Thunman H. Continuous catalytic tar reforming of biomass derived gas with Simultaneous catalyst regeneration. Industrial & Engineering Chemistry Research 2011;50:11553-11562.*

[4] *Adanez J, et al. Progress in chemical-looping combustion and reforming technologies - a review. Progress in Energy and Combustion Science 2011;38:215-282.*

It is easily realized that the sum of reaction (1) and reaction (2) is reaction (3), i.e. ordinary combustion of the fuel with oxygen.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H^o_{298} = -802\ kJ/mol_{CH4} \qquad (3)$$

The most interesting feature with CLC is that mixing between the fuel and nitrogen from air is avoided. Thus pure carbon dioxide for carbon capture and storage (CCS)[5] can be obtained simply by cooling and condensation of steam. It also makes formation of thermal NO_X impossible[6], albeit fuel NO_X may still be a problem for solid fuels.

Some oxygen carriers such as for example manganese (III) oxide are capable of releasing gas phase oxygen directly into an atmosphere with low oxygen fugacity, see reaction (4).

$$6Mn_2O_3(s) \rightarrow O_2(g) + 4Mn_3O_4(s) \qquad \Delta H^o_{298} = 195\ kJ/mol_{CH4} \qquad (4)$$

The mechanism described in reaction (4) is referred to as Chemical-Looping with Oxygen Uncoupling (CLOU)[7]. Oxygen released can react directly with gaseous or solid fuel in what could be described as a “pseudo-oxyfuel” combustion process in accordance with reaction (3). Subsequently the reduced oxygen carrier is oxidized a separate reactor vessel just as in ordinary CLC, and the cycle is complete. The ideal chemical-looping process could very well involve fuel oxidation both via reaction (1) and via reactions (4+3).

Researchers at Chalmers University of Technology are among the leaders in the development of chemical-looping technology and they have more than 15 years of experience in the field. As of late 2015, chemical-looping combustion has been demonstrated in >24 pilot units during >7500 h of operation (of which >4400 h by the group at Chalmers). The main motivation for this considerable research effort is that the cost for carbon dioxide avoidance using CLC would be much lower compared to more conventional technologies. The cost of CO_2 avoidance when using reactor systems similar to ordinary Circulating Fluidized Bed (CFB) boilers have been estimated to about 20 €/ton CO_2 avoided[8], a reduction with at least 50% compared to conventional and commercially available technology such as absorption in aqueous amine solution. There are currently about two dozen laboratory scale CLC plants[9] and the technology has been demonstrated in sizes up to 3 MW[10].

But despite its promises and the relatively swift development it is expected that large-scale deployment of CLC still is several years into the future. Such deployment will require both further development work and perhaps even more crucially, laws and economic incentives for allowing CCS as a technology for climate change mitigation. At present it is unclear when this could be in place.

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[5] *Carbon dioxide Capture and Storage. Intergovernmental Panel on Climate Change, 2005.*

[6] *Ryu HJ, et al. Demonstration of inherent CO_2 separation and no NO_x emissions in a 50 kW chemical-looping combustor: Continuous reduction and oxidation experiments. 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, 2004.*

[7] *Mattisson T, Lyngfelt A, Leion H. Chemical-looping with oxygen uncoupling for combustion of solid fuels. International Journal of Greenhouse Gas Control 2009;3:11–19.*

[8] *Lyngfelt A, Leckner B. A 1000 MW_{th} boiler for chemical-looping combustion of solid fuels - discussion of design and costs. Applied Energy, in press – available online 2015, DOI: 10.1016/j.apenergy.2015.04.057.*

[9] *Lyngfelt A. Chemical-Looping Combustion of solid fuels – status of development. Applied Energy 2014;113: 1869-1873.*

[10] *Revolutionary Chemical Looping Technology Advances Clean Coal. Power Engineering, 11/14/2013.*

While large-scale deployment of CLC does not seem to be imminent, the knowledge gained and oxygen carrying materials developed for the process over the last few years could very well be useful for other purposes. One option would be to use them to improve the performance of conventional facilities for biomass combustion in fluidized bed boilers, which is an important renewable energy technology on its own merit, capable of producing affordable heat and power with small environmental footprint. Such facilities are common in several countries, including Sweden. The concept, which is the subject of this report, will henceforth be referred to as Oxygen Carrier Aided Combustion (OCAC).

1.2 OXYGEN CARRIER AIDED COMBUSTION (OCAC)

Oxygen Carrier Aided Combustion (OCAC) is a combustion concept that could be directly implemented in Circulating Fluidized Bed (CFB) and possibly also in Bubbling Fluidized Bed (BFB) boilers. This makes it a potentially attractive concept for generation of heat and power with biomass as fuel, for which fluidized bed combustion is a commercially attractive and widely used technology.

OCAC is realized by partially or completely substituting the bed material used in conventional fluidized bed boilers (usually silica sand which is practically inert with respect to fuel and air) with a chemically active oxygen-carrying material, similar to what has been used during the development of CLC. The operating principle is straightforward and ingenious and existing boilers do not need extensive redesign. The active bed material will be reduced in fuel rich parts of the combustion chamber, as described in reaction (1). In oxygen rich parts it will be oxidized, as described in reaction (2). Materials capable of releasing gas phase oxygen, as described in reaction (4), would actively release oxygen in parts of the combustion chamber where it is lacking. Basically, the whole chemical-looping cycle will be realized within a single reactor vessel, see Figure 2.

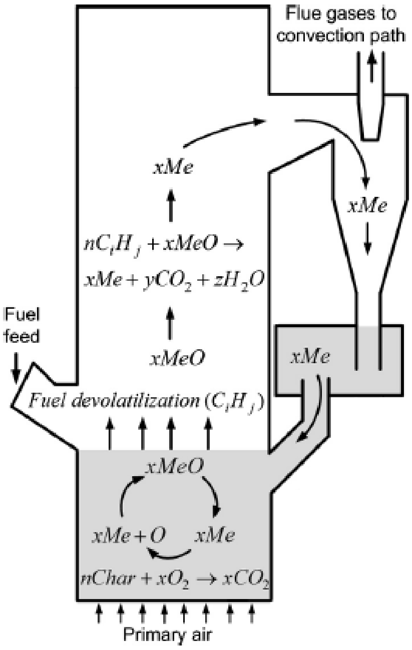

Figure 2. Schematic illustration of Oxygen Carrier Aided Combustion (OCAC) in a Circulating Fluidized Bed (CFB) boiler. MeO = oxidized oxygen carrier, Me = reduced oxygen carrier.

By means of OCAC, several interesting effects could potentially be achieved:

- The oxygen carrying bed material would provide entirely new mechanisms for bringing oxygen to the fuel, in addition to the usual mixing between fuel and air. The effect could be sufficient to significantly even out the oxygen potential throughout the combustion chamber and reduce the emissions of carbon monoxide and unburnt hydrocarbons, especially for combustion with low air-to-fuel-ratio.
- The amount of oxygen retained and available for fuel oxidation in the bed would be very significant, if compared to the air flow and fuel flow. Thus the oxygen in the bed will constitute a buffer, capable of thwarting negative effects of uneven fuel feeding. Thus the active bed material should be capable of evening out the oxygen potential in the combustion chamber, not only in the room space dimensions, but also in the time dimension. This could be a considerable advantage as fuel feeding of biomass can be somewhat problematic, especially in smaller facilities.
- In conventional power plant combustion of more stable fuel components such as methane does not take place in the dense bed in the bottom of the combustion chamber to any larger extent. This is because of the relatively low temperature (≈800-870°C) and huge thermal inertia of the bed, which effectively prevents formation of sufficiently hot flames. This will be completely different when using a bed material that can react directly with the fuel such as in reaction (1). This is because it has been shown in numerous studies[11] about CLC that complete methane conversion inside such beds is readily achieved even without addition of air, as will be the case for OCAC. The apparent reason is that direct reaction between methane and oxygen carrier is not hampered by temperature to the same extent as the homogeneous reaction. It can therefore be expected that conversion also of comparably stable fuel components could proceed rapidly already inside the dense bottom bed[12].
- The temperature profile of the combustion chamber will be affected, both due to improved conversion of methane in the dense bed and due to the reaction enthalpies of reaction (1-4). Direct reactions between fuel and oxygen carrier can be thermo-neutral or even endothermic. This opens up a range of possibilities such as for example heat extraction in the dense bed zone for reduced boiler height. In an unmodified plant the expected effect would be that heat generation will move “up-stream” in the system, resulting in reduced temperatures in the upper part of the combustor and cyclone and increased temperature in the lower part of the combustor such as the dense bottom bed.
- The substitution of bed material could possibly also offer opportunities to reduce problems with agglomeration and corrosion connected to combustion of biomass in fluidized beds[13] and possibly also other types of emissions such as NO_X.

The technological concept OCAC, using the general principles described above, has only very recently been proposed. However, it has already been demonstrated in the 12 MW circulating fluidized bed research boiler at Chalmers University of Technology with very promising results[14]. In that campaign the mineral ilmenite, which is a rich

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[11] *Adanez J, et al. Progress in chemical-looping combustion and reforming technologies - a review. Progress in Energy and Combustion Science 2011;38:215-282.*

[12] *Chadeesingh DR, Hayhurst AN. The combustion of a fuel-rich mixture of methane and air in a bubbling fluidised bed of silica sand at 700°C and also with particles of Fe_2O_3 or Fe present. Fuel 2014;127:169-77.*

[13] *Khan AA, de Jong W, Jansens PJ, Spliethoff H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Processing Technology 2009;90:21-50.*

[14] *Thunman H, Lind F, Breitholtz C, Berguerand N, Seemann M. Using an oxygen-carrier as bed material for combustion of biomass in a 12-MW_{th} circulating fluidized-bed boiler. Fuel 2013;113:300-309.*

titanium-iron ore, was used as oxygen carrier. Ilmenite is one of the most commonly used minerals in Chemical-Looping Combustion research and the one typically used in larger laboratory facilities[15]. It is characterized by being robust and durable, but has quite poor reactivity with fuel gases. Nonetheless, by substituting 40% of the sand bed with ilmenite, up to 80% decrease of carbon monoxide in the flue gases for a given air to fuel ratio could be achieved[14]. This is a remarkable effect. Further, up to 30% decrease in NO emissions could also be observed[14]. The latter could be an effect of less reliance on flame combustion, more even temperature throughout the combustion chamber or a reduction of hot spots. It is also possible that the addition of oxygen carrier material to the bed may have had a catalytic effect boosting NO reduction, as it is well established that some transition metal oxides (in particular Fe) can have this effect[16,17]. Three different ilmenites have also been examined for the OCAC concept in laboratory experiments in a batch fluidized bed[18], with promising results.

Ilmenite is quite affordable (≈150-200 €/ton) and is known to have good mechanical properties. However, as oxygen carrier it has its limitations. It has rather poor reactivity with hydrocarbons and cannot directly release oxygen in gas phase via the CLOU mechanism (see above). ***The aim of this project is to continue to investigate the concept OCAC of biomass, but now utilize oxygen carriers with better reactivity towards hydrocarbons and which are capable of releasing gas phase oxygen via reactions similar to reaction (4). Manganese ore has precisely these properties.***

1.3 MANGANESE ORE AS SOLID OXYGEN CARRIER

In the early years of CLC research the focus was on using synthetic particles with either nickel(II) oxide or iron(III) oxide as active phase[19]. By now it is widely recognized that both approaches have significant drawbacks. Nickel is far too expensive and in short supply and it is also carcinogenic and poisonous. Synthetic iron based particles are expensive to manufacture, especially if raw materials of high purity are used, while scarcely capable of achieving sustained high reactivity with hydrocarbons over numerous redox cycles. Within the CLC community there is still interest in high-performing synthetic particles for some applications, especially materials that can release gas phase oxygen via mechanisms such as reaction (4). Considerable work is carried out with oxides based on mono-metallic or mixed oxides of copper and manganese for this purpose[20,21]. However, these kinds of oxygen carriers are expected to be economically viable only for relatively pure fuels such as natural gas and possibly some niche applications.

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[15] *Ströhle J, Orth M, Epple B. Chemical looping combustion of hard coal in a 1MW$_{th}$ pilot plant using ilmenite as oxygen carrier. Applied Energy 2015, in press, doi:10.1016/j.apenergy.2015.06.035.*

[16] *Yao MY, Che DF. Catalytic effects of minerals on NO$_x$ emission from coal combustion. Energy Sources Part A: Recovery, Utilization, and Environmental Effects 2007;29:1005-16.*

[17] *Ohtsuka Y, Wu Z. Effect of metal cations present naturally in coal on the fate of coal-bound nitrogen in the fixed-bed pyrolysis of 25 coals with different ranks: Correlation between inherent Fe cations and N$_2$ formation from low rank coals. Energy & Fuels 2009;23:4774-4781.*

[18] *Zhao D, Schwebel G, Pour NM, Leion H, Lind F, Thunman H. Laboratory fluidized bed testing of ilmenite as bed material for Oxygen Carrier Aided Combustion (OCAC). 11th International Conference on Fluidized Bed Technology, CFB 2014. Beijing: Chemical Industry Press; 2014. p. 721-6.*

[19] *Adanez, J., et al., (2011), Progress in Energy and Combustion Science, 38, pp. 215-282.*

[20] *Mattisson T. Materials for Chemical-Looping with Oxygen Uncoupling. ISRN Chemical Engineering Volume 2013, Article ID 526375, http://dx.doi.org/10.1155/2013/526375*

[21] *Rydén M, Leion H, Mattisson T, Lyngfelt A. Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling. Applied Energy. 2014;113:1924-32.*

But as for solid fuel application, the focus is now almost exclusively on naturally occurring minerals and to some extent also on industrial waste products. The reason is that such materials have been shown to have performance comparable to that of synthetic iron based particles, while being readily available and much cheaper. Most commonly iron based materials are used. Rich ores such as ilmenite, hematite and magnetite, and iron rich industrial waste from the steel and aluminum industries, are all viable. At Chalmers we have chosen a different approach in the past few years, focusing on the development of manganese based oxygen carriers. We consider ourselves world-leading in this effort, both with respect to synthetic manganese based materials and the use of common minerals. We have shown in several laboratory experiments that manganese ores react much faster with fuels than iron based ores such as ilmenite[22]. We have also successfully operated manganese ores in various pilot reactors[23].

Manganese oxide has considerably higher oxygen transfer capacity per weight (7-10 wt% depending on temperature) compared to iron oxide (3.3 wt%). This is because complete conversion of fuel is possible both for reduction of $Mn_2O_3 \rightarrow Mn_3O_4$ and for $Mn_3O_4 \rightarrow MnO$, while iron is limited to the reaction $Fe_2O_3 \rightarrow Fe_3O_4$. The theoretical performance of different oxide materials can relatively easy be determined by means of thermodynamic equilibrium calculations[24]. Further, pure manganese (III) oxide have the ability to release oxygen directly in gaseous form into inert atmosphere via reaction (4). For manganese ores, which are not pure but also contains elements such as iron and silicon, other even more favorable mechanisms for oxygen release could also be available[25]. From a practical and economic perspective, manganese ores are rich ores which often contains more than 45 wt% manganese, in addition to other potential oxygen carrying components such as iron oxides. This means that the active metal content is similar to iron based ores, while oxygen capacity and reactivity should be much better. Based on our research we believe that no further enrichment will be required to turn manganese ores into highly reactive oxygen carriers. Oxygen carriers based on manganese ores could easily be prepared in very large quantities at low cost, by simply crushing naturally occurring minerals into the desired size range. This is in great contrast to other highly reactive oxygen carriers based on for example copper oxide or nickel oxide. Copper and nickel ores are leaner and often contains just 1-2% (or less) of the desirable metals and thus are not useful as oxygen carriers without extensive (and expensive) enrichment and processing.

For OCAC of biomass, it is likely that cheap and readily available oxygen carriers would be highly favorable or perhaps even necessary. This is because the presence of biomass ash, which is expected to interact with the bed material in various and not necessarily benign ways. For example, in the previous campaign in Chalmers Research Boiler with ilmenite it was noted that alkali metals diffused into the particle core which

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[22] *Arjmand M, Leion H, Mattisson T, Lyngfelt A. Investigation of different manganese ores as oxygen carriers in chemical-looping combustion (CLC) for solid fuels. Applied Energy. 2014;113:1883-94.*

[23] *Linderholm C, Lyngfelt A, Cuadrat A, Jerndal E. Chemical-looping combustion of solid fuels - Operation in a 10 kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite. Fuel 2012;102:808-822.*

[24] *Jerndal E, Mattisson T, Lyngfelt A. Thermal analysis of chemical-looping combustion. Chemical Engineering Research and Design 2006;84:795-806.*

[25] *Rydén M, Leion H, Mattisson T, Lyngfelt A. Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling. Applied Energy. 2014;113:1924-32.*

led to the formation of KTi_8O_{16}[26]. Such effects may very well limit the lifetime of the bed material. In conventional biomass combustion, the sand bed is regenerated and replaced with short intervals (time scale days, often about 30% of the bed is replaced each day). While it is not obvious that this will have to be the same for active oxygen carrier materials, the use of synthetic particles nonetheless seems inconvenient. High-performing synthetic oxygen carriers are likely to be at least one order of magnitude more expensive compared to ores and waste materials so the increased cost would be very significant. That leaves two options, to use rich iron based minerals or rich manganese based minerals. The latter clearly has higher reactivity with fuels and therefore was the choice of study for this project.

1.4 AIM OF THE PROJECT

The aims of the project stated in the applications were:

- To show that it is possible to achieve significantly reduced emissions of CO for a given air to fuel ratio by complete or partial substitution of sand with manganese ore in fluidized bed combustion.
- To show that complete or partial substitution with manganese ore could also contribute towards reduced emissions of NO.
- To study what effect manganese ore has on the practical operation of a semi-industrial circulating fluidized bed boiler.
- To examine a number of manganese ores during continuous operation in a small laboratory reactor system.

The methods utilized were practical experiments with manganese ores as bed material in a semi-industrial circulating fluidized bed boiler (Chalmers Research Boiler, 12 MW_{th}) and experiments in a small laboratory reactor. The goals were to achieve at least one week of operation in the semi-industrial power plant and to examine at least 5 different manganese ores in the small reactor. The goal with respect to process performance in Chalmers Research Boiler was to achieve better results than the previous study with ilmenite as oxygen carrier[27], i.e. better than the 80% reduction in CO and 30% reduction in NO that was achieved with 40% substitution of sand with ilmenite. As for the work in the laboratory reactor, no specific goals with respect to performance were defined. These experiments were meant for allowing testing of different qualities of bed materials and provide some understanding about issues such as attrition during operation. The combination of laboratory experiments and operation in large pilot scale should allow for robust conclusions, with respect to the attractiveness of the proposed concept.

As will be elaborated below, most project goals were achieved and the results are deemed as both scientifically interesting and possible to commercialize in the immediate future. In particular the experiments in Chalmers Research Boiler turned out very well. The one effect that could not be clearly verified was the possibility to reduce NO emissions, which is a topic that will have to be further examined.

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[26] *Corcoran A, Marinkovic J, Lind F, Thunman H, Knutsson P, Seemann M. Ash properties of ilmenite used as bed material for combustion of biomass in a circulating fluidized bed boiler. Energy and Fuels 2014;28:7672-7679.*

[27] *Thunman H, Lind F, Breitholtz C, Berguerand N, Seemann M. Using an oxygen-carrier as bed material for combustion of biomass in a 12-MW_{th} circulating fluidized-bed boiler. Fuel. 2013;113:300-309.*

2 Experimental work

The experimental work was divided into two parts. The first part was carried out in a small laboratory fluidized bed reactor. The focus of this part of the project was to examine a number of different manganese ores, both with respect to how they could be turned into viable oxygen carrier particles, their general properties and their performance in practical operation. The second part involved an experimental campaign in Chalmers Research Boiler, which is a CFB boiler of semi-industrial size. The focus of that part of the project was to generate industrially relevant performance data and get a picture of other relevant factors concerning operability, such as for example attrition behavior and tendency to form agglomerations.

2.1 WORK IN LABORATORY REACTOR

The goal of this part of the project was to prepare at least 5 batches of oxygen carrier particles from different manganese ores and examine them in continuous operation in a small laboratory reactor with the nominal thermal power of 300W.

2.1.1 Aims of experiments in laboratory reactor

The aims of this part of the project were:

- **Manufacturing of oxygen carrier particles from different kinds of manganese ores.** This includes choice of raw materials and handling such as i) crushing, ii) sieving, iii) heat treatment (calcination, sintering). By doing this a qualitative picture is given regarding the behavior of these kinds of materials and challenges with turning them into oxygen carrier particles suitable for use in fluidized bed reactors.
- **Fundamental examination in continuous operation.** This gives a quantitative evaluation of the materials i) capacity to transfer oxygen, ii) reactivity with fuel gases, iii) impact on nitrogen chemistry and iv) attrition behavior. Obtained results were to be compared with results by identical experiments performed with conventional bed material in form of silica sand.

2.1.2 Examined bed materials

Five manganese ores with distinctly different properties was chosen for examination. The elemental compositions of each ores are reported in Table 1. The analysis was performed by an accredited laboratory[28] (ALS Scandinavia) using methods capable of identifying 35 different elements[29]. In Table 1, balance is oxygen. The dominating oxidation state for the main elements after heat treatment should be Mn(II,III), Fe(III), Al(III), Si(IV) and Ca(II). Under this assumption the species balance in Table 1 is correct within a few % points, which is acceptable considering that much of the ores could be expected to consist of mixed oxides. See below for further discussion.

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[28] http://www.alsglobal.se/media-se/pdf/ackrediteringens-omfattning.pdf

[29] http://www.alsglobal.se/miljoanalys/paket/Branslen--aska-och-rokgaser_5/Grundamnen_5/MG-2-Grundamnen-i-aska-efter-syrauppslutningsmalta_3870

Table 1. Elemental composition of the examined manganese ores reported in wt%. Elements present in concentrations lower than 0.1 wt% in any of the ores are not included in the table. The elemental analysis was carried out after heat treatment at 950°C. Balance is oxygen (see below for discussion).

Material	Mn	Fe	Al	Si	K	Ba	Ca	Mg	P	Ti
NCH	42.6	12.0	0.2	1.6	<0.1	1.5	6.2	0.6	<0.1	<0.1
SF-AUS	51.3	10.0	2.3	3.6	1.2	<0.1	0.9	0.2	0.1	0.1
SIB-MG	66.4	3.0	3.1	1.4	0.7	0.3	0.1	0.1	0.1	0.1
SIB-SF	46.2	5.2	3.4	3.7	1.0	0.2	1.9	0.3	0.1	0.2
UMK	62.0	3.8	2.0	0.9	0.6	1.8	0.2	0.3	0.1	0.1

The ores were named according to the company suppling each ore:

- **NCH** = Nchwaning. A rather low grade manganese ore from South Africa. It is characterized by rather high Fe and Ca content, which possibly could be of importance for its oxygen uncoupling properties[30].
- **SF-AUS** = Sinfin-Australia. Intermediate metallurgical product consisting of >85% Australian manganese ore sintered together with slag products. Interesting as oxygen carrier as sintering could be expected to improve mechanical properties considerable compared to unprocessed ores.
- **SIB-MG** = Sibelco-Mangagran. Industrial product provided by Sibelco Nordic that is produced from untreated high grade manganese ores (unspecified but supposedly of Australian in origin). Characterized by very high manganese content and low level of impurities.
- **SIB-SF** = Sibelco-SF. Medium grade manganese ore (supposedly from Brazil) provided by Sibelco Nordic. Calcined before delivery which could be a significant advantage, as will be elaborated below.
- **UMK** = United Manganese of Kalahari. High grade manganese ore from South Africa. One of the largest actor on the manganese ore market today.

The obtained ores represent a wide range of qualities, from low grade to high grade, and from the most important countries for mining of manganese (South Africa, Australia and Brazil). It is not obvious which would be the most appropriate choice for OCAC. It is not given that high-grade ores are to be preferred as lower grade materials have an advantage in price and does not necessarily have less good oxygen carrying or mechanical properties. One motivation for doing screening experiments in small laboratory reactor is to provide a general understanding of the behavior of different kinds of manganese ores.

In order to be used in fluidized bed experiments the ores were crushed in a crushing machine and pre-sieved to the size interval 90-212 μm. The resulting particles were heat treated at 950°C for 24 h. The heat treatment serves two functions. Firstly, the predominant oxide in most manganese ores manganese (IV) oxide is calcined to manganese (III,II) oxide. This is important since the phase transfer from manganese(IV) oxide to manganese (III) oxide occurs at rather low temperature (below 600°C) and is very rapid. Therefore heating of manganese (IV) oxide is associated with massive and rapid O_2 release which weakens its structure or even outright fractures it. Secondly,

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[30] *Rydén M, Leion H, Lyngfelt A, Mattisson T. Combined oxides as oxygen carrier material for Chemical-Looping Combustion with oxygen uncoupling. Applied Energy 2014;113:1924-1932.*

heat treatment induces a certain level of sintering which makes the particles denser, harder and more durable.

The processing of SIB-SF was slightly different compared to the other ores. This material was acquired in very large quantity (>12 tonnes) for operation in Chalmers Research Boiler. The reason for choosing this ore was that it could be provided calcined from the source. In the context of this project, that was a very important advantage because heat treatment in accordance to the method described above is unfeasible for such large amounts of materials. In fact, finding an actor willing to calcine these amounts of materials at a cost that could be covered by the project budget proved to be difficult. Hence SIB-SF was examined in the form it was provided, i.e. pre-calcined to mainly Mn_2O_3 and in a size range deemed suitable for Chalmers Research Boiler of 100-400 μm. The procurement and preparation of this very large batch of material will be further elaborated later.

The elemental analysis of the manganese ores was carried out after heat treatment. Thus the metal fraction of the ores increases as oxygen is released from the solid in gas phase, compared to raw ore taken directly from the mine. The bulk of the remaining fraction not included in Table 1 is oxygen. It is very difficult to determine the precise crystal structure of all phases and compounds involved. This is because ores, which contains a lot of impurities, tend to produce blurry diffractograms when using conventional analysis methods tools such as X-Ray Diffractometry (XRD). Also mixed oxides containing both manganese and iron overlap with their monometallic analogues, further complicating detailed analysis. However, according to thermodynamic equilibrium calculations the dominating oxidation state for the main elements after heat treatment should be Mn(II,III), Fe(III), Al(III), Si(IV) and Ca(II). Under this assumption the species balance in Table 1 is correct within a few % points, which is acceptable considering that much of the ores could be expected to consist of mixed oxides.

The resulting heat treated particles were sieved once more and bulk density was measured as the mass poured into a known volume. The mean particle size and the bulk density of the materials are reported in Table 2.

Table 2. Mean particle size and bulk density of the examined materials. *Data is for the batch to the laboratory reactor. Later a larger batch was produced also for Chalmers Research Boiler which had a slightly lower mean particle size of 200 μm.

Material	Mean particle size (μm)	Bulk density (kg/m^3)
Sand 1	152	1550
Sand 2	127	1420
NCH	139	1130
SF-AUS	158	1990
SIB-MG	142	1880
SIB-SF*	234	1840
UMK	139	1370

In Table 2, two sand samples have been included. These were ordinary silica sands consisting overwhelmingly of SiO_2 and were provided by a company supplying bed material to fluidized bed combustion. These samples were used both for reference experiments and for mixing with ores. It can be noticed that most of the examined ores have considerably higher bulk density than sand. This is not unexpected if we consider than Mn_3O_4 has a solids density of 4.86 g/cm^3, which should be compared to 2.65 g/cm^3 for SiO_2. However, at the same time it can be seen that NCH actually has considerably lower bulk density than sand. Therefore it is evident that NCH is much more porous than sand and the other manganese ores. While this could be an advantage with respect to reactivity, it could also be a disadvantage with respect to hardness and durability.

2.1.3 Experimental setup

The experiments were carried out in a small laboratory circulating fluidised bed reactor designed for a thermal power of 300 W. The experimental setup was initially designed for small-scale operation of the carbon capture technology CLC, described in section 1.1 above. The aim of the design was to produce a compact apparatus for examination of oxygen carrier particles for this technology and therefore the design differs from conventional circulating fluidised bed boilers. The reactor was slightly modified for the current project, but the general characteristics were retained, with effects which will be elaborated below.

The experimental reactor is made of 253MA steel, which is a temperature, creep and deformation resistant stainless steel with the approximate composition 67.9% Fe, 21% Cr, 11% Ni, 1.6% Si and 0.1% C. It consists of three compartments: a combustion chamber, a secondary bubbling bed and a downcomer functioning as a loop seal. The reactor is depicted in Figure 3 with the combustion chamber coloured blue, the secondary bed coloured red and the downcomer coloured green.

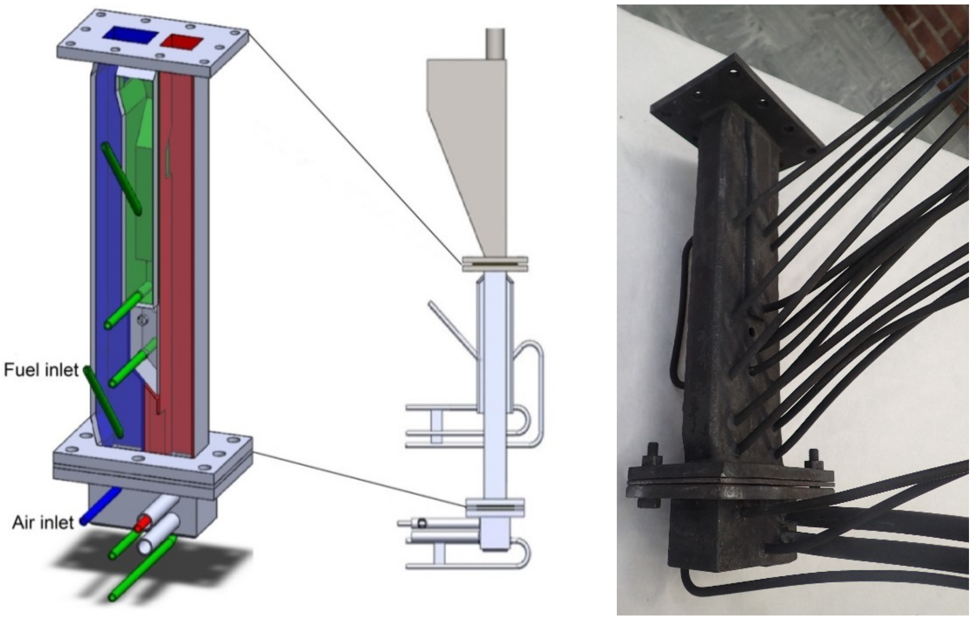

Figure 3. Left: Schematic illustration of the laboratory fluidised bed reactor: open front view to the left and side view including the particle separation box to the right. Right: Photo of the laboratory fluidised bed ractor.

The combustion chamber is divided into two parts with a lower bed section in which the cross section (40 x 25 mm) is larger than in the riser section above the bed (25 x 25 mm). The precondition for achieving solids circulation is a gas velocity in the combustion chamber high enough to carry the particles up from the bed surface and into the narrow riser section. When the gas with the suspended particles exits the combustion chamber it enters a separation box where the gas velocity decreases due to a dramatically increased cross section area. This low-velocity section results in a separation of gas and particles, and the latter will fall back towards the combustion chamber. A certain fraction of these particles will enter the downcomer between the combustion chamber and the secondary bed. The downcomer works as a J-type loop seal (25 x 25 mm) with an overflow exit into the secondary bed. After fluidising in the secondary bed the particles eventually return to the combustion chamber through a lower loop seal located in the bottom of the system between the wind box of the combustion chamber and the wind box of the secondary bed. Thus the reactor system in many ways works as a CFB reactor, but it lacks cyclone and utilize lower gas velocities (>1 m/s). The solids circulation rate between the two reactor parts is typically in the order of 2-3 g/s.

Prior to operation the reactor is filled with particles, typically in the size range 90-212 μm. The amount required depends on the bulk density of the material. In this project the amount of bed materials added to the system was adjusted to get the same bed height before fluidisation (13 cm) in the combustion chamber for all materials. The amounts used corresponded to a bed mass in the combustion chamber of 140-200 g.

The combustion chamber is fluidised with air through the bottom plate, which consists of a sintered permeable quartz plate. The target application for the technology examined in the project is combustion of solid biomass, but the use of solid fuel was not intended with the small reactor setup. Instead gaseous fuel is added through a pipe entering approximately 1 cm above the bottom plate. This option was added specifically for this project and no such function had previously been examined in this reactor.

Porous quartz plates are used as gas distributors in both the combustion chamber and the secondary bed. The secondary bed, the downcomer and the lower loop seal are fluidised with argon. In the loop seals, the fluidising gas is added through small holes in the pipes which can be seen in Figure 3. Since the combustor has a high area to volume ratio, there will be significant heat losses through the walls. Therefore it is enclosed in an electric furnace in order to keep the desired temperature.

The temperature is measured with one thermocouple in the combustion chamber and one in the secondary bed. The thermocouples are located approximately 1 cm above the distributor plate in each compartment. The pressure drops in the system are measured by pressure transducers which are connected to the combustion chamber, secondary bed and the downcomer via pressure legs. The pressure drops are measured in order to be able to assess the fluidisation behaviour and the solids inventory in the different parts of the system.

The reactor system has two outlets. One from the combustion chamber and one from the secondary reactor. Each outlet stream is lead through a particle filter and a gas conditioning unit before entering gas analysers. Methane, carbon monoxide and carbon dioxide are sampled online and analysed using IR-sensors (SICK MAIHAK) while oxygen is sampled online and analysed using a paramagnetic sensor (SICK MAIHAK). Nitric oxide and nitrogen dioxide are also measured online (Emerson X-Stream). The outlet from the combustion chamber is also analysed with a gas chromatograph (Varian micro-GC) which measures hydrogen and nitrogen, as well as the previously mentioned gases except nitrogen oxides. Further, it was calibrated for and has capacity for detecting also dinitrogen oxide, albeit none was detected at any occasion. The gas chromatograph samples gas approximately once every three minutes. For experiments involving examination of nitrogen chemistry, ammonia was measured directly in the gas stream with Dräger tubes. Since both ammonia and nitrogen dioxide are highly soluble in water, the condensate water was collected after each day and sent for an analysis of the nitrogen content. A summary of measuring equipment used can be found in Table 3.

Table 3. Overview of measured gas components, NDIR = Non-Dispersive Infrared Sensor, GC = Gas Chromatography, PMOD = paramagnetic oxygen detector, CL = Chemiluminescence

Gas component	Measuring method
Methane (CH_4)	NDIR, GC
Carbon monoxide (CO)	NDIR, GC
Carbon dioxide (CO_2)	NDIR, GC
Oxygen (O_2)	PMOD, GC
Hydrogen (H_2)	GC
Nitrogen (N_2)	GC
Nitric oxide (NO)	CL
Nitric dioxide (NO_2)	CL
Dinitrogen oxide (N_2O)	GC
Ammonia (NH_3)	Dräger tubes

2.1.4 Experimental methodology

The operation with the five manganese ores was carried out in two larger experimental campaigns:

- The first campaign consisted of operation with a mixture of 50 wt% manganese ore mixed with silica sand and the fuel used was pure methane. Methane was chosen as fuel since it is: i) comparably stable and difficult to oxidize, ii) a major component of biomass volatiles and iii) it decomposes to hydrogen and carbon monoxide which are two other important components of biomass volatiles. The campaign was carried out mainly at 850°C, which is the temperature commonly used for fluidized bed combustion. The campaign involved the use of NCH, SIB-MG and UMK manganese ores and the result were benchmarked to operation with Sand 1 as bed material. The results of this campaign have been summarized in a conference publication[31].
- The second experimental campaign consisted of operation with 100 wt% manganese ore. The fuel used was methane with 3 vol% ammonia, of which the latter was intended as substitute to organic nitrogen. Ammonia was chosen as the nitrogen source as it is the main volatile component originating from the nitrogen content in biomass[32]. Most nitric oxide formed during biomass combustion is

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[31] *Källén M, Rydén M, Lind F. Improved Performance in Fluidized Bed Combustion by the Use of Manganese Ore as Active Bed Material. 22nd International Conference on Fluidized Bed Conversion, Turku, Finland, 2015.*

[32] *Winter F, Wartha C, Hofbauer H. NO and N_2O formation during the combustion of wood, straw, malt waste and peat. Bioresour Technol. 1999;70:39-49.*

formed via release of ammonia, followed by subsequent oxidation to nitric oxide. During operation the combustion chamber was fluidised with a gas mixture consisting of 21 vol% oxygen in argon rather than air, in order to enable a nitrogen balance based solely on the added ammonia. This campaign was carried out at a constant temperature of 950°C. This setup was used for SF-AUS and SIB-SF and the results were compared to operation with 100 wt% Sand 2. Silica sands were used as references in both experimental campaigns since it is a commonly used bed material for circulating fluidised bed boilers.

It is acknowledged that the division into two campaigns with somewhat different operational conditions makes direct comparison between all five manganese ores complex. Therefore this procedure merit some clarifications. The background is as follow:

The first campaign was conducted during autumn 2014 while the second campaign was conducted during spring-summer 2015. During autumn 2014 only preliminary experiments with addition of ammonia were conducted. The reason was unexpected problems related to ammonia-induced corrosion on certain critical parts of the reactor system (gas expansion units, mass flow controllers). We had been lead to believe that the equipment we had access to would endure this, but this proved to be incorrect. Because of this parts of the reactor system needed to be upgraded with ammonia resistant parts, which was done prior two the second campaign. Despite this setback we felt that we needed to proceed and do experiments during the autumn in order to move forward with project implementation. While not optimal, we considered the effect on CO emissions and the operability of the manganese ores to be the most important factors to evaluate.

As for mixing with sand or using pure manganese ore, considerable trial and error was conducted over the course of the project without coming to a final conclusion of what would be most appropriate. The different manganese ores proved to have different fluid properties (density, size distribution etc, see table 2). In the beginning of the project we sought to diminish this effect by using mixtures between sand and manganese ore, but this approach was later dropped for reasons that will be further discussed below. For the campaign in Chalmers Research Boiler both partial substitution and operation with 100% manganese ore was examined, as will be discussed later.

It would have been desirable to do both kinds of experiments with a single oxygen carrier, such as for example perform NH_3 experiments also with SIB-MG or UMK. This was not done since the first campaign was performed with 50/50 mixtures with sand and we lacked sufficient amounts of fresh undiluted material to make a second batch of experiments.

Aside from the division into two campaigns, the general experimental methodology was the same for all experiments. For each campaign the laboratory circulating fluidised bed combustor was first operated with only silica sand as bed material over a course of relevant process parameters. Sand 1 was used for the autumn 2014 campaign while sand 2 was used for the spring-summer 2015 campaign. The reason for changing sand was that insufficient amount of sand 1 was available during the autumn. The sand experiments were later used as reference points for the results from the operation with partial manganese ores.

During operation, the air-to-fuel ratio was varied by keeping a fixed air flow and increasing or decreasing the fuel flow step-wise. Each set of gas flows was maintained for 20 minutes in order to ensure stable operating conditions. The reactor temperature was kept constant at 850°C or 950°C for all experiment, except one experiment with only silica sand as bed material when the temperature was set to 800°C.

2.1.5 Data evaluation

The main data from the experiments used to analyse the performance of the bed materials were the exhaust concentrations of carbon monoxide and nitric oxide as function of air-to-fuel ratio. A nitrogen balance was also done in order to validate the results from the experiments with ammonia in the fuel. Nitric oxide and nitrogen dioxide were continuously measured online and nitrogen and nitrous oxide were measured with the gas chromatograph. Ammonia was measured directly in the gas stream by Dräger tubes. Since both ammonia and nitrogen dioxide are highly soluble in water, the condensate water was collected after each day and sent for an analysis of the nitrogen content.

As mentioned above, the gas concentrations were directly measured during the operation. The air-to-fuel ratio (λ), however, has to be calculated and this can be made by different approaches. The air-to-fuel ratio can be calculated from the volumetric gas flows (V) into the combustion chamber by:

$$\lambda = \frac{l_t}{l_{ot}} \tag{5}$$

l_t = dry air volume added to the combustion chamber ($m_n^3/m_{n,fuel}^3$)

l_{0t} = dry air volume needed for stoichiometric combustion of the fuel mix ($m_n^3/m_{n,fuel}^3$)

The air-to-fuel ratio can also be calculated from either the carbon dioxide concentration or the oxygen concentration out from the combustion chamber. The following expressions are derived from mass balances and fuel data:

$$\lambda = 1 + \frac{g_{ot}}{l_{ot}}\left[\frac{(CO_2)_{ot}}{(CO_2)_t} - 1\right] \tag{6}$$

$$\lambda = 1 + \frac{g_{ot}}{l_{ot}} * \frac{(O_2)_t}{0.2095-(O_2)_t} \tag{7}$$

g_{0t} = dry flue gas volume for stoichiometric combustion ($m_n^3/m_{n,fuel}^3$)

$(i)_{0t}$ = concentration of component i in dry flue gas for stoichiometric combustion (-)

$(i)_t$ = observed concentration of component i in dry flue gas (-)

Both approaches should give a correct value of the air-to-fuel ratio and great care was taken to calibration of the mass flow controllers and gas analysers. However, in practice quite substantial uncertainties was observed nonetheless. The measuring error of the gas analysers is smaller than that of the mass flow controllers so expressions (6-7) could be expected to provide more robust results. Of these expression (7) proved to be less sensitive to minor changes in measured gas concentration and therefore was used here. Further, while operating at specific and measuring air-to-fuel ratio may seem straightforward, it turned out to be a considerable challenge for the experiments performed in this part of the study. As have been explained above the manganese ores contains a lot of oxygen, which potentially can be released from the bed material. The impact of this will be elaborated in section 3 below.

When using expressions 5-7 all gas concentrations had to be recalculated to an argon-free basis, since the theoretical values for exhaust gas flow, air flow and carbon dioxide concentration are valid for an undiluted exhaust gas stream. To recalculate the gas concentrations the following expression was used:

$$x_{i,new} = \frac{x_i}{x_{CO_2}+x_{O_2}+x_{CO}+x_{NO}+x_{N_2}} \qquad (8)$$

where x_i is the measured concentration of gas component *i*.

In addition to gas concentrations and air to fuel ratio, the rate of attrition of each material was also calculated. This was done by measuring the increased weight of the particle filters located downstream the gas exhaust. By taking the bed mass and time of operation into consideration, the breakdown of bed material as function of time could be expressed.

2.2 WORK AT CHALMERS RESEARCH BOILER

The objective of this part of the project was to study the effect of operating a semi-industrial CFB Boiler with manganese ore as bed material. The goal was to operate Chalmers Research Boiler for at least one week, with partial and/or complete substitution of sand with manganese ore. The goal was achieved, yielding very interesting results which are elaborated in section 3 below.

2.2.1 Aims of experiments at Chalmers Research Boiler

The aims of this part of the project were:

- **Procurement of >10 tons of manganese ore suitable for use as oxygen carrier.** This amount was deemed necessary for successfully achieving the project goals. This is also an interesting task in itself as it provides much improved understanding about availability, costs and methods required for full-scale implementation of the OCAC technology.
- **Examine general operability of CFB boiler with manganese ore.** It is not obvious that oxygen carriers based on manganese ore constitutes a suitable bed material for fluidized bed combustion, from a strictly operational perspective. Factors that were deemed as particularly interesting here were attrition behavior, tendency to form agglomerations and tendency to induce fouling of heat exchanger surfaces. All these factors provides certain constrictions on fluidized bed combustion using sand as bed material.
- **Characterization on the effect of emissions.** The goal of the OCAC process is to develop a straightforward method for reducing emissions, mainly of CO at low air-to-fuel ratios, but also of NO_x. Operation of a semi-commercial boiler provides an excellent indication whether these advantages can be realized.
- **Studying effect on different levels of manganese ore substitution.** Due to the presumably favorable oxygen carrying properties of manganese ore, it was assumed that a rather small substitution of sand could have considerable effect on emissions. The goal here was to examine the effect of different levels of substitution, but also of operating the plant with 100% manganese ore.

2.2.2 Procurement of large batch manganese ore

Over the course of the project several potential providers of ores and related services such as crushing and sieving were contacted and evaluated. Needless to say, it was not easy to find someone willing to provide exactly what we wanted in sufficient amount, especially since there were strict limitations with respect to time and cost. However, in the end it turned out well enough.

The manganese ore ultimately chosen for operation in Chalmers Research Boiler was the one with the designation SIB-SF, see Table 1 above. It shall be acknowledged that this was a choice of necessity rather than a free choice. The main reason for choosing this ore was that it could be provided calcined directly from the source. It would have been possible to acquire sufficient amounts of some other ores, such as for example Sib-Mg which performed excellent in the laboratory reactor. However, in the end it turned out that calcination of these amounts of ores was too complicated and costly to realize with the budget and time frame we had at our disposal. Therefore we settled for a pre-calcined material. Nevertheless, SIB-SF is a very typical medium grade manganese ore that should be representative for what ultimately looks likely to be used in large-scale OCAC applications.

Some more background regarding the need for pre-calcination may here be in order. In raw manganese ore the manganese atoms typically exists in the oxidation state +4 or +3, as MnO_2, Mn_2O_3 or Mn_7SiO_{12}. Especially the presence of highly oxidized Mn^{4+} is presumed to be problematic for use in fluidized bed combustion. At temperatures above ≈500°C Mn^{4+} decomposes rapidly to lesser oxidized compounds during the release of gaseous O_2, see reaction (9):

$$MnO_2(s) \rightarrow O_2(g) + 4Mn_2O_3(s) \qquad (9)$$

It is easily realized that addition of fresh MnO_2 to a boiler operating at 850°C, which will be necessary for example during regeneration of the bed, would result in rapid and very substantial release of gas phase O_2 into the boiler, until less oxidised form of manganese oxide reflecting thermodynamic equilibrium at boiler conditions is achieved. This rapid oxygen release would have multiple consequences. The most worrying is the potential for fragmentation or weakening of the particles due to build-up of internal gas pressure. This is a well-known phenomenon from addition of limestone to CFB boilers for sulphur capture, a process during which $CaCO_3$ is rapidly calcined to CaO(s) and $CO_2(g)$ under notable breakdown and weakening of the limestone particles[,33,34]. From research about CLC, there is a substantial amount of anecdotal evidence that the same phenomena could be relevant for manganese ores[35]. While Mn^{3+} could undergo similar decomposition at temperatures above ≈850°C, see reaction (4) above, this process is very much slower and less dramatic and not believed to be a problem of the same magnitude.

With this background knowledge and experience, one of the requirements on the ore we wanted for use in Chalmers Research Boiler was that it should be calcined and hence free from MnO_2. However, it turned out that it was hard to find an actor willing to calcine these amounts of manganese ore at a cost that could be covered by the project budget. The amount of material that needed to be calcined was too large for ordinary laboratory equipment and industrial actors in possession of rotary kilns of suitable size

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[33] *F. Scala, A. Cammarota, R. Chirone, P. Salatino, Comminution of limestone during batch fluidized-bed calcination and sulfation, AIChE Journal 43 (1997) 363–373.*

[34] *F. Scala, P. Salatino, R. Boerefijn, M. Ghadiri, Attrition of sorbents during fluidized bed calcination and sulphation, Powder Technology 107 (2000) 153–167.*

[35] *M. Rydén M, P. Moldenhauer, T. Mattisson, A. Lyngfelt, Attrition of oxygen carrier particles in fluidized bed – basic theory and screening measurements with a customized jet cup test rig. 3rd International Conference on Chemical Looping, Göteborg, Sweden, 2014.*

proved to worry a lot about contamination of their equipment. Because of these factors, the choice ultimately fell on the SIB-SF, as it could be supplied directly as pre-calcined chunks from the source. Hence we did not need to arrange for a separate calcination step.

The procedure for oxygen carrier procurement and manufacturing was as follows:

- The supplier of SIB-SF was the Sibelco Nordic AB. They received the material via their Belgian-based mother company Sibleco, a major global provider of industrial minerals, who in turn acquired the material from an undisclosed source. Based on the chemical composition of the ore it is extremely likely that it is of Brazilian origin, where the main producer is Vale.
- The provided ore was in the form of chunks, a few cm in diameter. One whole truckload of this material was ordered, which was about 25 metric tonnes. The amount ordered was limited to the weight allowed for road transport from provider to middlemen.
- The large chunks were turned into bed material suitable for use in CFB boilers by UVR-FIA GmbH in Freiberg, Germany. This is a Research Institute that focuses on mining operations, mineral processing etc. The procedure consisted of pre-crushing followed by grinding, sieving and dedusting in several stages. The final product was packed on big-bags of 1 tonne each.
- The product was picked up by Sibelco Nordic AB, who repackaged it in their facility in Baskarp. This was in order to be able to blow the material directly into the bed material silo at Chalmers Research Boiler with a blow truck. After repacking the material was delivered to Chalmers.
- The target size of the particles was 100-400 µm, which was readily achieved. The mean diameter of the final material was in the order of 200 µm (based on sieving of a few selected samples). This is somewhat smaller than what was achieved when UVR-FIA produced the test batch for laboratory equipment, see Table 2. The material was pretty much free of fines and dust and the received amount of oxygen carrier particles was 12.1 tonnes, i.e. a yield of almost 50%.

A summary of the properties of the large batch of oxygen carrier material can be found in Table 4.

Table 4. Characteristics of the large batch of oxygen carrier for Chalmers Research Boiler.

Material	SIB-SF
Chemical composition	46.2% Mn, 5.2% Fe, 3.7% Si, 3.4% Al, 1.9% Ca, 1.0% K, 0.3% Mg, 0.2% Ba, 0.2% Ti, 0.1% P, balance O
Provided as	Sintered lumps, a few cm in diameter
Treatment	Crushing, multi-step grinding, sieving, dedusting
Product sieved to size	100-400 µm
Mean particle size	200 µm
Bulk density	1840 kg/m^3
Batch size	12.1 tonnes
Yield in production process	≈ 50%

The raw material cost for the sintered manganese ore SIB-SF was 480 €/tonne. The price for unprocessed manganese ore generally is below 200 €/tonne (2015). This shall be compared with the price of silica sand typically used in CFB boilers, which is in the order of 50 €/tonne. Crushing and sieving in laboratory environment was a very considerable cost in the current project but would likely be smaller if done in large scale and in proper industrial environment. So while it is clear that manganese ore is more expensive, it is not obvious that partial substitution would end in greatly increased costs for bed materials. This will be elaborated in the discussion section below.

2.2.3 Experimental setup

The experiments were performed in Chalmers Research Boiler, which is a semi-industrial CFB-boiler/gasifier reactor system owned and operated by Akademiska Hus AB that is located at Campus Johanneberg of Chalmers University of Technology. It is typically fired with wood chips, although the fuel flexibility of the facility is very good.

The boiler is designed for a maximum load of 12 MW, when using coal as fuel. When using wood chips the maximum load is about 8 MW. Most often the boiler is operated at the slightly lower load of 5-6 MW.

Chalmers Research Boiler produces mainly hot water for district heating, with the major part of the produced heat being consumed within the campus and the remaining part being sold to Göteborgs Energi in accordance with an existing agreement and provided to the city grid. The Division of Energy Technology has an agreement with the plant operators that allows us to use the boiler in research activities. The boiler is operated around the clock during the colder half of the year, typically from November to April, when there is heavy demand for domestic heating. A schematic description of the boiler can be found in Figure 4.

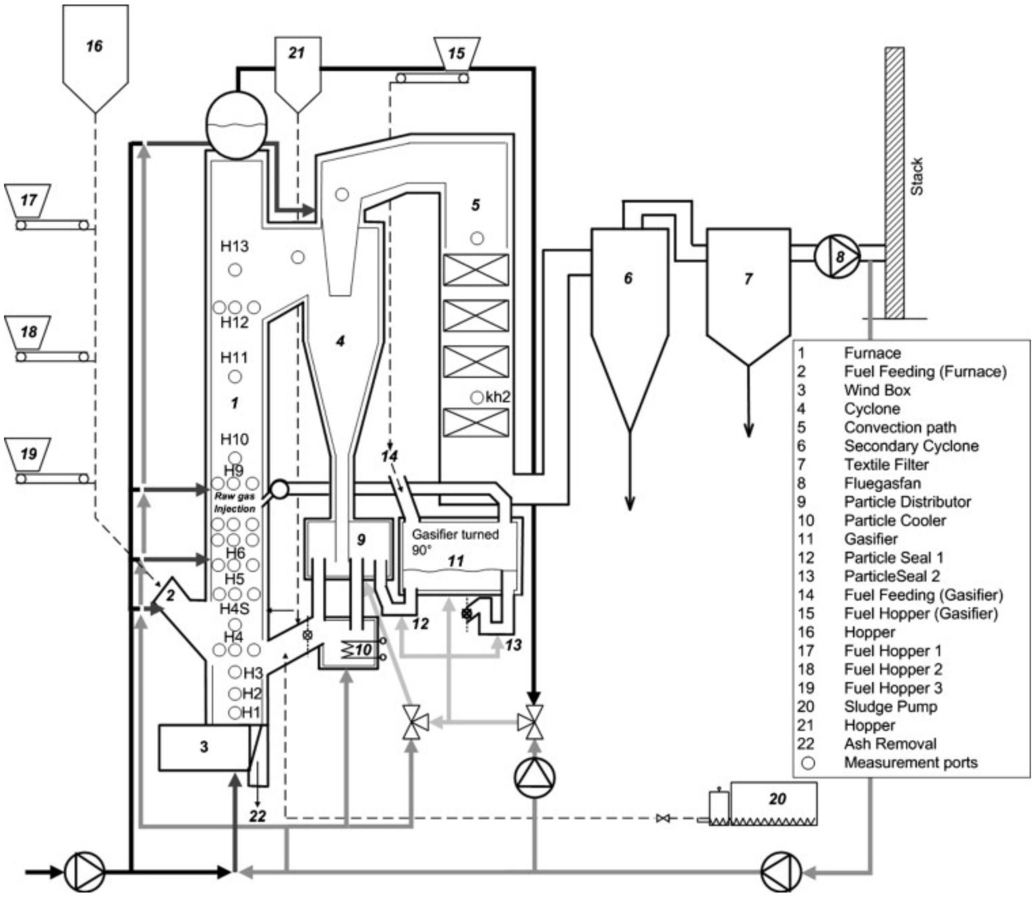

Figure 4. Schematic description of Chalmers Research Boiler/gasifier reactor system.

Regarding the components of the boiler, as depicted in Figure 4: the furnace (1) has a square cross-section of 2.25 m^2 and a height of 13.6 m; the fuel is fed at the top of the furnace bed via the fuel chute (2); the entrained bed material is separated from the flue gases in the water-cooled cyclone (4); and then transported to the particle distributer (9); through the particle distributer, it is possible to re-circulate the bed material back to the combustion furnace either via the gasifier (11) or the external particle cooler (10); the flue gases leave the furnace via the cyclone into the convection path (5), where the gases are cooled in heat exchangers using water, which is subsequently used for district heating; the flue gases that exit the convection path are cleaned of ashes in a secondary cyclone (6) and thereafter using bag filters (7).

About 25% of the total fuel load to the system can be fed into the indirect gasifier instead of the boiler. Approximately 70% of the fuel fed to the gasifier (14–15) is converted into a raw gas, and the remaining char follows the bed material back to the boiler where it is combusted together with the fuel fed to the boiler. The produced raw gas is then directed to the center of the furnace freeboard where it is injected and combusted. However, this aspect will not be discussed in this report, as the gasifier was not used for these experiments.

The combustion process can be followed in detail by monitoring a range of parameters throughout the furnace body such as i) gas composition, ii) temperature, iii) pressure, iv) solids inventory.

Gas compositions are measured using three parallel systems, measuring at three different locations. Each measuring system basically uses the same range of instruments and measures the same components as reported for the laboratory experiments in Table 3. However, NH_3 is not analyzed and the systems at the research boiler also have Flame Ionization Detector (FID) for measurement of total hydrocarbons (THC). The A system is measuring in the chimney while the B and C can be assigned to different measuring points. In the experimental campaigns reported here, the B system has been measuring in the convection path at location (location kh2 in Figure 4). In practice, the readings of the A system and the B system are almost identical. However, all data reported have been measured with the B system in the convection part The C system was mostly assigned to measure in the particle distributor (point 9 in Figure 4) and the readings here have no practical bearing on the conclusions of the study and will not be further discussed in this report.

Further, combustion gases can also be extracted in-situ by inserting a gas sampling probe through dedicated ports located throughout the furnace, referred to as H1–H13 in Figure 4, upstream and downstream of the cyclone, in the convection path, and downstream of the flue gas fan. The gas sampling probe is an electrically heated tube mounted inside a water-cooled jacket. The tip of the probe is equipped with a high-temperature filter, to prevent particles entering the gas analysis system. The gases are transported in heated Teflon tubes from the probe to the analysis instruments through an electrically heated pump. While the opportunity to do this kind of experiments was considered, it was not part of the original project plan and not done at this occasion. As the campaign turned out focus ended up elsewhere. In future projects, this opportunity could be utilized to provide improved understanding of fuel conversion inside the boiler.

2.2.4 Experimental methodology

The experimental methodology used for the experiments in Chalmers Research Boiler was rather straightforward. The goal was two-fold:

1. To study the use of manganese ore as bed material in a circulating fluidized bed boiler, with respect to operability and general behaviour.
2. To study the effect of a reduced availability of oxygen in the boiler in order to establish whether manganese ore would provide benefits (with respect to emissions) compared to sand, especially at reduced air-to-fuel ratio.

Point 1 was studied by overall observations and measurement of key operational parameters over the course of the experimental campaign. The following points actively measured and considered:

- Temperature at key locations in the boiler. This should show whether manganese ore facilitates fuel conversion in the dense bed and if less combustion takes place in the cyclone, compared to when sand is used.
- Pressure drop over key components. This shows whether the bed performs as expected or if it has tendencies to agglomerate. Also provides a first indication if there is excessive attrition of the bed material.

- Amounts of elutriated solids captured in the secondary cyclone and the subsequent textile filter. Will provide an imperfect measure about rate of attrition.

Further, over the course of the solid samples was collected in order to provide enhanced insights about practical and operational issues. This was necessary in order to establish an improved mass balance over the boiler and to monitor aging of bed material, adsorption of ash components etc. Each day samples were collected at the following locations:

- Bed material taken from inside boiler during operation. This was done using a special cooled collection probe and allows monitoring of the properties of bed material, as function of time.
- Ash samples from the secondary cyclone. This materials constitutes a rather course fraction of materials elutriated from the system during operation. Should consist of fly-ash and possibly bed material.
- Ash samples from textile filter. Consists of fine material elutriated from the system during operation. Should consist of fly-ash and possibly bed material.

The solid samples briefly examined in-house, albeit the current project did not include sufficient resources for a detailed characterization. Bed agglomeration tests in order to determine tendencies to agglomerate at severe conditions was performed by SP (Sveriges Tekniska Forskningsinstitut) on four samples and will be described in section 3.2.5 below.

Point 2 from above was studied by performing dedicated so called lambda experiments, which involved a step-wise reduction of air-to-fuel ratio during operation. The control system of the boiler regulates the oxygen concentration in the flue gases by adjusting the rate of fuel feeding. Further, it is possible to regulate temperature by changing the amount of flue gas recirculated to the boiler. The procedures during lambda experiments were as follows:

- The air flow was kept constant at 2.15 kg/s.
- The baseline fuel flow was in the order of 1800 kg/h, corresponding to roughly 5 MW_{th}. This is a very typical load for the boiler and corresponds to about two thirds of the maximum load when wood chips is used as fuel. The flow was adjusted depending on current moisture content in order to achieve an outlet oxygen concentration of 3.5 vol%.
- The set point for the oxygen concentration was step-wise decreased. This resulted in that the regulator system increased the fuel flow.
- The boiler is normally operating with an outlet oxygen concentration of 3.5 vol%, which was decreased in 0.5 vol% steps down to 1.5 vol%. Each operating point was kept until the oxygen concentration had stabilized around a certain level for at least 10 min.
- The target temperature was 870°C in the dense bottom bed. Flue gas recirculation was increased if necessary, but most often this option did not need to be used.

The measured emissions could then be expressed as function of air-to-fuel-ratio, by use of equation (6) or equation (7).

The fuel during all experiments were wood chips provided by Sjögårdens Energiflis AB. The wood chips was produced by chopping rather than crushing and therefore has a comparably uniform size distribution of 20-40 mm, lacking longer splinters. Since it is a commercial product the precise quality varied slightly over the course of the campaign. However, the raw material was overwhelmingly softwood (pine, spruce). The moisture content was measured each day and was in the range 33.6-42.1 wt%.

3 Results

3.1 RESULTS FROM WORK IN LABORATORY REACTOR

All results from the operation with the manganese ores in the laboratory reactor, as well as with the reference silica sands, are presented in this section. The results include fuel conversion, nitric oxide emissions and attrition behaviour of the active bed material.

3.1.1 1st campaign - experiments with methane as fuel

The results of this campaign have been summarized in a conference publication[36]. Sand 1 was used as reference bed material for the first experimental campaign. The air flow was kept 4.1 l_n/min and the methane flow was varied between 0.32-0.44 l_n/min. The variation of air-to-fuel ratio was carried out at two temperature levels: 800°C and 850°C. The concentrations of carbon monoxide and oxygen measured in the exhaust gases are shown in Figure 5.

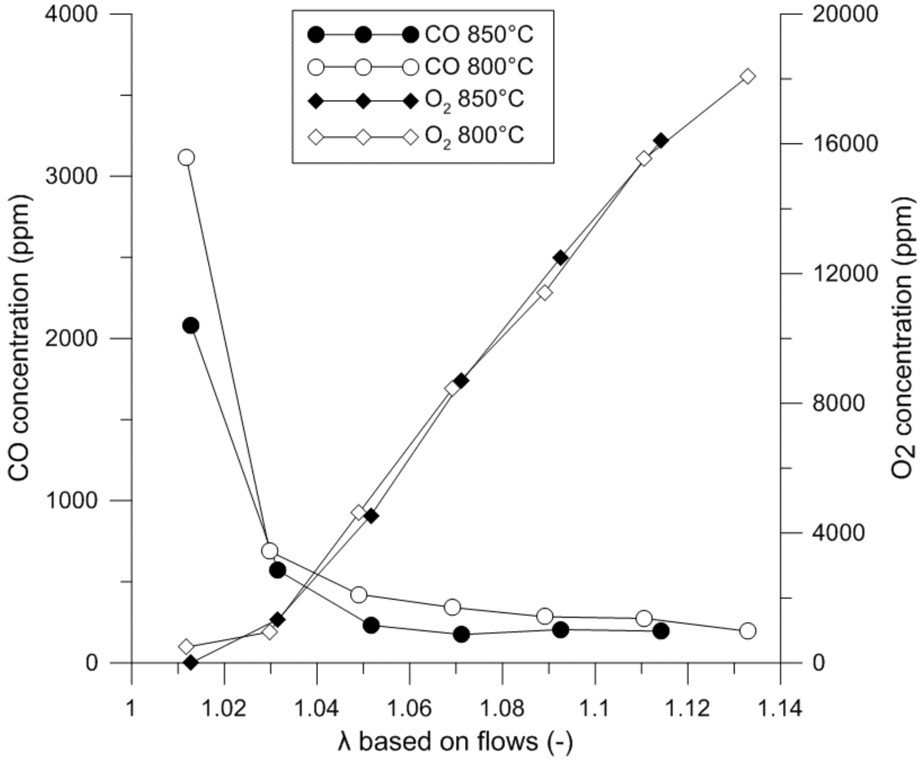

Figure 5. Measured outlet concentration of carbon monoxide and oxygen as a functions of air-to-fuel ratio based on flows during operation with sand as bed material.

In Figure 5, it can be seen that the carbon monoxide concentration remained at a rather stable level (≈200-300 ppm) until the air-to-fuel ratio was decreased below 1.05. This is

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[36] *Källén M, Rydén M, Lind F. Improved Performance in Fluidized Bed Combustion by the Use of Manganese Ore as Active Bed Material. 22nd International Conference on Fluidized Bed Conversion, Turku, Finland, 2015.*

somewhat higher than what one may have expected, but seems to constitute sort of a baseline for the reactor setup used. As have been explained above, conversion of methane in fluidized bed is complicated due to the thermal inertial of the bed material. For air to fuel ratios below 1.05 the carbon monoxide emissions increase rapidly to several thousand ppm.

As for the measured oxygen concentration, it decreases continuously and was almost zero when the air-to-fuel ratio was close to 1. This is in accordance with what could be expected. As can be seen in the figure, there was only minor difference between the two temperature levels, except for the carbon monoxide concentration at the lowest air-to-fuel ratio. The emissions were slightly higher for the lower temperature, as could be expected. Therefore it was decided that all other experiments in the first experimental campaign were to be carried out at 850°C. This was also deemed as the most relevant temperature for the target application, i.e. combustion of biomass in fluidized bed.

Following the experiments with sand, the same procedure was carried out with three different manganese ores. After certain trial and error it was decided to use a mixture of 50 wt% ore and 50 wt% sand (“sand 1”). It was also decided to vary the oxygen carrier mass so that a uniform bed height (13 cm) was obtained for all experiments, rather than to use a constant mass of oxygen carrier. The ores used were SIB-MG, UMK and NCH. SIB-SF was not used since it was not available during the initial campaign. SF-AUS was not used since it was available in small amount, so examining it with ammonia addition was prioritized. Of the three examined manganese ores, the experiments with SIB-MG and UMK turned out very well. The experiments with these ores were run over 3-5 days for each material.

In contrast, the experiments with NCH mixed with sand did not work properly. This was realized rather early, as not only carbon monoxide but also methane was detected in the outlet when the air-to-fuel ratio was lowered to 1.05. This was profoundly different compared to experiments with SIB-MG and UMK and could possibly have been caused by a poor contact between the fuel and air in the combustion chamber. Because of the very poor performance, the experiment was aborted and the reactor disassembled. Since no obvious reason for the behaviour could be found the reactor was reassembled and the experiments repeated, with the same result. The fact that the poor performance was repeatable and that no obvious physical phenomena such as for example agglomeration of bed material was experienced suggests that the effect was due to unfavourable hydrodynamic performance of the reactor under the conditions used. Pressure measurements in the reactor indicate that there was no particles present in the upper part of the reactor during experiments with NCH, which is in contrast to the other experiments performed. Also the pressure drop in the lower part of the reactor was low and also displayed low variance. These observations suggests that addition of fuel may have contributed to blowing particles away in the reactor zone, allowing formation of separate paths for fuel and air and poor mixing. This seems much more likely to be feasible for NCH compared to SIB-MG and UMG, due to the very low density of this material. Another possible explanation could be large bubbles forming slugs in the high narrow bed in the combustion reactor. The reactor system used is known to be susceptible to slugging and the very low bulk density of NCH could increase the chances for this occurring. Slugging could allow for sufficiently poor mixing in the upper part of the reactor to result and the much greater level of emissions experienced with this manganese ore. Because of the irate behaviour no results are presented for this material.

During the initial campaign, no ammonia was fed to the reactor, for reasons which have been explained in section 2 above. In combination with the rather low temperature this means that there should be no formation of nitric oxide and none was detected. Therefore, the emission of immediate interest was carbon monoxide. Measured concentrations as the air-to-fuel ratio was decreased are shown in Figure 6 for SIB-MG and for UMK. The operation with 100 wt% "Sand 1" has also been included as a reference.

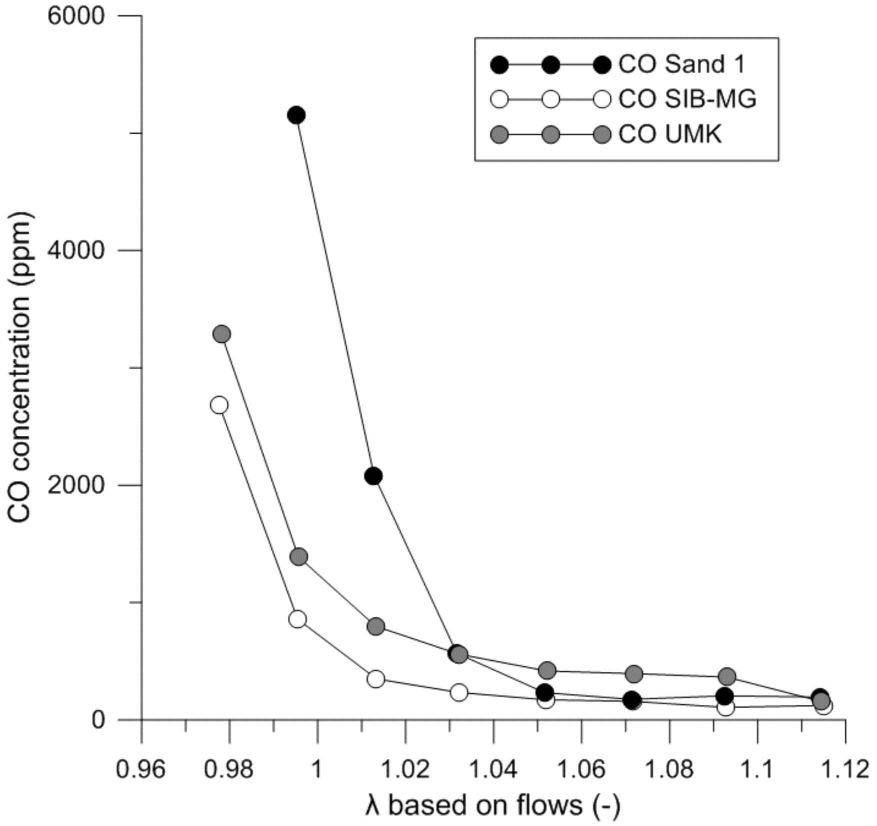

Figure 6. Measured outlet concentration of carbon monoxide as a function of the air-to-fuel ratio based on flows during operation with 100 wt% Sand 1, 50 wt% UMK ore in sand and 50 wt.% SIB-MG ore in sand. The temperature was set to 850°C.

In Figure 6, it can be seen that a dramatically reduced carbon monoxide emission was achieved for low air-to-fuel ratios when manganese ore was used as bed material, compared to when sand was used. This is in accordance with what could be expected. Switching from inert to active bed material should improve fuel conversion via several mechanisms. Direct reaction between bed materials in fuel inside the dense bed should now be possible and the bed material should contribute to distributing oxygen more evenly throughout the combustion reactor.

However, in Figure 6 it can also be seen that at several of the higher air-to-fuel ratios, the concentration of carbon monoxide was higher for UMK ore than for sand. This is unexpected, for the same reasons as pointed out above. The most likely explanation is that this was caused by hydrodynamic effects such as slugging in the combustion chamber. As have been explained above the experimental setup uses high thin beds and thus is susceptible to such behavior. This is not a very satisfying explanation, but as of this moment this is our belief.

The measured outlet concentrations of oxygen for the same experiments are shown in Figure 7.

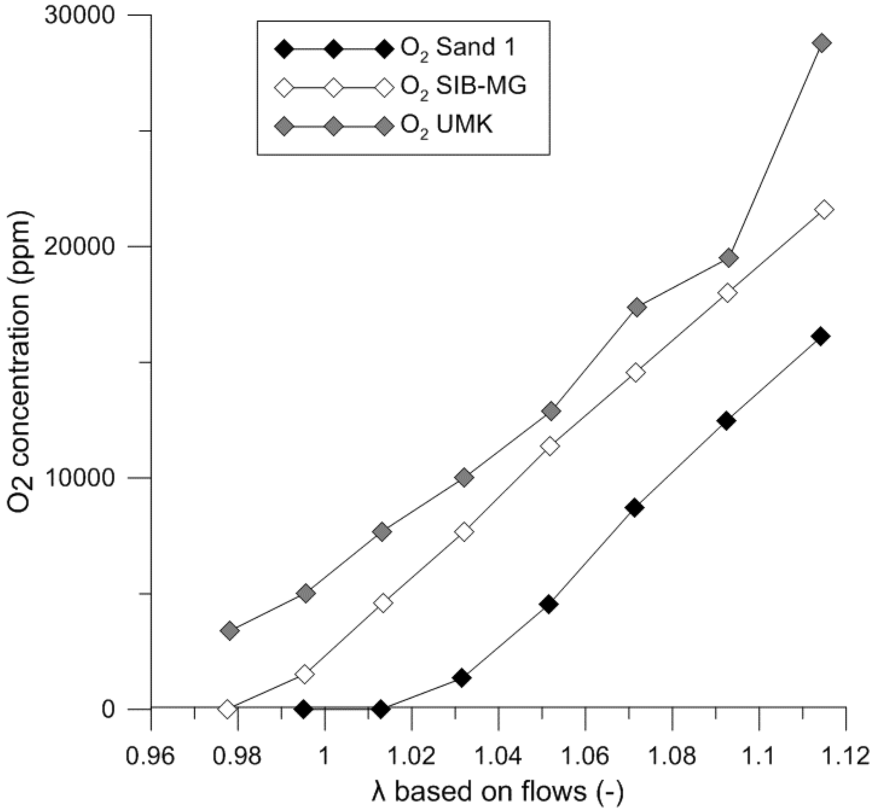

Figure 7. Measured outlet concentration of oxygen as a function of the air-to-fuel ratio based on flows during operation with 100 wt% "Sand 1", 50 wt% UMK ore in sand and 50 wt% SIB-MG ore in sand. The temperature was set to 850°C.

In Figure 7 it can be seen that both manganese ores provided higher concentrations of oxygen in the exhaust gas than sand. This is obviously a very important observation as it shows the effect of the oxygen release ability of the manganese ores during fuel addition. ***However, it also shows that the experiments with manganese ores may not have been conducted at true steady state conditions.*** At the true steady state, the amount of oxygen leaving the reactor for a given flow should be the same as for experiments with sand. Instead, the oxygen buffer in the bed appears to have been contributing actively to fuel conversion, leaving more oxygen in the outlet gas than what could have been expected. The presence of more oxygen in the exhaust compared to the experiments with sand suggests that the bed material is in average continuously slowly reduced, a topic that will be further discussed in numerical terms below.

Both SIB-MG and UMK was also capable of releasing gaseous oxygen in inert atmosphere at 850°C. This was shown by fluidizing all parts of the reactor system with argon. During such conditions the measured outlet oxygen concentration stabilised at 3000-8000 ppm. These numbers are not true equilibrium concentrations and are also influenced by factors such as argon added to the downcomer. But it clearly illustrates that the ores not only are capable of direct solid-gas reactions with fuel gases, but also are capable of releasing gas phase oxygen, if the surrounding oxygen fugacity is low. This means that in theory, the oxygen concentration in a combustion zone where an excess of such particles occur should not fall below these numbers. This could potentially greatly reduce emissions of unburnt.

The oxygen release phenomena described above are obviously somewhat problematic when evaluating the experimental results. The amount of oxygen available in the bed is very considerable compared to what is needed for combustion of the fuel. For example, a rich manganese ore such as SIB-MG has an oxygen carrier capacity of up to 10 wt% (corresponding to reduction of Mn_2O_3 to MnO). With 200 g such manganese ore in the bed this is sufficient oxygen for complete oxidation of 0.25 l/min methane for roughly 1 hour. During OCAC an overwhelming majority of the oxygen will be provided with the combustion air instead, meaning that it would take tens or even hundreds of hours to reach true steady state conditions. This illustrates both the immense potential benefit with oxygen carrying bed materials in fluidized bed combustion and why extensive experiments at true steady state conditions could not be achieved in the experimental campaigns reported here.

As was described in the methodology section each data points included in the figures above represent the average of 20 min of operation at stable conditions. In order to examine whether these results could be expected to be greatly influenced by being performed at non-steady-state conditions, experiments with longer duration and fixed parameters were also carried out. The result of two such experiments are shown in Figure 8 below.

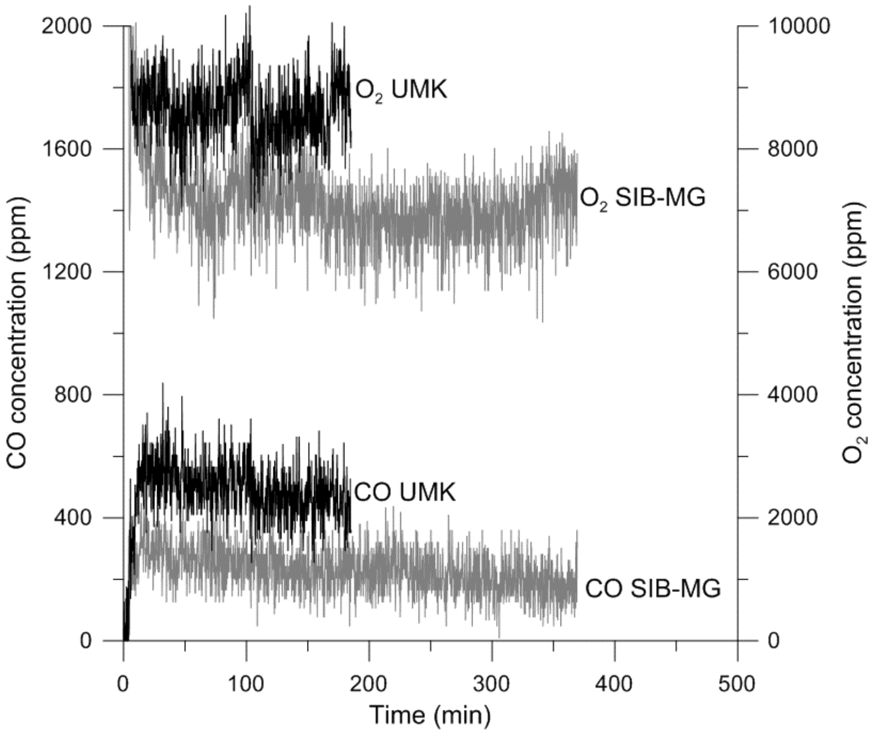

Figure 8. Measured outlet concentrations of carbon monoxide and oxygen during operation with 50 wt% SIB-MG ore in Sand 1 and with 50 wt% UMK ore in Sand 1 at a constant air-to-fuel ratio of 1.05 (based on flows). The temperature was set to 850°C.

As can be seen in Figure 8, the outlet concentrations of both carbon monoxide and oxygen were reasonably stable and at the same levels as for the base experiments. Both carbon monoxide and oxygen seems to decrease slowly as function of time, but in reality the decrease is small and basically within the margin of error. The instruments used are calibrated at start-up each day, but slow drifting over the course of hours is commonly occurring. So Figure 8 seems to suggest that the decrease in oxygen content of the bed material is too slow to influence the results, or that it is not a factor greatly influencing the results.

The air-to-fuel ratios reported in Figures 5-7 above are calculated from the flows entering the combustion chamber, i.e. via reaction (5). As was explained in section 2.1.5 above it is also possible to calculate air-to-fuel ratio based on gas concentrations, for example from the measured oxygen concentration via equation (7). This would provide a ***λ based on concentrations*** in which the ***oxygen provided by the oxygen carrier has been internalized***.

In Figure 9, the carbon monoxide concentrations are shown as functions of the air-to-fuel ratios calculated from the outlet oxygen concentration on an argon-free basis. This is basically Figure 6, but with oxygen provided from reduction of the oxygen carrier internalized in accordance with equation (7).

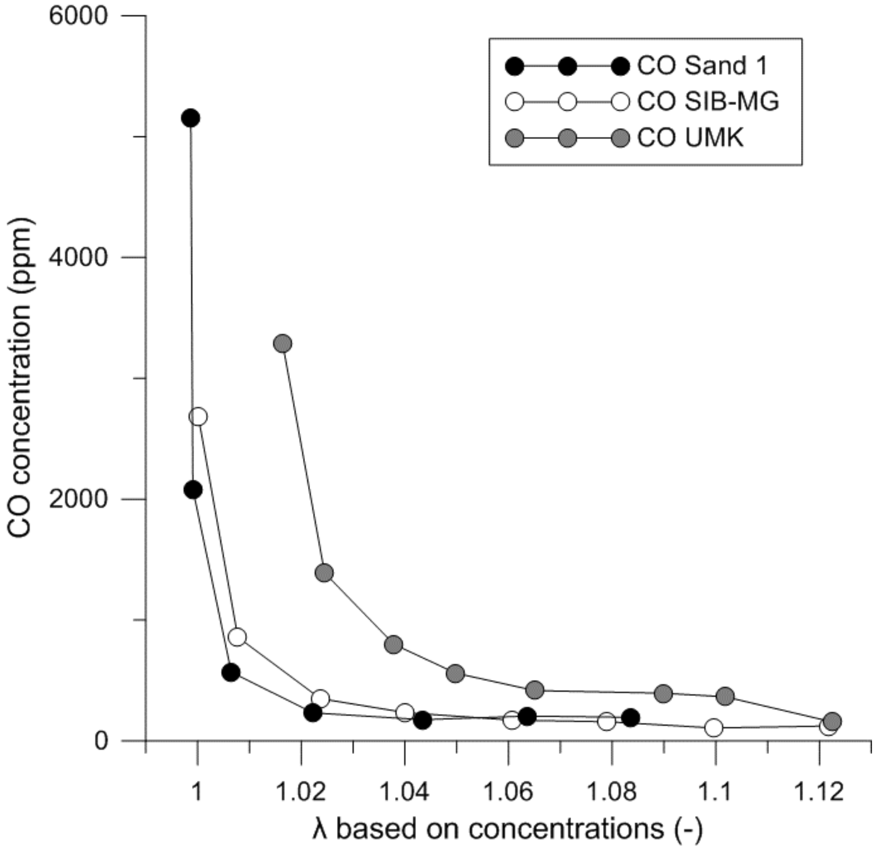

Figure 9. Measured outlet concentration of carbon monoxide as a function of the air-to-fuel ratio based on oxygen concentrations during operation with 100 wt.% Sand 1, 50 wt.% UMK ore in sand and 50 wt.% SIB-MG ore in sand. The temperature was set to 850°C.

Interestingly, when we use this method for calculating the air-to-fuel ratio the strong decrease in carbon monoxide concentration for the mixtures of manganese ore with sand can no longer be seen. In fact, 100 wt% "Sand 1" and SIB-MG seem to perform rather equally. This can be interpreted as that it does not matter for the combustion results whether oxygen is provided by the air or by the oxygen carrier. Now it is clearly shown in Figures 6-8 that the oxygen carrier does provide extra oxygen to the process which, as could be expected, reduces CO emissions. But the question remains whether this effect will still be there when the true steady state is reached. That is a question that these experiments cannot answer. As for the experiments with UMK, Figure 9 emphasises previous observations, namely that the combustion performance was poor when this manganese ore was used. While UMK is capable of carrying extra oxygen to the fuel, seen in Figure 6-8, the emissions for a given amount of oxygen is in fact larger than for sand, see Figure 9.

In order to examine attrition behaviour, the particle filters located downstream the reactor before the gas analysis equipment and the chimney, were weighed before and after the six hours of operation of SIB-MG shown in Figure 8. The amount of fines produced during this day was assumed to consist only of manganese ore. The loss of manganese ore would then be 0.027 wt%/h which would correspond to a particle lifetime of 3 700 h for the SIB-MG ore. This is very much longer than the typical turnover time in circulating fluidised beds, where sand typically has a residence time in the boiler of only a few days. The other ores examined did not generate excessive amounts of fines either.

This was good news. Early CLC experiments with manganese ore as oxygen carrier in this type of reactor typically resulted in massive attrition[37]. It is possible that the less reducing conditions used for OCAC may be one reason for the better performance, but we also believe that pre-calcination of the ore is important. Preventing dissolution of MnO_2 in the reactor and avoiding the weakening of the particle structure related to this reaction should definitely be positive with respect to attrition resistance and is a phenomenon that merits closer examination. To summarize, the experiments in the laboratory reactor suggests that attrition may not be a big concern.

However, it shall be pointed out that the reactor used for these experiments lacks cyclone and use rather low gas velocities (below 1 m/s). An industrial facility use higher gas flows (≈ 3-5 m/s), high velocity nozzles, cyclones and other arrangements that could result in greater mechanical stresses[38]. Therefore the experiments at Chalmers Research Boilers will be of greater interest when it comes to attrition behaviour.

3.1.2 2nd campaign - experiments with methane and ammonia as fuels

The second experimental campaign was carried out with 3 vol% ammonia added to the fuel. The ammonia was premixed with methane in a separate gas bottle. The reason for adding ammonia has been briefly outlined above. Basically, ammonia is considered as the main precursor for formation of nitric oxide during biomass combustion. During pyrolysis, a substantial fraction of the reactive fuel-nitrogen is removed from the fuel as

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[37] *Rydén M, Lyngfelt A, Mattisson T. Combined manganese/iron oxides as oxygen carrier for chemical looping combustion with oxygen uncoupling (CLOU) in a circulating fluidized bed reactor system. Energy Procedia 2011;4:341–348.*

[38] *Rydén M, Moldenhauer P, Lindqvist S, Mattisson T, Lyngfelt A. Measuring attrition resistance of oxygen-carrier particles for chemical-looping combustion with a customized jet cup. Powder Technology 2014;256:75-86.*

ammonia, which in subsequent steps is partially oxidized to nitric oxide. Because of this, ammonia is commonly added to fuels when examining nitric oxide formation in combustion.

The use of ammonia required certain changes to the reactor system for corrosion reasons, notably mass flow controllers and pressure regulators needed to be replaced. Further, the use of ammonia caused problems in the calibration procedures for the mass flow controller. The method used includes passing the gases through a detergent solution of water, which cannot be carried out with the ammonia containing gas as it would dissolve in the water. Therefore the calibration values for pure methane had to be used. However, it turned out that the addition of ammonia in the gas resulted in a slightly different mass flow of gas than pure methane did. Therefore the air-to-fuel ratio was not calculated from flows for the second campaign. Instead the air-to-fuel ratio based on measured gas concentrations had to be used.

The focus of the second campaign was to examine the potential effect on the emissions of nitric oxide. In order to do this, we needed to establish operating conditions for which a reasonable level of emissions would be experienced for the reference case sand. After trial and error, it was decided to perform the second campaign at experiments at 950°C instead of 850°C. The reason for this is that formation of nitric oxide is favoured at higher temperatures and the emission was barely measurable at the lower temperature level.

A few other changes were also made, based on lessons learned from the first campaign. Firstly, it was decided to use 100% manganese ore rather than mixtures of 50% manganese ore and sand. The reason for this was that, based on the experiences with UMK and NCH from the first campaign, it was not obvious that the hydrodynamic behaviour of the bed would be more similar to the case with 100% sand for mixtures. Thus it was deemed that using 100% manganese ore would simplify evaluation and provide clearer results, highlighting the difference between each material. In hindsight, it is not obvious that this was a good choice. It was noticed during handling and operation that the flow and fluidisation behaviour of crushed manganese ore differed quite significantly from that of silica sand and it seems likely that these differences would be less pronounced for mixtures with sand.

Figure 10 shows the measured outlet concentrations of carbon monoxide and nitric oxides as functions of the air-to-fuel ratio, when calculated based on the undiluted oxygen concentration in the gas exhaust. It can be seen that the carbon monoxide concentration was rather similar for all three bed materials. However, it shall be pointed out that the oxygen provided by the oxygen carrier is internalized in the same fashion as was done in Figure 9 above, meaning that less oxygen should be provided by air. The baseline level is lower and the effect of approaching low air-to-fuel ratio is less dramatic, which most likely is an effect of the significantly higher temperature used in the second campaign. It is well known that the rate of combustion reactions increase greatly as function of temperature.

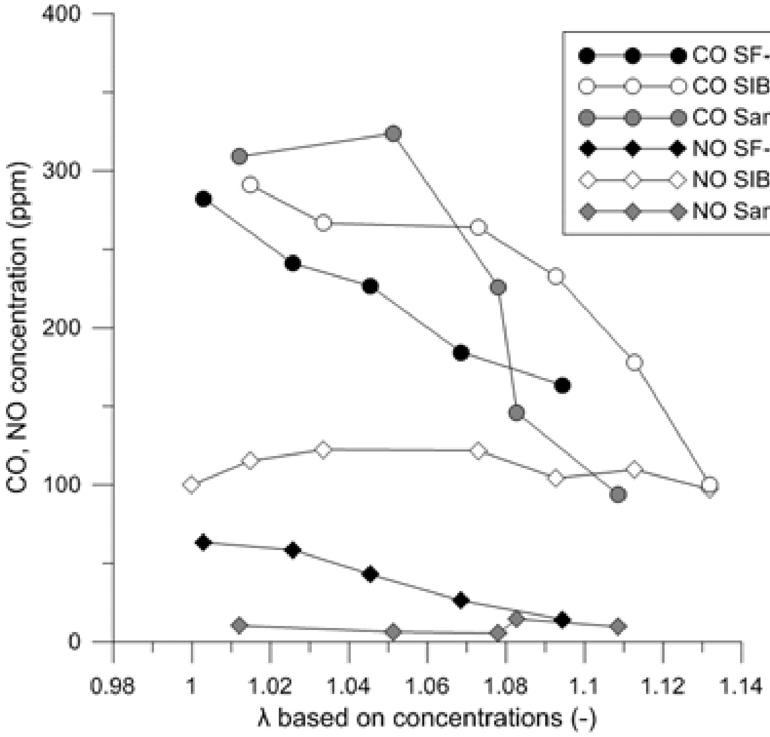

Figure 10. Measured outlet concentration of carbon monoxide and nitric oxide as functions of the air-to-fuel ratio based on oxygen concentrations during operation with 100 wt% "Sand 2", 100 wt% SF-AUS ore and 100 wt% SIB-SF ore. The temperature was set to 950°C.

A nitrogen balance was calculated in order to validate the results for the operation with ammonia addition. It was found that the ammonia formed mainly nitrogen gas and smaller amounts of nitric oxide while no nitrous oxide or gaseous ammonia were detected. A minor fraction of the nitrogen was found as ions in the condensate water, probably originating from ammonia and nitrogen dioxide. The average fractions of the nitrogen atoms added during one day measured as nitric oxide and as ions in the condensate for each bed material are reported in Table 5. The measured outlet nitrogen species corresponded well to the added amount of ammonia.

Table 5. Average fractions of nitric oxide and of ions dissolved in the condensate for the three bed materials reported. Since no N_2O, NO_2 or NH_3 was observed, balance should be N_2.

Species	Sand 2	SF-AUS	SIB-SF
NO (%)	0.29	1.86	5.34
N in water (%)	0.011	0.0056	0.0063

In Table 5, the balance was nitrogen gas (N_2), which also was verified by gas chromatography. While the equipment used was not ideal for measuring nitrogen at these low concentrations, measured concentrations corresponded quite well to the added amount of ammonia.

To summarize the impressions from the experiments with ammonia addition, it has to be concluded that it is hard to draw convincing conclusions. Even though high ammonia concentration (3%), comparably high temperature (950°C) and a range of air-to-fuel ratios was examined, the conversion of ammonia to nitric oxide was very low. At least an order of magnitude lower than anticipated. Great effort was put into calibrating instruments, measure all potential nitrogen species, ensure that the correct amount ammonia entering the reactor with the methane and collect and analyse condensate water. Therefore the most likely explanation for the low emissions of nitric oxide is that it was an effect of the reactor system used. Here it shall be recalled that the system was not originally designed for combustion and that this is the first series of experiments exploring this possibility. It has large surface area as function of fuel flow which could be important for catalytic reduction of nitric oxide. The small scale of the equipment may hamper formation of hot flames which would be more likely to generate NO than N_2. Also the residence time for gas and gas velocity differs from conventional facilities. So when considering that all three experiment series provided very low conversion of ammonia to nitric acid, it seem reasonable to believe that this was an effect of the properties of the reactor system.

As for the potential effect of switching from sand to manganese ore, it is apparent in Figure 10 that the emission of nitric oxide was greater when manganese ore was used. While this does not look promising the actual emissions was still very low, so it is not clear how much bearing these experiments has.

In recently conducted work associated with, but not conducted under the framework of this project, the phenomena of nitric oxide formation during biomass combustion in in fluidized bed in presence of oxygen carrier particles has been examined in detail[39]. In this detailed study a small batch reactor of quartz was utilized and wood char was used as fuel. Also in this study data evaluation turned out to be tricky. Much higher nitric oxide emissions was seen when manganese ore was used compared to when sand was used, if only looking at measured raw data for similar experiments. However, if plotted as function of carbon monoxide emissions, considerably lower emissions of nitric oxide was seen for manganese ore for a given emissions level. Again the ability of manganese ore to supply oxygen for fuel oxidation made interpretation of data difficult.

3.2 RESULTS FROM WORK IN CHALMERS RESEARCH BOILER

The experiments in Chalmers Research Boiler worked well and more experiments than originally anticipated could be carried out. While the original goal was to achieve one week of operation with partial substitution of sand with manganese ore, more than two weeks of operation was actually achieved, some of which used 100% manganese ore. The campaign will be described also in one or two articles in an appropriate scientific journal in the near future[40]. A summary can be found in Table 6.

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[39] *Zhao D. Oxygen Carriers in Combustion. ÅForsk final report ref. nr. 13-428.*

[40] *Will be submitted for publication during spring 2016.*

Table 6. Overview over experiments performed in Chalmers Research Boiler.

Test	Day	Sand [wt%]	Manganese ore [wt%]	Comment
I	1	100	0	Reference experiment
II	2	90	10	
III	3	70	30	
	4	70	30	
IV	5	50	50	
Boiler stop during weekend (day 6-7). This was necessary in order to remove material contaminated with sand and allow for operation with 100% manganese ore.				
	8		100	Start-up with only manganese ore
V-VI	9		100	Also operation at 800°C
	10		100	
	11		100	
	12		100	
Operation with 100% manganese ore during weekend (day 13-14) by the plant operator (Akademiska Hus AB). No experimental activities during this time.				
VII	15		100	Experiments with sulphur feeding
VIII	16		100	Regenerated bed, sulphur feeding
After day 16 the official campaign was ended and the plant was left to the plant operators. The desire was to gradually replace the manganese ore with sand. After more than a week we learned that they still had approximately 10% manganese ore in the plant and that things worked very well, so two more days of experiments were conducted.				
IX	24	≈90	≈10	
X	25	≈90	≈10	

In Table 6 it can be see that the boiler was in fact operated for more than 23 days with at least 10% manganese ore. Except for the planned stop day 6-7 the plant was in continuous operation over this whole time period. Research personnel (on average ≈5 persons) were actively working in the facility day 1-5, 8-12, 15-16, 24-25 (14 days in total). The column "Test" indicates period during which complete so called lambda tests have been performed, which constitutes the main indicator for combustion performance during these experiments. The procedure for these was explained in section 2.2 above.

As with the laboratory experiments, the experiments in the research boiler can be divided into two sub-campaigns. Day 2-5 and day 24-25 the plant was operated with partial substitution of sand with manganese ore (SIB-SF), while during day 8-16 the plant was operated with 100% manganese ore.

For the first campaign, great care was taken to adjust the amount of manganese in the bed in order to achieve the values reported. This was done at the morning each day of operation, principally by screwing out material from the bottom bed and adding fresh manganese ore. The amounts removed and added were adjusted in order to achieve a fixed pressure drop of about 5.5 kPa, from the bottom of the bed to the top of it. To be able to do this a number of assumptions had to be made:

- It was assumed that the composition of the bed material removed corresponded to what theoretically should be if the whole bed was perfectly mixed, i.e. that there was no segregation of solids.
- It was assumed that there was no accumulation of ash in the bed.

The methodology used has some limitations. One obvious problem is that it was not immediately possible to distinguish between ash, manganese ore and sand in the solid material collected in the secondary cyclone and filters. This made the precise concentration of manganese ore in the boiler impossible to follow in real time. However, the numbers reported in Table 6 for test I-IV should be very close to the actual numbers. For test IX-X, the numbers are more uncertain.

For the experiments with only manganese ore, this did not constitute a problem. Here new material was added in the morning in order to obtain a pressure drop over the boiler of about 5.5 kPa. A partial regeneration was done day VIII, during which 50% of the bed material was removed and replaced with fresh manganese ore. Aside from this, the bed was not regenerated over the course of the experimental campaign. The potential effects of this will be discussed below.

3.2.1 Effect on CO emissions during reduced air-to-fuel ratio

The most important process parameter to look at when evaluating these experiments is the emissions of CO in the flue gas leaving the boiler. The main attractiveness with switching from sand as bed material to manganese ore would be to facilitate fuel conversion, thus allowing for reduced air-to-fuel ratio without increasing the emissions of unburnt such as CO. Summaries of the measured CO emissions during operation at certain air-to-fuel ratios can be found in Figure 11-12.

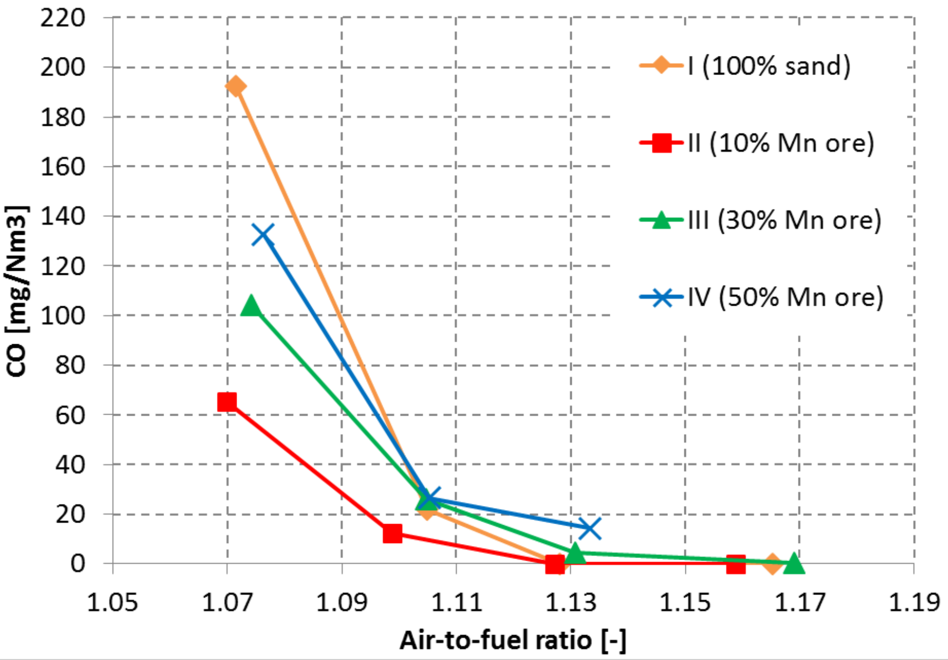

Figure 11. Measured concentrations of CO (mg/nm³, at 6% O₂) at position kh2 in the convection path as a function of the air-to-fuel ratio for experiments with partial substitution of sand with manganese ore.

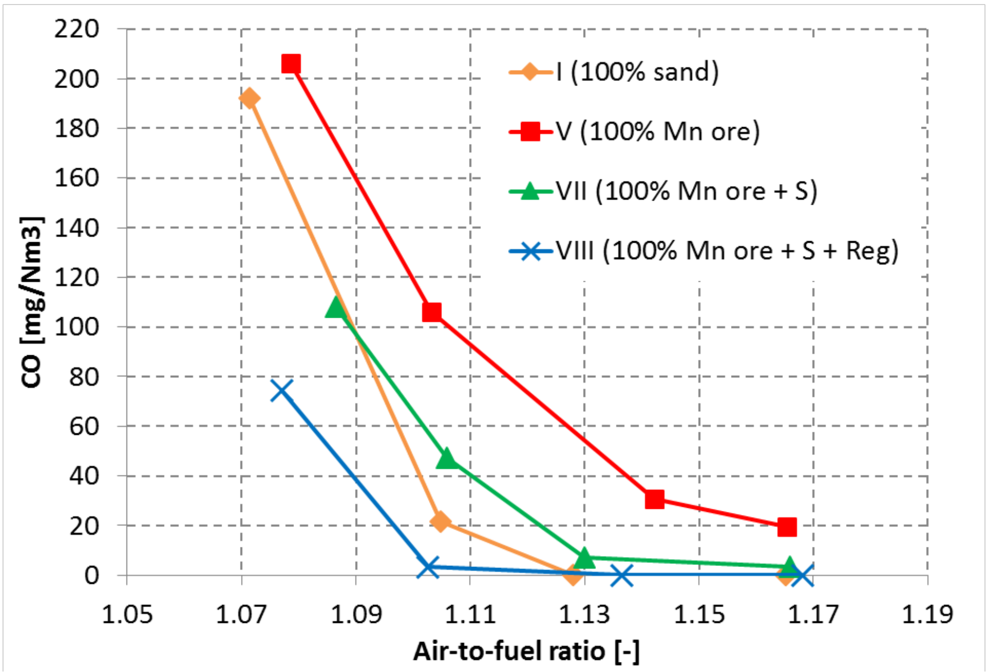

Figure 12. Measured concentrations of CO (mg/nm³, at 6% O₂) at position kh2 in the convection path as a function of the air-to-fuel ratio for experiments with 100% substitution of sand with manganese ore.

The results shown in Figure 11-12 may not seem totally intuitive. However, after some evaluation we believe that they are explainable, as will be elaborated below. Basically, Figures 11-12 show two things:

- ***By substituting sand with manganese ore it was possible to achieve very substantial reduction in CO emissions compared to the sand reference.*** For example, at the specific air-to-fuel ratio of 1.07 experiments with 10% manganese ore has ≈70% less emissions of CO compared to experiments with fresh sand, while the experiments with 100% manganese ore (with sulphur feeding and partially regenerated bed) has ≈55% less at an air-to-fuel ratio of 1.07 and ≈90% less at 1.10. Operation at as low air-to-fuel ratio as 1.10 or even lower appears perfectly conceivable.
- ***However, the positive effect is not a given.*** For the experiments with partial substitution of sand, it can be seen that during the following days of operation (with 30% and 50% manganese ore) the CO emissions increased. For the experiments with 100% manganese ore, no positive effect is seen until active measures to remove alkali from the bed is taken.

It is not straightforward to explain some of the phenomena from Figure 11-12. It seems counterintuitive that CO emissions should decrease considerably when adding 10% manganese ore, but that the effect should be significantly reduced when fraction is increased to 30%. However, compared to ordinary combustion, a number of things were changed for the present experimental campaign that has implications on the removal of such components from the boiler:

- During normal operation of Chalmers Research Boiler about 30% of the sand used as bed material is replaced each day. This is referred to as "regeneration" of the bed. In practice, this means that alkali components absorbed by the bed material is continuously removed from the process. However, this common procedure was not followed during the experiments performed here. This was done in order to save manganese ore. What this means is that alkali metals were not continuously removed from the boiler and thus may have accumulated in the bed material and inside the boiler.

- Manganese ore typically contains considerable amounts of alkali metals and the present ore has a potassium content of 1 wt%, see Table 1. This suggests that the bed material in this case may already be saturated with alkali and unable to absorb more.

Both points suggest that the mechanisms normally used to remove alkali from the boiler may not have been present to adequate extent. The bed was not sufficiently regenerated and its potential to absorb alkali may have been poor to begin with.

Accumulation of alkali and other ash compounds in fluidized bed combustion of biomass is well-known to create a range of difficulties. This includes agglomerations and presence of KCl in the flue gas, which in turn may result in deposits on super-heater tubes[41]. In small-scale CFB boilers saturation of KCl and other ash components in the flue gas can also be associated with CO emissions. The precise mechanism does not seem to be universally accepted. One mechanism that have been suggested is that biomasses do not necessarily combust in accordance with the shrinking core model, but rather via a shrinking sphere model, which could result in that the ash layer surrounding the fuel particle could makes the oxygen diffusion difficult[42]. Considering the reactive nature of alkali metals, heterogeneous effects could also be a possibility. So even though the precise mechanism may not be established, increased emissions of CO as function of time should not be surprising for the experiments illustrated in Figure 11. So while increased amounts of manganese ore could be expected to result in lower emissions according to the reasoning presented in section 1 of this report, what may have happened is that saturation of the bed with alkali and other ash compounds could have countered this, as the mechanism for their removal may have been inadequate. This will be further discussed below in connection with the section describing analysis of ash and bed samples.

In Figure 12, it can be seen that the initial experiment with 100% manganese ore as bed material resulted in surprisingly high emissions of CO, much higher than the sand reference. The operation as such worked fine, but for several days we were unable to achieve decently low CO emissions. While the first day of operation were focused on fundamental aspects of operating a new bed material, there were signs that low CO could not readily be achieved even then. This may suggests that the potassium already present in the ore (1 wt%) could have prevented further adsorption of alkali. Rethinking our procedures, we started to feed a small amount of elemental sulphur (1 kg/h) to the bed on day 15 of operation. This was done based on the theory presented above, namely that the CO emissions were related to poor removal of alkali from the bed.

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[41] *Davisson K O, Åmand L-E, Steenari B-M, Elled A-L, Eskilsson D, Leckner B. Countermeasures against alkali-related problems during combustion of biomass in a circulating fluidized bed boiler Biomass combustion in fluidized bed boilers: Potential problems and remedies. Chemical Engineering Science 2008;63:5314-5329.*

[42] *Khan A A, de Jong W, Jansens P J, Spliethoff H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Processing Technology 2009; 90:21-50.*

Addition of elemental sulphur should result in sulphation of potassium ultimately forming solid K_2SO_4 [43], thus reducing the influence of gaseous alkali compounds on the combustion results. As can be seen in Figure 12, this resulted in improved performance from day one. After having regenerated half of the bed and applying the concept of sulphur feeding, greatly improved combustion results were achieved also when 100% manganese ore was used as bed material.

Here some care should be taken when interpreting the results. This is because sulphur feeding to CFB combustion have in fact occasionally been applied to reduced CO emissions[44,45]. The mechanism for this improvement is not universally accepted either, but a heterogeneous mechanism have been suggested that involves formation of oxidative aerosols[46] of K_2SO_4. This mechanism is perfectly compatible with the reasoning above, but it makes comparison with the sand reference without sulphur addition problematic.

To summarize, the experiments conducted clearly show that it is possible to achieve considerable improvements with respect to CO emissions when manganese ore as bed material during CFB combustion. However, it is also clear that this positive effect is not a given. While not certain, we believe that the alkali balance over the bed is an issue that needs to be carefully studied in order to determine the possible mechanism. This issue will be discussed further in the discussion section below.

3.2.2 Effect on reactor temperature profile during experiments

Measuring local temperature in different parts of the boiler is a complex issue. Things that needs to be considered includes the cooling effect of air and flue-gas used to fluidized the bed, cooling from the tube walls, potential for uneven temperature over the cross-section etc. Detailed studies of the said phenomena were beyond the scoop of the current project. Still, also a relatively simple analysis could provide important insights. Below are two plots. Figure 13 describes the temperature in 4 different measuring points when the boiler was operated at high air-to-fuel ratio, while Figure 14 describes the same temperatures when operating the boiler at low air to fuel ratio. These temperatures was measured with conventional thermocouples type-K.

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[43] *Kassman H, Bäfver L, Åmand L-E. The importance of SO_2 and SO_3 for sulphation of gaseous KCl – an experimental investigation in a biomass fired CFB boiler. Combustion and Flame 2010;157: 1649-1657.*

[44] *Lindau L, Skog E. CO-reduktion i FB-panna via dosering av elementärt svavel. Värmeforsk rapport 812 (2003).*

[45] *Kassman H, Andersson C, Carlsson J, Björklund U, Strömberg B. Minskade utsläpp av CO och NO_x genom dosering av ammoniumsulfat i förbränningsrummet. Värmeforsk rapport 908 (2005).*

[46] *Christensen K A, Livbjerg H. A Plug Flow Model for Chemical Reactions and Aerosol Nucleation and Growth in an Alkali-Containing Flue Gas. Aerosol Science and Technology 2000;33:470-489.*

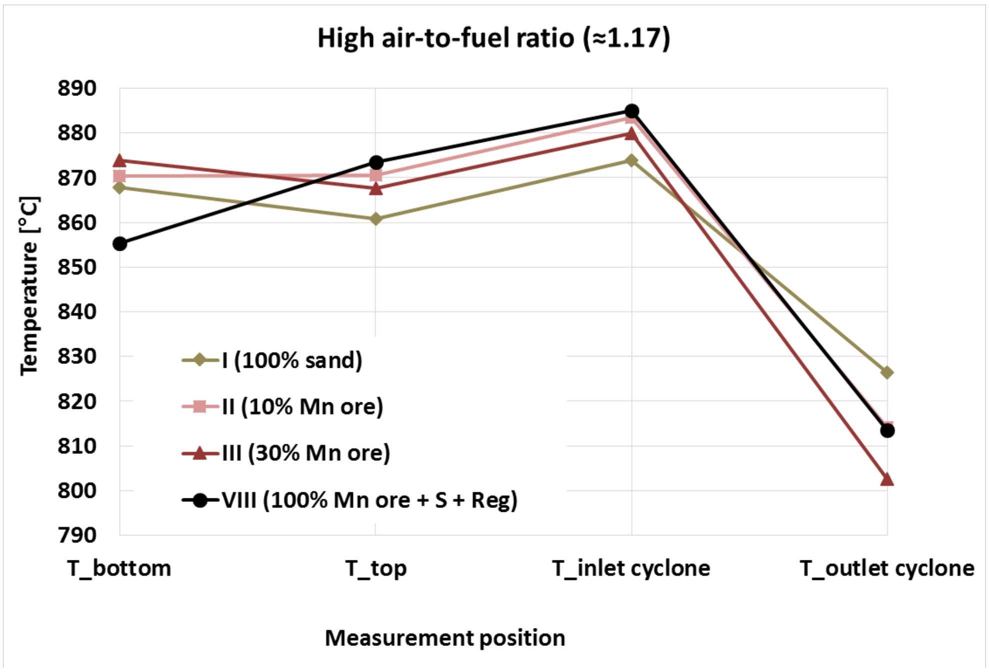

Figure 13. Temperature profile over the boiler when operated on high air-to-fuel-ratio.

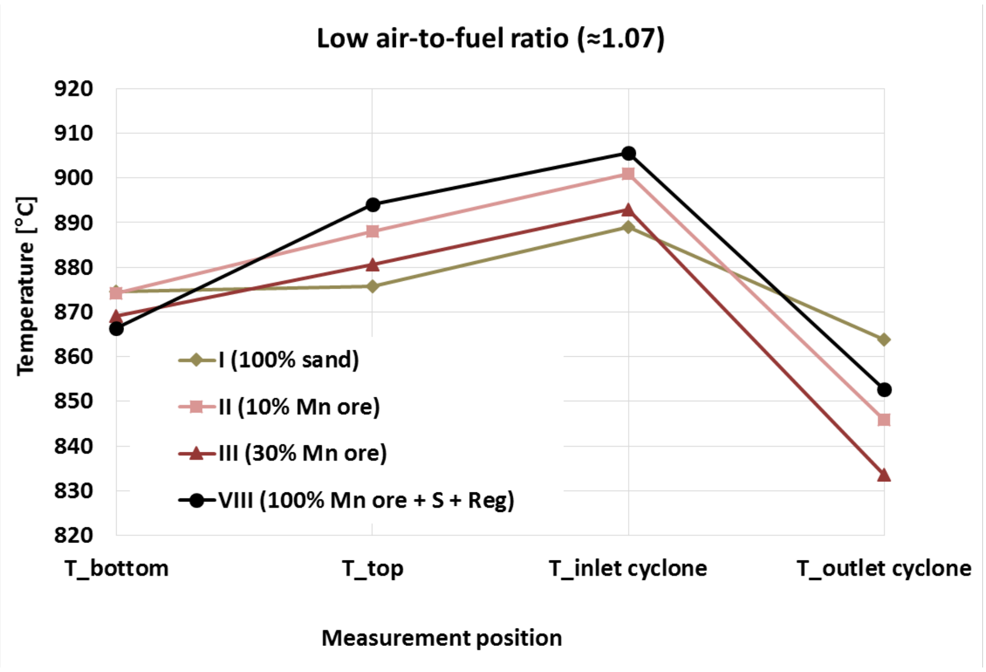

Figure 14. Temperature profile over the boiler when operated on low air-to-fuel-ratio.

In Figure 13-14 the following phenomena can be identified:

- The temperature drop over the cyclone is much more pronounced for experiments involving manganese ore than when sand is used. This clearly illustrates that much less combustibles enters the cyclone and burns here. The obvious explanation is that more combustion takes place in the boiler itself, i.e. that the presence of manganese ore in the bed facilitates combustion.

- The temperature difference between the top of the boiler and the bottom of the boiler also differs considerable between the different cases, and the general pattern suggests that more combustion takes place here when manganese ore is present. With 100% manganese ore there is considerable temperature increase for both high and low air-to-fuel ratio, which should be compared to slight temperature decrease when sand is used. The two cases with partial substitution is somewhere in between.

Figures 13-14 are consistent with what could be expected. Addition of an oxygen carrying bed material is supposed to facilitate combustion in the dense part of the bed and in the freeboard above it, so that less combustibles remain to be burned in the cyclone.

Figures 13-14 also indicates that the case with 100% manganese ore has superior ability to facilitate combustion in the boiler, compared to partial substitution. This is interesting since the effect on CO emissions is not superior, which suggests that there are other factors that influence the ultimate combustion results. In this context it shall be pointed out that the final emissions is equal to what actually leaves the cyclone, not what leaves the boiler. The problem with 100% manganese ore seems connected to final burnout, which normally takes place in the vortex finder, i.e. the exit tube from the cyclone.

3.2.3 Effect on NO emissions during reduced air-to-fuel ratio

A second performance parameter to look at when evaluating these experiments is the emission of NO in the flue gas leaving the boiler. As was described in section 1 above there are reasons to believe that switch of bed material could have positive impact also for this aspect. Summaries of the measured NO emissions during operation at certain air-to-fuel ratios can be found in Figures 15-16.

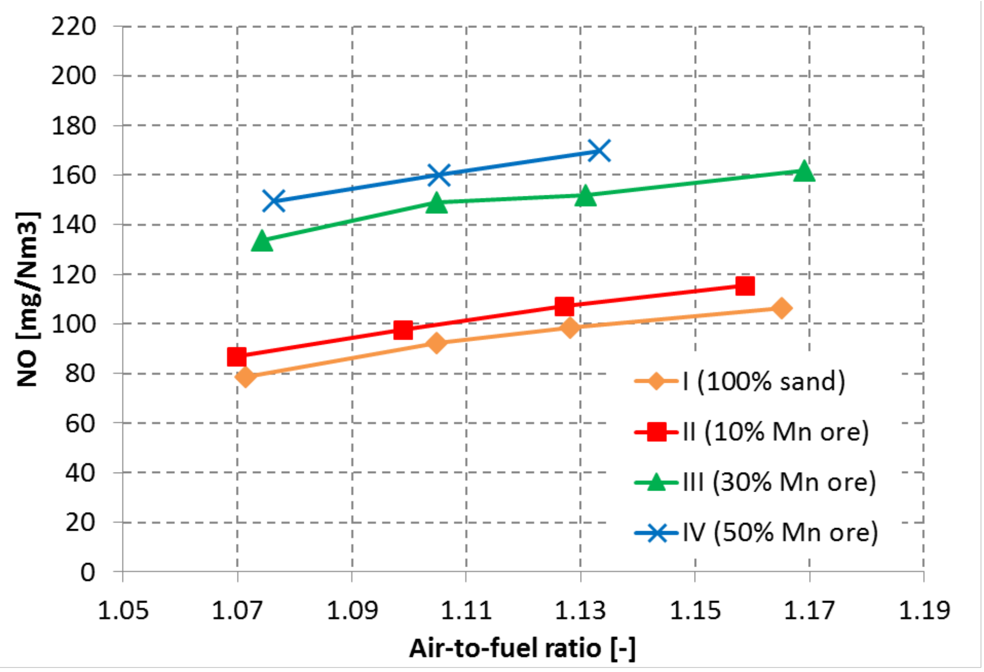

Figure 15. Measured concentrations of NO (mg/nm³, at 6% O₂) at position kh2 in the convection path as a function of the air-to-fuel ratio for experiments with partial substitution of sand with manganese ore.

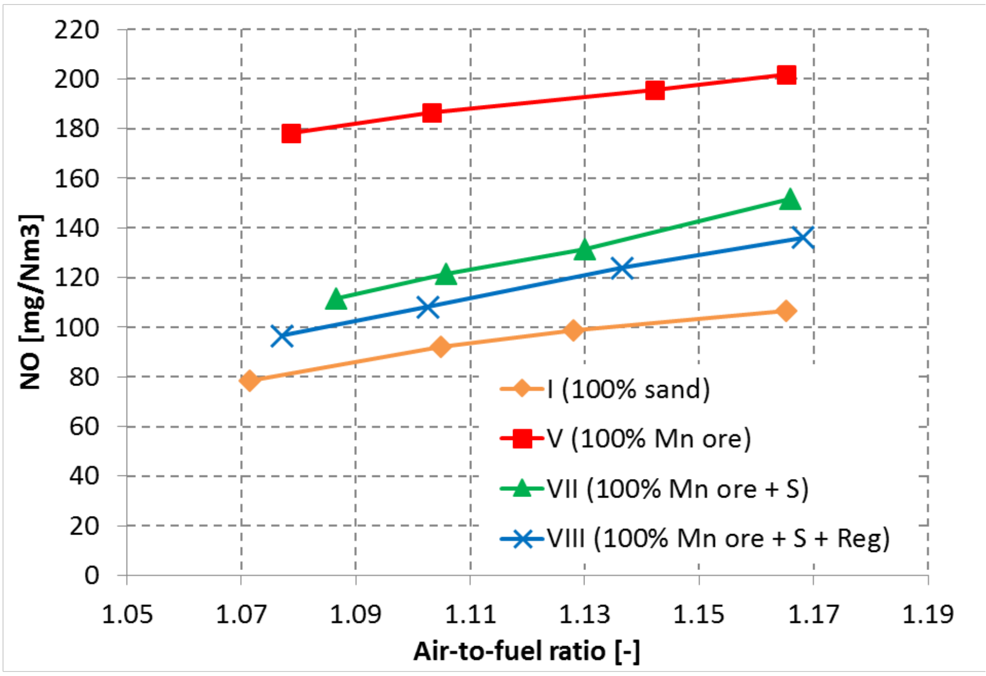

Figure 16. Measured concentrations of NO (mg/nm³, at 6% O₂) at position kh2 in the convection path as a function of the air-to-fuel ratio for experiments with 100% manganese ore.

Based on the results presented in Figures 15-16 the following points can be made:

- High air factor results in higher NO emissions, a well-known phenomenon within combustion chemistry that requires no further comment.

- The sand reference has the lowest NO emissions, meaning that no improvements could be verified by using manganese ore as bed material.
- Of the experiments where manganese ore is used, those who perform good also with respect to CO emissions (10% manganese ore and 100% manganese ore with sulphur addition) performs decently also with respect to NO emissions. A connection between the two seems very likely and could be associated with the concerns related to inadequate removal of ash components from the bed discussed in section 3.2.1 above.

These results suggest that the positive effect of up to 30% reduction of NO shown during partial substitution of sand with ilmenite[47] could not be replicated with manganese ore. This observation is in line with the observations from the laboratory experiments presented in section 3.1.2 above. This issue will be further discussed in the discussion section below.

3.2.4 Observations with respect to general operability

Over the course of the experimental campaign, which as can be seen in Table 6 totalled 23 days with more than 10% manganese ore in the bed, no issues related to general operability was encountered. There were no tendencies to form agglomerations or other problems related to operation of the plant. In this context it shall also be pointed out that rather high temperatures were used with the target temperature in the bed most often being 870°C, see Figures 15-16. This is near the maximum temperature of operation for sand. Also the lack of proper bed regeneration between day 8 and day 15 would normally be assumed to favour agglomeration.

Finally, it should be mentioned that the boiler temporarily shut itself down at two occasions. For security reasons, Chalmers Research Boiler has an automated control system that shuts down fuel and air if certain abnormal conditions are fulfilled. The first occasion was related to a failure in a fan and left the boiler without air for about a minute. The second occasion was related to a disruption of power to the boiler, which shut the boiler down for about 30 minutes. None of these disruptions had anything to do with the performance of the boiler or the bed material. At both these occasions fluidization was suddenly disrupted during operation, which when it happens could result in agglomeration of the bed. The fact that no such problems were experienced suggests that manganese ore certainly are not worse than sand in this respect.

3.2.5 Performance in agglomeration tests

In order to characterize the manganese ore with respect to its tendency to form agglomerations, dedicated defluidization tests were also conducted by the research institute SP (Sveriges Tekniska Forskningsinstitut). Four samples were examined, three of which had been extracted from the bed during operation:

- Fresh manganese ore
- 10% Manganese ore in sand (extracted day 2 at 15:10)
- 100% manganese ore (extracted day 9 at 16:30)
- 100% manganese ore operated with sulphur feeding (extracted day 16 at 14:20)

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[47] *Thunman H, Lind F, Breitholtz C, Berguerand N, Seemann M. Using an oxygen-carrier as bed material for combustion of biomass in a 12-MW$_{th}$ circulating fluidized-bed boiler. Fuel 2013;113:300-309.*

The experimental methodology was as follows. A sample of about 200 g was placed in a reactor, which was located to an electrically heated furnace capable of reaching up to 1100°C. The reactor consisted of a metal tube with the length 140 cm and an inner diameter of 7 cm. A sintered metal plate is located in the middle of the tube, on which the sample is located. The sintered metal plate also acts as gas distributor. The sample is fluidized by air provided by a mass flow controller. The flow is set to 20 l_n/min, which corresponds to a superficial gas velocity of about 0.5 m/s at 750°C. The pressure drop over the bed is measured with a pressure transducer and the temperature is monitored with a K-type thermocouple. Both variables are measured and logged over the course of the test. The experiments are started when the bed temperature are stabilized at 750°C. From this point bed temperature is increased by 3.5°C/min. The maximum temperature was 1100C. After reaching this temperature the sample was allowed to cool in the reactor by roughly 10°C/min.

When the bed agglomerates the pressure drop is reduced. Three temperatures were reported:

- T_{A1} (first tendency towards agglomeration): This is the lowest temperature when a disturbance in the pressure drop over the bed can be verified,
- T_{A2} (apparent agglomeration): The lowest temperature when agglomeration clearly is taking place. The bed is considered to be agglomerating when the pressure drop is reduced continuously with 5 Pa/min or more.
- T_{A3} (complete agglomeration): The temperature when the pressure drop is stabilized at its minimum value.

The results of the agglomeration tests can be found in Table 7 below:

Table 7. Results of agglomeration tests.

Sample	T_{A1} (°C)	T_{A2} (°C)	T_{A3} (°C)	Comments
Fresh manganese ore	-	-	-	Successfully reached 1100°C. Some very soft agglomerates was formed, likely during cooldown.
10% Manganese ore in sand	876	941	958	
100% manganese ore	959	959	998	Sample contained numerous mm-sized agglomerates.
100% manganese ore operated with sulphur feeding	775 (1000)	820 (1000)	1025	Sample contained numerous mm-sized agglomerates.

Some further comments on the results is in place. The fresh ore performed excellently and showed no tendencies towards agglomeration. The very soft flake-like agglomerates found in the sample are not expected to have any impact on operability. Also the sand ore mixture and 100% used manganese ore performed well, showing no tendency to agglomerate at the temperature levels typically used in CFB combustion (<870°C).

The sample of manganese ore that had been operated with sulphur feeding showed peculiar behaviour. At 820°C the pressure drop over the bed started to decrease (from 200 Pa to about 90 Pa). However, the pressure drop stabilized at this level and continued to show variance, suggesting that it fluidized well. Further tendencies towards decreased pressure drop was not seen until 1000°C and complete agglomeration did not happen until 1025°C. It is not easy to explain the initial decrease in pressure drop based on fluid dynamics. This would have to involve defluidization of about half of the bed, while air would still be provide to the rest of the bed in such manner so that it fluidized properly. The higher numbers reported also fit better with practical experience from Chalmers Research Boiler, which was operated with this mixture at 870°C without problems.

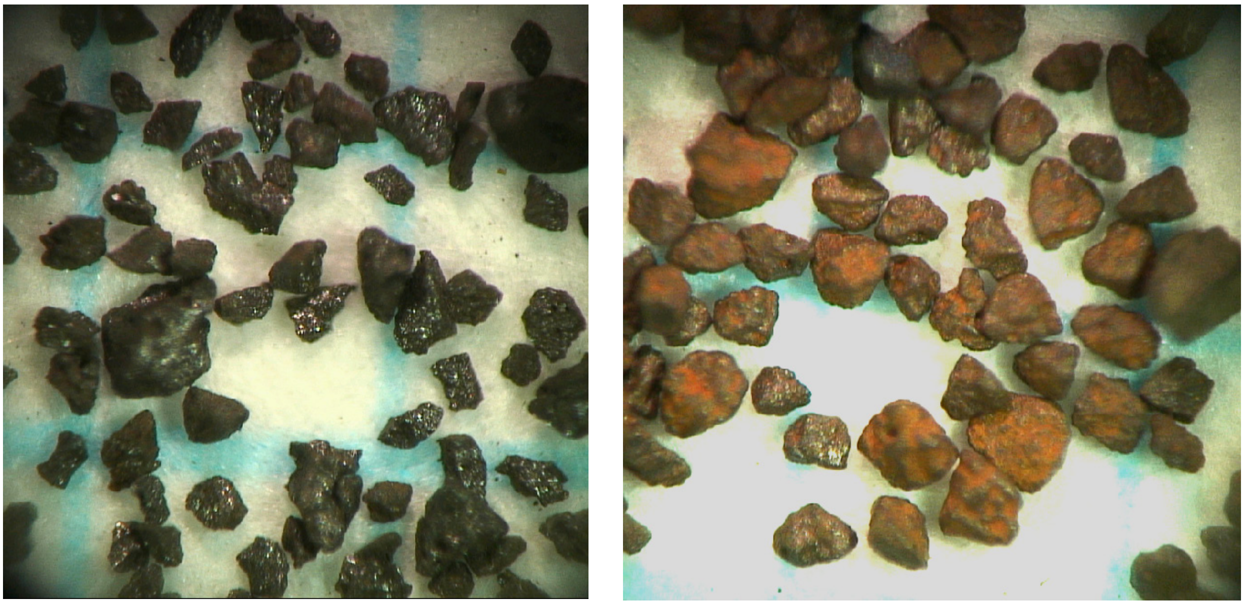
To summarize the agglomeration tests, they suggest that manganese ore seems likely to have equal or less tendency towards defluidization and agglomeration than ordinary silica sand. With fresh ore it was possible to reach 1100°C without problems and also with used ore no problems were seen until >959°C. The mixture with sand showed some tendencies to agglomerate at lower temperature, albeit operation at standard temperatures should not be a problem.

3.2.6 Properties of bed materials and ash samples

As explained in section 2.2.4 above, solid samples from different sources were collected over the course of operation. This included:

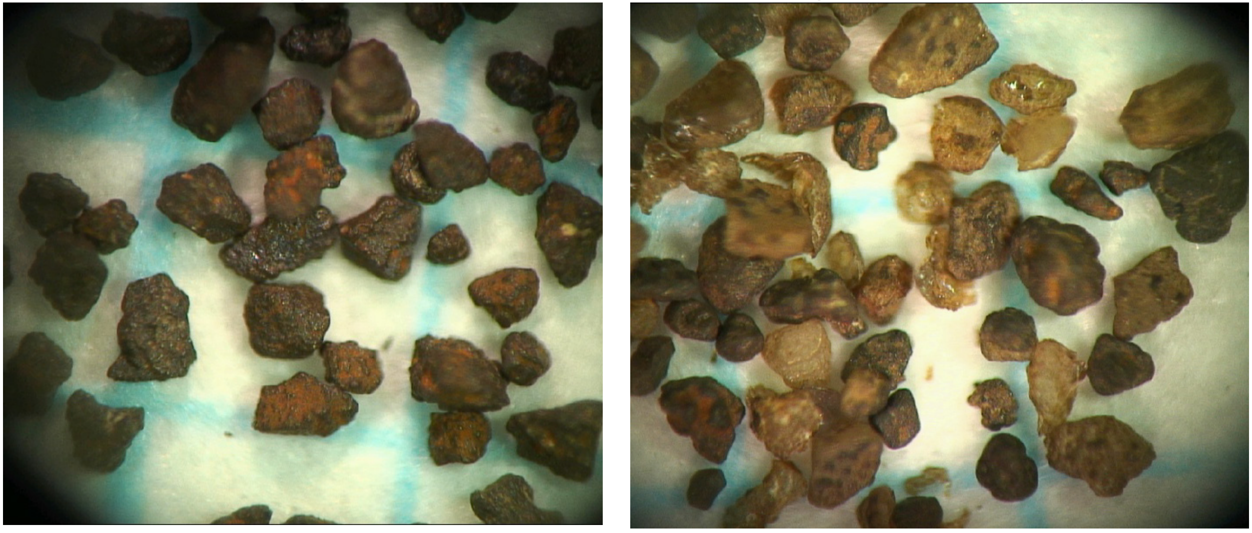
- Bed material taken from inside boiler during operation. This was done using a special cooled collection probe and allows monitoring of the properties of bed material, as function of time.
- Ash samples from the secondary cyclone. This materials constitutes a rather course fraction of materials elutriated from the system during operation. Should consist of fly-ash and possibly bed material.
- Ash samples from textile filter. Consists of fine material elutriated from the system during operation. Should consist of fly-ash and possibly bed material.

The project did not include resources for detailed analysis and characterization of the samples, but a handful were selected and examined in a high-resolution light microscope in order to examine morphological irregularities. Pictures of four such samples can be found in Figure 17 below:



Fresh manganese ore.

100% manganese ore after 20 h of operation.



100% manganese ore after 172 h of operation.

After >300 h of operation (mixed with sand).

Figure 17. High-resolution light microscope pictures of fresh manganese ore from the large batch of oxygen carrier and three bed samples extracted during operation of Chalmers Research Boiler.

In Figure 17 it can be seen that the manganese ore did undergo considerable changes over the course of the campaign. The fresh material is rough-edged, as could be expected from particles produced by crushing and grinding. Material that has been used in operation is smother around the edges, albeit the general shapes are not substantially altered. There is also a noticeable change in colour, with fresh particles being almost black while used particles are dark brownish with rusty red also being present.

A detailed examination and characterization of used samples could possibly provide additional information about the material samples, such as for example their tendencies for reaction with ash components. Such detailed characterization was not covered by the current project, but will be considered in the future, if time and resources allows for it.

3.2.7 Material balance and attrition behavior

The overall impression was that the manganese ore used as bed material in Chalmers Research Boiler had excellent resistance toward attrition. Experiments with 100% substitution could readily be done without excessive elutriation of bed material. For example, between day 8 and day 15 no material was added while the bed inventory remained approximately constant.

Over the course of the experimental campaign, care was taken to record any instance of addition or removal of solids from the boiler. This includes:

- Sand and oxygen carrier added to the boiler at the start of each day. Estimated by scale in the material silos and pressure drop in the boiler.
- Bed material removed with the bottom screw each day. Estimated by scale in the material silos and pressure drop in the boiler.
- Material elutriated from the boiler and captured in the secondary cyclone each day. Measured by scale.
- Material elutriated from the boiler and captured in the textile filter each day. Measured by scale.
- Ash added with the fuel. Can be calculated from fuel flow.

While all these parameters are measured continuously, the degree of uncertainty for each is considerable. For example, the vessels for captured ash are placed on scales that are known to show irregularities when a lot of people are walking around in parts of the boiler house in its close proximity, exact amount of ash varies depending on fuel quality and moisture content etc. Also calibration of scales for bed material silo and bottom screw material is complicated and not done on regular basis.

Available data should allow for making a rough material balance over the boiler in order to establish the rate of attrition of manganese ore. However, the degree to which ash components are adsorbed by the manganese ore is unknown and considerably influence the conclusions. During most days of operation elutriated material corresponds well to the amount of ash added with the fuel. This seemingly suggests that attrition of the manganese ore was low and most elutriated material was ash from the fuel. However, it shall be acknowledged that it is possible that ash components could be adsorbed by the bed material, meaning larger than expected elutriation of manganese ore.

Basically, an extensive analysis of ash samples would be needed in order to make a thoroughly comprehensive mass balance over the boiler. As pointed out in Section 3.2.6 above such extensive analysis was not covered by the project. Until that is done no numerical data for attrition can be presented. However, the general impression was that operation with manganese ore worked flawlessly with very little attrition of the bed material.

4 Discussion

4.1 COMPARISON WITH PARTIAL SUBSTITUTION WITH ILMENITE

As was explained in the background and elsewhere, similar experiments with partial substitution of sand with the titanium-iron ore ilmenite was conducted a few years ago in Chalmers Research Boiler[48]. These experiments was deemed as highly interesting and the idea has since been picked up and demonstrated in a power plant on commercial basis for more than seven months.

Because of the apparent success of ilmenite as bed material for biomass combustion, it is of great interest to compare the effect of partial substitution with ilmenite and partial substitution with manganese ore. This could give an idea whether manganese ore would be more suitable for the application than ilmenite, or vice versa.

The experiments with ilmenite in Chalmers Research Boiler were performed during three days using very similar methodology to the one used in this study, which makes such benchmarking possible. A comparison of the effect on CO emissions between these experiments ant the current experiments with manganese ore can be found in Figure 18 below.

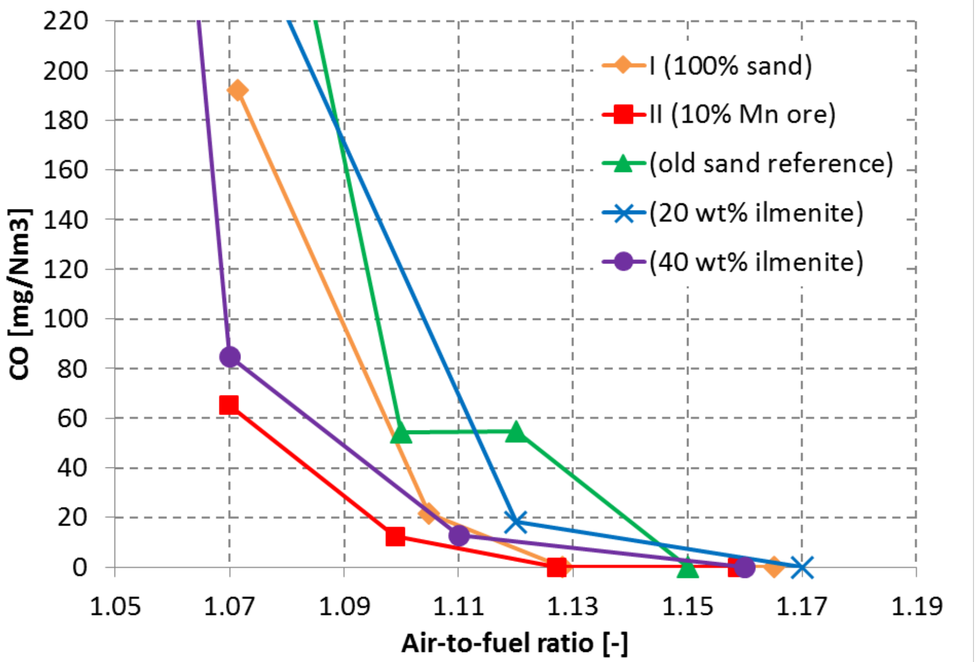


Figure 18. CO emissions as function of air-to-fuel ratio, comparison between partial substitution of manganese ore and partial substitution of ilmenite.

In Figure 18 it can be seen that it is not completely trivial to compare the two cases. The following observations should be carefully considered before drawing conclusions:

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[48] *Thunman H, Lind F, Breitholtz C, Berguerand N, Seemann M. Using an oxygen-carrier as bed material for combustion of biomass in a 12-MW$_{th}$ circulating fluidized-bed boiler. Fuel 2013;113:300-309.*

- One striking difference is the low emissions from the sand reference used in the current study, compared to the old sand reference. This could possibly be associated with the fact that the current reference was recorded at the immediate start of the combustion season and using a full batch of new high quality S36 silica sand. The old sand reference was presumably recorded under less benign circumstances. Because of this, a third reference series should probably be recorded when the opportunity arises. Also care should be taken when the effects of oxygen carrier substitution is small.
- The ilmenite experiments were recorded in a rather short experimental campaign lasting only three days. Fresh ilmenite was added each day replacing parts of the bed. Hence it can be said that these experiments were conducted while using reasonable procedures for bed regeneration. In contrast, manganese ore was used for many days with very limited bed regeneration. Therefore we have only included the case with 10% manganese ore in the comparison in Figure 18, which was recorded already on day 2.
- The subsequent experiments with 30% and 50% manganese ore yielded less good results than the experiments with 10%, as have been discussed above.

Figure 18 suggests that substitution of just 10 wt% of the sand bed with manganese ore allows for at least as good performance as substitution with 40 wt% ilmenite. This is remarkable but not unexpected, considering that manganese ore generally is considered as a superior oxygen carrier.

On the other hand, ilmenite reportedly had a positive effect on NO emissions[49]. Also, ilmenite have showed improved capability to absorb alkali metals[50] and thus have not required extensive regeneration or addition of sulphur or other additives in order to perform well. This could potentially be a very useful property reducing problems related to emissions, attrition and agglomeration. The fate of alkali metals when using manganese ore is currently not known and will have to be examined in detail in the future.

To summarize, with the information currently available it seems premature to tell for sure whether manganese ore is a distinctively better alternative than ilmenite for the application OCAC of biomass. The oxygen carrying capacity is probably better, but this was known already thanks to previous research about oxygen carrying materials for CLC. Also the mechanical properties of the manganese ore used in thus study proved to be excellent. However, current uncertainties with respect to impact on combustion chemistry and adsorption and removal of alkali metals from the boiler make it hard to draw strong conclusions. It is likely that a well thought-through scheme for regeneration of the bed is needed if manganese ore is to be used, but this may not be a big issue in practice.

4.2 PARTIAL SUBSTITUTION OR 100% MANGANESE ORE

In the project, the opportunity both to exchange the whole sand bed with manganese ore and the opportunity to just exchange part of it have been examined. So which option looks more promising? A comparison on the effect on CO emissions for 10%

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[49] *Thunman H, Lind F, Breitholtz C, Berguerand N, Seemann M. Using an oxygen-carrier as bed material for combustion of biomass in a 12-MW$_{th}$ circulating fluidized-bed boiler. Fuel 2013;113:300-309.*

[50] *Corcoran A, Marinkovic J, Lind F, Thunman H, Knutsson P, Seemann M. Thunman H, Lind F, Breitholtz C, Berguerand N, Seemann M. Ash properties of ilmenite used as bed material for combustion of biomass in a circulating fluidized bed boiler. Energy & Fuels 2014;28:7672-7679*

substitution and experiments with 100% manganese ore and sulphur feeding can be found in Figure 19.

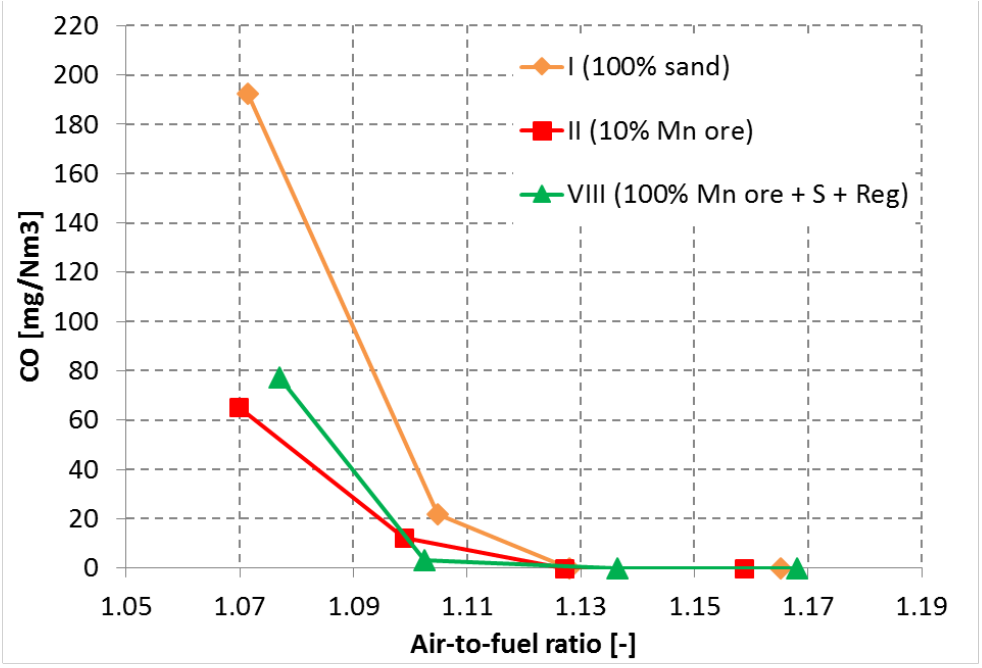

Figure 19. CO emissions as function of air-to-fuel ratio, comparison between 10% manganese ore and 100% manganese ore with sulfur addition and 50% regenerated bed.

In Figure 19 it appears that the performance of each alternative is rather equal. However, as has been explained above it took considerable trial-and-error and sulphur addition to achieve good results with 100% manganese ore. Just replacing sand with manganese ore resulted in increased CO emissions. Also, the results with partial substitution declined as function of time when the bed was not continuously regenerated.

On the other hand, the temperature profile reported in section 3.2.2 above suggests that 100% manganese ore is more efficient to facilitate combustion within the boiler chamber. Thus, it seems premature to conclude whether partial substitution or complete substitution is to prefer.

It is clear that methodology and general philosophy concerning bed regeneration will have to be a crucial part of the concept. Here factors not considered in this study will also be important, such as for example waste handling and the possibility to use spend manganese ore as raw material for metallurgic purposes.

4.3 EFFECT ON NITRIC OXIDE EMISSIONS

As have been explained above, neither the laboratory experiments nor the experiments at Chalmers Research Boiler suggested that the proposed method could provide a considerable improvement with respect to NO emissions. This is rather disappointing, considering that this was a working hypothesis of the project. On the contrary, the results suggest that substitution of sand with manganese ore could even result in increased NO emissions. General comments:

- Manganese ore may in fact enhance *NO formation* in the combustion chamber, by consuming reducing gas components such as H_2 and CO and forming oxidizing products such as H_2O and CO_2. This is because NO formation is hampered by reducing atmosphere, but facilitated by oxidizing atmosphere.
- The assumption prior to the project was that manganese ore would facilitate *NO reduction*, since transition metal oxides are known to catalyse this[51].
- The ultimate NO emissions released from combustion is equal to *NO formation* minus *NO reduction*.

The reasoning above suggests that although the work presented here does not look promising with respect to NO reduction, it cannot be dismissed that such reduction could in fact be possible. It may just have been that the process conditions used just were incapable to unlock the conditions suitable to achieve an overall reduction of NO. The impact of important factors such as air-staging was not examined, which is known to have great impact in NO formation. The understanding of this subject would likely benefit from further studies.

It shall also be pointed out that for experiments performing well with respect to CO (10% manganese ore day 2 and when sulphur feeding was used) the increase was modest, i.e. 10-20%. It is conceivable that the overall NO emissions could be reduced since NO is also a function of air-to-fuel-ratio. Therefore, if sustained operation on lower air-to-fuel ratio could be facilitated this could indirectly result in reduced NO emissions.

4.4 COMMENTS ON COMMERCIAL POTENTIAL

At this moment, it is difficult to comment on the commercial potential of the concept. However, considering that already 10% manganese ore provided a considerable improvement it is tempting to do so. And while the current project do not allow for detailed analysis about economics some general observations can still be made.

It is clear that there could be significant gains if addition of manganese ore would allow operation at reduced air-to-fuel ratio without increasing emissions of CO and unburnt hydrocarbons. Let us for example assume that a reduction from 30% excess air to 15% excess air would be possible:

- Firstly, if we consider the boiler being dimensioned for a certain gas flow (a simplification) this would allow for a 13% increase in fuel flow and production in a given facility. This would translate to a 13% reduction in capital expenditures (for the boiler) per kWh power and heat produced. With capital expenditures being approximately half of the total expenditures and the boiler being the by far most capital intensive piece of equipment in a fluidized bed power plant, a reduction in the cost of generating power and heat of ≈5% based on reduced capital expenditures seems plausible.
- Secondly, fan power would be reduced with the air flow, in our example by 13%.
- Thirdly, thermal efficiency would increase due to reduced flue gas losses. With wood as fuel and a flue gas temperature in the stack of 160°C the thermal efficiency would improve ≈1%-point in our example.

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[51] *Yao MY, Che DF. Catalytic effects of minerals on NO_x emission from coal combustion. Energy Sources Part A: Recovery, Utilization, and Environmental Effects 2007;29:1005-16.*

Let us then assume that the problems related to poor performance which arouse as function of time had to do with inadequate bed regeneration, as we suggested above. We can also assume that these problems can be solved by proper regeneration, i.e. replacement of about 30% of the bed per day. What would the cost be of this procedure?

- The price for unprocessed manganese ore generally is below 200 €/tonne (2015) or considerably lower for low-grade ores. The cost for the bed material used here which was produced from an expensive raw material (480 €/tonne) by a research institute was about 4200 €/tonne. Let's assume that it would be possible to produce useful oxygen carrier particles at the intermediate price of 500 €/tonne, assuming a dedicated large-scale process rather than a research institutive. This shall be compared with the price of silica sand typically used in CFB boilers, which is in the order of 50 €/tonne. With the assumptions suggested above, a 10% mixture would increase the cost of bed material with 90% while a 5% mixture would increase the cost 45%. These are substantial increases, albeit the cost for bed material is a very minor post in the overall costs for operating a CFB boiler. The procedure could possibly add some complications with respect to ash disposal. However, the general impression is that this opportunity does look interesting and worth considering.
- Alternatively, a dedicated process utilizing 100% manganese ore and novel schemes for bed regeneration and reuse of the bed material could possibly be developed. That goes beyond the scope of this report though.

The reasoning presented above suggests that there could be considerable economic incentives to develop OCAC with manganese ore. A dedicated study with respect to process economy would likely provide more definite answers.

4.5 DISCUSSION ABOUT PROJECT AIMS AND OBTAINED RESULTS

As was outlined in section 1.4 above, the aims of the project stated in the project plan were:

I. To study what effect manganese ore has on the practical operation of a semi-industrial circulating fluidized bed boiler. The goal was to achieve at least one week of operation in Chalmers Research Boiler with partial (or complete) substitution of sand with manganese ore.

II. To examine a number of manganese ores during continuous operation in a small laboratory reactor system. The goal in strictly numerical terms was to examine at least 5 different manganese ores.

III. To show that it is possible to achieve significantly reduced emissions of CO for a given air to fuel ratio by complete or partial substitution of sand with manganese ore in fluidized bed combustion. In numerical terms, the goal with respect to performance in Chalmers Research Boiler was to achieve at least 80% reduction in CO compared to sand reference.

IV. To show that complete or partial substitution with manganese ore could also contribute towards reduced emissions of NO. The goal with respect to performance in Chalmers Research Boiler was to show at least 30% reduction in NO compared to sand reference.

The fulfillment of each goal will be briefly discussed below:

I. We consider this project goal fulfilled. A very large batch (>12 tons) of manganese ore was procured and operated in Chalmers Research Boiler for 23 days, out of which 14 days involved active research. Also both partial substitution of sand and the use of 100% manganese ore were examined. This allows for a much better insight about the operational behavior of manganese ore than envisioned in the project plan. From an operational point of view, it turned out that switching from sand to manganese ore did not involve challenges with respect to factors such as attrition and agglomeration. If anything, the behavior of manganese ore in this application was much better than we had dared to hope. From our point of view this specific activity involved considerable challenges and large uncertainties. Therefore we are particularly pleased about how this turned out.

II. We consider this goal fulfilled as well. The envisioned number of manganese ores was obtained, prepared and examined in the laboratory reactor (point IV). The experiments themselves did not turn out to be as good indicator for the combustion performance of OCAC of biofuels as we had envisioned, but they allowed for providing proof-of-concept and studying a number of materials and their properties. We also learned a lot about how a dedicated laboratory reactor for OCAC experiments could be designed to provide answers to the questions raised in this project.

III. It was shown that considerable reduction in CO for a given air to fuel ratio was indeed possible, so we consider this goal fulfilled. While good results were not a given at all operational conditions it was shown beyond doubt that the potential is there. For example, at the specific air-to-fuel ratio of 1.07 experiments with 10% manganese ore has ≈70% less emissions of CO compared to experiments with fresh sand, while the experiments with 100% manganese ore (with sulphur feeding and partially regenerated bed) has ≈55% less at an air-to-fuel ratio of 1.07 and ≈90% less at 1.10. As explained in detail above, we believe that the key to unlocking the potential of OCAC with manganese ore is improved understanding of interactions between bed material and fuel ash. It could be argued that the importance of such interactions should have been evident before the project was initiated. While this is true, the overall aim of the current project was limited and focused mainly on providing credible proof-of-concept rather than studying details. After all, ash chemistry in biomass combustion is a highly complex issue and would need different resources to study than what was at our disposal in the current project.

IV. This project goal was not reached. No improvement was seen with respect to NO emissions. Neither in Chalmers Research Boiler nor in laboratory experiments. On the contrary, NO increased in all cases. For conditions with favorable performance with respect to CO the increase in NO emissions was very small but it still increased. The goal with 30% reduction was based on results from the previous study using ilmenite in Chalmers Research Boiler[52]. The cited paper does not present any definite conclusion whether the NO reduction was due to decreased NO formation or increased NO reduction, but suggests that the latter could be the case due to catalytic properties of the bed materials. When determining the project goals we reasoned that manganese ore should be equal to ilmenite with respect to

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[52] *Thunman H, Lind F, Breitholtz C, Berguerand N, Seemann M. Using an oxygen-carrier as bed material for combustion of biomass in a 12-MW$_{th}$ circulating fluidized-bed boiler. Fuel 2013;113:300-309.*

> NO reduction since it is known that transition metal oxides (especially iron oxides) can catalyze such reactions[53,54]. Manganese ores are rich in iron oxide and manganese oxides themselves could also be expected to have similar effect. We also thought that the use of an oxygen carrier would reduce the presence of hot spots, which could contribute to lower NO formation. As have been explained in detail above, this issue is probably more complicated than we imagine. While we believe that the potential for enhanced NO reduction is there we now tend to believe that NO formation may be enhanced due to fast reaction between the reducing gases CO and H_2 and manganese oxide, resulting in less reducing conditions during combustion which should facilitate NO formation.

To conclude, three out of four project goals were clearly fulfilled. The central part of the project which was practical experiments in Chalmers Research Boiler worked out considerably better than expected. The project results were highly interesting and suggests that the concept could have commercial value. Further studies in areas related to interactions between manganese ore and biomass ash as well as mechanisms for NO formation and NO reduction in presence of manganese ore would provide a more complete picture.

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[53] *Yao MY, Che DF. Catalytic effects of minerals on NOx emission from coal combustion. Energy Sources Part A: Recovery, Utilization, and Environmental Effects 2007;29:1005-16.*

[54] *Ohtsuka Y, Wu Z. Effect of metal cations present naturally in coal on the fate of coal-bound nitrogen in the fixed-bed pyrolysis of 25 coals with different ranks: Correlation between inherent Fe cations and* N_2 *formation from low rank coals. Energy & Fuels 2009;23:4774-4781.*

5 Conclusions

Based on the experiments in Chalmers Research Boiler, the experiments in laboratory reactor and theoretical considerations, the following conclusions can be drawn:

- Oxygen Carrier Aided Combustion (OCAC) of biomass using manganese ore as bed material appears to be a viable concept with potential to significantly improve performance of existing Circulating Fluidized Bed (CFB) boilers.
- Substitution of just 10% of the sand bed with manganese ore makes it possible to reduce the air to fuel ratio considerably, without generating large amounts of CO. In the experimental campaign in Chalmers Research Boiler up to 70% reduction was achieved, compared to a sand reference. This suggests that higher fuel flow may be feasible in existing facilities, and that fan power and heat loss with flue gases could be reduced.
- During multi-day operation in Chalmers Research Boiler issues with respect to CO and NO emissions manifested itself. It is believed that this was related to accumulation of alkali compounds in the boiler, which seems natural since the bed was not regenerated to the same extent as during operation with sand. The manganese ore used also had rather high alkali content and may have been unable to adsorb more. This is an issue that needs further examination.
- Using 100% manganese ore as bed material show similar or greater potential than partial substitution, with up to 90% reduction in CO emissions compared to the sand reference. However, such results were only achieved when combining manganese ore with sulphur feeding for removal of alkali, in accordance with the theory suggested above.
- Without sulphur feeding the use of 100% manganese ore as bed material resulted in higher emissions of CO than the sand reference.
- From an operational point of view not considering emissions, manganese ore was shown to work excellent as bed material in fluidized bed boilers. No problems were encountered related to factors such as attrition and agglomeration. Also the material was easy to handle, to fill into and remove from the reactor.
- In laboratory experiments several manganese ores were shown to be viable as oxygen carrier particles, but it was clear that different ores have very different mechanical properties. Especially bulk density varied in a wide range, suggesting that not all ores are suitable for the application without pre-treatment.
- It is clear from the temperature profile of Chalmers Research Boiler that the presence the oxygen carrier is active in the process and facilitates fuel conversion inside the reactor vessel. Basically, the temperature in the bottom bed and the temperature drop over the cyclone increases as function of the amount of manganese ore added. This means that more fuel burns inside the dense section of the bed and that there is much less combustibles entering the cyclone, compared to operation with sand. This effect did not always translate to reduced CO emissions though, as explained above.
- The method did not show great potential for reduction of NO emissions. For a given air-to-fuel ratio, NO emissions was always higher when manganese ore was included in the bed compared to when only sand was used. For experiments performing poorly also with respect to CO, an increase of up to 100% was seen. For experiments performing well with respect to CO (10% manganese ore day 2 and when sulphur feeding was used) the increase was more modest, i.e. 10-20%.

- It is conceivable that the overall NO emissions could be reduced since NO is also a function of air-to-fuel-ratio. Therefore, if sustained operation on lower air-to-fuel ratio could be facilitated this could indirectly result in reduced NO emissions.

IMPROVED COMBUSTION IN FLUIDIZED BED WITH MANGANESE ORE AS BED MATERIAL

En av de viktigaste faktorerna som påverkar förbränningsresultatet i biomass-eldade kraftverk är omblandning av bränsle och syre. Oxygen Carrier Aided Combustion, OCAC, är ett nytt förbränningskoncept. Förbränning sker då i en fluidiserad bädd innehållande ett fast syrerikt material som har förmågan att kunna reagera med både bränsle och syre. Det möjliggör nya reaktionsvägar och mekanismer för hur syre och bränsle kan mötas.

I den här rapporten beskrivs experiment med manganmalm som syrebärande material. Här beskrivs experiment både i laboratoriemiljö och i semi-industriell skala i en forskningspanna som innehåller flera ton manganmalm.

Resultaten visar att en betydande minskning av luft-bränsle-förhållandet för förbränning skulle vara möjlig utan att mängden oförbränt material ökar jämfört med en referens. Alla processförhållanden leder dock inte till goda förbränningsresultat, vilket kan vara knutet till hur manganmalm interagerar med askkomponenter som kalium.

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