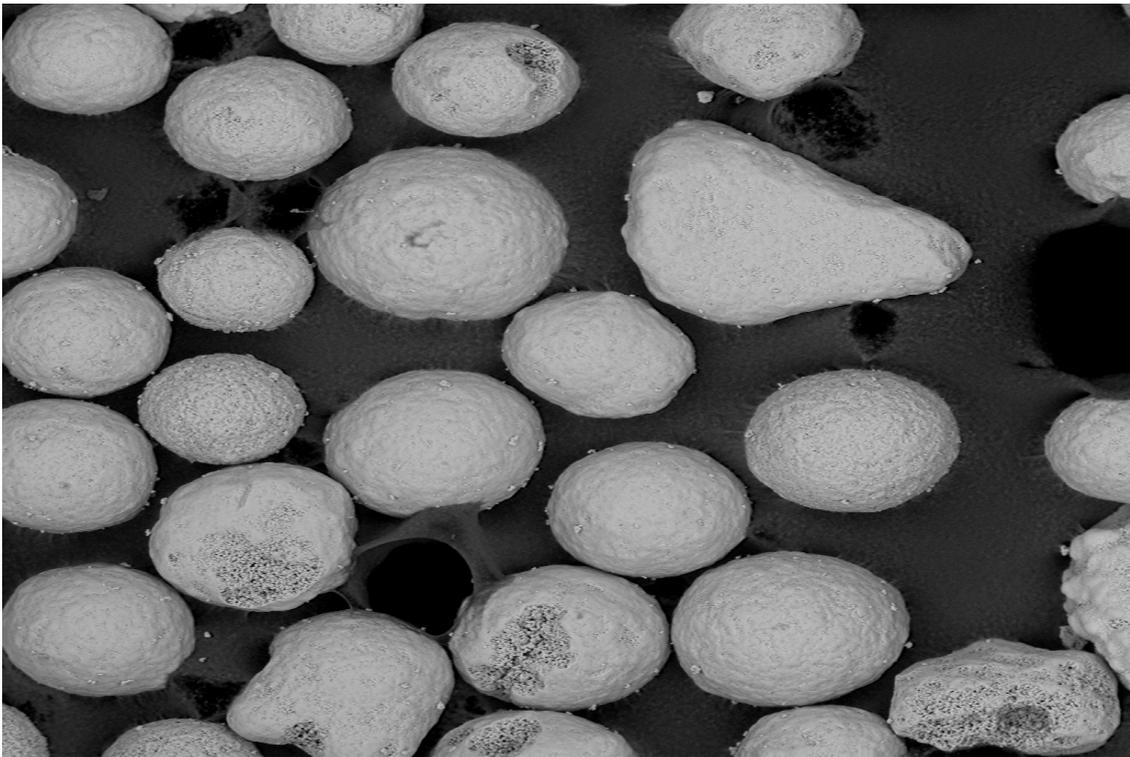




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Experimental Investigation of Alkali Release From Different Oxygen Carrier's used in CLC

Thermogravimetric Analysis (TGA), Surface Ionization
Detection (SID) and Scanning Electron Microscope (SEM)
Analysis of Oxygen Carrier and Alkali Interaction

Master's thesis in Innovative and Sustainable Chemical Engineering (MPISC)

BINIAM O. KIFLEYESUS

MASTER'S THESIS 2020:NN

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Cover: SEM image of the 5 wt.% alkali dosed fresh C28 oxygen carrier ($CaMn_{0.755}Ti_{0.125}Mg_{0.1}O_{3-\delta}$) which later treated in a furnace at a heating rate of 5 °C/min to 900 °C with an isotherm for 1 hour at 900 °C and then cooled at the same rate to room temperature.

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Abstract

Continuous summits and conferences have been and are being held to address alarming situation of global warming and climatic change. Such conference is the Paris 2015 United Nation Climatic Change Conference. But it is not enough, we should take actions not only to limit and eliminate emissions, but also to remove and reduce the already emitted green house gases such as CO₂. One of the technologies that has the potential of negative CO₂ circulation in the environment is chemical looping combustion (CLC) by using biomass. CLC is an energy production method with inherent CO₂ capture which can be used for negative emission if biomass is used as fuel.

Challenges in using biomass as energy source are the diverse inorganic content of biomass such as alkali metals. Alkali metals cause corrosion and deterioration of down stream equipment such as heat exchangers and piping systems. They can also cause bed agglomerate, deactivate and cause fouling to the oxygen carrier (OC) used in CLC. To narrow the gap of our understanding on CLC, developing an on-line measurement technique for all components would help mitigating these challenges either by taking proactive or counteractive measures. In this paper therefore, a concept which uses thermal ionization known as Surface Ionization (SI) was used to detect alkali from exhaust gas of a redox reaction of CLC technology on OC material used in CLC using thermogravimetric analysis (TGA). The TGA analysis was conducted on different oxygen carriers subjected to typical CLC environments which are inert, oxidising and reducing.

The system was able to detect alkali metals released from intentionally KCl dosed fresh oxygen carrier (C28), and was able to determine different desorption dynamics of alkali metals. Surface and cross sectional SEM-EDX analysis was used to analyse different locations of the potassium on the oxygen carrier particle. The analysis was then expanded to fresh oxygen carrier (C28), oxygen carrier from lab-reactor (C28) and oxygen carrier from a pilot plant (mixture of 80 wt.% of ilmenite and C28).

Based on the results from the SEM-EDX cross sectional elemental analysis, the oxygen carrier from the lab reactor and pilot plant found to contain alkali mainly potassium absorbed in a very low concentration, however the alkali metal was found to exist independent of chlorine. The TGA and SID integration was able to detect low alkali release from both the oxygen carriers with relatively higher release from the pilot plant during all TGA environments.

Keywords: Oxygen carrier, Manganese ore, Ilmenite, Alkali metals, Biomass combustion, Chemical loop combustion.

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Contents

List of Figures	xi
List of Tables	xv
1 Introduction	1
1.1 Literature Study of CLC Technology	2
1.2 Problem approach	4
1.2.1 Pilot plant	5
1.2.2 Lab reactor	5
1.2.3 TGA System	6
1.3 Objective	6
1.4 Limitation	6
2 Experimental	7
2.1 Instrumentation	7
2.1.1 Thermogravimetric Analysis	7
2.1.2 Surface Ionization Detection	7
2.1.3 TGA and SID Arrangement	8
2.1.4 Scanning Electron Microscope	9
2.2 Experimental procedure	9
3 Results and Discussion	11
3.1 System Analysis	11
3.1.1 Empty pan Analysis	11
3.1.2 Alkali dosed fresh C28 Oxygen Carrier Analysis	13
3.2 SEM-EDX Analysis	18
3.2.1 Oxygen carrier from the lab-reactor	18
3.2.2 Oxygen carrier from the 100 kW unit pilot plant	20
3.3 TGA and SID Analysis	21
3.3.1 Inert Environment	21
3.3.2 Oxidation Environment	23
3.3.3 Reduction Environment	23
3.3.4 Cycle	24
4 Conclusions	27
4.1 Recommendations	28

Bibliography

29

List of Figures

1.1	Schematic diagram of Chemical Looping Combustion (CLC)	2
1.2	Implication of biomass fuel in CLC for negative environmental CO_2 circulation	2
2.1	Experimental set-up of the TGA and SID integration for alkali detection.	8
3.1	TGA temperature ramp at the rate of 20 °C/min and SID signal of alkali concentration from the exhaust gas. The amplification ratio of the SID-system is 10^8	11
3.2	TGA temperature ramp at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8 .	12
3.3	TGA temperature ramp analysis after treating the old pan with HNO_3 and heated for 20 min. The ramp temperature was set at the rate of 20 °C/min to 1000 °C and SID signal corresponding to alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8	12
3.4	New alumina and Platinum pan of TGA temperature ramp at the rate of 20 °C/min and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8 .	13
3.5	TGA temperature ramp at the rate of 20 °C/min and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8	14
3.6	TGA temperature ramp at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8 .	14
3.7	Surface elemental combined map SEM analysis on the alkali dosed OC (color identified)	15
3.8	Cross sectional elemental combined map SEM analysis on the alkali dosed OC (color identified)	15
3.9	Cross sectional elemental combined map SEM analysis on the alkali dosed oxygen carrier (Potassium)	16
3.10	Cross sectional elemental combined map SEM analysis on the alkali dosed oxygen carrier (Chlorine)	16

3.11	Extended isotherm condition of TGA and SID analysis to examine the peaks observed on figure 3.6 and the alkali detected on the SEM analysis of figures 3.9, 3.10. The amplification ratio of the SID-system is 10^8	16
3.12	Double isotherm TGA and SID analysis (repeat of the single isotherm process experiment with out opening the system) on the alkali dosed oxygen carrier. The amplification ratio of the SID-system is 10^8 . . .	17
3.13	Double isotherm TGA temperature and Weight analysis (repeat of the single isotherm process experiment with out opening the system) on the alkali dosed oxygen carrier.	17
3.14	Surface elemental combined map SEM analysis on the alkali dosed OC after the TGA analysis (see figure3.6(color identified)	18
3.15	Cross sectional elemental combined map and point SEM-EDX analysis on different particles of the oxygen carrier from the lab reactor .	19
3.16	Cross sectional elemental combined map SEM-EDX analysis of the oxygen carrier from the lab reactor	20
3.17	Cross sectional elemental combined map SEM analysis of the oxygen carrier from the 100 kW unit pilot plant at chalmers university (color identified)	20
3.18	Cross sectional elemental combined map SEM analysis of the oxygen carrier from the 100 kW unit pilot plant at Chalmers University color identified for individual elements	21
3.19	Inert condition: Empty pan TGA and SID analysis. TGA ramp temperature at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C with an isotherm for 25 min at and 1000 °C then cooling at a rate of 20 °C/min to 200 °C. Alkali signal detected by the SID corresponding to alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9	22
3.20	Inert condition: Repeat of experiment on figure 3.19 with a new empty platinum pan (System check). TGA ramp temperature at the rate of 20 °C/min to 500 °C then at 10 °C/min to 1000 °C with an isotherm condition at 1000 °C for 25 min and again 20 °C/min to 200 °C. SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9	22
3.21	Inert condition: Empty pan (Blue), Fresh C28 OC (Green), oxygen carrier from the lab reactor experiment (Yellow), oxygen carrier from the pilot plant (Violet) and Temperature (Red).TGA ramp-temperature at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9	23
3.22	Oxidation condition: Empty pan (Blue), fresh C28 OC (Green), oxygen carrier from the lab reactor experiment (Yellow), oxygen carrier from the pilot plant (Violet) and Temperature (Red). TGA ramp-temperature at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9	23

-
- 3.23 Reduction condition: Empty pan (Blue), fresh C28 OC (Green), oxygen carrier from the lab reactor experiment (Yellow), oxygen carrier from the pilot plant (Violet) and Temperature (Red). TGA ramp-temperature at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9 24
- 3.24 Cycle experiments: Starts with temperature ramp to 900 °C at a rate of 25 °C/min then Isotherm for 100 min at 900 °C where 10 min Inert, 15 min Oxidation, 10 min Inert and 15 min Reduction environmental conditions repeats twice and proceeds to temperature ramp to 1000 °C at the rate of 10 °C/min where the same cycle as in the 900 °C repeats for 100 min. Cooling to 200 °C at rate of 25 °C/min. 25

List of Tables

3.1	Elemental weight concentration of the surface SEM analysis of the alkali dosed fresh OC	15
3.2	Elemental weight concentration of the Cross sectional SEM analysis of the alkali dosed fresh OC	15
3.3	Elemental weight concentration of the surface SEM analysis of the alkali dosed fresh OC after the TGA analysis (see figure3.6	18
3.4	Elemental weight concentration of the Cross sectional SEM-EDX combined elemental map analysis of the oxygen carrier from the lab reactor exposed to 0.32 mgKCl/min for 5 hours of reactor environmental cycle	19
3.5	Elemental weight concentration of the Cross sectional SEM analysis of the oxygen carrier from the 100 kW unit pilot plant at Chalmers University	20

1

Introduction

Growing environmental concern and climate change are issues that the world should act on today. These are human made problems that are caused from the lack of thinking sustainably and taking unsustainable development measures. Summits are continuously held to address these issues in order to reduce greenhouse gas emissions to the environment (Paris Summit 2015), but this is not enough, we should not only think on reducing the greenhouse gases emission. It is time to think and work on how to reduce the already released greenhouse gases in the environment. Chemical looping combustion (CLC) is one of the hot topics that has the potential to address CO_2 deposition in the environment. The potential of CLC is not only to reduce the emission of CO_2 to the environment, but also to capture the CO_2 that has already being released to the environment. This can be achieved by using biomass as a fuel source for the combustion.

Biomass is the product of organic material that is being used as a major fuel source for energy production across the globe. Wood, sawdust, animal and municipal waste and other residues including purposefully grown plants can be classified as biomass materials that can be used as bio- energy resources. Biomass is considered as environmentally manageable renewable energy resource with neutral CO_2 emission. This is because the CO_2 in the environment released by burning a plant is used in the photosynthesis of the same plant. However, the lack of proper management of biomass energy resources such as forests could lead to environmentally unsustainable biomass use.

CLC is a technology of combustion whereby synthesised or naturally existing metal oxides are used to carry the oxygen needed in the combustion process as air in the conventional combustion process. CLC is built using two fluidized bed reactors known as air reactor (AR) and fuel reactor (FR), see circulating fluidized reactors Figure 1.1. The metal oxide (MeO) particles circulates between these two reactors carrying oxygen hence the name oxygen carrier (OC). In the AR, air is used to oxidise the oxygen carrier before they are transported to FR where they release oxygen when being reduced by the fuel. From the AR, oxygen depleted nitrogen is released and from the FR, CO_2 and H_2O are major gaseous products. Therefore, the energy intensive separation of CO_2 from N_2 in the conventional combustion process is avoided in CLC where H_2O is easily condensed, and pure CO_2 can be captured and stored and managed. The main advantage of chemical looping combustion is the low penalty in energy compared to conventional combustion process which makes it a competitive sustainable candidate of combustion technology in the energy industries

[1][2] [15].

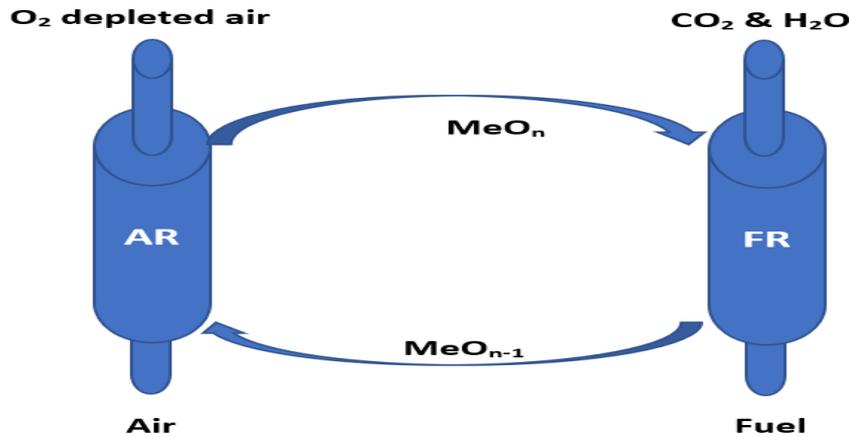


Figure 1.1: Schematic diagram of Chemical Looping Combustion (CLC)

Biomass is CO₂ neutral, this is because the same plant used to produce energy and release CO₂ will use the same CO₂ in the environment for its photosynthesis. CLC captures CO₂, so if biomass is burnt using CLC technology then there will be a negative CO₂ circulation in the environment. This circulation is depicted in the below figure 1.2.

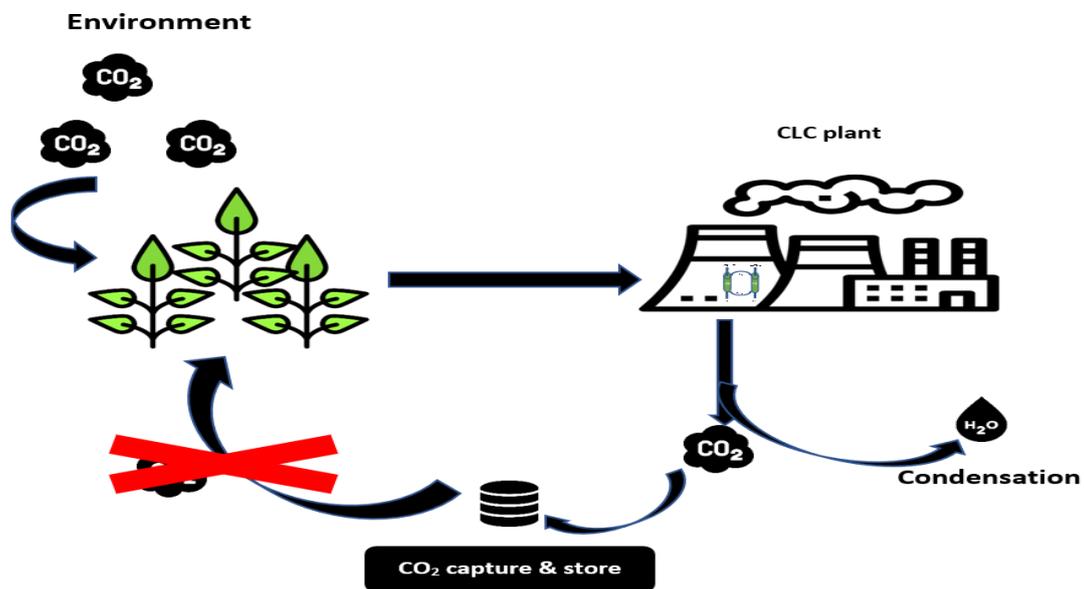


Figure 1.2: Implication of biomass fuel in CLC for negative environmental CO₂ circulation

1.1 Literature Study of CLC Technology

Some of the challenges that CLC have is the choice of the oxygen carrier with good fuel conversion, durable, environmentally sound, high reactivity and economically

feasible [3]. Lyngfelt, A.(2011) summarises an overview of 41 studies on the development of oxygen carriers. Several oxygen carriers such as Ni, Co, Cu, Fe, Ca, Mn oxides and their combinations were being studied. Nickel based oxygen carrier showed good fuel conversion and high reactivity with low attrition, but they are expensive, toxic to environment and health with thermal constraint for full conversion. This was further supported by Rydén [4] and Jing [1]. According to Rydén and Jing Nickel based oxygen carriers showed severe deterioration when using biomass fuel comparing coals, probably due to the presence of sulphur in the biomass which indicates its unsuitability to be used with renewable energy resource [1] [4].

From the discussion by Lyngfelt A. 2011 the main challenge of CLC also lies on oxygen carrier inventories, that is to create fuel-oxygen carrier contact area specially for solid fuels. However, this can be encountered by the potential of some oxygen carriers to release gaseous oxygen from their oxides as such copper-based oxygen carriers [3]. This potential is called oxygen uncoupling. Oxygen carrier inventory is the amount or mass of oxygen carrier used by the system. CuO oxygen carrier particles showed good oxygen uncoupling effect with relatively low oxygen carrier inventory that resulted in complete fuel conversion.

In terms of reactivity and price Ni, Cu, Mn, Fe are ordered from high to low respectively. Generally speaking, these metals and their oxide forms, showed good fuel conversion for gaseous fuels and can be scaled to large commercial production. However, more research is needed for the use of solid fuels. The main challenge with solid fuels lies on the limited contact area between the fuel and oxygen carrier. The ash and char formation is also another challenge that may lead to short life and uneconomical use of oxygen carriers. Based on the reactivity and price hierarchy, the next candidate OC material is CuO-based oxygen carriers using Al_3O_3 , ZrO_2 , $MgAl_2O_4$, TiO_2 and SiO_2 as a support materials. The potential of good oxygen uncoupling and high oxygen transfer capacity makes it an ideal candidate. However, its defluidization behaviour and formation of agglomerates at moderate temperatures along with its affinity to react with Al_3O_3 and lose its oxygen uncoupling effect makes it difficult to scale for large scale production and operation [1].

Ilmenite (Fe_2TiO_5) is a naturally occurring mineral with the potential of high reactivity when using synthetic fuel gases (CO and H_2). Ilmenite is a cheap, non-toxic, naturally abundant material with favourable thermodynamical properties that has the potential of providing high combustion efficiency. The main advantage with Fe-based oxygen carrier is its low cost and the main disadvantage is the lack of oxygen uncoupling and poor oxygen transferring capacity [2],[5]. A paper by Chen L. discusses on how to improve the ilmenite-based oxygen carrier performance by introducing alkali or alkali earth metals and transition metals. Based on the finding's alkali metals were found to facilitate reactivity of the oxygen carrier with wet syngas and coal char [5].

Another approach on the study of oxygen carrier development is to use the combination of different metal oxides. One of the heavily studied combination metal oxides

is, MnO with Fe-, Cu-, Mg- Si- and Ti- oxides. Thus combinations of metal oxides are reported to have good reactivity with methane and good oxygen uncoupling effect [1]. $CaMnO_{3-\delta}$ is with perovskite structure that can be categorised under these combined metal oxides oxygen carriers. The delta (δ) - represents the oxygen deficiency in the structure that is dependent on oxygen partial pressure of the environment to which it is operating and hence release or uptake oxygen. A recent study on the development of Ca-Mn-based oxygen carrier is the European SUCCESS (2013-2017) project where a large scale of cheap material has been produced. Good attrition resistance with good oxygen uncoupling effect and high reactivity are the main advantages of this oxygen carrier. However it is prone for sulphur poisoning [1].

CLC is proved to perform well through different experiments using synthesised or manufactured oxygen carriers when using syngas and methane. Syngas (CO and H_2) and methane (CH_4) can be produced from biomass through technologies such as gasification and pyrolysis for environmentally sustainable energy forms. However from economical feasibility perspective the ability to use solid biomass as fuel directly in CLC would be a ground brake. But due to the aggressive nature of the inorganic compounds of biomass solid fuels, oxygen carrier could be lost as fines or gets contaminated which leads to uneconomical use of the oxygen carriers. The slow or insufficient conversion of solid fuel due to less reaction contact area with the solid oxygen carrier is also another reason which affects the reactivity and thereby conversion efficiency in time. An oxygen carrier that suits for solid bio-fuels should have CLOU properties. This, since the gaseous oxygen will lead to fuel gasification and thereby the OC-fuel interaction will go from solid-solid to solid-gas interaction with greatly enhanced conversion efficiency [2].

Industrial countries utilize technologies such as gasification and pyrolysis to produce gaseous fuels from biomass. Large power plants and district heating factories utilize municipal wastes as fuel in combustion. Carbon monoxide, hydrogen and methane commonly known as syngas are mainly the major gaseous components often produced when burning biomass. Though, biomass contains impurities such as tar, particulate matters, acidic gases and alkali metals, biomass gasification is considered a promising thermochemical conversion technology in delivering these easily accessible fuel components for CLC process where side effect of these impurities can be avoided [7] [6] [8].

1.2 Problem approach

This thesis is part of the research on the development and up-scaling process of the CLC technology. One main challenge of CLC technology is the choice of economically feasible oxygen carrier for commercially operable and environmentally sustainable CLC plant. To address this challenge, it is crucial to understand the interaction of the OC and alkali metals. Studying and understanding this interaction would allow us to use, regenerate and manufacture feasible OCs. The 100 kW unit pilot plant, a lab scale reactor and in this thesis a small TGA unit are some of these

hierarchy study of the problem study.

1.2.1 Pilot plant

The 100 kW pilot plant setup at Chalmers have similar design as the CLC setup depicted on diagram 1.1. More description of the setup can be found in [8], [9].

In a study by Gogolev I., the system used synthesised calcium manganite perovskite ($CaMn_{0.755}Ti_{0.125}Mg_{0.1}O_{3-\delta}$) here by it is referred as C28 and natural ilmenite oxygen carriers to convert four types of biomass fuels with varied alkali contents. The four biomass fuels are black pellets, black pellets impregnated with K_2CO_3 , a mixture of 50/50 wt.% black pellets and straw pellets and wood char. This experimental study was the first of its kind to study the fate of biomass alkali on both reactors in CLC technology. The study found that most of the alkali were found to be accumulated on the oxygen carrier and the alkali release from the AR was found to be higher or the same as the alkali release from the FR flue gas. However it was also noted that toward the end of the campaign the ilmenite ratio was increased to 80-90 % to compensate the inventory of the oxygen carrier as there were no-more fresh C28 present to add. Oxygen carrier sample from this project will be analysed in different TGA environments to analyse the release and association of alkaline from the oxygen carrier [8].

1.2.2 Lab reactor

A research on a batch wise fluidized bed reactor is under way on the study of alkali and C28 interaction at Gothenburg University by Andersson V.. The reactor operates as AR (oxygen carrier oxidation) and FR (oxygen carrier reduction) at different times with inert transition. The reactor operates at 800, 850 and 900 °C temperature which is typical CLC operation temperature. To mimic the biomass nature of an actual CLC operation using biomass fuel, 13% synthetic-gas (50% CO and H₂) in nitrogen is fed as fuel to the reactor. However synthesized-gas does not contain alkali, hence to represent the alkali content of biomass fuel, 0, 7 and 14 mgKCl/m³ mass concentration of potassium chloride are fed with the fuel. This mass concentration corresponds to "no-alkali", "medium loading" and "high loading" respectively. To ensure well specified and controllable, stable and repeatable introduction of alkali species dosage, alkali are injected in the form of aerosols in a carrier gas of nitrogen to represent a more realistic CLC-system. These KCl aerosol particles evaporates before reaching the OC bed material and thus, the alkali are in gas phase when reaching the bed. A redox cycle of the system is defined as oxidation (3 Vol.% O₂ in N₂)-inert-reduction-inert operation. C28 exposed to 10 mM KCl for whole cycle means that the system was fed with 14 mgKCl/m³ of potassium chloride during all operating environments. More about the system and its experimental set-ups can be referred to [10].

1.2.3 TGA System

Another approach that can be utilised in smaller scale study of the system is thermal analysis. One of these experimental methods used is thermogravimetric analysis. Thermogravimetric analysis (here by it will be referred as TGA) is an experimental method used to analyze the weight change of a substance against temperature in time. Whereby physic-chemical information such as oxidation and/or reduction, adsorption and/or desorption, quantitative content, thermal stability and/or performance of the substance can be obtained [12]. The TGA has been used for different purposes in regards of chemical looping combustion technology. Such studies can be [1, 5] which studied oxygen carrying capacity of an oxygen carrier material.

1.3 Objective

The main objective of this project is to make scientific contribution to the research study undergoing for the commercial CLC up-scaling to use biomass as fuel energy source.

Thus the project investigates the interaction of oxygen carrier and commonly found alkali in biomass by focusing on:

- Develop simple methodology of alkali detection analysis.
- Alkali detection analysis from C28 and ilmenite to predict alkali-oxygen carrier interaction

1.4 Limitation

Below are listed as limitations of this paper:

- Only two oxygen carrier were examined i.e. Ilmenite and C28
- Oxygen carriers from the pilot plant was a mixture of of ilmenite and C28, it would have been more informative if they were investigated individually.

2

Experimental

2.1 Instrumentation

2.1.1 Thermogravimetric Analysis

In this master thesis project, TGA environments are being setup as the following compositions. Reduction environment (13 vol.% syngas in nitrogen), oxidation environment (5 vol.% oxygen in nitrogen) and inert environment with pure nitrogen. A sample is placed in a platinum pan inside a quartz furnace, where it is hanged on a thin platinum thread that continuously measures the weight of the sample. The maximum temperature that the TGA can reach is 1000 °C. Since the reactors in CLC system are usually operated around 850 -950 °C and gaseous alkali can be found even at lower temperatures , the ramping from low to high temperature can also be very significant. The TGA is equipped with a thermocouple to have online temperature measurement inside the furnace. Heating of the sample starts at room temperature and will be increased at different rate, suitable to the sample. The TGA is connected to two stream of gas flow, one that supplies the gas required to create the environment and the other stream that provides nitrogen gas for the balance purge flow.

2.1.2 Surface Ionization Detection

The principle of surface ionization (SI) process has been employed on various application [14]. Recently it has successfully used as alkali detection instrument in combustion systems on both small [10] and larger scales [8, 11]. Surface Ionization Detector (SID) is connected to the TGA exhaust gas stream to measure gaseous alkali metals (K and Na) released from the sample. The TGA exhaust gas is diluted by nitrogen to take 700 mL/min which has been used in similar set up of the same SID in previous studies [11]. The dilution ratio is later used to match the actual concentration of alkali in the exhaust gas. High alkali concentration in the gas stream to be analysed has the risk to overdose the platinum filament in the SID system. The flow for dilution is regulated using mass flow controller (MFC). SID utilises thermal excitation of targeted ions to detect alkali in the exhaust stream. In this process alkali containing exhaust gas flows through the measurement cell of the SID. When the alkali come into contact with hot platinum filament located inside the cell, alkali ions are generated. These positively charged alkali ions will then be excited to the nearest, negatively charged, electrode metal detector. When the alkali ions hit the electrode, they send out signal current which is amplified and

logged. The signal is proportional to the alkali mass concentration in the exhaust gas stream. The temperature of the filament is controlled by a power supply (set approximately 4.7A) and the voltage of the metal detector is controlled by a high voltage supply (set -300V). The current signal can be calibrated using commercial Scanning Mobility Particle Sizer (SMPS) which gives the particle (in this case alkali) to correspond alkali mass concentration.

2.1.3 TGA and SID Arrangement

The TGA will be used to analyze the weight change of the oxygen carrier as a function of temperature in different environments, and the SID will be used simultaneously to measure alkali concentration in the exhaust gas.

Similar SID setup has been used to measure alkali concentration by Gogolev I. [8] in larger scale at the 100 kw pilot plant at Chalmers University and a smaller scale experiment is underway from Gothenburg University by Viktor Andersson [10]. However, it is noted by [8] that the reading by the SID on alkali detection showed significant fluctuation from the sensitivity analysis conducted. This fluctuation is highly suspected caused due to the lag in calculating the value of dilution ratio and reactor pressure fluctuation. Dilution ratio is the ratio of diluting inert N_2 stream to the alkali carrying TGA exhaust gas stream. A lag in calculating the dilution ratio can highly influence the alkali concentration reading by the SID. However, the dilution and exhaust streams in this study are assumed constant i.e. 7 for all experiments which eliminates the drawbacks stated. The experimental arrangement of TGA and SID integration can be seen on the figure 2.1 below.

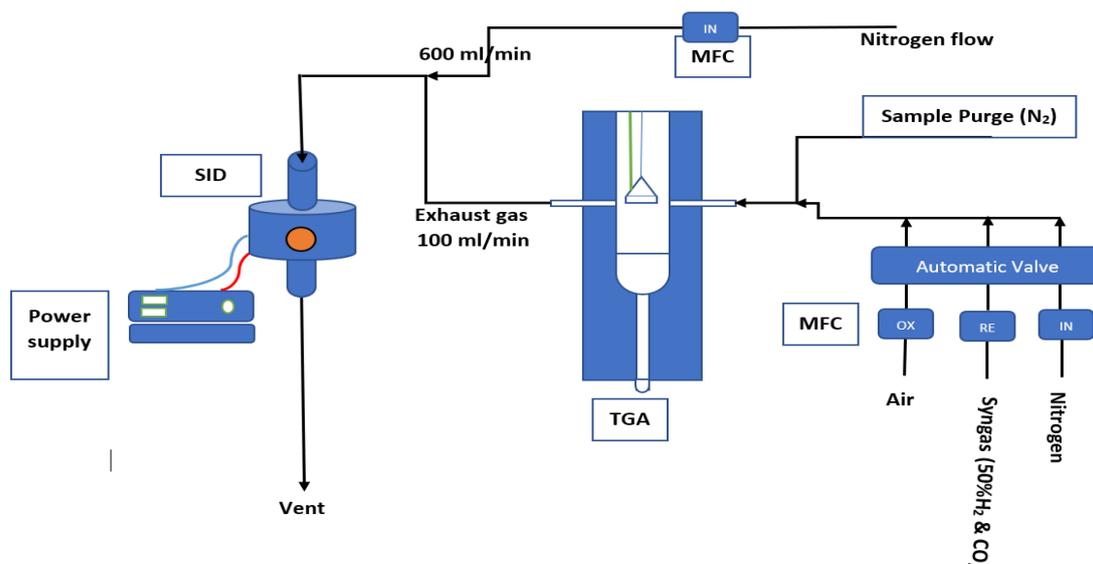


Figure 2.1: Experimental set-up of the TGA and SID integration for alkali detection.

2.1.4 Scanning Electron Microscope

Scanning Electron Microscope Electron Dispersive X-ray (SEM-EDX) utilizes electron beams and electromagnetic radiation to analyse and acquire information of a sample. It is a process of surface analysis of a sample which uses a beam of electrons to obtain high image resolution at very high magnification from the back-scattered electron beams which behaves according to the matter-electron interaction. By doing SEM-EDX analysis both qualitative (type of elements) and quantitative (atomic or weight percentage of the elements) information of a sample can be obtained [13]. Such instrument is the Desktop Phenom SEM analyser. In this experiment the Desktop phenom SEM analyser was used to analyse the elements and take images of different oxygen carrier samples that has been exposed to different forms of alkali concentrations in different environments. The elemental analysis along with the resolution images will be used to identify presence of alkali in the oxygen carrier sample which will supplement the TGA and SID analysis result. In this project two SEM-EDX analysis will be conducted i.e. surface and cross sectional elemental analysis before and after experiments. The cross-sectional analysis are obtained by moulding the OC sample in an epoxy material and grinding them. The surface and cross sectional SEM-EDX analysis will be used to identify surfacely attached and internally absorbed alkali on and in of the oxygen carrier sample.

2.2 Experimental procedure

The analysis was started by doing temperature ramp heating at the rate of 10 °C/min to 1000 °C from room temperature on OC samples followed by isotherm analysis at 1000 °C. In this experiment two types of pans, alumina and platinum were used, where a pan that refers as an old alumina pan, is a pan which has been used in unknown experiments previously and new alumina and platinum pans which never has been used previously. The new pans were used to examine the usage of old alumina as a sample holder for alkali-containing OCs and the background of the system. As described in the previous topic the experiment was conducted with three TGA environmental gas compositions.

After separate experiments on each gas conditions a redox cycle was also conducted. The redox cycling starts with inert condition temperature ramp at a rate of 25 °C/min to 900 °C. After it reached 900 °C first cycle starts with inert then follows oxidation, inert, reduction consecutively with inert gas flow for 10 min and oxidation and reduction gas flow for 15 min each where 10 min inert is in between. After two cycle on the 900 °C it follows a ramp temperature at rate of 100 °C/min to 1000 °C where similar set-up as in the isotherm 900 °C repeats. Finally the process cools to 200 °C at a rate of 25 °C/min.

Initially temperature ramp and isotherm experiment were conducted on inert condition with empty pan, fresh C28 oxygen carrier sample (fresh oxygen carrier is referred as C28 oxygen carrier which never have been introduced to any alkali), deliberately alkali dosed fresh C28 oxygen carrier, C28 oxygen carrier sample from the lab-scale

2. Experimental

reactor (oxygen carrier exposed to 0.044 mgK/min for total 5 hours and 80 wt.% Ilmenite/C28 mixture of oxygen carrier sample from the pilot plant.

Temperature ramp was used to spot where the interesting points happen then isotherm condition was used to analyze more what is being observed at the points of interest. After enough experiments with the inert conditions similar experiments was conducted with reducing and oxidising conditions.

The experiment was started by doing empty pan and fresh oxygen carrier sample experiment with the old alumina pan was conducted. Based on the results obtained new alumina and platinum pan was then used to understand the system and use it as background analysis for the later experiments. Then experiment conducted on the deliberately alkali dosed fresh C28 oxygen carrier was used to analyse the alkali detection ability of the TGA-SID integration in relation to the SEM-EDX analysis.

Finally TGA-SID experiments and SEM-EDX analysis on the oxygen carrier samples from the pilot plant and from the lab-scale reactor experiment was conducted. Random experiments were then repeated to check consistency and trends of results.

3

Results and Discussion

3.1 System Analysis

3.1.1 Empty pan Analysis

Empty pan experiment was conducted to examine the background in order to understand the system. The experiment on the analysis of the background was started using a previously used alumina pan, based on the premise's alumina is inert toward alkali. However, the SID detected some alkali starting at around 900 °C (see figure 3.1) which seems some alkali are being released either from the system or from the pan.

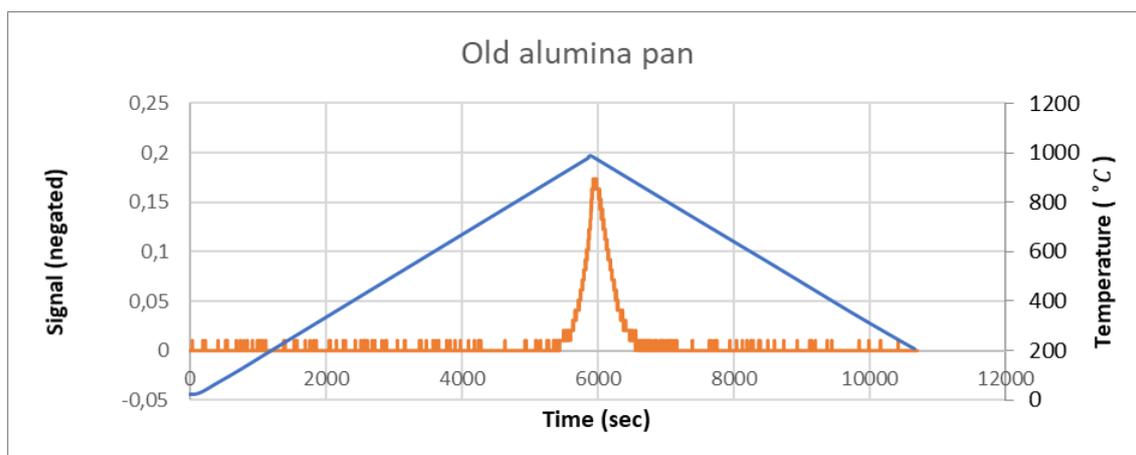


Figure 3.1: TGA temperature ramp at the rate of 20 °C/min and SID signal of alkali concentration from the exhaust gas. The amplification ratio of the SID-system is 10^8

A repeat experiment was conducted on the same pan with slow ramp starting from 700 °C at the rate of 2 °C/min to 1000 °C to see if there are undetected peaks at the 20 °C/min temperature ramp. In addition an isotherm condition at 1000 °C (i.e. the temperature where the peak was observed at the higher ramp) to resolve the peak in time. As it can be seen in Fig 3.2; no other peak or release is observed prior to 900 °C and a constant signal corresponding to the isotherm temperature can be observed by the SID at 1000 °C.

To understand the source of the signal the pan was treated with HNO_3 and distilled water to dissolve and wash away possible alkali contamination from the pan then it

3. Results and Discussion

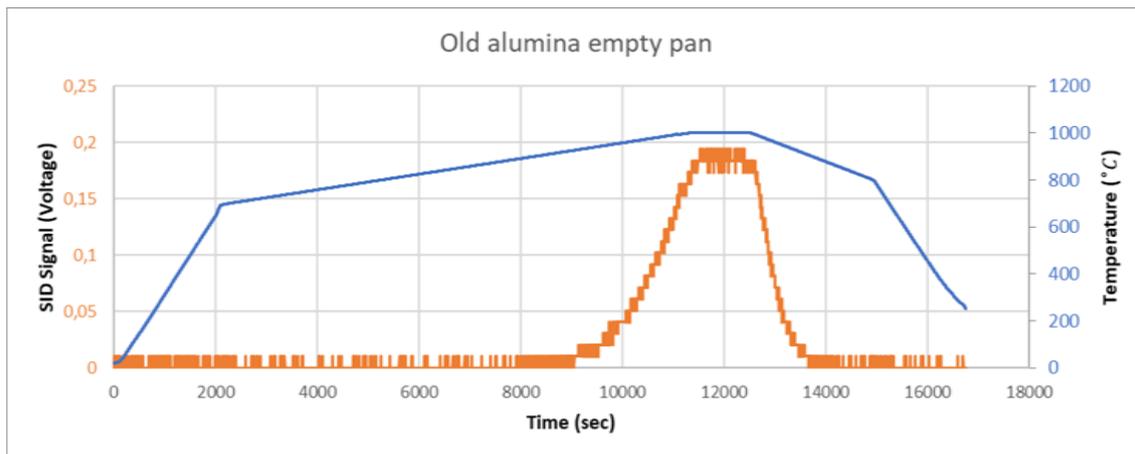


Figure 3.2: TGA temperature ramp at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8

was heated for 20 min to eliminate possible alkali on the pan surface. Interesting results (figure 3.3) was then observed with two peaks which indicate the release of alkali at different ranges of temperatures. The first peak gives the clue that there might have been some alkali deposited on the surface of the pan. These alkali which might have been strongly attached on the pan surface gets detached by the HNO_3 and then evaporates when they are subjected to heat.

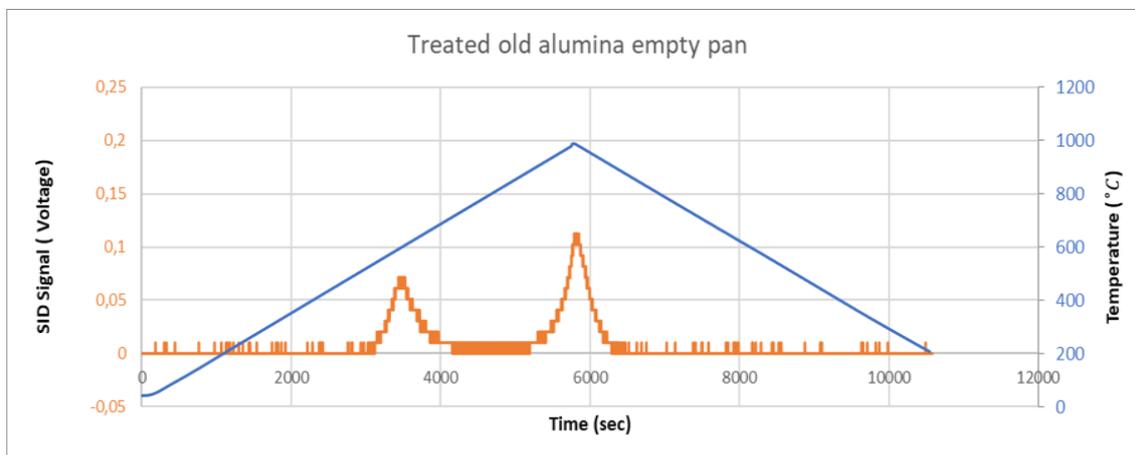


Figure 3.3: TGA temperature ramp analysis after treating the old pan with HNO_3 and heated for 20 min. The ramp temperature was set at the rate of 20 °C/min to 1000 °C and SID signal corresponding to alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8

To further analyse the system two new pans (new alumina pan and platinum pan) were used to expand the reproducibility and consistency of the result. Fig 3.4, shows no alkali detection when both a new alumina pan and a new platinum pan were used. The figure also shows that the TGA furnace is clean of alkali contamination.

Based on the previous experiment on the old alumina, it is observed that the old alumina released alkali, this implies that alumina somehow adsorbs alkali. Therefore alumina cannot be used while studying alkali release from the OC samples in this study and platinum will henceforth be used for all future experiments.

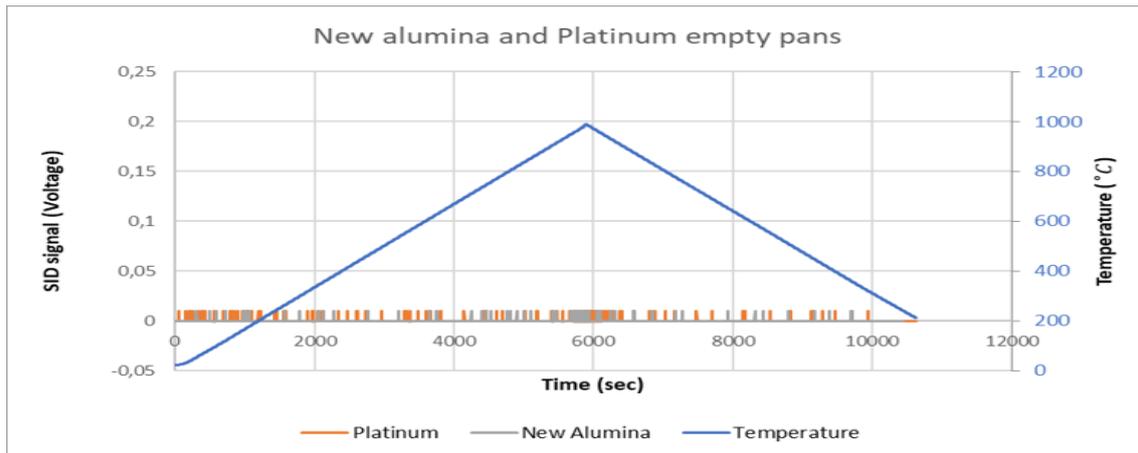


Figure 3.4: New alumina and Platinum pan of TGA temperature ramp at the rate of 20 °C/min and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8

3.1.2 Alkali dosed fresh C28 Oxygen Carrier Analysis

To investigate if the system could detect alkali released from oxygen carriers, a batch of fresh C28 oxygen carrier was treated with 5 wt.% KCl. This was done by mixing the oxygen carrier with the salt and then heated up to 900 °C where it was kept in an isotherm for 1hr at 900 °C in pure nitrogen. The sample was first subjected to TGA temperature ramp analysis at heating rate of 20 °C/min to 1000°C. The signal from the SID alkali detection was very high starting from around 500 °C. As it can be seen in the figure: 3.5, the signal exceeded the maximal detection level that is 10 V. This implies that the true value of signal might be higher than what is seen in the figure.

3. Results and Discussion

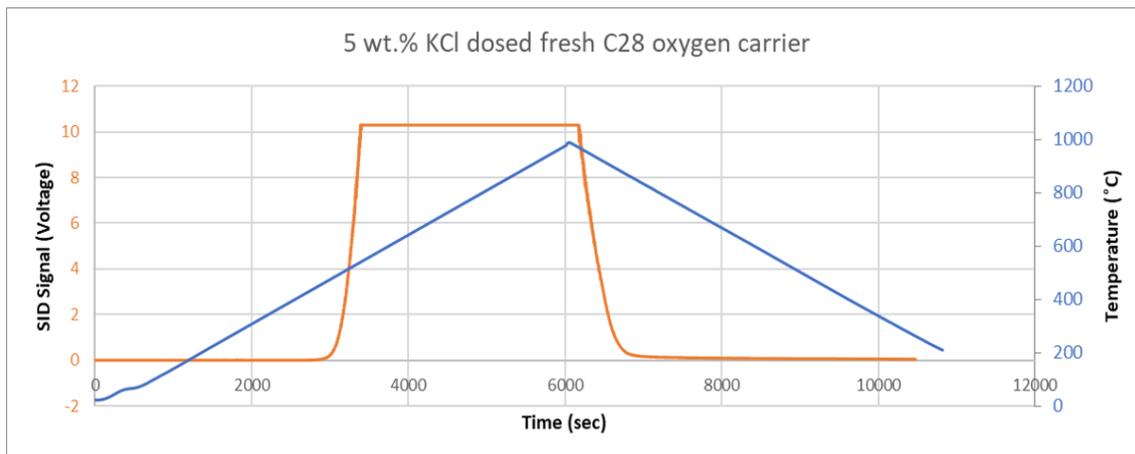


Figure 3.5: TGA temperature ramp at the rate of 20 °C/min and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8

A slow ramp to further capture the detail with an isotherm at 1000 °C were used to characterise the alkali behaviour on the same oxygen carrier. As it can be seen on figure 3.6; the three peaks can relate to different alkali release mechanisms. For example, the first peak is most likely to be related to the evaporation of alkali salts on the surface of the oxygen carrier which is around 500 °C. Second one might be associated with chemical reaction from the surface and the third is more appropriate with desorption of alkali from the core of the oxygen carrier and therefore it slowly decreases to about 1 V where then the temperature is low for alkali desorption.

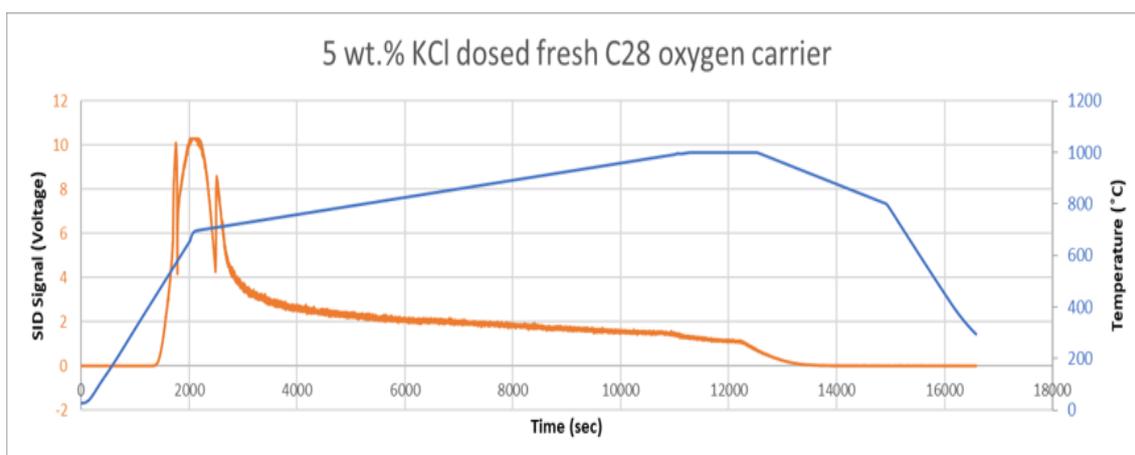


Figure 3.6: TGA temperature ramp at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^8



Figure 3.7: Surface elemental combined map SEM analysis on the alkali dosed OC (color identified)

Table 3.1: Elemental weight concentration of the surface SEM analysis of the alkali dosed fresh OC

Element Name	Weight Conc.
Calcium	41.38
Manganese	38.70
Magnesium	5.33
Titanium	7.59
Iron	3.59
Chlorine	1.45
Silicon	0.93
Potassium	0.70
Aluminium	0.33

As it can be seen in figure 3.7 and table 3.1 clearly, the surface SEM-EDX elemental analysis confirms that there exists some alkali attached on the oxygen carrier surface. Hence the early alkali detection by the SID can be justified by the evaporation of these surface attached alkali. Further SEM-EDX analysis on the cross section of the oxygen carrier was conducted to see if the alkalis also penetrate the oxygen carrier. Based on the combined map SEM-EDX elemental analysis see figure 3.8 and table 3.2; it shows that significant concentration of alkali (potassium) is present. However, the presence of chlorine is uniform and not necessarily on where the sites where the potassium is located as it is seen in figures 3.9 and 3.10.

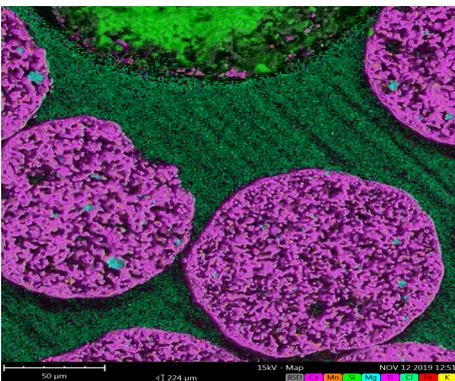


Figure 3.8: Cross sectional elemental combined map SEM analysis on the alkali dosed OC (color identified)

Table 3.2: Elemental weight concentration of the Cross sectional SEM analysis of the alkali dosed fresh OC

Element Name	Weight Conc.
Calcium	36.51
Manganese	34.38
Silicon	16.26
Magnesium	5.15
Titanium	5.61
Chlorine	1.20
Iron	0.55
Potassium	0.34

3. Results and Discussion

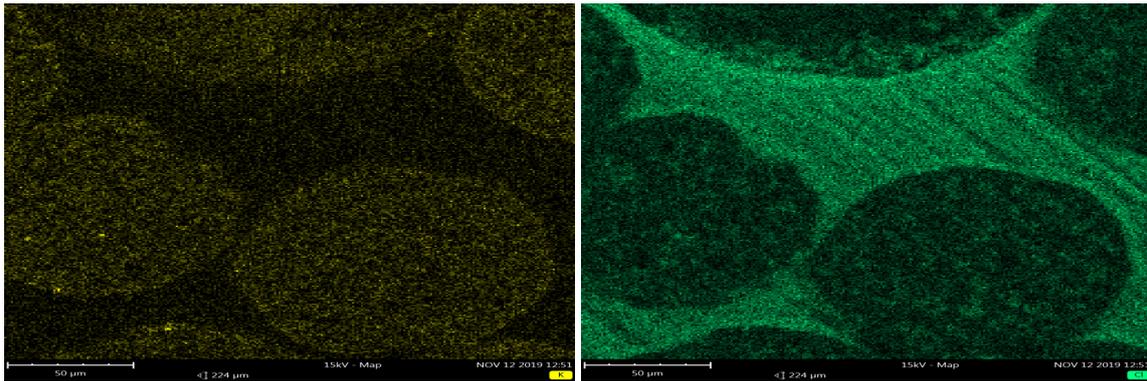


Figure 3.9: Cross sectional elemental combined map SEM analysis on the alkali dosed oxygen carrier (**Potassium**)

Figure 3.10: Cross sectional elemental combined map SEM analysis on the alkali dosed oxygen carrier (**Chlorine**)

To analyse the three peaks in figure 3.6; an isotherm for long time at 560 °C and at 1000 °C to account for higher time resolution and examine how the outer and inner absorbed alkali evolve in longer isotherm condition. Figure 3.11 illustrates this case, as it can be observed in the figure, the amount of alkali also decreases steadily during these isotherm conditions.

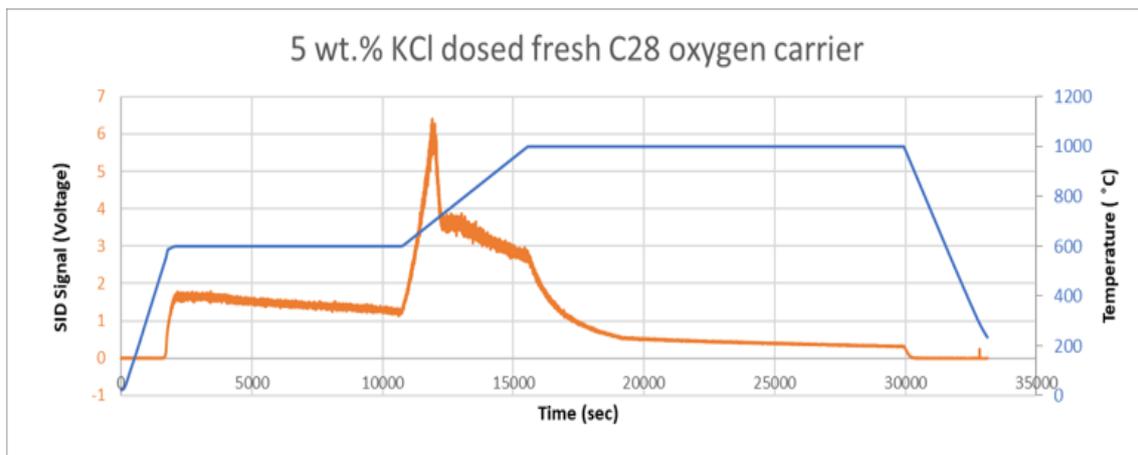


Figure 3.11: Extended isotherm condition of TGA and SID analysis to examine the peaks observed on figure 3.6 and the alkali detected on the SEM analysis of figures 3.9, 3.10. The amplification ratio of the SID-system is 10^8

Further a double isotherm analysis was conducted on the oxygen carrier to examine how the oxygen carrier retains the alkali even after it was subjected to 1000 °C of the TGA temperature. Figure 3.12 shows the SID signal and TGA temperature shows similar alkali release trend as the above; higher early alkali release from the surface of the OC which then gets significantly low at the higher temperature which is likely from the core of the OC. On the repeat, no alkali release is observed at around 500 - 800 °C which was previously observed on the first ramping, meaning no surface alkali remains to be released. However, at 1000 °C, moderate alkali, though lower signal than the first ramping is observed. This indicates that the alkali in the core

of the first ramping isotherm is not entirely depleted and it will take long time to completely remove it. Figure 3.13; shows the weight and temperature graph in time. The sample experiences about 2 wt.% (0.215 mg) mass loss during the consecutively repeated isotherm analysis. However the majority of the mass change happened before the loop. Based on this result it can be deduced that either the alkali have been removed or they are chemically bonded to the oxygen carrier that they can no longer evaporate below 1000 °C.

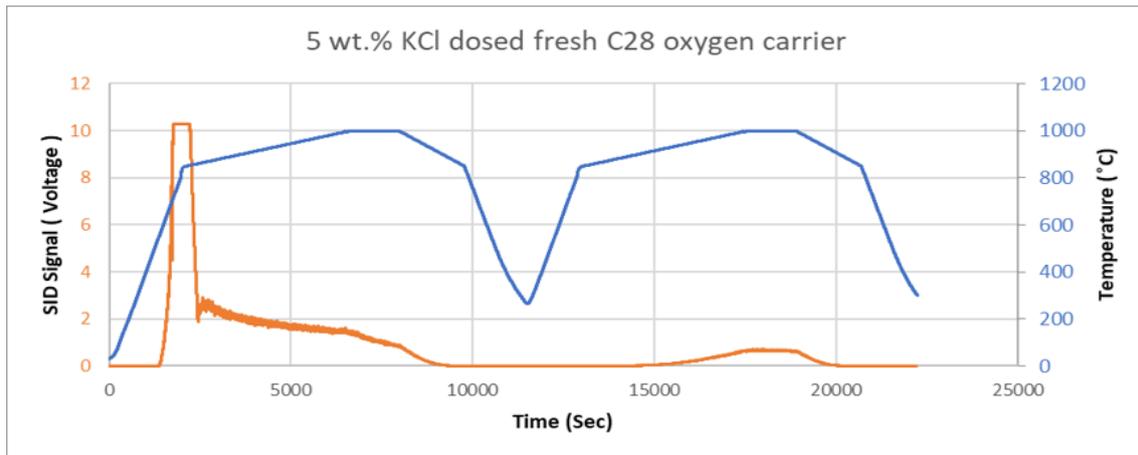


Figure 3.12: Double isotherm TGA and SID analysis (repeat of the single isotherm process experiment with out opening the system) on the alkali dosed oxygen carrier. The amplification ratio of the SID-system is 10^8

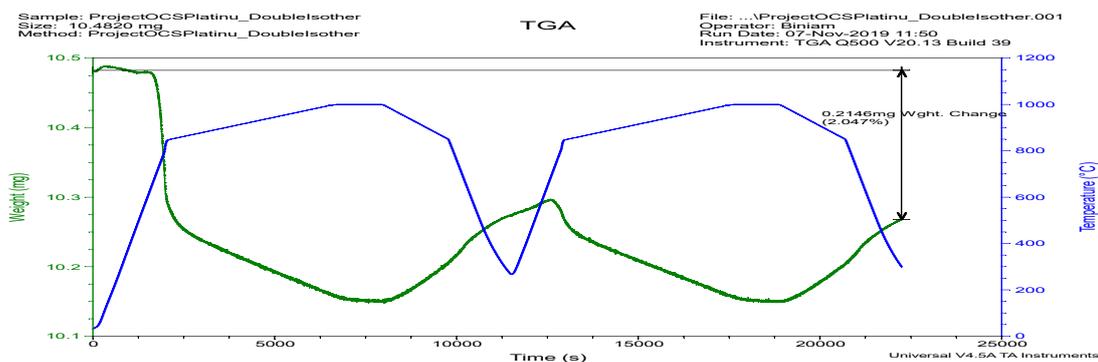


Figure 3.13: Double isotherm TGA temperature and Weight analysis (repeat of the single isotherm process experiment with out opening the system) on the alkali dosed oxygen carrier.

A SEM-EDX analysis was conducted on the alkali-dosed C28 sample that has been subject to 1000 °C TGA experiment (figure 3.6). This analysis was to investigate if any alkali remains on the surface of the oxygen carrier after the TGA experiment. The combined map elemental SEM analysis and its weight based elemental concentration can be seen in figure 3.14 and table 3.3 respectively. Since the weight

concentration of potassium and chlorine which are below the detection limits, no alkali remains attached on the surface of the oxygen carrier after it has been exposed to 1000 °C TGA isotherm analysis. Thus the second lower peak observed on figure 3.12 strengthens the assumption that the release of alkali in-fact from the core of the OC.

Table 3.3: Elemental weight concentration of the surface SEM analysis of the alkali dosed fresh OC after the TGA analysis (see figure3.6

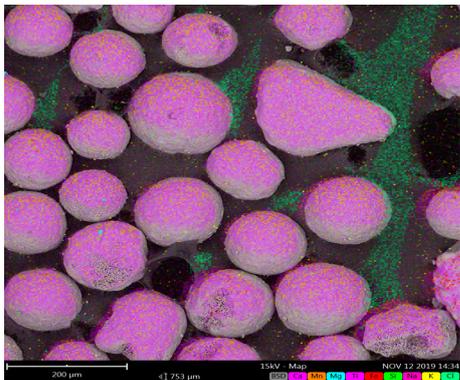


Figure 3.14: Surface elemental combined map SEM analysis on the alkali dosed OC after the TGA analysis (see figure3.6(color identified)

Element Name	Weight Conc.
Calcium	42.33
Manganese	41.66
Magnesium	5.35
Titanium	7.20
Iron	2.91
Silicon	0.55
Sodium	0.00
Potassium	0.00
Chlorine	0.00

The above analysis on the deliberately KCl dosed fresh C28 oxygen carrier demonstrates that the integration of TGA-SID can be used to detect alkali release from oxygen carrier. Based on the result it can clearly be shown that the experimental setup can be expanded to analyse alkali and oxygen carrier interaction. The result from the SEM-EDX elemental analysis also supports this conclusion by providing information on circa location of the alkali on the OC.

3.2 SEM-EDX Analysis

In this section of SEM-EDX analysis, oxygen carrier from the pilot plant and the lab reactor will be analysed.

3.2.1 Oxygen carrier from the lab-reactor

A combined map and point elemental analysis were conducted on the cross section of the oxygen carrier from the lab reactor. Result from the combined map SEM-EDX elemental analysis, (figure 3.16) shows that there is a uniform concentration of potassium throughout the bulk of the oxygen carrier sample, but the concentration is below the detection limit looking at the overall elemental weight concentration table 3.4. However analysing the sample carefully, one can see in figure 3.15 that all the oxygen carrier sample does not have same particle structure. Looking into the potassium concentration, relatively denser potassium on a different particle structure

(spot B in figure 3.15) is observed. Based on the SEM-EDX combined map elemental analysis, it was found that the sample of C28 oxygen carrier from the lab reactor to have ilmenite contamination in it. This can be justified from figure 3.16 where high Fe-Ti concentration is observed. A point analysis was made on the two types of particles, seen in figure 3.15, These points depicted in figure 3.15, show ilmenite particle (point B) and C28 particle (point A). The elemental weight concentration shown in table 3.4 indicates that the potassium concentration in the ilmenite particle is 1.75 wt.% while the concentration in the C28 particle remains below the detection limit. Chlorine does not seem to be associated with any kind of these particles, rather it seem to exist uniformly distributed on the epoxy background.

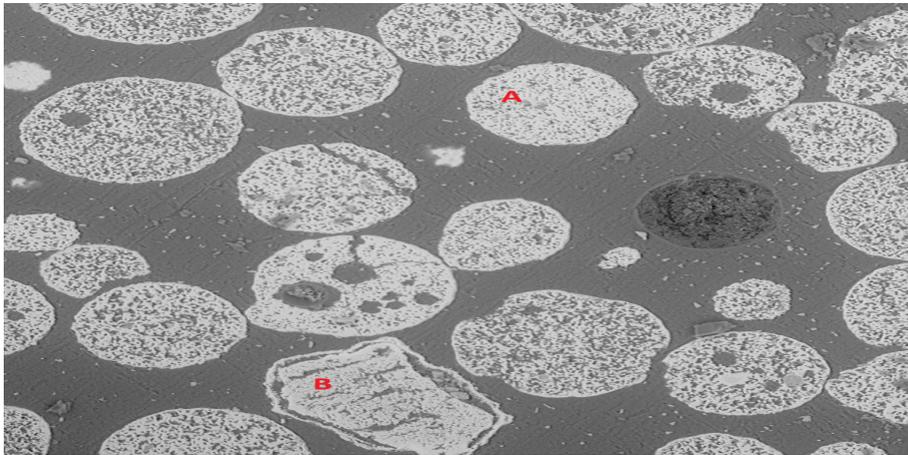


Figure 3.15: Cross sectional elemental combined map and point SEM-EDX analysis on different particles of the oxygen carrier from the lab reactor

Table 3.4: Elemental weight concentration of the Cross sectional SEM-EDX combined elemental map analysis of the oxygen carrier from the lab reactor exposed to 0.32 mgKCl/min for 5 hours of reactor environmental cycle

Element Name	Overall Wt.%	Wt.% (Spot A)	Wt.%(Spot B)
Oxygen	44.64	45.61	38.81
Calcium	21.69	23.58	2.76
Manganese	21.12	24.09	3.71
Magnesium	3.17	2.22	1.78
Titanium	4.94	3.35	32.87
Silicon	1.82	0.75	0.68
Iron	1.80	-	15.37
Chlorine	0.53	0.10	0.12
Aluminium	0.30	0.29	-
Potassium	0.00	0.00	1.75
Carbon	-	-	2.15

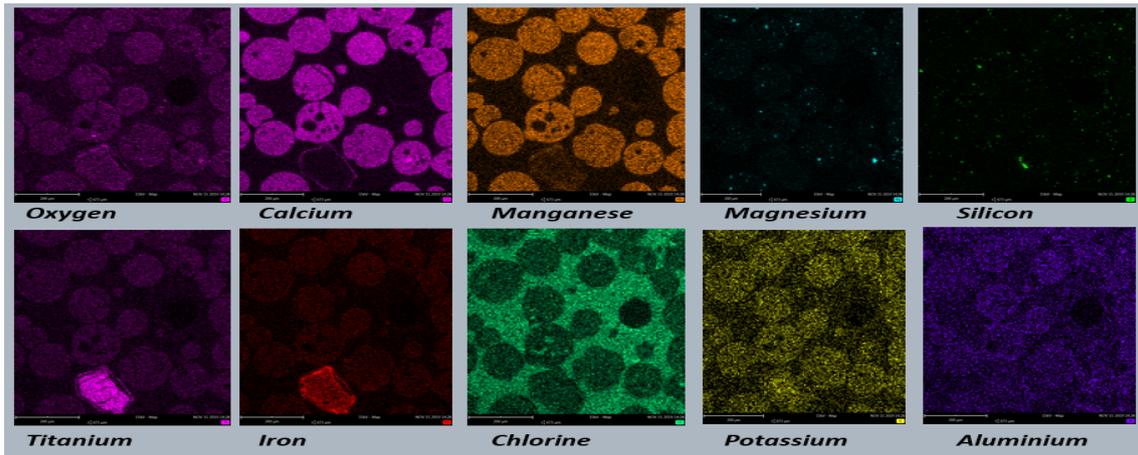


Figure 3.16: Cross sectional elemental combined map SEM-EDX analysis of the oxygen carrier from the lab reactor

3.2.2 Oxygen carrier from the 100 kW unit pilot plant



Figure 3.17: Cross sectional elemental combined map SEM analysis of the oxygen carrier from the 100 kW unit pilot plant at Chalmers University (color identified)

Table 3.5: Elemental weight concentration of the Cross sectional SEM analysis of the oxygen carrier from the 100 kW unit pilot plant at Chalmers University

Element Name	Weight Conc.
Iron	39.72
Titanium	31.19
Magnesium	5.25
Calcium	8.02
Manganese	10.47
Silicon	4.43
Chlorine	0.73
Potassium	0.17

Figure 3.17 and table 3.5 shows the SEM image and weight concentration of the elemental composition of the oxygen carrier sample taken from the pilot plant. Table 3.5 shows presence of certain amount of potassium concentration. From figure 3.18 one can observe relatively high potassium concentration on the sites of the illemnite particles.

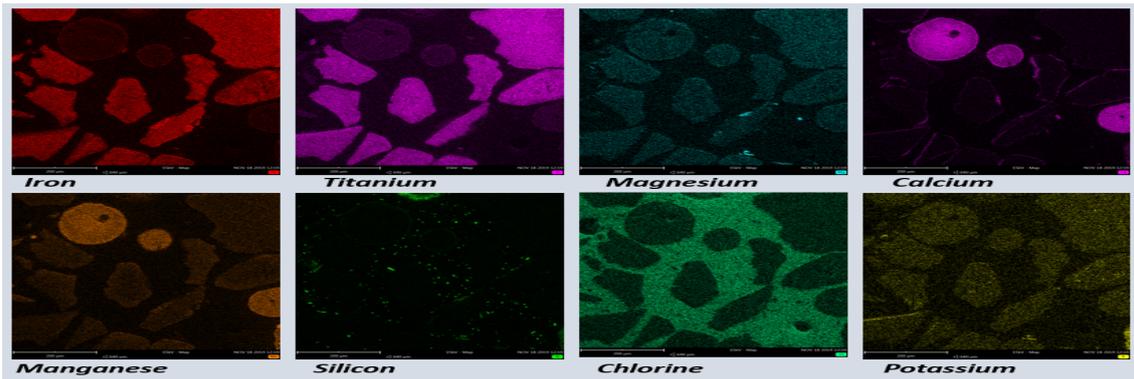


Figure 3.18: Cross sectional elemental combined map SEM analysis of the oxygen carrier from the 100 kW unit pilot plant at Chalmers University color identified for individual elements

3.3 TGA and SID Analysis

On the previous topics of SEM-EDX analysis of the oxygen carrier samples from the lab reactor and the pilot plant, it was clearly that they contain certain amount of alkali. Now these oxygen carrier samples along with an empty pan and a fresh oxygen carrier will be analysed in the integrated TGA and SID analysis. This, is to examine if the alkali in the OC material can be released in different temperature ranges or gas environments.

3.3.1 Inert Environment

First an isotherm TGA analysis on an empty platinum pan was done in an inert condition where no detection was observed, hence the amplification ratio of SID system was increased from 10^8 to 10^9 , the same result can be seen in figure 3.19. From the figure it is evident that some alkali is being detected starting around 950 °C and during the 1000 °C isotherm condition and continues to about 950 °C during the cooling condition. However this was not expected since the platinum pan was supposed to be inert toward alkali (see figure 3.4) regardless the amplification ratio, hence therefore a new platinum pan was used with fast ramp to validate if the alkali is released from the pan or the system. The experiment with new platinum seem also to release a signal with almost similar strength (see figure 3.20). Since some detection level was obtained at 10^9 , all future experiments continued with the new amplification while all previous experiments were conducted at an amplification ratio of 10^8 .

3. Results and Discussion

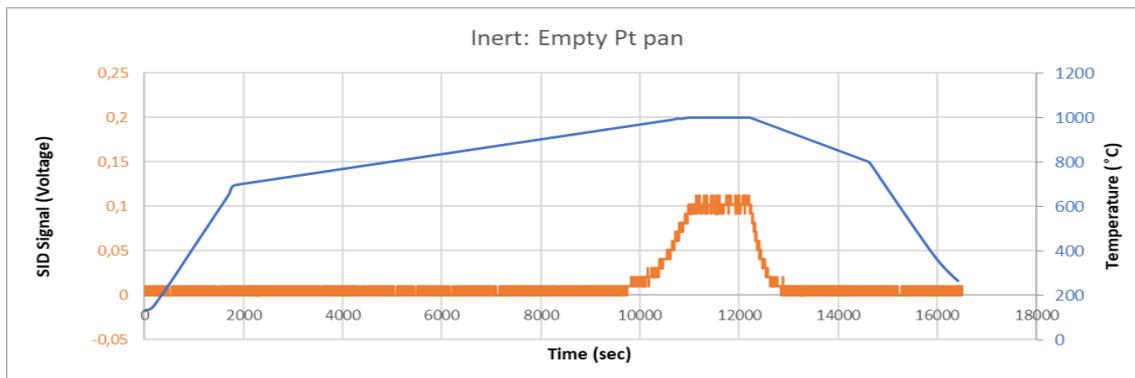


Figure 3.19: Inert condition: Empty pan TGA and SID analysis. TGA ramp temperature at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C with an isotherm for 25 min at and 1000 °C then cooling at a rate of 20 °C/min to 200 °C. Alkali signal detected by the SID corresponding to alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9

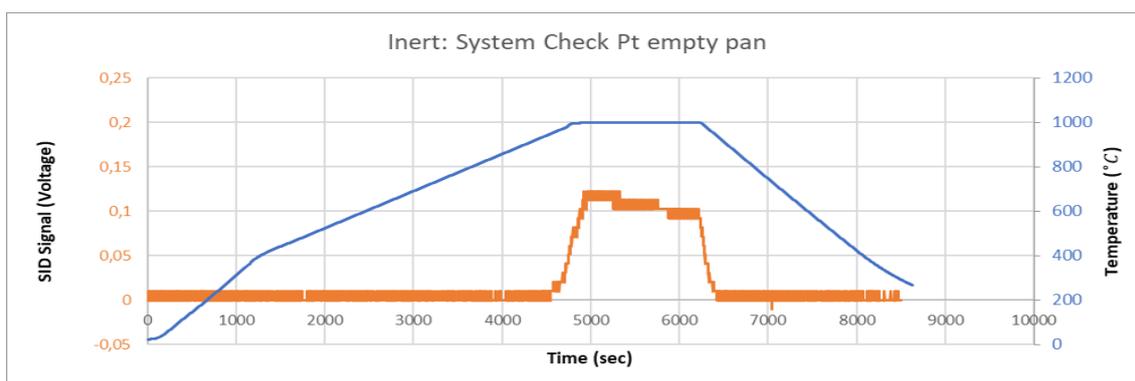


Figure 3.20: Inert condition: Repeat of experiment on figure 3.19 with a new empty platinum pan (System check). TGA ramp temperature at the rate of 20 °C/min to 500 °C then at 10 °C/min to 1000 °C with an isotherm condition at 1000 °C for 25 min and again 20 °C/min to 200 °C. SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9

Further similar an inert condition experiment was conducted on the fresh C28, oxygen carrier from the lab reactor and the oxygen carrier from the pilot plant. Figure 3.21 shows these experiments with colour labels. As it can be seen in the figure almost all the oxygen carriers show similar trends and strengths of alkali release detection by the SID. Since the empty pans and the fresh oxygen carriers have almost the same trend and signal, therefore it can be said that the signal is actually from the system. Finally since empty pan and all experimental OCs show similar level of alkali release, it is assumed the OC does not release any significant amount of alkali in inert condition at 1000 °C.

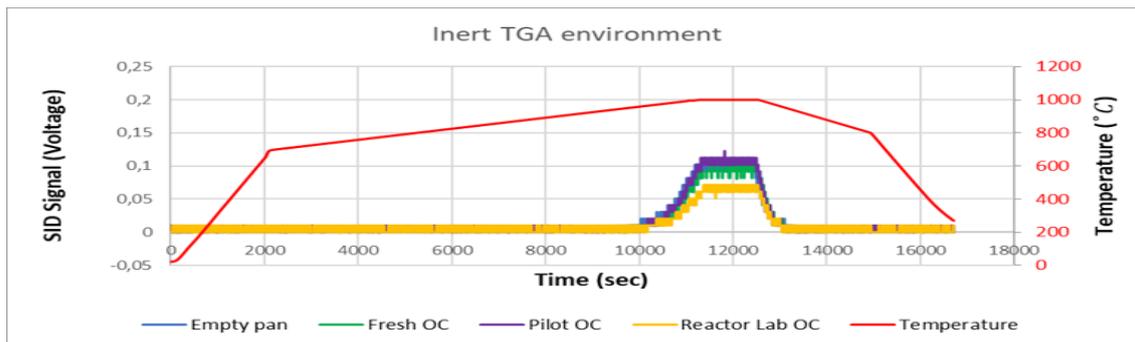


Figure 3.21: Inert condition: Empty pan (Blue), Fresh C28 OC (Green), oxygen carrier from the lab reactor experiment (Yellow), oxygen carrier from the pilot plant (Violet) and Temperature (Red). TGA ramp-temperature at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9 .

3.3.2 Oxidation Environment

The environment of the TGA thermal analysis was then changed to oxidising environment. Analysis of the four cases empty pan, fresh C28 oxygen carrier, oxygen carrier from the lab reactor experiment and the pilot plant oxygen carrier was conducted. The result of the SID signal can be seen in the figure 3.22. The results seem to be more or less similar to the results of the inert condition that is no significant amount of alkali is released by any of the OC sample.

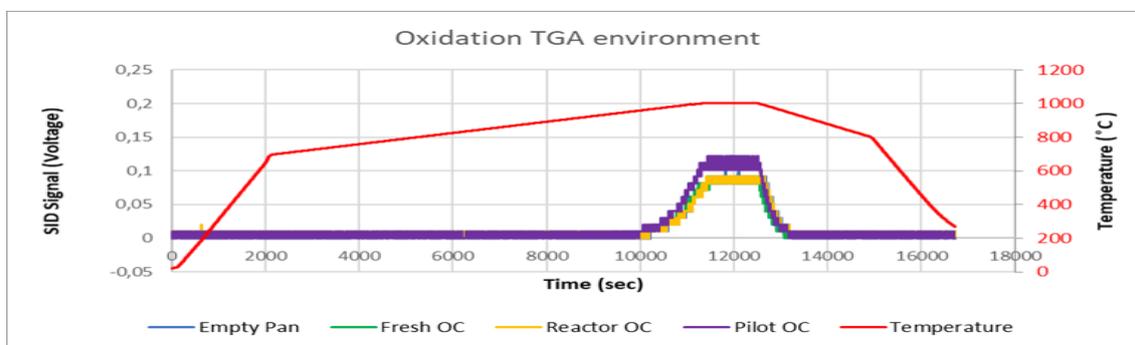


Figure 3.22: Oxidation condition: Empty pan (Blue), fresh C28 OC (Green), oxygen carrier from the lab reactor experiment (Yellow), oxygen carrier from the pilot plant (Violet) and Temperature (Red). TGA ramp-temperature at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9 .

3.3.3 Reduction Environment

Finally TGA analysis with reducing environment was used to analyse the four cases. As it is shown in figure 3.23, the SID signal from the fresh C28 and lab reactor

experiment oxygen carriers in the reduction environment was observed to be lower than the SID signal inert and oxidation environment. However the SID signal from the empty pan and that of the pilot plant oxygen carrier seem to be higher than what was observed in the inert and oxidation environment (see figure 3.22 & 3.21). From this analysis it can be deduced that since the background of the system (empty pan) is higher, it means that the system releases more alkali during reducing than Inert and oxidising environment. And the pilot plant SID signal remains the same amplitude during all gas conditions which indicates that there is neither alkali adsorption or desorption from or to the pilot OC from the system. Thus pilot OC is not affected by the system gas condition. However, analysis on the lab reactor and fresh C28 OCs resulted in a way lower SID signal that means the C28 OC samples adsorb the alkali released from the background of the system.

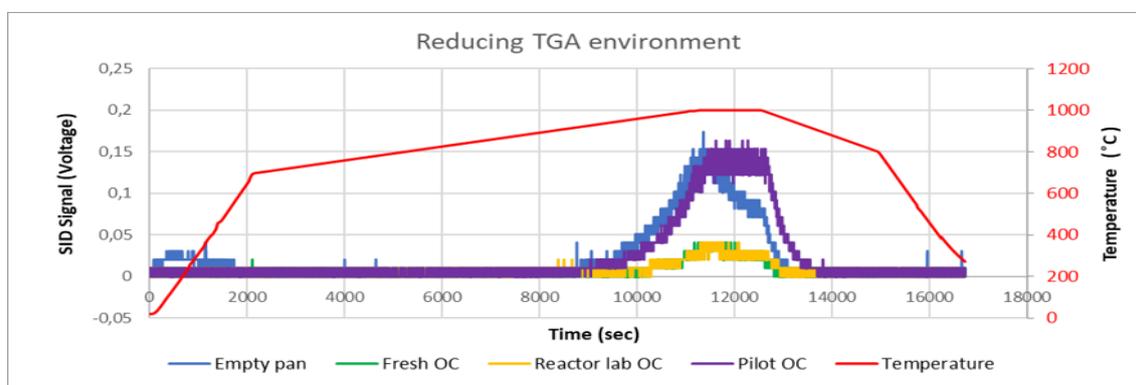


Figure 3.23: Reduction condition: Empty pan (Blue), fresh C28 OC (Green), oxygen carrier from the lab reactor experiment (Yellow), oxygen carrier from the pilot plant (Violet) and Temperature (Red). TGA ramp-temperature at the rate of 20 °C/min to 700 °C then at 2 °C/min to 1000 °C and SID signal of alkali concentration from the TGA exhaust gas. The amplification ratio of the SID-system is 10^9 .

3.3.4 Cycle

At last all the above TGA environmental conditions (Inert, Oxidation and Reduction) were combined to form typical CLC redox operation cycle. The cycle was set at an isotherm of TGA furnace temperature 900 °C and 1000 °C for 100 min at each isotherm.

From the result shown on figure 3.24, strong SID signal is shown during the reduction from the most of the oxygen carrier. However there is high background signal during all environmental conditions which was the problem reading signals during the experiments of the oxygen carrier. From the cycle experiment it was observed that higher SID signal at 1000 °C than at 900 °C mostly during the reducing condition. Oxygen carrier from the lab reactor showed high SID signal during the initial ramp temperature at around 500 °C, this does not seem plausible given results from the inert.

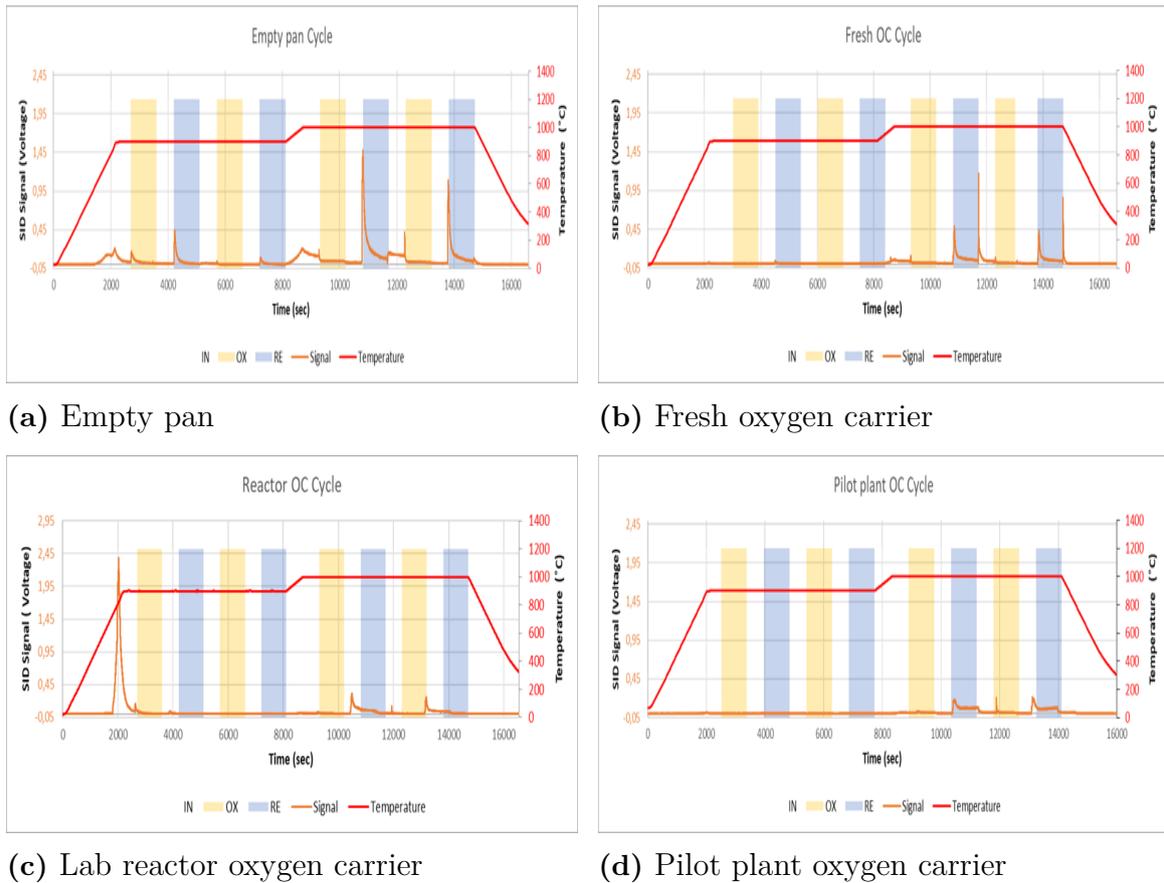


Figure 3.24: Cycle experiments: Starts with temperature ramp to 900 °C at a rate of 25 °C/min then Isotherm for 100 min at 900 °C where 10 min Inert, 15 min Oxidation, 10 min Inert and 15 min Reduction environmental conditions repeats twice and proceeds to temperature ramp to 1000 °C at the rate of 10 °C/min where the same cycle as in the 900 °C repeats for 100 min. Cooling to 200 °C at rate of 25 °C/min.

4

Conclusions

This paper has shown, how TGA-SID integration system can be used to detect gaseous alkali. From the system analysis it also can be seen how the system can be used to analyse the release behaviour of alkali from an oxygen carrier in relation to a surfacely attached alkali or internally absorbed alkali.

The OC from the pilot plant is unaffected by the gas environment while the fresh C28 OC and the OC from the lab reactor adsorbed the alkali release from the background of the system during reducing environment which means that C28 might adsorb alkali during reducing gas condition at 1000 °C.

From the experiments conducted on different TGA environments, there is higher alkali release during the reduction, there is no empirical finding that supports why higher alkali release is observed during reduction environment. However the alkali release during inert and oxidation environments is more or less similar to each other. The signal amplification ratio is higher in this project than what is being used in previous studies [10], [11], hence the signal detected or the alkali release in this project is considered as very low.

Based on this project result, it can be deducted that ilmenite OC showed neutrality toward alkali desorption and adsorption during all environment conditions and C28 absorb alkali during reducing condition but showed similar behaviour during inert and oxidation gas conditions. This implies that the effect of alkali on the oxygen carrier needs further investigation. Like effects toward regeneration and activation of the oxygen carrier, oxygen carrying capacity, oxygen gas uncoupling and other effects which related criterion's of the OC similarly reactivity and conversion capability of the oxygen carrier.

Results from the SEM-EDX cross sectional elemental analysis shows that the oxygen carrier from the lab reactor and pilot plant found to contain alkali mainly potassium absorbed. Alkali release most of the time correlated to the availability of chlorine [8]. This might have affected the mobility of potassium, hence strong alkali signal were not detected by the SID as the alkali might remained intact to the oxygen carrier. The TGA-SID analysis found low to no alkali release from both the oxygen carriers due to high background signal of the system. The alkali release of the OCs is either equal or less from the background (empty pan) signal. This was not expected as the oxygen carrier from the pilot plant contain ilemnite, and ilemnite is known to absorb alkali.

4.1 Recommendations

Replica of this project on pure ilmenite and C28 and mixture of both oxygen carriers by dosing known amount of alkali would have been interesting of future work. Where the concentration of the alkali is tracked continuously. thus, then OCs are subjected to TGA-SID integrated analysis to investigate the alkali- oxygen carrier interaction would have a great scientific implication and contribution.

The alkali concentration detected by the SID in this system is not related to the minimum alkali concentration effect on the down stream equipment. Standardisation of the SID measurement could also have a great implication on the CLC development.

Bibliography

- [1] Jing, D. Z., T. Mattisson, M. Ryden, P. Hallberg, A. Hedayati, J. Van Noyen, F. Snijkers and A. Lyngfelt (2013). "Innovative Oxygen Carrier Materials for Chemical-Looping Combustion." *Ghgt-11* 37: 645-653.
- [2] Leion, H., A. Lyngfelt, M. Johansson, E. Jerndal and T. Mattisson (2008). "The use of ilmenite as an oxygen carrier in chemical-looping combustion." *Chemical Engineering Research & Design* 86(9a): 1017-1026.
- [3] Lyngfelt, A. (2011). "Oxygen Carriers for Chemical Looping Combustion-4000 h of Operational Experience." *Oil and Gas Science and Technology-Revue D Ifp Energies Nouvelles* 66(2): 161-172.
- [4] Ryden, M., M. Johansson, E. Cleverstam, A. Lyngfelt and T. Mattisson (2010). "Ilmenite with addition of NiO as oxygen carrier for chemical-looping combustion." *Fuel* 89(11): 3523-3533.
- [5] Chen, L. Y., J. H. Bao, L. Kong, M. Combs, H. S. Nikolic, Z. Fan and K. L. Liu (2017). "Activation of ilmenite as an oxygen carrier for solid-fueled chemical looping combustion." *Applied Energy* 197: 40-51.
- [6] Kirkels, Arjan & Verbong, Geert. (2011). Biomass gasification: Still promising? A 30-year global overview. *Renewable and Sustainable Energy Reviews*. 15. 471-481. 10.1016/j.rser.2010.09.046.
- [7] Asadullah, M. (2014). "Biomass gasification gas cleaning for downstream applications: A comparative critical review."
- [8] Gogolev, I., C. Linderholm, D. Gall, M. Schmitz, T. Mattisson, J. B. C. Pettersson and A. Lyngfelt (2019). "Chemical-looping combustion in a 100 kW unit using a mixture of synthetic and natural oxygen carriers - Operational results and fate of biomass fuel alkali." *International Journal of Greenhouse Gas Control* 88: 371-382.
- [9] Pontus Markström, Carl Linderholm, Anders Lyngfelt (2013), Chemical-looping combustion of solid fuels – Design and operation of a 100kW unit with bituminous coal, *International Journal of Greenhouse Gas Control*, Volume 15, Pages 150-162, ISSN 1750-5836, <https://doi.org/10.1016/j.ijggc.2013.01.048>. (<http://www.sciencedirect.com/science/article/pii/S1750583613000790>).
- [10] V. Andersson, A. H. Soleimanisalim, X. Kong, F. Hildor, H. Leion, T. Mattisson, and J. B. C. Pettersson (2020). "Online Measurements of Alkali in a Stainless-Steel Reactor while Simulating Chemical Looping Combustion of Biomass" Submitted for publication, *Fuel Processing Technology*.
- [11] Gall, D. (2018). "Alkali Metals and Tar in Biomass Thermochemical Conversion: Development and Application of Online Measurement Techniques."

- [12] Coats, A. W. and J. P. Redfern (1963). "Thermogravimetric analysis. A review." *Analyst* 88(1053): 906-924."
- [13] A. Nanakoudis (2019 August 22). EDX Analysis with a Scanning Electron Microscope (SEM): How Does it Work? [Thermo Fisher Scientific] Accessed on January 2020 from <https://blog.phenom-world.com/edx-analysis-sem>.
- [14] Angelika Hackner, Sebastian Beer, Gerhard Müller, Thomas Fischer, Sanjay Mathur,(2012) Surface ionization detection of amphetamine-type illicit drugs, *Sensors and Actuators B: Chemical*, Volume 162, Issue 1, Pages 209-215, ISSN 0925-4005, <https://doi.org/10.1016/j.snb.2011.12.068>. (<http://www.sciencedirect.com/science/article/pii/S0925400511011580>)
- [15] Lyngfelt, A. (2007). "Chemical Looping Combustion of Solid Fuels."