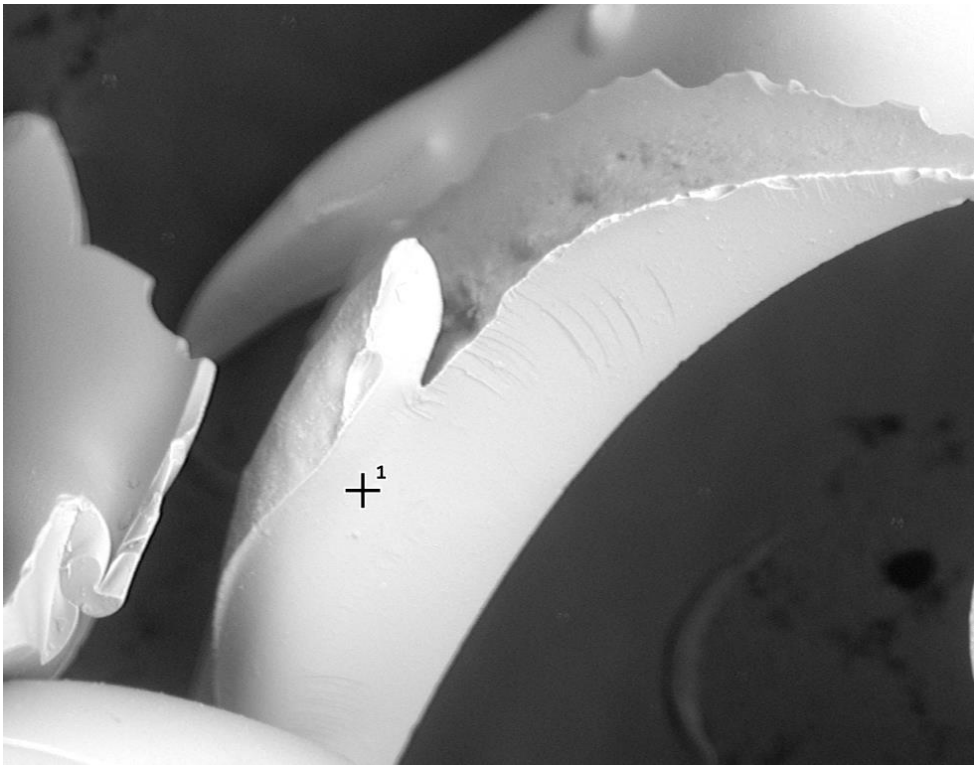

Agglomeration of granulated copper smelter slag in oxygen carrier aided combustion

Bachelor's thesis in the bachelor's programme of Chemical Engineering

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Cover: [A surface sweep electron microscope picture of the surface of a fresh granulated copper smelter slag sample]

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Abstract

Oxygen carrier aided combustion (OCAC) is a concept used in fluidized bed boilers. The oxygen carrier used in OCAC functions as an oxygen buffer, which allows for better oxygen distribution which in turn decreases incomplete combustion and the excess air flow need. A promising potential oxygen carrier is granulated copper smelter slag, commonly known as iron sand. However, in unpublished research it's been observed that granulated copper smelter slag has agglomerated (lumped together) when rapidly heated from its fresh state to around 800 °C during OCAC. As agglomeration could cause the fluidized bed boiler to stop fluidizing (defluidization), investigation seemed prudent. The project aimed to investigate the cause of the agglomeration, and potential solutions. A laboratory scale fluidized bed was used in conjunction with a sweep electron microscope to try to find the cause of agglomeration. The study found that defluidization of granulated copper smelter slag occurred both in the presence and absence of air, at around 650 ºC. In other words, oxidation is unlikely to be the primary cause for defluidization and in turn agglomeration. Additionally, it was found that oxidation of copper smelter slag affected defluidization and higher oxidation levels hindered defluidization. As the oxidation affected defluidization it could be possible to avoid defluidization by slowly heating copper smelter slag. In conclusion additional research on the oxygen free defluidization would be required to understand the underlying cause for the agglomeration of granulated copper smelter slag in OCAC.

Acknowledgments

I'd like to thank my examiner Henrik Leion for the chance to do this fun project and for his time. I'd like to thank Victor Purnomo for acting as my supervisor in the early parts of the project and helping me get acquainted with the lab equipment. And finally, I'd like to thank my supervisor Felicia Eliasson Störner for her patience and helpfulness during all of the project.

Ati Thorpe 2023

Keywords: granulated copper smelter slag, OCAC, iron sand, agglomeration, defluidization, fluidized bed

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1 Introduction

Copper smelter slag commonly referred to as “iron sand” is a granular material produced as a side product from the copper smelter industry. The copper smelter slag studied is from Boliden in Sweden has been suggested for use in fluidized bed boilers as a replacement for quartz sand [1]. Due to the extensive mining of quartz sand, finding quartz sand sources with low ecological impact could become harder in the future. Copper smelter slag on the other hand is a side product with low price and demand [1,2]. Additionally, copper smelter slag could potentially act as an oxygen carrier [1] in oxygen carrier aided combustion (OCAC). Oxygen carriers are bed materials that contain transition metals which can reduce and oxidize at the operational temperature of fluidized bed boilers. As oxygen carriers can bind and release oxygen in redox reaction it helps increase the availability of oxygen in boilers during combustion, which is why it’s called oxygen carrier aided combustion (OCAC). The increased oxygen availability helps avoid incomplete combustion products such as CO. [3,4]

As of the writing of this report copper smelter slag is not used commercially as a bed material [3] as it has been insufficiently studied. One problem with copper smelter slag is that it has been observed to agglomerate (lump together) when rapidly heated to around 800 °C. The lumps negatively affect the fluidization and can even cause the fluidization of the bed to stop, defluidization [5]. Defluidization generally decreases heat transfer and the evenness of combustion. That said, defluidization and agglomeration can occur independently, but the two are correlated. The agglomeration isn’t a problem on its own, but as it is usually accompanied by defluidization once sufficiently agglomerated, the report will treat the two like the same problem unless otherwise specified.

To solve the problem of copper smelter slag defluidization caused by agglomeration, this project studied the oxidation of copper smelter slag on its own to better understand the underlying mechanisms behind the agglomeration. To achieve this, copper smelter slag would be oxidized using air at temperatures around 800 °C in a series of fluidized bed experiments. The final goal being information about the copper smelter slag’s reactivity with air, the phases present during different temperatures and hopefully the reason for the agglomeration and in turn defluidization.

2 Purpose

The purpose of this thesis has been to investigate the defluidization of granulated copper smelter slag when used in oxygen carrier aided combustion.

To investigate the defluidization several questions were asked:

What is the cause of defluidization?

Is there a way to avoid defluidization?

Where in the particle is the iron located?

How reactive is copper smelter slag with air?

How are the phases present in the copper smelter slag affected by temperature?

3 Background

Bed fluidization is a technology that allows high mass and heat transfer between solid particles by blowing air through a granular material. The high heat transfer is the reason the technology is used in boilers. A problem with the technology is that defluidization can occur due to agglomeration (lumping together) of particles which can happen due to ash components [5] or melting of components in the bed material. Agglomeration of particles can be hard to reverse which could necessitate removal of the bed material and restarting of the boiler. Another problem is that while fluidized bed boilers have high fuel conversion due to the fluidization, there are still some parts of the fluidized bed that have incomplete fuel conversion due to oxygen deficiency. An answer to the oxygen deficiency found in fluidized bed boilers has been oxygen carriers. Oxygen carriers could replace the silica sand typically used as bed material today [6]. One such potential oxygen carrier is copper smelter slag.

On a chemical level copper smelter slag is primarily composed of Fe oxides and Si-oxides with smaller amounts of oxidated Al, Ca and Mg. [1] As it is composed in large part of Fe oxides it has the ability to further oxidize and could allow it to be used as an oxygen carrier in oxygen aided combustion. OCAC is a technique in which the bed material used can act as an oxidizing agent in the absence of oxygen gas and be re-oxidized when oxygen gas is present allowing the bed material to carry oxygen and function as an oxygen buffer [7]. OCAC allows better, and more even, distribution of oxygen in boilers which can in turn decrease need of high excess airflow [7] as well as decreasing the amount of incomplete combustion products. OCAC has previously been performed with Ilmenite ore, but copper smelter slag could serve as a cheaper alternative. Copper smelter slag is currently used in the building industry due to its low price, unfortunately, a significant amount of it goes unused [2]. Being able to use copper smelter slag in OCAC would likely be very helpful in increasing fluidized bed boiler efficiency and reducing boiler emissions of gases such as carbon monoxide (CO).

Unfortunately, copper smelter slag tends to defluidize when oxidized from its fresh state to around 800 °C. This defluidization could prove quite problematic in starting boilers and figuring out how to avoid agglomeration could be key in making copper smelter slag commercially viable as a OCAC bed material. Previous studies of Ilmenite, another promising oxygen carrier, had found that the bed material agglomerated and that an iron rich surface was formed when used in a fluidized bed boiler [8]. This led to a hypothesis that the iron rich surface was causing the agglomeration in Ilmenite; Copper smelter slag is also iron rich. Could the formation of an iron rich layer be the reason for agglomeration in copper smelter slag? To complicate things further fluidized bed boilers are usually run continuously rather than batch wise. As the fluidization continues the bed material gets more worn and absorbs more ash product which in turn can promote agglomeration. To avoid this many fluidized bed boilers, remove old bed material and add fresh bed material as the process goes on. The bed is regenerated, which is why it’s known as bed regeneration. The addition of fresh bed material is in other words very important to commercial fluidized beds. Could the addition of fresh bed material cause any

problems? Agglomeration, defluidization, surface formation, and bed regeneration, how can these phenomena be studied?

4 Method

4.1 Calcination

To study the defluidization, granulated copper smelter slag from Boliden was divided into 5 batches. 4 of the batches were slowly heated in a calcination oven at 4 different temperatures: 750, 850, 950, and 1100 ºC and the remaining batch was fresh (untreated) copper smelter slag. The batches were calcinated at different temperatures to change how strongly they reacted with oxygen and in turn how much oxygen they absorbed. Each batch was then sieved to obtain particles in the 125-250 µm size. Bed material and sweep electron microscope samples were the primary purposes of the 5 batches as it allowed observation of how oxidation affected defluidization, particle composition, and particle structure.

4.2 Fluidized bed tests

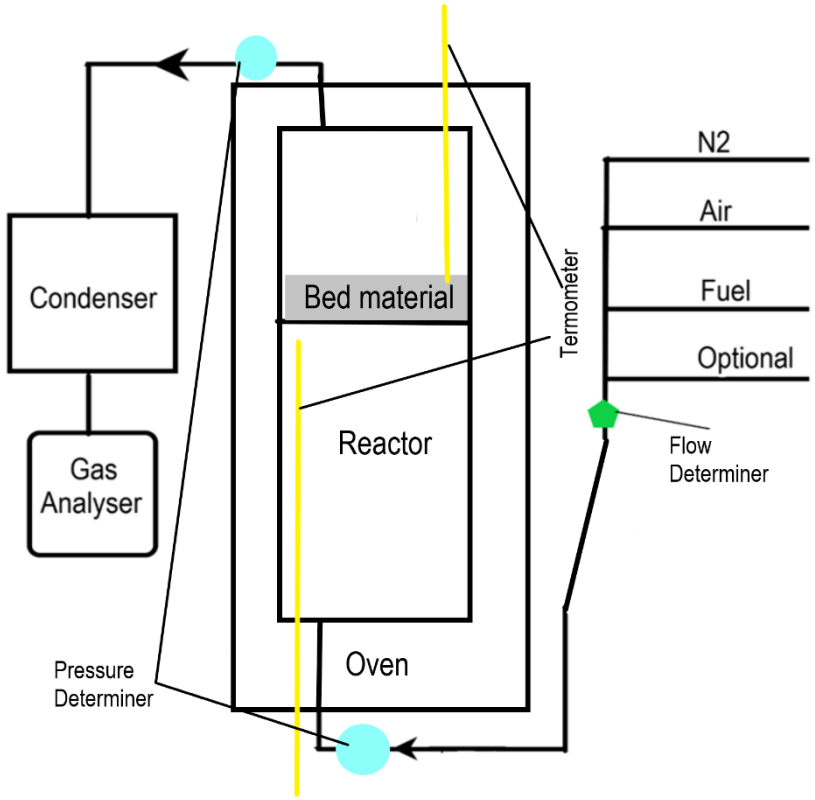


Figure 4.1. A very rough sketch of the system used in the fluidized bed tests

The fluidized bed tests used the lab scale fluidized bed system described in [9]. The general setup of the system can be seen in figure 4.1 and was composed of 4 valve-controlled gas inlets that led leads into the bottom of the reactor housing the bed material. The reactor is in an oven that heats the incoming gas to a set temperature. Once the heated gas exited the reactor it was cooled and led to a gas analyser capable of analysing CO, CO2, O2, CH4, and SO2. In addition to the gas analyser the system was equipped with thermometers for the bed and heated incoming gas, pressure meters to measure pressure drop over the reactor, and a flow determiner. The pressure drop, temperature, flow, and concentrations were logged in a computer during the experiment.

The reactor itself was a stainless-steel reactor that was used and described in [5]. The reactor had an inner diameter of 26 mm and is made up of a lower and higher portion, each part 530 mm and 270 mm long respectively with a perforated plate separating the portions and serving as the bottom for the bed material. The top of the reactor has an opening for inserting bed material or fuel. The opening is typically closed during operation of the fluidized bed.

The data logged into the computer during the test can be used to understand what is happening in the reactor. The pressure drop can be used as a sort of proxy for fluidization and in turn agglomeration. As fluidization means the bed is acting as a fluid, that means the bed material is stirred around and bouncing up and down, this in turn leads to that the loss of pressure over the reactor fluctuates as the resistance the bed poses varies. When fluidization stops the bed material starts acting as a

solid and gives a more stable pressure drop. Another use for the data is quantifying the oxygen absorption of the bed material. By combining the flow and oxygen concentration data and integrating it, it could be possible to obtain a rough measure of the mass of oxygen absorbed over a test. Additionally, the concentration of CO2, CO, and CH4 can used to quantify fuel conversion in the fuel tests performed.

4.3 Tests

Seven bed fluidization tests were performed, with varying bed material, heating methods and gas flow. Unless otherwise stated, the gas flow used was 1 l/min, 20 g of bed material was used, and what is referred to as air flow was a 60% air and 40% N2 gas flow.

4.3.1 Test 1. Slow oxidation of fresh copper smelter slag

The first test involved slowly heating fresh copper smelter slag with an air flow to observe how temperature affects oxygen absorption. The bed material was heated in N2 gas to 400 ºC, to avoid oxidation. This was done to ease data analysis. After the bed temperature stabilized at 400 ºC the gas flow was switched to air flow while retaining the same temperature. The oxygen level was allowed to stabilize, and the temperature was then raised to 500 ºC. The stabilization of oxygen and the increase in temperature were repeated at the following temperatures: 500, 600, 700, 750, 800, 850, and 900 ºC. Once the oxygen level at 900 ºC had stabilized the heating was turned off and the reactor was left to cool.

4.3.2 Test 2. Defluidization test of 750 ºC calcinated copper smelter slag
The second test involved quickly heating 750 ºC calcinated copper smelter slag in air to investigate the defluidization and agglomeration tendency. The bed material was heated in air flow to 700 ºC. Once the temperature had stabilized the temperature was increased to 800 ºC. The stabilization of the temperature was repeated, and the temperature was increased to 900 ºC. The reactor was left running for around an hour after the temperature stabilized at 900 ºC to observe if any additional changes occurred and then the reactor was left to cool.

4.3.3 Test 3. Defluidization test of fresh copper smelter slag, with air
Much like the second test, the third test was to quickly heat copper smelter slag with an air flow to cause defluidization. But this time the bed material used was fresh copper smelter slag. The temperatures 700, 800, and 900 ºC were used and the temperature was increased after the temperature had stabilized. Once the temperature stabilized at 900 ºC the heating was turned off and the reactor was left to cool.

4.3.4 Test 4. Defluidization test of fresh copper smelter slag without air
The fourth test was to compare how a different gas flow affected the defluidization of fresh copper smelter slag. Like the third test, fresh copper smelter slag was rapidly heated, but instead of an air-N2 mix the gas flow was only N2 gas, thus hindering oxidation. The temperatures 700, 800, and 900 ºC were used and the temperature was increased when the temperature stabilized. Once the temperature stabilized at 900 ºC the heating was turned off and the reactor was left to cool.

4.3.5 Test 5. Regeneration of bed with fresh copper smelter slag
The purpose of the fifth test was to investigate how copper smelter slag would react when used to regenerate (replace) bed material during fluidized bed operation. To do this 13 g of 950 ºC calcinated copper smelter slag was heated in an air flow to 600 ºC. Once the temperature stabilized at 600 ºC the heat was increased to 850 ºC. Once the temperature had stabilized at 850 ºC a 7 g sample of fresh copper smelter slag was added from the top of the reactor. Using a flow of N2 gas the 7 g sample was flushed down into the reactor in several parts, as the sample was too big to be inserted in one go. Around 40 minutes after inserting the 7 g sample the heating was turned of and the reactor was left to cool.

4.3.6 Test 6. Reactivity test of 750 ºC calcinated copper smelter slag with methane

The sixth test was to check the reactivity of copper smelter slag with fuel. 750 ºC calcinated copper smelter slag was heated to 750 ºC. Once the oxygen level had stabilized the system was set to cycle through 4 different phases in which the gas flow varied according to the schedule found below.

Gas flow	Time (s)
N2	180
50% methane: 50% N2	40
N2	60
60% O2: 40% N2	Until oxygen level stabilized

Once the system had gone through the 4 phases it started a new cycle. The system did 4 cycles at 750 ºC according to the schedule above and then a fifth cycle where the second phase was 60 seconds instead of 40 seconds. The temperature was then raised to 850 ºC, the temperature was stabilized and then 4 additional cycles were done with the schedule above. A tenth cycle was done with a modified schedule where the second phase was 60 seconds instead of 40 seconds. The reactor was then left to cool.

4.3.7 Test 7 Reactivity test of 950 ºC calcinated copper smelter slag with methane

The seventh test was a repeat of test 6 but with 950 ºC calcinated copper smelter slag.

4.4 SEM-EDS

Sweep electron microscope with energy dispersive X-ray diffraction or SEM-EDS or just SEM for short is an analysis method that allows observation of particles structure and determination of the elemental composition of a sample. [4] 11 SEM analyses were performed with varying samples and sample preparation.

5 SEM analyses where surface scans were the sample was glued to a sample holder. As the sample was held in place the surface of the particles could be analysed with SEM. The 5 surface SEM analyses were performed on fresh copper smelter slag and 750, 850, 950, and 1100 ºC calcinated copper smelter slag.

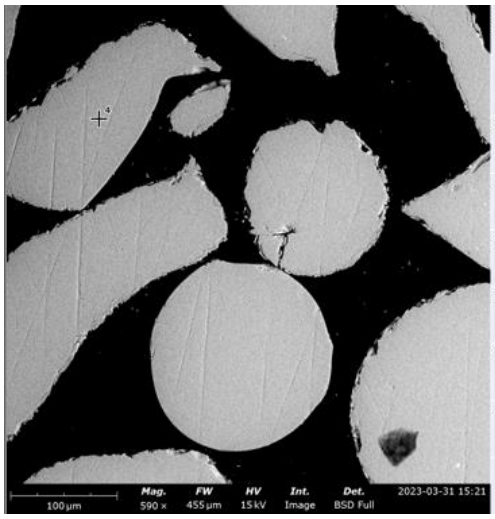
6 of the analyses where cross section analyses were the samples were cast in epoxy plastic. If the sample had agglomeration both an agglomerated part and a non-agglomerated part of the sample was cast in epoxy. Once the epoxy had hardened the samples were ground down with abrasive paper to give a cross section of the copper smelter slag particles. The samples were then polished with sandpaper. The cross-section SEM was performed on fresh and 1100 ºC calcinated copper smelter slag and on the bed material from test 1, 3, 4, and 5.

Once the samples were under the electron microscope, pictures of their structure were taken. In addition to the pictures, elemental analysis was performed on specific spots on the particles, so called spot analyses. Maps were also taken where a square area was specified and divided into a set number of smaller squares. The SEM analysed the small squares one by one and marked to most abundant element in each square, creating a coloured map. Line maps were also taken in which a line was drawn, and the SEM analysed the elemental composition across the line.

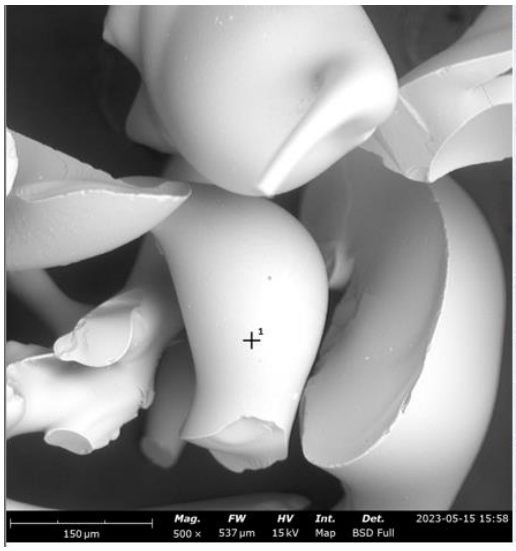
5 Result and discussion

Below are the results from the SEM and fluidized bed tests. The results start with the SEM pictures for the fresh and the calcination oven samples and then goes onto the fluidized bed tests complemented with SEM.

5.1 SEM for calcinated samples



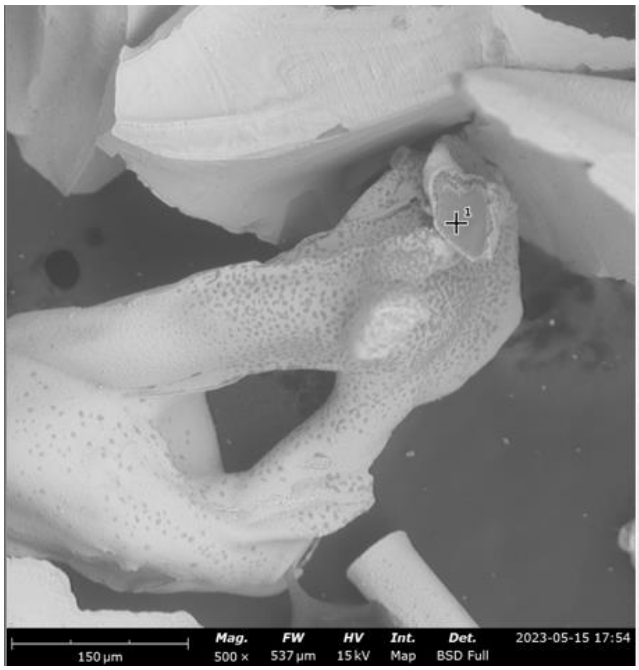
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	70.42	48.64
14	Si	Silicon	13.32	16.15
26	Fe	Iron	12.44	30.00
13	Al	Aluminium	1.80	2.09
20	Ca K	Calcium	1.45	2.51
12	Mg	Magnesium	0.58	0.61



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	61.32	46.92
26	Fe	Iron	20.88	31.78
29	Cu	Copper	5.89	10.19
20	Ca K	Calcium	6.61	7.22
13	Al	Aluminium	5.30	3.90
12	Mg	Magnesium	0.00	0.00
30	Zn K	Zinc	0.00	0.00
16	S	Sulfur	0.00	0.00

Figure 5.1 & 5.2. Above: A cross section SEM picture of fresh copper smelter slag and the results of a point elemental analysis. Below: A surface SEM picture of fresh copper smelter slag and the results of a point analysis.

Figure 5.1 and 5.2 shows SEM pictures of fresh granulated copper smelter slag. To note is that the surface and interior of the fresh sample appears smooth and homogenous. The homogeneity can likely be attributed to that the material is amorphous.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
26	Fe	Iron	91.81	91.34
29	Cu	Copper	4.07	4.61
30	Zn K	Zinc	2.75	3.21
16	S	Sulfur	0.93	0.53
20	Ca K	Calcium	0.44	0.31
12	Mg	Magnesium	0.00	0.00
13	Al	Aluminium	0.00	0.00
14	Si	Silicon	0.00	0.00

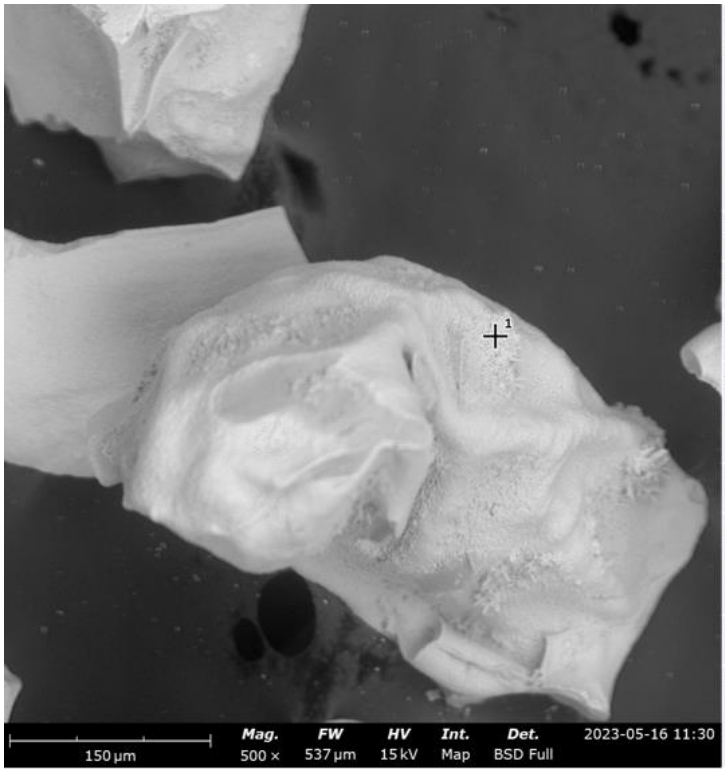
Figure 5.3 shows an SEM picture of the surface of 750 ºC calcinated copper smelter slag particles. The picture also shows the result of a point analysis.

Figure 5.3 shows the surface of 750 ºC calcinated particles. Unlike the very homogenous fresh sample, the 750 ºC sample is slightly porous and has dark spots and streaks. Additionally, the spot analysis shows that the surface is very iron rich. The iron rich surface could be attributed to oxidation as shown in [10] in which iron is drawn out to the surface to react with the air.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
26	Fe	Iron	74.80	74.62
29	Cu	Copper	16.29	18.49
30	Zn K	Zinc	2.44	2.85
20	Ca K	Calcium	3.38	2.42
14	Si	Silicon	2.12	1.06
16	S	Sulfur	0.96	0.55
12	Mg	Magnesium	0.00	0.00
13	Al	Aluminium	0.00	0.00

Figure 5.4 shows an SEM picture of the surface of 850 ºC calcinated copper smelter slag particles. The picture also shows the result of a point analysis.

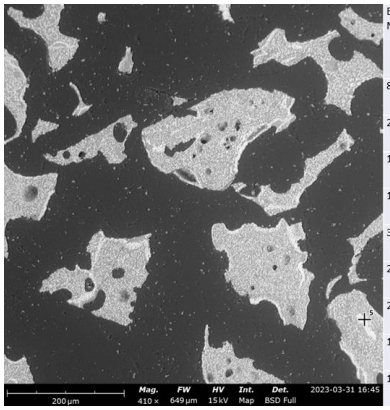
Figure 5.4 shows 850 ºC calcinated copper smelter slag particles. The dark spots found in the 750 ºC calcinated sample are no longer as abundant, instead the surface of the sample has iron rich furrows. The furrows could be attributed to an increase in the height of the iron rich layer due to further oxidation.



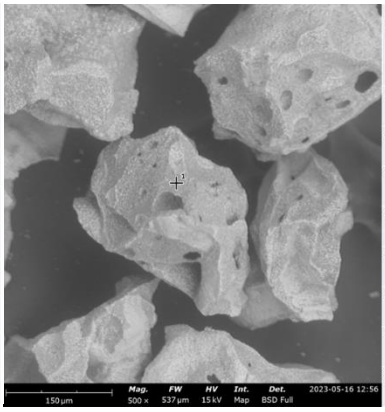
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
26	Fe	Iron	79.76	79.58
29	Cu	Copper	10.95	12.44
30	Zn K	Zinc	5.06	5.91
12	Mg	Magnesium	2.09	0.91
14	Si	Silicon	1.64	0.82
20	Ca K	Calcium	0.40	0.29
16	S	Sulfur	0.09	0.05
13	Al	Aluminium	0.00	0.00

Figure 5.5 shows an SEM picture of the surface of 950 ºC calcinated copper smelter slag particles. The picture also shows the result of a point analysis.

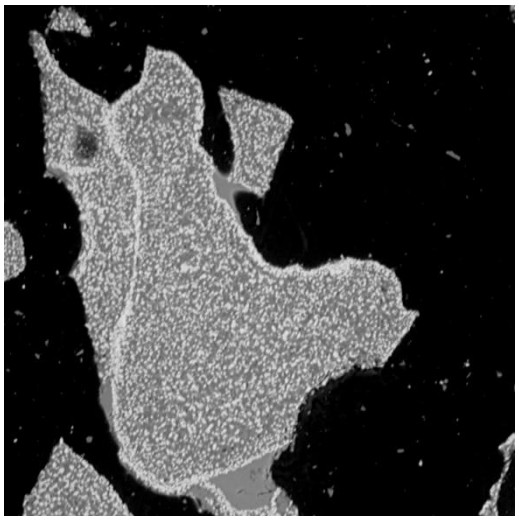
The 950 ºC calcinated sample shown in figure 5.5 is much like the 850 ºC calcinated sample but appears to have crystals forming on the surface. Judging from the point analysis the formed crystals are iron rich. The crystals could be attributed to further growth of the iron rich layer due to further oxidation.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	72.15	45.50
26	Fe	Iron	20.24	44.54
14	Si	Silicon	5.10	5.64
13	Al	Aluminium	1.06	1.12
30	Zn K	Zinc	0.61	1.57
20	Ca K	Calcium	0.47	0.74
29	Cu	Copper	0.31	0.79
16	S	Sulfur	0.07	0.08
12	Mg	Magnesium	0.00	0.00



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	63.63	50.35
26	Fe	Iron	24.31	38.26
13	Al	Aluminium	7.33	5.57
20	Ca K	Calcium	3.53	3.98
29	Cu	Copper	0.84	1.51
16	S	Sulfur	0.36	0.33
12	Mg	Magnesium	0.00	0.00
30	Zn K	Zinc	0.00	0.00



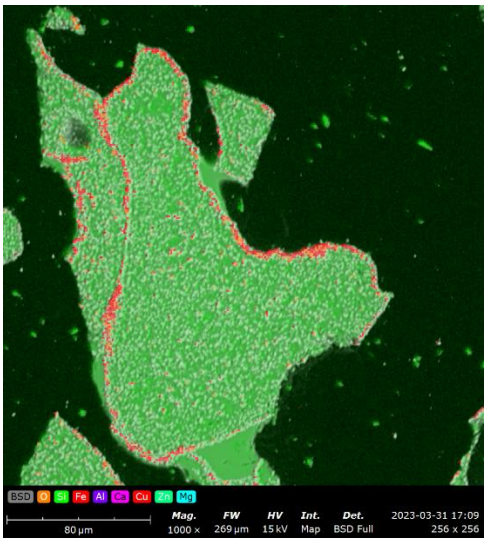
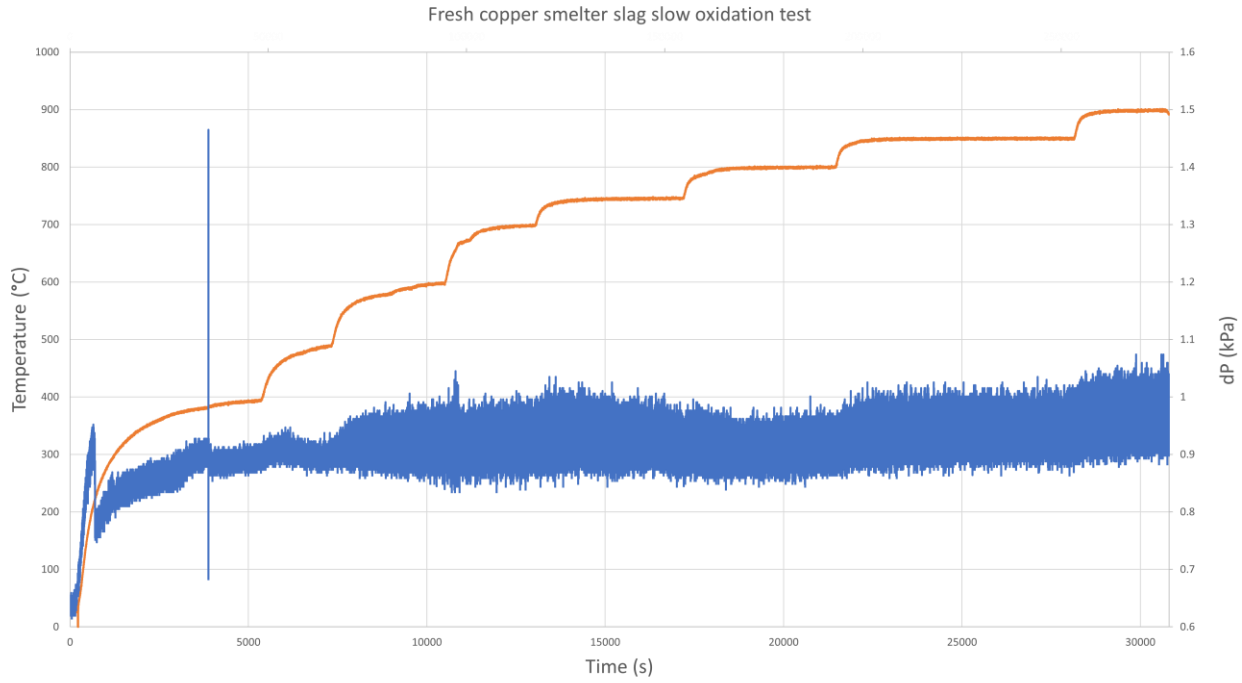


Figure 5.6, 5.7, 5.8 & 5.9. Top-left 5.6: A cross section SEM picture of 1100 ºC calcinated copper smelter slag. Top-right 5.7: A surface SEM picture of 1100 ºC calcinated copper smelter slag. Both 5.6 & 5.7 show the results of a point analysis. Bottom- left 5.8: A cross section SEM picture of 1100 ºC calcinated copper smelter slag. Bottom-right 5.9: An SEM map of a cross section of 1100 ºC calcinated copper smelter slag.

In figure 5.6 and 5.7 the cross section and surface view of 1100 ºC calcinated copper smelter slag is shown. To note is that both pictures look very similar despite that the 850 and 950 ºC samples had a very clear iron rich surface. This is likely due to the sample preparation as the sample had agglomerated and had to be broken in pieces in order to be analysed. Both pictures show a surface speckled with dark dots, similar to the 750 ºC sample. In addition, the cross section shows iron rich light spots that could be the same kind of iron rich surface found in the 850 and 950 ºC sample. The SEM map of 5.8 in 5.9 further shows that the light dots are iron rich and the dark spots silica rich.

5.2 Fluidized bed tests

5.2.1 Test 1: Slow oxidation of fresh copper smelter slag



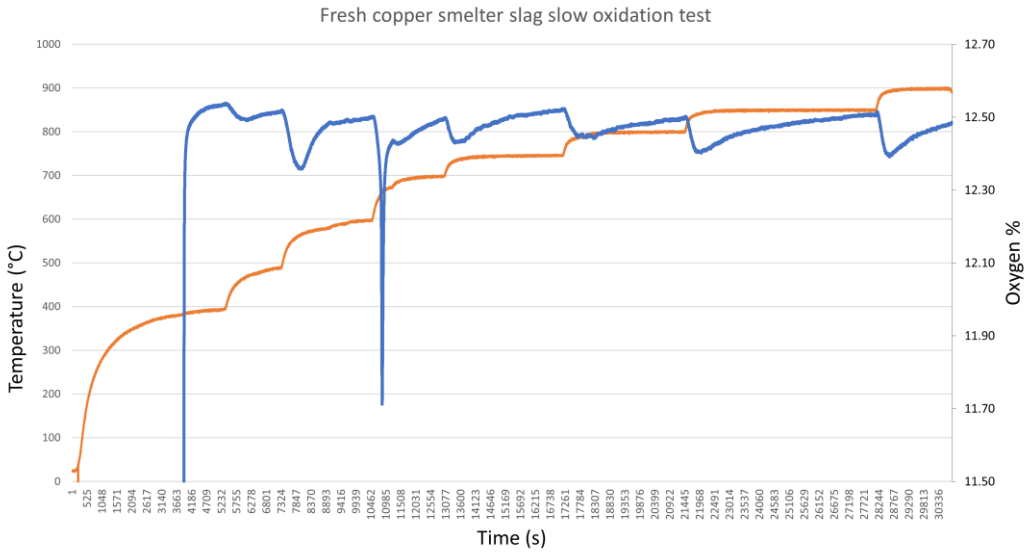


Figure 5.10 & 5.11. Above: A graph of the temperature (orange) and pressure drop (blue) over the course of the slow oxidation test. Below: A graph of the temperature (orange) and oxygen fraction (blue) over the course of the slow oxidation test.

Figure 5.10 shows the pressure drop over the course of the test. A fluidized bed is typically shown by fluctuations in the pressure drop. A defluidization is typically marked by a sudden fall in amplitude of the pressure drop, that said the pressure drop isn't a measurement for fluidization but simply a proxy. Since there is a lack of an obvious fall in amplitude in figure 5.10, there was likely no defluidization during test 1. However, when the sample was removed from the reactor it was partially

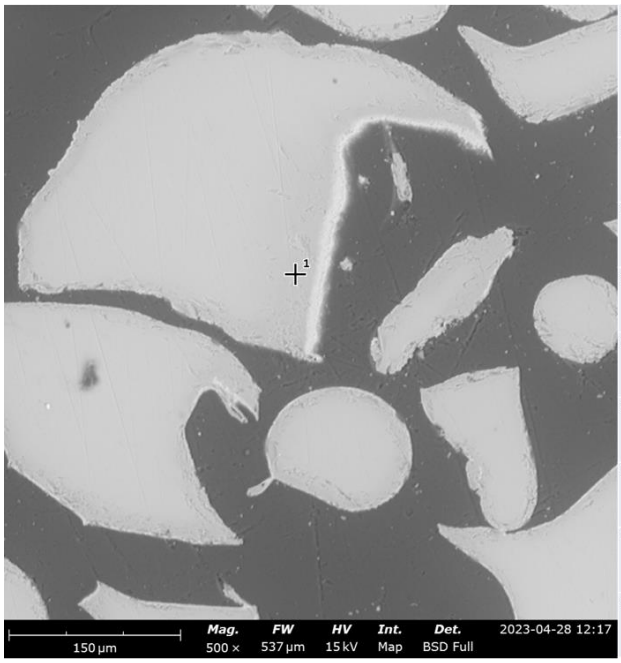
agglomerated with around a third of the sample agglomerated into a few big pieces, the rest of the sample did not show signs of agglomeration. The agglomeration was loosely bound together, and the particles were easily separated. Unfortunately, the loose nature of the agglomeration also made SEM analysis of the place where the particles have lumped together difficult, as the agglomeration broke during sample preparation. The reason why it agglomerated despite not visibly defluidizing could have multiple explanations. The agglomeration could have been weak enough to be broken by the gas flow, the agglomeration might not have affected fluidization, or the agglomeration could have happened during cooling or overnight. Figure 5.11 shows that a significant increase in oxygen absorption occurs around 650 ºC.

By integrating the oxygen absorption in figure 5.11 a rough measure of the amount of oxygen absorbed by the test 1 sample could be made. The quantification is shown in the table below.

	Weight (g)	Weight increase (g)
Start of test	20	0
End of test	20.507	+0.507
Calcination		+0.225*
Sum	20.732	+0.732

**. The actual value was 0.2 g, but it was adjusted to account for loss of bed material by multiplying with the calculated weight of the bed material at the end of the test divided by the mass calcinated, 20.507 / 18.2.*

It took around 7 hours of oxidation for the 20 g sample to absorb 0.507 g oxygen. To check if the sample was fully oxidized, the sample was weighted and put in a calcination oven at 900 ºC for 24h to measure the weight increase from oxidation. After calcinating in the oven and accounting for mass loss from transferring the sample the total mass oxygen absorbed was 0.732 g. In other words, the oxidation of the fresh copper smelter slag was around 70% done even after 7 hours. Judging from that information, copper smelter slag oxidizes slowly.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	51.76	37.88
26	Fe	Iron	35.08	51.05
13	Al	Aluminium	8.66	6.09
20	Ca K	Calcium	2.62	2.74
16	S	Sulfur	0.78	0.65
30	Zn K	Zinc	0.63	1.08
12	Mg	Magnesium	0.25	0.16
29	Cu	Copper	0.21	0.35

Figure 5.12. 5.12 shows a cross section SEM picture of test 1's bed material. It also shows the result of a point analysis.

Figure 5.12 shows a cross section SEM picture of test 1's bed material. It lacks the speckled pattern found in 1100 ºC calcinated copper smelter slag. The lack of the speckled pattern could be due to incomplete oxidation. It has an iron rich layer on the surface of the particle similar to 850 and 950 ºC calcinated samples.

5.2.2 Test 2: Defluidization test of 750 ºC calcinated copper smelter slag

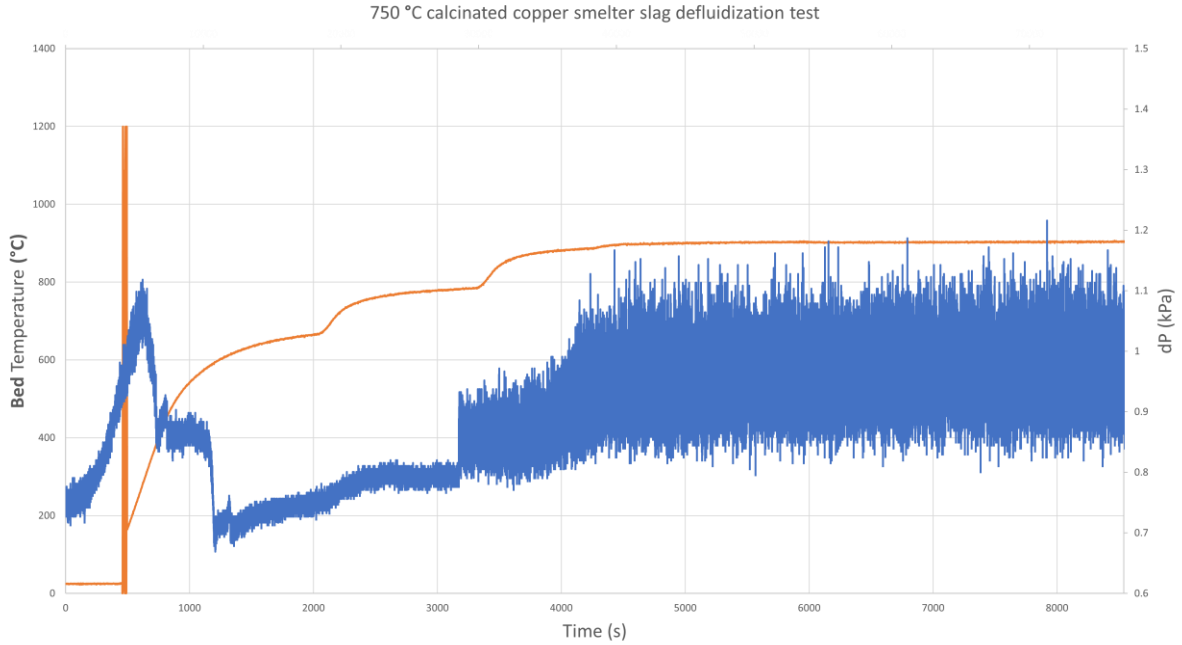


Figure 5.13. A graph showing the pressure drop (blue) and temperature (orange) over time for test 2.

Figure 5.13 shows a lack of an obvious fall of pressure drop amplitude. No signs of defluidization were observed. However, the sample, once taken out was slightly agglomerated in a similar manner to test 1.

5.2.3 Test 3 & 4: Defluidization test of fresh copper smelter slag, with and without air

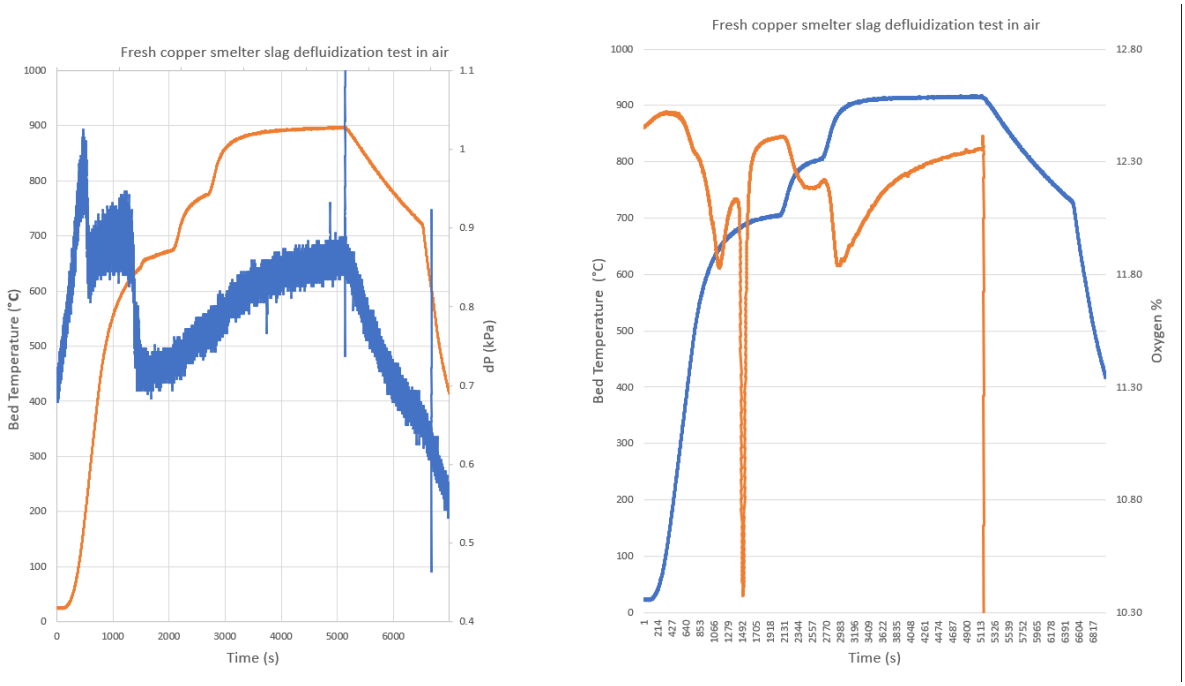


Figure 5.14. Left: A graph of the pressure drop (blue) and temperature (orange) over time for test 3. Right: A graph over the temperature (blue) and oxygen fraction (orange) over time for test 3.

Figure 5.14 shows what is likely a defluidization at around 650 ºC in test 3. Additionally, oxygen absorption increased sharply at around 650 ºC. The coincidence of the oxygen absorption and defluidization led us to hypothesize that the defluidization was caused by the formation of iron rich surfaces found in the 850 and 950 ºC samples.

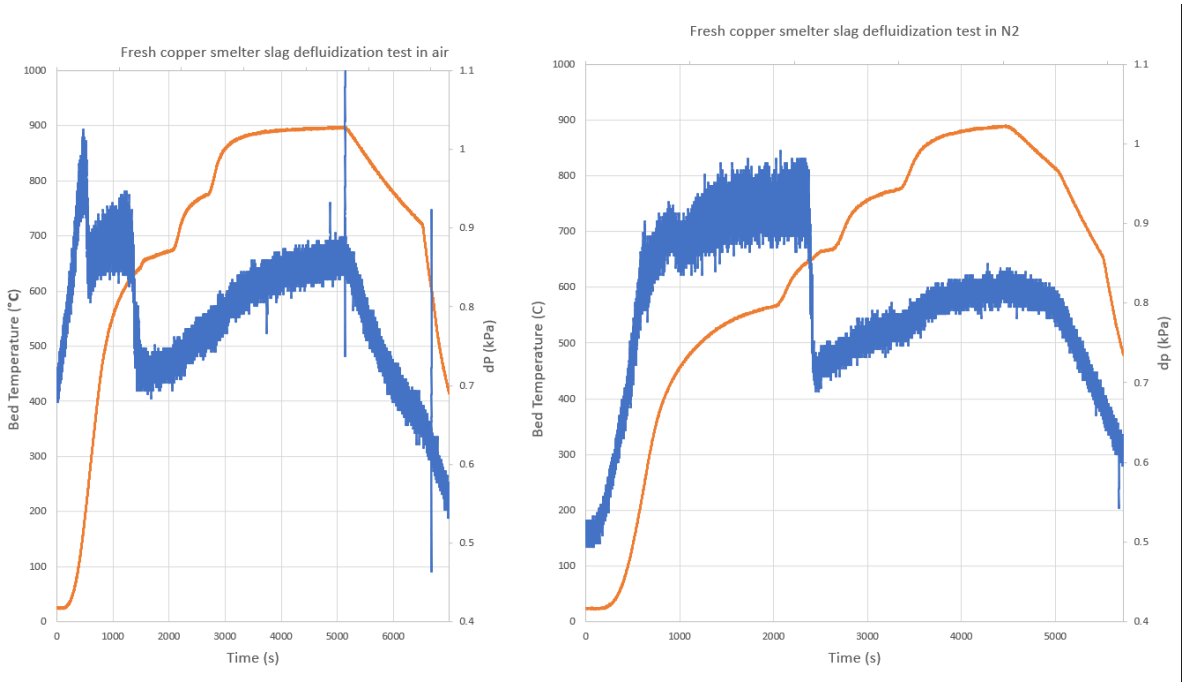
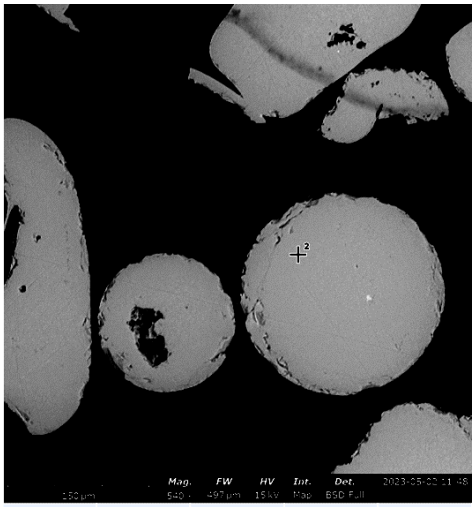


Figure 5.15. Left: A graph of the pressure drop (blue) and temperature (orange) over time for test 3. Right: A graph of the pressure drop (blue) and temperature (orange) over time for test 4.

Figure 5.15 compares the pressure drop in test 3 and 4. In both tests defluidization can be observed at around 650 ºC. The initial hypothesis that the defluidization was caused by oxidation turned out to be false as defluidization occurred even when no oxygen was present. It could be that some kind of phase transition happens at around 650 ºC, which increases the availability of iron to the air. That said, we don't know and to understand the cause of the defluidization, further studies would be required.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	46.33	33.13
26	Fe	Iron	36.93	52.51
13	Al	Aluminium	7.62	5.23
20	Ca K	Calcium	4.55	4.65
12	Mg	Magnesium	2.09	1.29
16	S	Sulfur	1.08	0.88
30	Zn K	Zinc	0.87	1.45
29	Cu	Copper	0.54	0.87



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	45.81	32.02
26	Fe	Iron	40.29	55.99
13	Al	Aluminium	7.44	5.00
20	Ca K	Calcium	3.20	3.20
16	S	Sulfur	0.95	0.76
30	Zn K	Zinc	0.91	1.48
29	Cu	Copper	0.72	1.14
12	Mg	Magnesium	0.68	0.41

Figure 5.16. Left: A cross section SEM picture of the test 3 bed material. Right: A cross section SEM picture of the test 4 bed material.

Figure 5.16 compares the SEM cross sections of the samples from test 3 and 4. The main difference between the two is that test 3 has a light iron rich surface layer.

5.2.4 Test 5: Regeneration of bed with fresh copper smelter slag

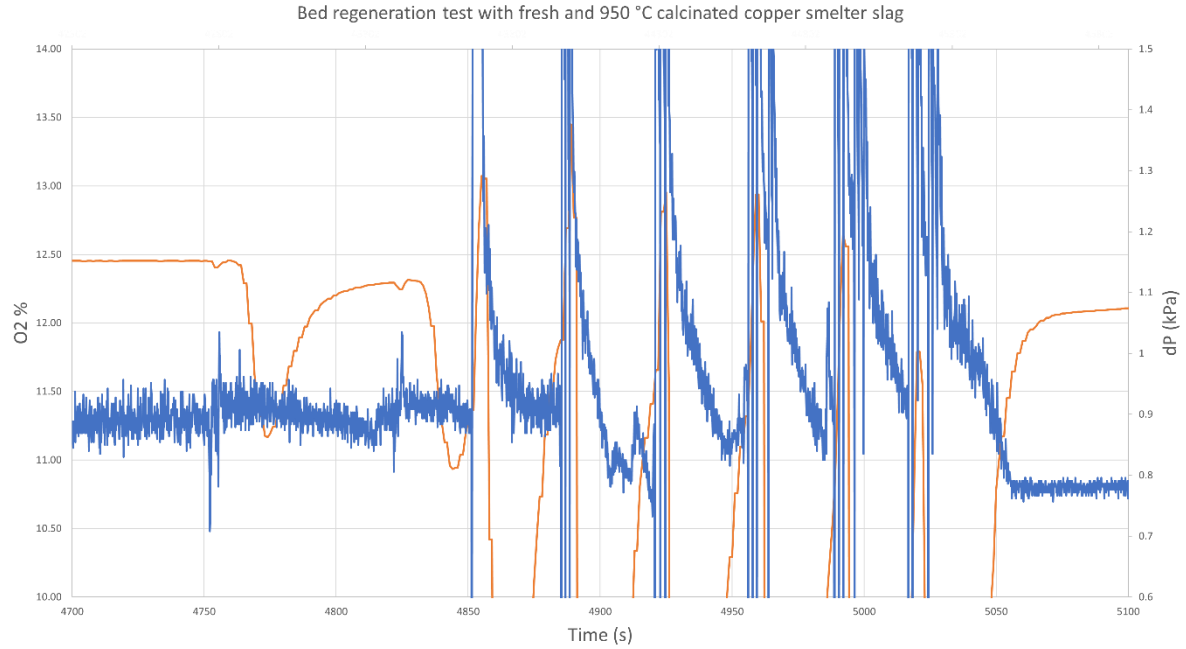
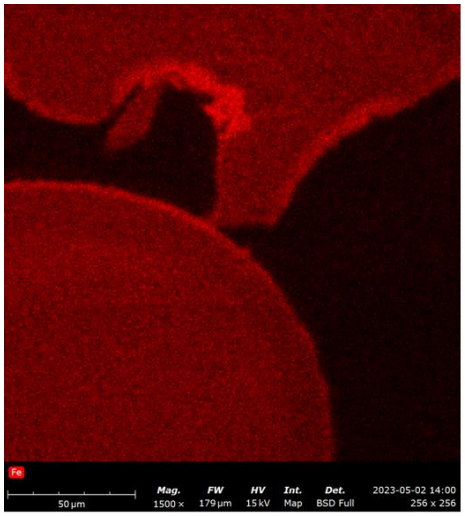
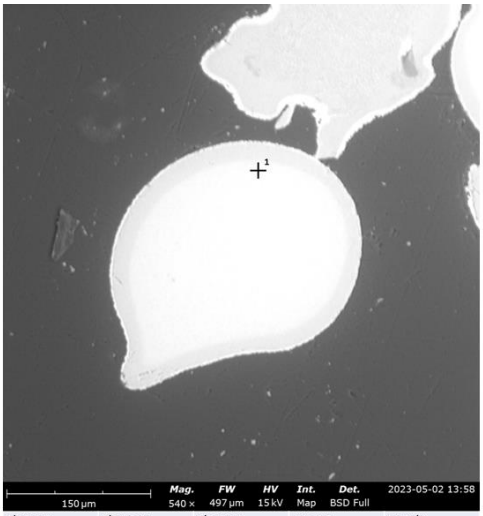


Figure 5.17. A graph of the pressure drop (blue) and oxygen fraction (orange) during the insertion of the fresh copper smelter slag bed in test 5.

Figure 5.17 shows the fluidization and oxygen fraction during the insertion of the new bed. As the added bed was too big to insert in one go the insertion took several minutes as can be seen in figure 5.17. The high and lows in pressure drop and oxygen levels is because the added bed was flushed down with nitrogen gas. After the 7 g fresh copper smelter slag sample was added, defluidization occurred very quickly, as can be seen in the decrease of amplitude and level of pressure drop.



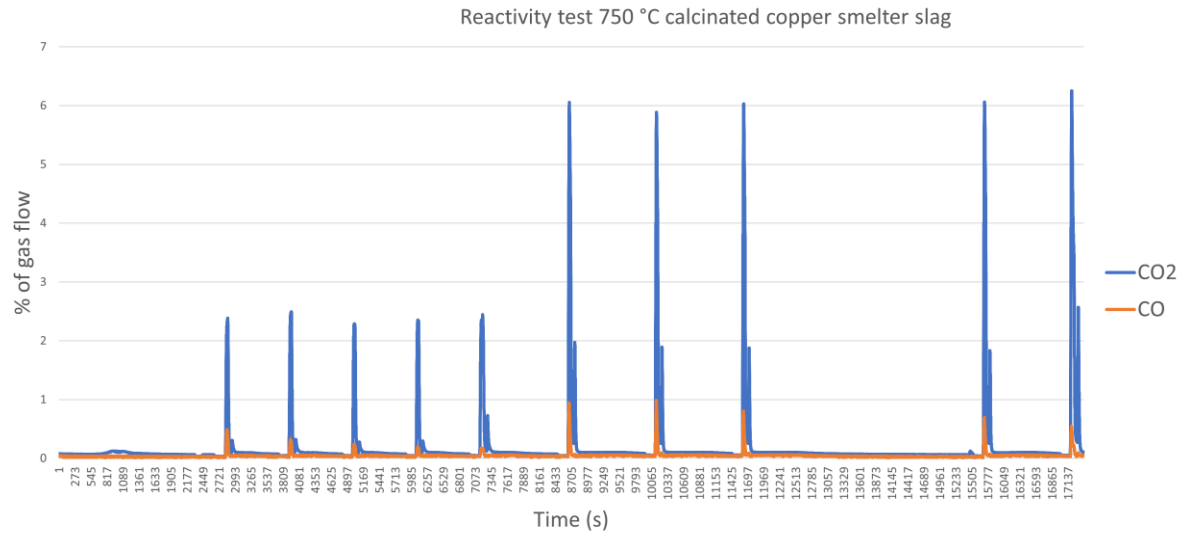


Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	45.95	32.70
26	Fe	Iron	38.07	53.88
13	Al	Aluminium	7.31	5.00
20	Ca K	Calcium	3.06	3.11
12	Mg	Magnesium	3.00	1.85
16	S	Sulfur	0.96	0.78
29	Cu	Copper	0.88	1.42
30	Zn K	Zinc	0.76	1.26

Figure 5.18. Left: A SEM map of a cross section of the test 5 bed material. Right: A cross section SEM picture of the test 5 bed material. The result of a point analysis is shown.

Figure 5.18 shows the cross section of two different particles. To note is that the particles look different. The upper particle is speckled in a similar manner to the 1100 ºC calcinated sample. The upper particle is likely from the 950 ºC calcinated batch and the lower particle is likely from the fresh batch that was inserted. The lower particle has three different layers. Judging from the SEM map the outer layer is iron rich, the middle layer is silica rich, likely due to the iron travelling to the surface. The inner layer appears to be neither rich nor poor in iron, possibly due to not being very oxidized.

5.2.5 Test 6: Reactivity test of 750 ºC calcinated copper smelter slag with methane



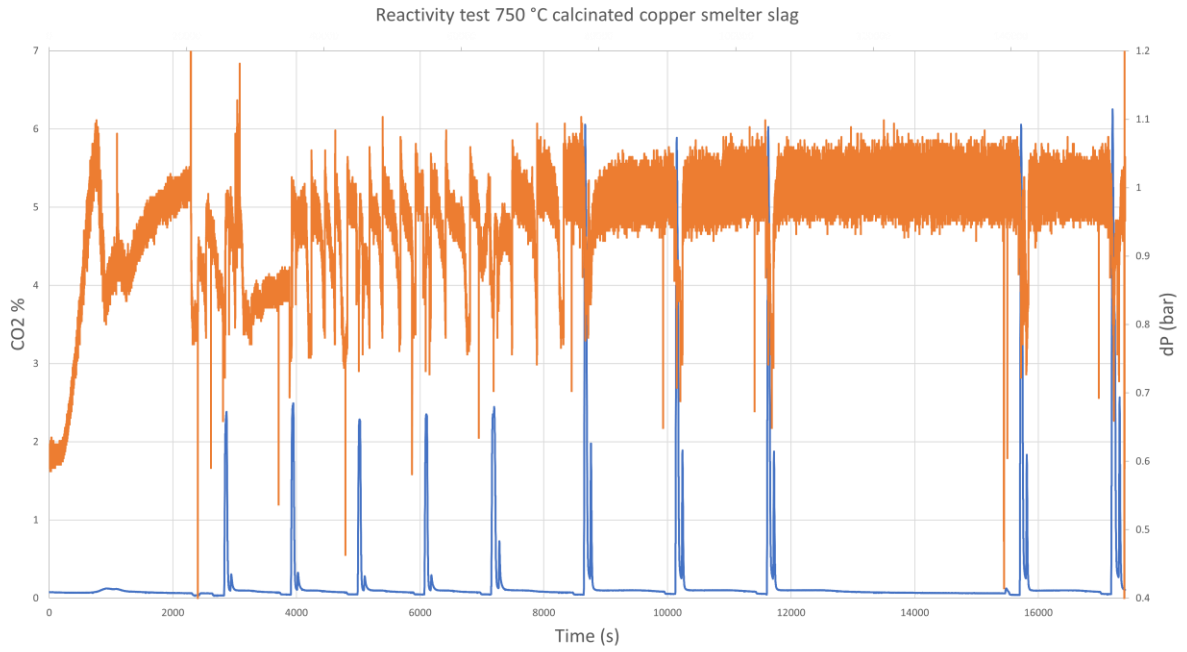
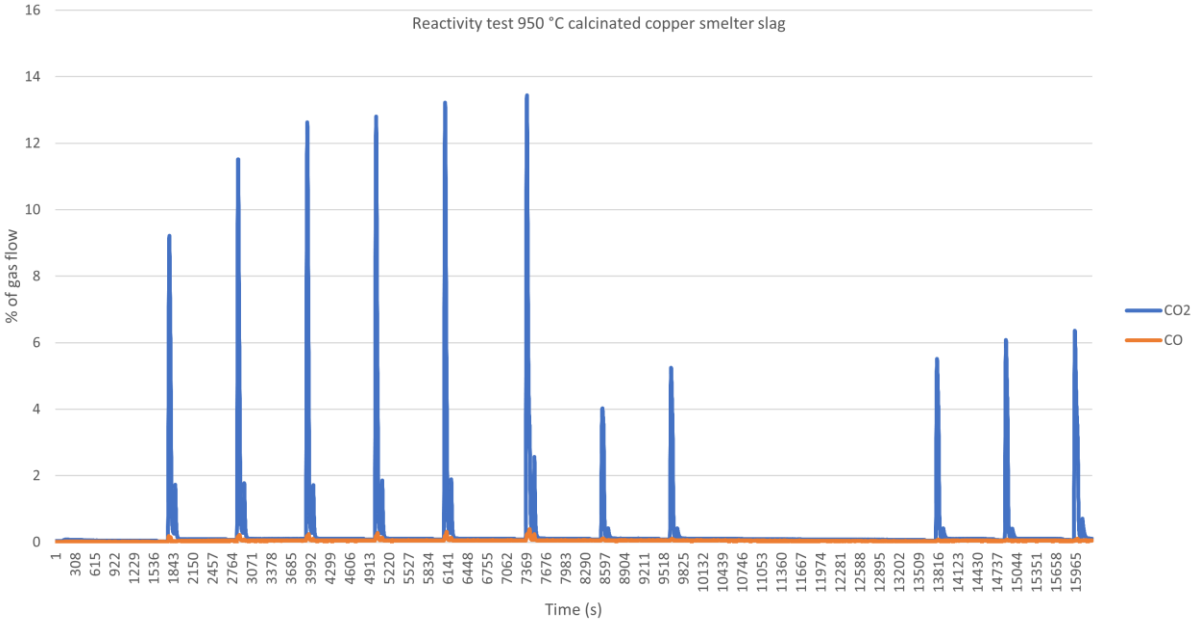


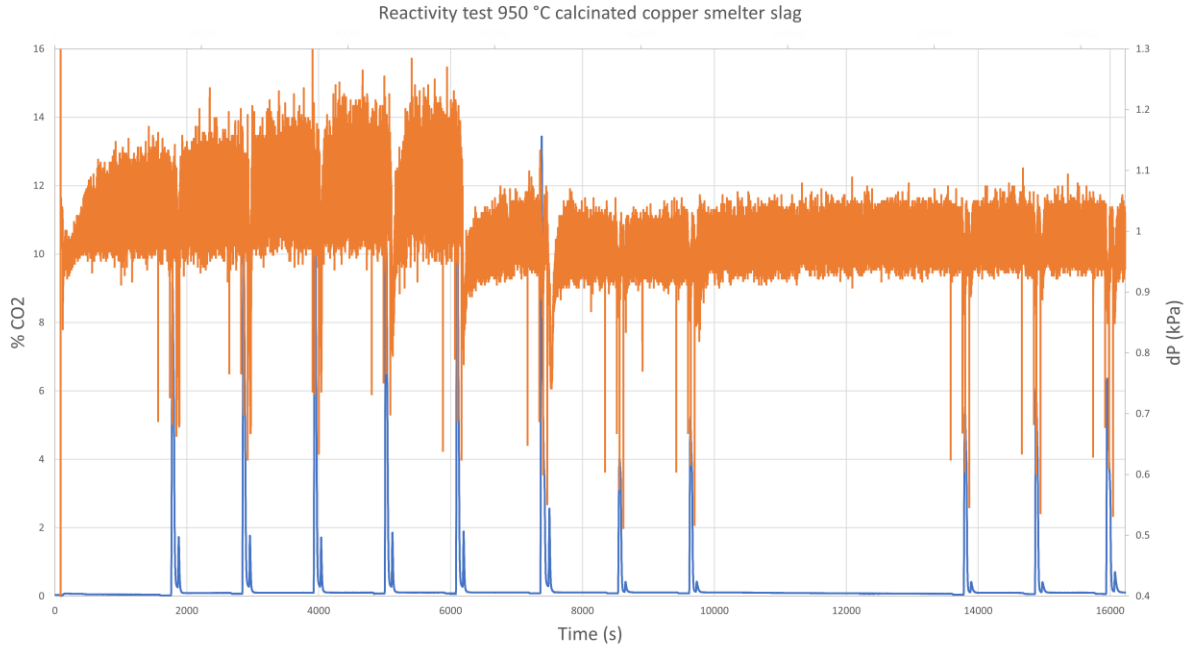
Figure 5.19 & 5.20. Above: A graph showing the CO2 (blue) and CO (orange) fraction over time during test 6. Below: A graph showing pressure drop (orange) and CO2 (blue) fraction over time during test 6.

Figure 5.19 and 5.20 shows the 10 cycles during test 6. 5.20 shows that the CO2 fraction increased when the temperature changed from 750 ºC to 850 ºC. The increase in the CO2 fraction is expected as a higher temperature generally leads to better conversion of the fuel. 5.20 shows that the sample tried to defludize at multiple instances. As previous test had shown that the agglomeration was weak, a light tap to the reactor with a spanner was enough to continue the fluidization. The refluidziation via spanner was done at sign of defluidization. Judging from figure 5.20 the tendency to defluidize was high when the temperature was 750 ºC and

decreased when the temperature was 850 ºC. Typically, extra heating encourages defluidization but in this case it seems to decrease the tendency to defluidize. The reason for this is unknown and would require additional research to understand.

5.2.6 Test 7 Reactivity test of 950 ºC calcinated copper smelter slag with methane





5.21 & 5.22. Above: A graph showing the CO2 (blue) and CO (orange) fraction over time during test 7. Below: A graph showing pressure drop (orange) and CO2 (blue) fraction over time during test 7. The fifth cycle and peak can be ignored as that cycle was improperly done.

Test 7 began with 5 cycles at 850 ºC and subsequently 5 cycles at 750 ºC. Figure 5.21 shows that methane conversion increased over time but decreased when the temperature dropped to from 850 ºC to 750 ºC. Figure 5.22 shows that the test 7 sample had a low tendency to defludize at both temperatures. To note is the difference between the CO2 and in turn methane conversion between test 6 and 7.

Despite operating at the same temperature, test 6 has a 6% CO_2 fraction at 850 ºC while test 7 had a 13% CO_2 fraction. In other words, the calcination level of copper smelter slag greatly affects methane conversion. This could be due to more iron transferring to the surface in the 950 ºC sample due to a higher calcination temperature.

6 Conclusion

In conclusion the cause of defluidization is still unknown, but at the very least defluidization isn't only caused by oxidation. Instead, there is some kind of phase transition at around 650 ºC that happens regardless of the presence of oxygen, but additional research would be required to understand the specifics. As for ways to avoid defluidization, oxidation at 950 ºC seemingly decreases the tendency to defluidize. Additionally, as the agglomeration is weak very little force is required to refluidize and increasing the temperature may be sufficient if the defluidization tendency is weak as in test 6. Also, oxidizing sufficiently before heating above 650 ºC as in test 1 may stop the bed material from defluidizing.

SEM analyses have shown that iron forms an iron rich layer on the surface of the particle during oxidation, making it accessible to the gas flow. Test 1 has shown that copper smelter slag takes a long time to oxidize. Additionally test 6 and 7 has shown that different oxidation level makes very large difference in reactivity and conversion of fuel.

The thesis did not study what phases were present at each temperature as it was beyond the time constraints and would require XRD analysis.

7 Future work

Future work could consist of XRD analysing copper smelter slag heated slightly above and under 650 ºC. Further investigation of ways to avoid defluidization could also be possible, mixing in quartz sand or investigating at what rate copper smelter slag can be used to regenerate a bed, or finding out just how much oxidation is required to avoid the 650 ºC defluidization. Understanding the great change in fuel conversion due to oxidation level as seen when comparing test 6 and 7 could also be interesting.

8 Sources

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