

Investigation of Cu and Zn interactions with ilmenite during waste incineration

Modelling of phases and reactions using a thermodynamic modelling approach

Master's thesis in Chemical Engineering

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CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2020 www.chalmers.se Investigation of Cu and Zn interactions with ilmenite during waste incineration

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SUMMARY

In 2018, approximately 2.01 billion tons of waste was generated in the world. By 2050, this number is expected to increase drastically to 3.40 billion tons of waste annually as lower income countries develop and the world population increases (Kaz, Yao, Bhada-Tata, & Van-Woerden, 2018). Some of the waste can be combusted to produce heat and power, leaving residual ash behind. This also decreases the volume of the waste flow by 90 % (Lam, Ip, Barford, & McKay, 2010). As waste generation is expected to increase while the land available for landfilling decreases, it is of interest to recycle as much as possible from waste, as well as from ash, and move towards a more circular economy in which no new raw materials are needed.

One technology that can be used for waste incineration is Oxygen Carrier Aided Combustion (OCAC). OCAC is a type of fluidized-bed combustion, in which the conventional inert bed material is replaced fully or in part with metal oxides, called oxygen carrier. The oxygen carrier is reduced in fuel rich parts of the reactor and oxidized in oxygen rich parts during the combustion, thereby improving the distribution of oxygen in space and time. This improves the combustion efficiency. The interaction between the oxygen carrier and fuel ash can lead to an uptake of certain elements such as zinc, copper, potassium, calcium and phosphorous among others.

The aim of the thesis was to investigate how major ash components (Si, Al, Fe, Mg, Ca, K, Na and Cl) and the minor ash components Cu and Zn interact with the oxygen carrier bed material ilmenite (FeTiO₃) during waste incineration. A focus on Cu and Zn was chosen since these usually have the highest concentrations out of the trace metals that can be valuable for recycling, as they are high-cost metals and energy intensive to produce. The investigation was carried out by simulating different boiler conditions and performing thermodynamical equilibrium calculations (constructing phase diagrams) using the software FactSage 7.2.

The simulations indicated that ilmenite interacts with Al₂O₃, CaO/CaCO₂, Na₂O, K₂O, MgO, ZnO and Cu/Cu₂O but does not interact with SiO₂. The compounds formed from interactions between ilmenite and ash which could be relevant for OCAC applications are FeAl₂O₄, CaTiO₃, (Na₂O)(TiO₂)₃, (Na₂O)(TiO₂)₆, ZnFe₂O₄, (ZnO)₂TiO₂, (Cu₂O)(Fe₂O₃) (s2) and (CuO)(Fe₂O₃) (s3). Experimentally, potassium has been found as KTi₈O₁₆ in ilmenite particles rather than as K₂Ti₃O₇ and K₂Ti₆O₁₃ as indicated by the simulations. The compound KTi₈O₁₆ is missing in the software database, therefore giving inconclusive results not corresponding to experimental findings.

Keywords: FactSage, copper, zinc, major ash elements, interactions, bed material, combustion, ilmenite, thermodynamical equilibrium calculations, phase diagram, oxygen carrier, ash interaction

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1. Introduction

Global climate change has already had observable effects on the environment such as loss of sea ice, accelerated sea level rise and more intense heat waves (NASA, 2020). The global temperature is also expected to rise as an effect of greenhouse gases produced by human activity (NASA, 2020). At the same time, the world population is increasing and is producing increasingly more waste that must be managed (Kaz et al., 2018). With the world becoming more aware of the effects of climate change and the waste generation increasing; while the land available for landfilling decreases, it is of interest to focus on process effectivization and to recycle as much as possible from waste and move towards a more circular economy in which no new raw materials are needed. This also, since the planet's resources are limited and spent materials must be reused. As more emphasis is put on recycling, there has been an increasing interest in finding new ways to recycle materials from Municipal Solid Waste (MSW) incineration ashes, mainly with a focus on precious metals such as copper, zinc and vanadium as these are expensive and energy intensive to produce. Solid metal pieces are already separated, but metals bound in different forms in ash particles are not. Previous studies have investigated leaching of heavy metals such as Fe, Al, Mg, As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Sr, V and Zn with different acids; not only for their monetary value but also to decrease the volume going to landfill, and since some metals are toxic (such as Cr, Cu, Ni and Pb) and would be beneficial to remove before landfilling (Tang, 2015), (Karlfeldt-Fedje, 2010), (Huang, Inoue, Harada, Kawakita, & Ohto, 2011), (Pöykiö, Mäkelä, Watkins, Nurmesniemi, & Dahl, 2016), (Hykš, 2008). Some studies have focused on Cu and Zn in particular as they often are the trace metals found in the highest concentrations in waste (Tang, 2015), (Karlfeldt-Fedje, 2010). Leaching has been found to be more efficient for fly ashes (volatile ash compounds) than the heavy bottom ashes, as the bottom ash is more heterogeneous and contains larger particles (Tang, 2015), (Karlfeldt-Fedje, 2010).

1.1. Background

The definition of waste according to the EU Waste Framework Directive is "any substance or object which the holder discards or intends or is required to discard" (Falkenberg, 2012). Waste occurs when any organism returns substances to the environment. Usually, these substances are recycled by other organisms (EnvironmentalLiteracyCouncil, 2015). Humans, however, produce a large flow of material residues (items consumers throw away) that would overload the capacity of natural recycling processes and therefore must be managed. Solid and fluid, hazardous and non-toxic wastes are generated in households, offices, schools, hospitals, and industries. Municipal Solid Waste (MSW) is waste collected from households, commercial buildings, hospitals and schools. MSW consists primarily of paper, containers and packaging, food wastes, yard trimmings, and other inorganic wastes (EnvironmentalLiteracyCouncil, 2015). In 2018, approximately 2.01 billion tons of waste was generated in the world. By 2050, this number is expected to increase drastically to 3.40 billion tons of waste annually as lower income countries develop and the world population increases (Kaz et al., 2018).

For managing waste, there is a waste hierarchy: a set of priorities for the efficient use of resources based on the Waste Avoidance and Resource Recovery Act 2001. The waste hierarchy is (as reproduced from EPA (2017):

- 1. **avoidance** including action to reduce the amount of waste generated by households, industry and all levels of government
- 2. **resource recovery** including re-use, recycling, reprocessing and energy recovery, consistent with the most efficient use of the recovered resources
- 3. **disposal** including management of all disposal options in the most environmentally responsible manner.

MSW (as well as other wastes and biomass) can be combusted to produce heat and power. For example, in 2017 approximately 240 million tons of municipal solid waste was generated in the U.S., (EPA, 2020). Out of the 240 million tons, 12.7 % were combusted with energy recovery (EPA, 2020). The incineration of waste, which falls under resource recovery in the waste hierarchy, is desirable over disposal as it (of course) recovers energy instead of directly sending it to landfill. In addition to this it also decreases the volume of the waste flows with the remaining ash being on average 10% of the volume of the input, and around 30% of its weight (Lam et al., 2010). Although the volume decreases significantly, the resulting ash (the residual material left after combustion), which must be disposed is still left behind. The ash can be seen as a new waste flow that can follow the waste hierarchy. The ash is usually landfilled or reused for secondary materials (Lam et al., 2010).

The combustion/incineration of waste and biomass is usually done with a grate-fired or fluidizedbed boiler. Fluidized beds offer advantages such as better contact between the fuel and air, rapid heat and mass transfer rates (created by the turbulence of the bed) and reduction of sulphur dioxide emissions (when using limestone). As a result of this, the combustion temperature can be lower; which in turn reduces the formation of nitrogen oxides (Dryden, 1982). In fluidized-bed combustion, material of for example coal ash, silica an inert bed sand and/or limestone is conventionally used (Dryden, 1982). For combustion of waste and biomass, silica sand is the usual choice of bed material (Rydén, Hanning, Corcoran, & Lind, 2016). There are two main categories of atmospheric fluidized bed combustors: bubbling fluidized-bed combustors (BFBC) and circulating fluidized-bed combustors (CFBC). The main difference between the two is that the fluidizing velocity is low in a bubbling bed which keeps most of the bed in the combustor (at a depth around 1 m); whereas the fluidizing velocity is significantly higher in a circulating bed. The higher velocity in the CFBC results in a higher uniform bed and some of the particles are entrained out of the combustor. They are then guided back to the bed through a cyclone. The heat and mass transfer rates are higher in a CFBC as a result of a higher slip velocity (difference between gas and solid velocity), longer residence and contact times and more intense mixing (Sarkar, 2015). Apart from the different fluidizing velocities and circulation, the different combustors operate similarly. As mentioned, they operate in the same temperature interval (Caneghem et al., 2012). Air is introduced below the bed in the combustor and goes through a perforated plate on which the fluidized bed rests. The fuel is introduced into the bed where it burns. Volatile compounds (fly ash) exit in the top of the boiler and is lead into the convective section where they are cooled and removed. Heavier compounds (bottom ash) in the bottom (Miller, 2017), (Sarkar, 2015). A simplified schematic of an atmospheric fluidized-bed combustor can be seen in Figure 1 below.



Figure 1. Simplified schematic of an atmospheric fluidized-bed combustor

In a fluidized bed, the air and thereby oxygen is dispersed by mixing as a result from turbulence of the bed. Insufficient mixing in the bed results in oxygen rich and oxygen poor zones, which can cause local temperature variations and emission of unburned species.

Another technology for fluidized-bed combustion is called Oxygen Carrier Aided Combustion (OCAC). In this process, the conventional inert bed material in the fluidized combustion reactor is replaced fully or in part with oxygen carriers. In OCAC, the oxygen carrier bed material is reduced in fuel rich parts of the reactor and oxidized in oxygen rich parts during the combustion. This improves the distribution of oxygen in space and time, which is especially beneficial for managing heterogeneous fuels such as waste and biofuels. OCAC has been found to have positive effects on emissions compared to other methods, whilst also having the advantage of increasing combustion efficiency and capacity (Gyllén, 2019), (Ryden, Hanning, & Lind, 2018). Although the dispersion of oxygen is improved, the oxygen carrier itself is subjected to both oxidizing and reducing conditions; which corresponds to the partial pressure of oxygen.

One oxygen carrier that is used in the OCAC process is ilmenite (FeTiO₃), which is the oxygen carrier that will be studied in this thesis. It can be found in natural mineral ores. Although ilmenite cannot achieve as high of a conversion rate as some other oxygen carriers, such as for example Fe_2O_3 , Al_2O_3 and MnO, it has the advantage of having a lower cost (Breault, 2018) and is the most studied oxygen carrier in the world. It is also the only one that has been applied in industrial scale.

The intent behind the thesis is to investigate interactions between ilmenite (oxygen carrier bed material) and ash-forming components from the waste fuel in a fluidized-bed combustor. For simulating the system, a fluidized bed combustor, some conditions must be specified. There are different types of fluidized-bed combustors, but they all usually operate at a temperature between 800-900 °C (Caneghem et al., 2012). There are vessels operating under pressurized and atmospheric conditions respectively, but for this study an atmospheric boiler has been chosen as it has the widest application globally (Sarkar, 2015). The operating pressure in the boiler is thereby 1 atm. Chemical looping combustion (CLC) is a technology in which two interconnected fluidized beds, a fuel reactor and air reactor are used. Metal oxides called oxygen carriers are circulated between the two, transporting oxygen, so that direct contact between fuel and air is avoided. This results in an outlet stream consisting of CO₂ and H₂O allowing for CO₂ capture (Lyngfelt, 2013). The air reactor in CLC can be thought to correspond to the maximal oxidizing conditions. Thereby the highest partial pressure of oxygen) and the fuel reactor in CLC the most reducing conditions. Thereby the highest partial pressure of 10^{-15} atm can be said to represent the most reducing conditions.

1.2. Ash formation

The interaction between the oxygen carrier and fuel ash can lead to an enrichment of certain elements such as zinc, copper, potassium, calcium and phosphorous among others in the oxygen carrier particles. As previously mentioned, there has been an increasing interest in recycling trace metals from ashes. As the bed material in fluidized bed boilers can contain a preconcentration of the metals found in waste, it is interesting to evaluate the possibilities to extract trace metals from it as well. Although research has shown that leaching is generally more effective for fly ash than bottom ash (Tang, 2015), (Karlfeldt-Fedje, 2010), spent ilmenite presents an opportunity as it can be magnetically separated from the rest of the bottom ashes and thereby present a more uniform fraction. For better understanding of how metals can be extracted from the ilmenite and how the different ash components interact with the bed material there are two different approaches: experiments with material characterization and theoretical simulations. In this thesis, theoretical simulations are

performed. Experiments were also initiated but not able to be finished. They can however be continued as future work.

For investigating how ash forming components interact with ilmenite, the fuel chemistry must be understood in order to choose the components to simulate. When a fuel is burned, it can be said to undergo three different steps: drying, pyrolysis and char burning. After the particles have been heated up and dried, pyrolysis starts and organic volatile species are released and burn with a visible flame. In this step, some reactive ash-forming elements are released. In the next step, char burning, most of the ash-forming elements end up in the residual ash. The released ash-forming matter reacts with flue gas components and with each other (Zevenhoven, Yrjas, & Hupa, 2010). When investigating interactions with ilmenite in the boiler, both ash-forming matter and compounds formed from interactions between the ash-forming matter and flue gas components should be considered.

In waste, the major elements are Si, Al, Fe, Mg, Ca, K, Na and Cl. The most common oxides found in ash from waste are SiO₂, Al₂O₃, CaO, Fe₂O₃, Na₂O, K₂O and MgO (Lam et al., 2010). Silicon is present in the fuel and/or bed material as silica (SiO₂) and does not react substantially under the combustion conditions but can have some interactions with the ash. Aluminum is present in waste in many forms, and in the furnace processes they all form alumina, Al₂O₃. The organic calcium compounds will be converted into calcium oxide (CaO) with CaCO₃ as an intermediate middle step. All the forms of iron will yield iron oxides, and finally Fe₂O₃. Magnesium behaves similarly to calcium and forms MgO. Sodium and potassium mainly primarily react with Cl (Zevenhoven et al., 2010), but can also form oxides as Na₂O and K₂O (Lam et al., 2010). For investigating interactions between ilmenite and major ash components, the components of interest are SiO₂, Al₂O₃, CaO, CaCO₃, Na₂O, K₂O and MgO. Fe₂O₃ is unlikely to have any significant interaction since the system is already iron rich and does therefore not need to be investigated. CaCO₃ needs to be investigated as it is a possibility that it might significantly interact with ilmenite before forming CaO. Other carbonates such as Na₂CO₃, K₂CO₃ and MgCO₃ are not investigated as Ca is expected to be in higher concentrations in MSW. K₂CO₃ which is considered as a main component in biomass, should under the conditions in the boiler mostly exist in the form of KOH and K₂O. When investigating potassium and sodium, it is especially important to also look at the subsystems of potassium/sodium, ilmenite and Cl as reactions with this component might be favored over interactions with ilmenite. Sodium and potassium form NaCl and KCl.

Waste also contains minor elements such as Cu and Zn, which are the main focus in this study as these trace metals usually have the highest concentration in waste and are valuable in recycling, as they are high-cost metals and for saving energy. Copper is used mainly for electrical purposes in and generation, wiring for buildings, telecommunication power transmission and electronics/electrical products (USGS, 2019). A lot of pigments also contain copper (Sward, 1972), but these compounds are unfortunately not available in the FactSage database for simulation. Zinc predominantly exists as ZnO as it is used as an additive in a range of products such as rubber and heat resistant glass among others (Jones, Bisaillon, Lindberg, & Hupa, 2013). Zinc as metal is primarily used for galvanizing steel (stainless steel), die casting machine parts, in batteries and other electrical applications. It is also used alloyed with copper to form brass (MadeHow, 2020).

Ash from a fluidized bed boiler fired with municipal solid waste has been shown to contain copper metal, Cu₂O, CuO and mixed oxides, such as CuCr₂O₄ (Lasseson & Steenari, 2013). Fly ash from municipal solid waste incineration has been shown to contain ZnS, ZnO, hydrozincite $(Zn_5(OH)_6(CO_3)_2)$, gahnite $(ZnAl_2O_4)$, and willemite (Zn_2SiO_4) (Struis, Ludwig, Lutz, & Scheidegger, 2004). Both zinc and copper also readily react with Cl to form ZnCl₂ (Struis et al., 2004) (Jones et al., 2013) and CuCl (Lasseson & Steenari, 2013). From all compounds mentioned, the main

compounds of interest to investigate for interaction with ilmenite are ZnO, Cu₂O and CuO since they are volatile ash-forming components. Secondary products ZnS, hydrozincite $(Zn_5(OH)_6(CO_3)_2)$, gahnite $(ZnAl_2O_4)$, willemite (Zn_2SiO_4) , ZnCl₂ and CuCl indicate that the ash-forming components interact with each other and flue gas components to form other stable zinc and copper compounds. The interactions between Zn-S, Cu/Zn-Cl, Zn-H₂O-CO₂, Zn-SiO₂ and Zn-Al₂O₃ also have to be investigated to evaluate which interaction is favored. If one of these interactions is favored, it might significantly affect to what extent Zn and Cu interact with ilmenite. Cl can be considered to be in the forms NaCl, KCl and Cl₂.

1.3. Aim

The aim of the thesis is to investigate how major ash components (Si, Al, Fe, Mg, Ca, K, Na and Cl) and the minor ash components Cu and Zn interact with ilmenite ($FeTiO_3$) during waste incineration. A focus on Cu and Zn was chosen since these usually have the highest concentrations out of the trace metals that can be valuable for recycling in the waste fuel.

The investigation was carried out by simulating different boiler conditions and performing thermodynamical equilibrium calculations using the software FactSage 7.2. The results from the calculations were compared to an elemental analysis of a sample obtained from an industrial OCAC plant.

1.4. Limitations

This thesis will not:

- Investigate interactions of other minor ash elements than Cu and Zn
- Investigate other bed materials or compare them to ilmenite
- Verify the simulated results experimentally
- Discuss the influence of process type on the accumulation of Cu and Zn.

1.5. Specification of issue under investigation

During the thesis, the following questions are to be answered:

• How does ilmenite interact with major ash components (Si, Al, Fe, Mg, Ca, K, Na and Cl), what phases are formed?

- What phases may be formed when Cu and Zn interacts with ilmenite during waste incineration?
- How do the formed phases vary with different boiler conditions?
- What reactions may the copper and zinc phases be formed by?
- How may the ilmenite oxygen carrier properties be affected practically based on the theoretically calculated phases formed from interactions?

2. Methodology

In this section, the method for how the project was executed is presented; which includes SEM-EDX-analysis of a sample of spent ilmenite, how parameters were defined and how the simulation and calculations were carried out. A sample of ilmenite used during waste incineration was provided by the company E.ON from their CHP plant at Handelö. A short description of how the software and its modules work is also included.

2.1. SEM-EDX-analysis of obtained sample

A sample of ilmenite used during waste incineration was provided by the company E.ON from their CHP plant at Handelö. As mentioned in the introduction, experiments were also initiated in the thesis but not able to be finished. A SEM-EDX-analysis (Scanning Electron Microscope - Energy-dispersive X-ray spectroscopy) of the ilmenite sample obtained from Handelö was however carried out. SEM-EDX-analysis with a Phenom ProX was used in an attempt to qualitatively map the trace elements and look at the distribution throughout the particles. Both samples prepared by immobilizing in epoxy and on carbon tape were analyzed as they give different types of information. The epoxy samples were grinded to a flat surface and coated with Au. The samples enclosed in epoxy gave information about the cross section of the particles, whereas the samples immobilized on carbon tape gave information about the particle surface. Both a mapping of the whole particles and point analysis in points of interest were performed. The settings were set to maximum obtainable HV and the intensity to "map". Detector "BSD Full" was used. With the SEM analysis, images of the particles and the distribution of chemical elements were obtained. For the mapping, the map resolution was set to 256, the pixel time to 20 ms and number of passes to one.

2.2. Simulation conditions

This section describes how the simulation of the system and how the calculations were carried out. It also includes short descriptions of how the software and its modules work. The software FactSage 7.2 (FactSage, 2020a) is used for the simulation and calculation of the system in this thesis. FactSage is an integrated database computing system in chemical thermodynamics. It can be used for many applications of which one is combustion. The program has access to data for thousands of compounds as well as to evaluated databases for solutions of metals, liquid and solid oxide solutions, mattes, molten and solid salt solutions, aqueous solutions, etc. From the databases available in the program, the most relevant ones for the combustion boiler system is FactPS (pure elements) and FToxid (oxide mixtures). FTsalt is also relevant when investigating subsystems with Cl. With FactSage it is possible to calculate conditions for multiphase, multicomponent equilibria (thermodynamical equilibrium calculations) and there are several tabular and graphical output modes (FactSage, 2018). The program contains different "modules" for different types of calculations, as for example FactSage phase diagram which is used in this thesis. It is however important to keep in mind that the results are heavily dependent on the chosen database and input (ratio between species) and that the calculations do not consider chemical limitations such as activation energies, diffusion limitations and reaction rates.

2.2.1. FactSage Phase Diagram

In the FactSage Phase diagram module unary, binary, ternary and multicomponent phase diagram sections can be calculated plotted and edited. The axes can be various combinations of T, P, V, composition, activity, chemical potential, etc. The results can be presented in a Y vs X or Gibbs triangle plot. The phase diagram calculations work in the same manner as in the Equilib module, but over intervals (FactSage, 2010). The FactSage Equilib module uses Gibbs free energy minimization to calculate the concentrations of chemical species when specified elements or compounds react to

reach a state of chemical equilibrium (FactSage, 2020b). A point in the phase diagram corresponds to an Equilib calculation. The diagram shows in which phases the compounds/products exist in the intervals that were specified before the calculations (FactSage, 2010).

2.2.2. Inputs to the software

The sample of ilmenite used during waste incineration (provided by the company E.ON from their CHP plant in Handelö) was used to estimate the fractions of the different ash components (by elemental analysis) for finding the region of interest in the phase diagrams. The elemental analysis can be found in Appendix i.

The different component systems that were simulated in the present work (as motivated under 1.1. Background) are summarized in Table 1 below, in which the components, number of ideal gases, solids and species/solutions can be seen. For a full list of what compounds were included in the simulation of the different systems, see Appendix ii.

Table 1. Summary of simulated component systems, including components, number of ideal gases, solids and species/solutions. Detailed information about all components included in the simulation can be found in Appendix ii.

Component system	# ideal gases	# pure solids	#solution phases: species/solutions
$FeTiO_3 - O_2$	8	29	32/9
$FeTiO_3 - SiO_2 - O_2$	13	50	38/10
$FeTiO_3 - Al_2O_3 - O_2$	15	40	43/9
$FeTiO_3 - CaO - O_2$	11	43	39/11
$FeTiO_3 - CaCO_3 - O_2$	21	53	39/11
$FeTiO_3 - Na_2O - O_2$	21	52	37/9
$FeTiO_3 - K_2O - O_2$	11	39	34/9
$FeTiO_3 - Na_2O - Cl - O_2$	35	63	41/10
$FeTiO_3 - K_2O - Cl - O_2$	35	51	34/9
$FeTiO_3 - MgO - O_2$	11	35	50/9
$FeTiO_3 - ZnO - O_2$	9	32	44/10
$FeTiO_3 - CuO/Cu_2O - O_2$	11	39	34/9
$FeTiO_3 - Zn - H_2O - CO_2 - O_2$	49	46	44/10
$FeTiO_3 - Zn - SiO_2 - O_2$	14	54	58/13
$FeTiO_3 - Zn - Al_2O_3 - O_2$	16	43	80/12
$FeTiO_3 - Zn - Cl - O_2$	32	39	56/13
$FeTiO_3 - Zn - S - O_2$	24	56	54/10
$FeTiO_3 - Cu - Cl - O_2$	34	47	45/12

Firstly, a system of only ilmenite and oxygen was simulated to investigate the oxidation/reduction behavior of ilmenite and for using as a reference for the other phase diagrams. Then, interactions with the major ash components SiO₂, Al₂O₃, CaO, CaCO₃, Na₂O, K₂O and MgO were investigated with three component systems of ilmenite – major ash component – oxygen. For the major ash components Na₂O and K₂O four component systems including Cl were also investigated as sodium and potassium are known to readily react with Cl and to evaluate which interactions are favored.

The minor ash components copper and zinc were also investigated by three component systems of ilmenite – ash component – oxygen as well as four component systems including Cl as copper and zinc have been known to form ZnCl₂ and CuCl. CuO and Cu₂O can be investigated by the same simulation as the systems both contain copper and oxygen. The software is then expected to determine in what areas the respective compounds are stable. In addition to investigating the favored reactions between Cu/Zn-Cl/ilmenite, four component systems of FeTiO₃ – Zn – S – O₂, FeTiO₃ – Zn – H₂O –

 $CO_2 - O_2$, FeTiO₃ - Zn -Al₂O₃- O₂ and FeTiO₃ - Zn - SiO₂- O₂ were investigated as zinc has also been known to form ZnS, hydrozincite (Zn₅(OH)₆(CO₃)₂), gahnite (ZnAl₂O₄) and willemite (Zn₂SiO₄).

For the investigation of the oxidation/reduction behavior of ilmenite, the temperature range of 800 - 900°C in which a fluidized bed boiler usually operates was chosen as the x-axis. This since the component fraction is known (=1) and to investigate how the behavior of the ilmenite varies with temperature. A temperature of 900°C was chosen for the other systems, as the simulation of the system ilmenite – oxygen showed that this is the temperature that captures the largest number of possible stable phases formed from the ilmenite.

The three-component systems were simulated, and the phase diagrams constructed at 900°C, at atmospheric pressure with a logarithmic oxygen partial pressure $(\log_{10}p(O_2))$ ranging from 0 to -20 as the y-axis. An additional diagram with a temperature of 800°C was constructed for the system ilmenite – CaCO₃ – oxygen as CaCO₃ forms CaO and CO₂ (gas) at 893°C. The ash component fraction between 0 and 1 was used for the x-axis, as the concentrations can vary significantly in the heterogeneous fuel. This, to get an overview of what happens as the concentration of the ash component increases. The fraction of ash component obtained from the elemental analysis of the sample obtained from Händelö (Appendix i) was marked on the images as an estimation of the area of conditions that the ilmenite particles are exposed to. If the phase diagrams were difficult to interpret in the marked area, an additional phase diagram was constructed within the intervals suggested by the sample content (estimation with included error margins) as the x-axis, thus enlarging the same phase diagram to the area of interest.

Four component systems were constructed in a similar manner, but with the additional component having a constant fraction.

For easier labeling and understanding of the resulting phase diagrams, the stable phases appearing in the diagrams were numbered according to the list in Appendix iii. All diagrams were marked with an estimation of the ash component fraction based on the elemental analysis of the sample obtained from Händelö, seen in Appendix i.

3. Results & Discussion

The following sections present and interpret the phase diagrams resulting from the simulations. In the thesis "oxygen carrier performance" is discussed based on the stable redox-phases of ilmenite, referring to the oxygen release between different phases and conditions. It is important to note that the diagrams can be interpreted differently if different purposes are defined from the beginning. The results obtained from the simulations are applicable for OCAC, and analyzed from that perspective, but could be used for understanding interactions in the CLC systems, where the highest oxygen partial pressure corresponds to the air reactor and the lowest to the fuel reactor.

The y-axis displaying the logarithmic oxygen partial pressure (in atm) can be interpreted as locations in the boiler with different concentrations of oxygen (depending on the fuel density and burning) but also as different locations within the particle (different depths of the formed layers). At the surface of the particle, the oxygen access is high, but moving inward in the particle, the conditions become increasingly reducing with less free oxygen present. An oxygen partial pressure of -20 is highly reducing, and very unlikely to occur for the circulating ilmenite particles as the bed is fluidized and the particles are in constant motion. It is however still of interest to investigate this pressure, as it can be said to represent the internal parts of the particles. The molar fraction of ash component on the xaxis can be interpreted as the ash component concentration surrounding the ilmenite particles in the boiler, but also as a concentration increasing due to accumulation of ash compounds on the particle surface. Lines in the plots that are believed to be representative for the conditions that the ilmenite particles are subjected to in an industrial application, will be marked in the figures based on ash component concentrations determined for sample obtained from Händelö by elemental analysis.

Once again it is important to keep in mind when analyzing the results, that the software does not take reaction rates or diffusion limitations into account. It is therefore possible for compounds that are not stable over the entire diagram to still be found in the sampled as bottom ash ilmenite fraction, due to the compound having a low reaction rate or getting encapsulated in a layer built up on the ilmenite particle surface and thereby not being able to react with other compounds in the boiler. The formation of a layer could be observed with SEM-analysis of the Händelö sample. Unexpected phases not showing up in the phase diagrams may also be found experimentally on the ilmenite due to missing data for those components in the software database. This was for example found for the compound KTi₈O₁₆, that has been the main potassium phase found experimentally on used ilmenite particles. This compound is missing from the software database and other phases were therefore predicted as stable by the software. During combustion, iron has also been found to migrate to the surface of the ilmenite particles (Corcoran, Knutsson, Lind, & Thunman, 2018b). Although the stable phases shown in the phase diagram contain titanium, interactions that form iron containing phases may be favored instead if only iron is available for reaction.

3.1. SEM-EDX-analysis of obtained sample

With the SEM-EDX, an ash-layer on the ilmenite particles' surface could be observed, see an example in Figure 2 below. The EDX-analysis indicated that the layer consisted mainly of calcium, as previously described by Corcoran, Knutsson, Lind, and Thunman (2018a).



Figure 2. SEM and EDX image of an ilmenite particle with a visible ash-layer formed on the surface

The layer formation on the particles means that they are not uniform and that there are concentration gradients. This must be kept in mind when analyzing the simulated system, as the software does not take layer formation or gradients into consideration; rather it considers a "perfectly mixed" system.

The SEM-EDX-analysis was mainly intended to map the Cu and Zn trace elements (along with the other elements) and to observe their distribution within the ilmenite particles. Upon analysis of the samples it was however discovered that the trace element concentration was too low to be reliably detected/mapped. If the software of the microscope did not identify the copper or zinc by default and a mapping was requested, the obtained information was misleading, where according to the obtained results copper and zinc were present throughout the particles and all over the image. An example of an intensity map over a cross-section of particles can be seen in Figure 3 below.



Figure 3. A SEM-EDX mapping of Zn and Cu showing the distribution of Cu and Zn throughout the particles which was considered incorrect

As can be seen in the figure, Zn and Cu appear all over the image, including in the epoxy background. As this is considered as impossible, the results were not further used. As the mapping time was only approximately an hour and a half, this background noise could possibly have been decreased (and the image become more reliable) if the time was increased. This would result in a higher picture resolution.

In addition to the mapping, point analysis was used to follow the concentration of Cu and Zn in various parts of the particles. According to the point analysis no Zn nor Cu were detected within the particles. A small unidentified peak could however be seen for one point-analysis in one of the EDX-spectra, which likely is a copper or zinc signal. This point was located toward the outer surface of the ilmenite particle. Looking at Figure 3, it appears that there is a brighter green layer (higher concentration) toward the particle surfaces. This observation together with the unidentified peak may indicate that there is an enrichment of zinc in the outer layer of the particles.

For another sample, an aggregation of Cu could however be detected, see Figure 4, confirming that Cu can accumulate on the ilmenite particles.



Figure 4. SEM-EDX mapping displaying an aggregation of Cu, seen as a bright red spot indicated by the red arrow

The Cu aggregation (rightmost image in Figure 4) could be seen as a bright red spot in the mapping, as indicated by the red arrow. It appears that the mapping works better when there is a more intense reference point. Although this SEM-EDX worked for detecting larger aggregations of Cu, it did not work for the purpose intended; mapping the trace elements throughout the particles. It appears that the concentration of the elements is too low to be able to separate them from background noise. The results may however have been improved if an increased mapping time was used.

3.2. Oxidation/reduction behavior of ilmenite

The resulting phase diagram for the system ilmenite – oxygen can be seen in Figure 5 below.



Figure 5. Phase diagram for the system ilmenite-oxygen over the boiler temperature interval, for investigating oxidation/reduction behavior of ilmenite. The M_2O_3 (corundum) structure is Fe_2O_3 , the spinel Fe_3O_4 and the titania spinel Fe_2TiO_4 , found as the main stable phases by FactSage.

The partial pressure intervals in which the phases are stable vary with approximately $log_{10}p(O) = 1$ atm over the entire temperature interval. At a $log_{10}p(O_2)$ of under -18, there is a variation in which phases are stable. Ilmenite is stable between a $log_{10}p(O_2)$ of approximately -19 to -12. Note that a $log_{10}p(O_2)$ of 0 corresponds to 1 atm which is the conditions in the boiler at which the ilmenite is in contact with the maximum amount of oxygen. Starting by looking at the interval where ilmenite (FeTiO₃) and the spinel phase are stable, it can be seen when through equilibrium calculations that the stable spinel phase is principally negligible. More than 99 % of the formed stable phase is ilmenite. Looking at what happens when the oxygen partial pressure changes, the ilmenite becomes unstable when the oxygen pressure increases. Based on the diagram it should then instead form rutile (TiO₂) and spinel (together with oxygen). The spinel structure has the general form AB₂O₄ where A, B= Al-Co-Cr-Fe-Mg-Mn-Ni-Zn. As the system only contains iron out of these compounds, the spinel structure in this case is Fe₃O₄, which is also called magnetite. A general reaction for this formation is presented in Equation (1):

$$6 \text{ FeTiO}_3 + 19 \text{ O}_2 \rightarrow 2 \text{ Fe}_3 \text{ O}_4 + 6 \text{ TiO}_2 \tag{1}$$

As can be seen in the equation, through this reaction the ilmenite is oxidized. Upon further increase of the oxygen partial pressure, it can be seen in the diagram that the spinel phase becomes unstable

and transforms into M_2O_3 (corundum), which in this case is Fe_2O_3 , also called hematite. The rutile phase remains stable. A general reaction for this can be described by Equation (2):

$$4 \operatorname{Fe}_3 O_4 + 17 O_2 \to 6 \operatorname{Fe}_2 O_3 \tag{2}$$

As can be seen in Equation (2), magnetite is further oxidized. Going back to the interval in which ilmenite "and spinel" are stable, it can be seen that the spinel structure (Fe_3O_4) becomes unstable and instead forms titania spinel, which in this case is Fe_2TiO_4 . The amount of titania spinel is very small compared to the amount of ilmenite, with there being roughly 355 times more stable ilmenite (in moles). For this titania spinel to be formed from magnetite, it must react with some ilmenite according to the general Equation (3) below:

$$2 \operatorname{Fe}_3 O_4 + 6 \operatorname{FeTi}O_3 \to 6 \operatorname{Fe}_2 \operatorname{Ti}O_4 + 25 O_2$$
 (3)

As can be seen in Equation (3), oxygen is released when magnetite reacts with ilmenite and therewith the compounds are reduced. When looking at a further reduction in low oxygen pressure, the resulting phases vary with temperature. At temperatures below 815° C, there is no further reduction of the compound (further release of oxygen) but at temperatures between approximately $815 - 840^{\circ}$ C there is one additional reduction. At temperatures above 840° C there are two further reductions, which are described by Equation (4) and (5) below. Looking at the first reduction, the titania spinel becomes unstable and forms Fe and ilmenite:

$$2 \operatorname{Fe}_2 \operatorname{TiO}_4 \to 2 \operatorname{FeTiO}_3 + 2 \operatorname{Fe} + \operatorname{O}_2 \tag{4}$$

At lower oxygen partial pressures, ilmenite decomposes to Fe and rutile (TiO₂):

$$2 \operatorname{FeTiO}_3 \to 2 \operatorname{TiO}_2 + 2 \operatorname{Fe} + \operatorname{O}_2 \tag{5}$$

From these results it can be concluded that there are two higher levels of oxidation of ilmenite, and three lower levels / levels of reduction. Looking at the phase diagram, oxygen partial pressures above approximately -12 can be said to result in oxidizing conditions, and partial pressures below -14 in reducing conditions. Ilmenite is oxidized to magnetite, which is further oxidized to hematite. Ilmenite is reduced by reaction with magnetite to form titania spinel, TiFe₂O₄, which is further reduced by decomposition to ilmenite and Fe. At the lowest pressures for the present study, ilmenite is reduced by decomposition to rutile and Fe. This is however not desirable practically because there is a larger energy barrier to oxidize Fe back to Fe₃O₄ than when oxidizing Fe₃O₄ to Fe₂O₃. Furthermore, defluidization of ilmenite has been linked to highly reduced oxygen carriers (Leion, Lyngfelt, Johansson, Jerndala, & Mattisson, 2008). In addition to this, an oxygen partial pressure of -20 is highly reducing, and very unlikely to occur for the ilmenite particles as the bed is fluidized and the particles are in constant motion. The highly reducing conditions can however be seen as representative for the inner intact parts inside of the ilmenite particles, depending on how the oxygen migrates in the particles (which is dependent on for example cracks in and on the particle).

It is also important to note, as earlier mentioned, that the software does not consider any chemical limitations such as diffusion limitations and reaction rates. In full scale application, the different compounds in the phase diagram can therefore exist simultaneously at the different pressures if limited by diffusion or reaction rates to form the predicted stable phases. The software assumes that every molecule is available for reaction (not limited by diffusion). Practically, the whole bed particle volume would not be available for reacting with oxygen, as the particle is only in contact with the surrounding oxygen at the surface.

Leion et al. (2008) investigated the reactivity of ilmenite towards methane and syngas experimentally in a laboratory setup, simulating a CLC process at temperatures in the range of 970 – 980°C, alternating between reducing and oxidizing conditions. They found through X-ray diffraction that the phases indicated for particles after oxidation were Fe₂TiO₅, Fe₃Ti₃O₁₀, Fe₂O₃ and possibly some FeTiO₃. For particles after subsequent reduction the indicated phases were FeTiO₃, Fe₃O₄, some TiO₂ and FeO and possibly some Fe₃Ti₃O₁₀. This is somewhat consistent with the results in Figure 5. The phases shown in the figure are stable, but kinetics play a role practically, making different reactions between the oxidation levels possible. This results in phases not predicted by the thermodynamical equilibrium calculations being able to form. The experimental findings also show that the maximal reducing atmosphere (as in a CLC reactor) is not enough to initiate the reaction in Equation (5). In addition to Equation (1) – (5), Equation (6) – (14) below are also possible, as reproduced from Leion et al. (2008). Level 0 corresponds to the oxidation state 2⁺ for iron (Fe^{II}) and level 2 has the oxidation state 3⁺ for iron (Fe^{III}), whereas level 1 is a mixture of 2⁺ and 3⁺, Fe^{2II}₂Fe^{II}.

• Oxygen release from level 1 to 0:

$$2 \operatorname{Fe}_3 \operatorname{Ti}_3 \operatorname{O}_{10} \to 6 \operatorname{FeTiO}_3 + \operatorname{O}_2 \tag{6}$$

$$2 \operatorname{Fe}_{3} \operatorname{Ti}_{3} \operatorname{O}_{10} \to 6 \operatorname{FeO} + 6 \operatorname{TiO}_{2} + \operatorname{O}_{2}$$
(7)

$$2 \operatorname{Fe}_3 \operatorname{O}_4 \to 6 \operatorname{FeO} + \operatorname{O}_2 \tag{8}$$

• Oxygen release from level 2 to 1:

$$6 \operatorname{Fe}_2 \operatorname{TiO}_5 + 6 \operatorname{TiO}_2 \to 4 \operatorname{Fe}_3 \operatorname{O}_4 + 12 \operatorname{TiO}_2 + \operatorname{O}_2 \tag{9}$$

$$6 \operatorname{Fe}_2 \operatorname{TiO}_5 + 6 \operatorname{TiO}_2 \to 4 \operatorname{Fe}_3 \operatorname{Ti}_3 \operatorname{O}_{10} + \operatorname{O}_2 \tag{10}$$

$$6 \operatorname{Fe}_2 O_3 + 12 \operatorname{Ti} \to 4 \operatorname{Fe}_3 \operatorname{Ti}_3 O_{10} + O_2 \tag{11}$$

• Oxygen release from level 2 directly to 0:

$$2 \operatorname{Fe}_2 \operatorname{TiO}_5 + 2 \operatorname{TiO}_2 \to 4 \operatorname{FeTiO}_3 + O_2 \tag{12}$$

$$2 \operatorname{Fe}_{2} \operatorname{TiO}_{5} + 2 \operatorname{TiO}_{2} \to 4 \operatorname{FeO} + 4 \operatorname{TiO}_{2} + O_{2}$$
(13)

$$2 \operatorname{Fe}_2 \operatorname{O}_3 \to 4 \operatorname{FeO} + \operatorname{O}_2 \tag{14}$$

The additional reactions should not affect the simulated results significantly with regards to ilmenite – ash component interactions, as the additional compounds (Fe_2TiO_5 and $Fe_3Ti_3O_{10}$) are very similar to the stable phases considered from the simulation in Figure 5.

3.3. Interactions between ilmenite and ash-components

3.3.1. Interactions with major ash component SiO_2

The resulting phase diagram for the system ilmenite $-SiO_2$ (silica sand) - oxygen can be seen in Figure 6 below. SiO₂ is not only an ash component but can be mixed with the ilmenite as bed material.



SiO₂/(FeTiO₃+SiO₂) (mol/mol)

Figure 6. Phase diagram for system ilmenite $-SiO_2 - O_2$ for investigating interactions between SiO2 and ilmenite. The M_2O_3 (corundum) structure is Fe₂O₃, the spinel Fe₃O₄ and the titania spinel Fe₂TiO₄.

When comparing the phase diagram (Figure 6) to Figure 5, ilmenite seems to display exactly the same behavior, apart from spinel not showing up as a stable compound in the oxygen partial pressure interval between -12 - -10. A possible explanation for this is that the number of moles of spinel is low and thus is neglected in the calculations. The titania spinel formed from the spinel in the adjacent lower partial pressure interval is however included (although it is formed from the spinel phase), as 3 moles of titania spinel form from 1 mol of spinel according to Equation (3) leading to a number of moles sufficiently high to be included in the calculations and show up on the phase diagram. It does not seem probable for ilmenite (FeTiO₃) to decompose to titania spinel (TiFe₂O₄) as additional iron is needed to form titania spinel.

Looking at the behavior of SiO_2 (silica sand), it is stable over the entire interval and no new compounds appear. It is therefore not expected to interact with ilmenite under the specified boiler conditions.

3.3.2. Interactions with major ash component Al₂O₃

The resulting phase diagram for the system ilmenite $-Al_2O_3 - oxygen$ can be seen in Figure 7 below. The green line indicates the aluminum fraction (approximately 2.4 %) found in the sample obtained from Händelö.



Figure 7. Phase diagram for system ilmenite $-Al_2O_3 - O_2$ used for investigating interactions between Al_2O_3 and ilmenite. The number 2 denotes rutile, and 6 - M_2O_3 (Corundum) where M = Al, Fe. The green line indicates the Al fraction (approximately 0.024) found in the sample obtained from Händelö. Note that the fraction based on the elemental analysis was divided by two as the compound (Al_2O_3) contains two Al atoms.

As the phase diagram in Figure 7 is more complex, it can immediately be seen that Al_2O_3 is not inert in its behavior. M_2O_3 (corundum) in the diagram denotes both Fe₂O₃ and Al_2O_3 . After performing equilibrium calculations in various points in the diagram, the main spinel structures were identified as Al_3O_4 and Fe₃O₄. The main titania spinel structures are FeAl₂O₄, and FeTi₂O₄. This means that there are interactions between ilmenite and aluminum oxide forming the titania spinel structure FeAl₂O₄. The FeAl₂O₄ forms under the same conditions as FeTi₂O₄, which is stable under reducing conditions. Looking at the phase diagram, it can be seen that Al_2O_3 behaves very similar to ilmenite, forming similar structures. At oxidizing conditions, the FeAl₂O₄ is again oxidized to Al_3O_4 and/or Al_2O_3 , which suggests that aluminum should not be stable and is not expected to accumulate on the ilmenite particle surface over time. However, some aluminum may accumulate in the system as the titania spinel FeAl₂O₄ is stable under reducing conditions and can be blocked from oxygen contact through layer formation on the particle. Besides the interactions forming FeAl₂O₄, the oxidation/reduction behavior of the ilmenite seems practically unchanged. The expected oxygen carrier performance should also be unchanged as FeAl₂O₄ contains the same amount of oxygen as FeTi₂O₄ and therefore behaves similarly over the same pressure interval.

As it is hard to distinguish the phases in the region around the aluminum fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 8 below.



Figure 8. Phase diagram for system ilmenite $-Al_2O_3 - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating interactions between Al_2O_3 and ilmenite.

In the figure, the oxygen partial pressure intervals can be seen for the region of most interest based on the sample obtained from Händelö. However, the same compounds are formed as earlier mentioned: Fe_2O_3 , Al_2O_3 , Al_3O_4 , Fe_3O_4 , $FeAl_2O_4$ and $FeTi_2O_4$ with an addition of the compound (FeO)₂(TiO₂) in a small interval.

3.3.3. Interactions with major ash component CaO

The resulting phase diagram for the system ilmenite -CaO - oxygen can be seen in Figure 9 below. The green lines indicate the calcium fraction interval (approximately 14 - 20 %) found in the sample obtained from Händelö. Some problems occurred with the FactSage software when trying to construct this curve. Not all tie-lines were drawn on the diagram and the phases displayed were incorrect. As the software indicated that the specified conditions did not result in any stable gas phases, the problem could be solved by simulating the system without ideal gases. This resulted in a complete phase diagram.



CaO/(FeTiO₃+CaO) (mol/mol)

Figure 9. Phase diagram for system ilmenite – $CaO - O_2$ used for investigating interactions between CaO and ilmenite. The green lines indicate the Ca fraction interval (approximately 0.14- 0.20) found in the sample obtained from Händelö.

In the phase diagram it can be seen that calcium interacts with the titanium in the ilmenite and forms the various structures CaTiO₃, Ca₃Ti₂O₇, Ca₅Ti₄O₁₃,Ca₃Ti₂O₆, Ca₂Fe₂O₅, CaFe₂O₄ in different parts of the diagram with CaTiO₃ being the most predominant one. At lower concentrations calcium interacts with the titanium in the ilmenite, and only at concentrations above roughly 50 % it reacts with the iron. One or more of these calcium compounds are stable through all pressures and concentrations. This indicates that calcium should interact readily with ilmenite when it is present in the boiler and accumulate on the particles over time, mainly in the form of CaTiO₃. The results from the modelling correspond well to experimental findings, as an outer layer consisting of mainly calcium and phosphorus has been shown to form on the ilmenite particles during combustion (also confirmed by the SEM-EDX analysis performed on the sample obtained from Händelö) and the main phase found with X-ray diffraction is CaTiO₃ (Gyllén, 2019). Calcium has also been shown to

sometimes increase the reactivity/catalytic ability of ilmenite. This increase in catalytic ability can be explained by the calcium rich layer promoting the water-gas shift reaction and reducing tars in the produced gas (Gyllén, 2019).

The diagram also shows a change in the oxidation/reduction behavior of ilmenite. When calcium is present in high concentrations, above 50 %, (at the particle surface) the pressure intervals in which spinel is stable are shifted, and the ilmenite and titania spinel structures become unstable. At very high concentrations, the spinel structure also becomes unstable. This indicates that the oxygen carrier performance may be affected if a too thick layer of calcium builds up on the ilmenite particles. $Ca_2Fe_2O_5$, which is instead stable, does itself work as an oxygen carrier but with only two levels of oxidation. Highly reducing conditions are required to release oxygen. It is hard to determine how this would impact the oxygen carrier practically. The elemental analysis however indicated that the calcium content in the sample obtained from Händelö of spent ilmenite was approximately 14 - 20%. Within this interval calcium is only stable as $CaTiO_3$.

3.3.4. Interactions with major ash component CaCO₃

The resulting phase diagram for the system ilmenite – $CaCO_3$ – oxygen can be seen in Figure 11. The green lines indicate the calcium fraction interval (approximately 14 – 20 %) found in the sample obtained from Händelö. Some problems occurred with the software when trying to construct the curve. Not all tie-lines were drawn on the diagram and the phases displayed were incorrect. As CaCO₃ forms CaO and CO₂ (gas) at 893°C, as determined from Figure 10 below, including ideal gases in the simulation is essential and the problem could not be solved in the same way as for the CaO curve in Figure 9 (by excluding ideal gases).



Figure 10. Phase diagram displaying the temperature at which $CaCO_3$ decomposes to CaO and CO₂, as indicated by the green dashed line. Gas-ideal denotes CO_2 .

As CaO is formed from CaCO₃ at 893°C and the curve is constructed at 900°C, the curve should be almost identical to the CaO curve. The temperature used for the construction of the phase diagram (900°C) being so close to the reaction temperature of for CaCO₃ to form CaO and CO₂ may be related to the software having problems constructing the correct curve. The problem was solved, and the correct curve produced, by superimposing the CaO diagram on the "unfinished" CaCO₃ diagram (a function in the software). The finished diagram for a temperature of 900°C can be seen in Figure 11.



Figure 11. Phase diagram for system ilmenite $- CaCO_3 - O2$ used for investigating interactions between CaCO₃ and ilmenite at a temperature above 893 °C. The green lines indicate the Ca fraction interval (approximately 0.14- 0.20) found in the sample obtained from Händelö.

As can be seen in Figure 11, the phase diagram for $CaCO_3$ at temperatures above 893°C looks fairly similar to the one for CaO. The ilmenite behaves in a similar way with regards to oxidation/reduction behavior and oxygen carrier performance, compared with the behavior illustrated by Figure 9. In the fraction interval based on the sample obtained from Händelö the calcium is stable as CaTiO₃ over the entire pressure interval. The carbon present in the system only interacts with the ilmenite and forms Fe₃C under very reducing conditions, below an oxygen pressure of -19, corresponding to the inside of the particle. This means that the carbon would have to diffuse inward to be able to react with the ilmenite. This indicates carbon is unlikely to significantly interact with ilmenite. Apart from this small interval carbon is otherwise stable as CO_2 .

As an OCAC-boiler usually operates closer to 850 °C, at which the CaCO₃ is stable as a solid, it is in this case insufficient to only look at the phase diagram constructed at 900 °C for evaluating the interactions with ilmenite. Therefore, an ilmenite – CaCO₃ – oxygen phase diagram was constructed at the lower temperature of 800 °C for investigating how the CaCO₃ interacts with the ilmenite below the temperature of 893 °C. Again, the software had problems constructing the curve. This was solved

by excluding the gas phase in the simulation. This phase diagram can be seen in Figure 12 below. The solid carbon in the graph would form CO_2 .



Figure 12. Phase diagram for system ilmenite $- CaCO_3 - O2$ used for investigating interactions between $CaCO_3$ and ilmenite at a temperature below 893 °C. The green lines indicate the Ca fraction interval (approximately 0.14- 0.20) found in the sample obtained from Händelö. C in this graph corresponds to CO_2 .

As can be seen in the phase diagram in Figure 12, a temperature below 893 °C results in stability of CaCO₃ in the oxidizing region and only interacting with ilmenite under reducing conditions, forming CaTiO₃, Fe₃C and a Ca₃Ti₂O₇-Ca₃Ti₂O₆ solid solution (at very high concentrations).

3.3.5. Interactions with major ash component Na₂O (and Na₂O/Cl)

The resulting phase diagram for the system ilmenite $-Na_2O - oxygen$ can be seen in Figure 11 below. The green line indicates the sodium fraction (approximately 1.1 %) found in the sample obtained from Händelö.



Figure 13. Phase diagram for system ilmenite – $Na_2O - O2$ used for investigating interactions between Na_2O and ilmenite. The green line indicates the Na fraction (approximately 0.011) found in the sample obtained from Händelö. Note that the fraction based on the elemental analysis was divided by two as the compound (Na_2O) contains two Na atoms.

In the phase diagram for the system ilmenite $-Na_2O - oxygen$ (Figure 13) it can be seen that there are many compounds formed as a result of interactions between ilmenite and Na₂O. These are: $(Na_2O)(TiO_2)_3$, $(Na_2O)(TiO_2)_6$, Na_2TiO_3 , Na_4TiO_4 , $Na_8Fe_2O_7$, $Na_8Ti_5O_{14}$ and $NaFeO_2$. The software indicated that $Na_3Fe_5O_9$ also is a stable phase that can be formed, but the area in which it is stable was too narrow to mark on the plot. At low and intermediate concentrations $(Na_2O)(TiO_2)_6$ and $Na_8Ti_5O_{14}$ are the major phases containing sodium and at higher concentrations the stable phases from ilmenite interaction are mainly $Na_8Fe_2O_7$ and $NaFeO_2$. At lower concentrations the sodium seems to mainly interact with the titanium in the ilmenite, and at higher concentrations the iron. This means that the sodium will mainly interact with the titanium in ilmenite, and only react with the iron if it is already is present at the surface in very high concentration. There are however stable sodium compounds containing iron or titanium in practically all areas in the phase diagram (through the entire condition intervals specified in the study). This indicates that sodium will accumulate on the ilmenite particles over time.

Already at low concentrations the sodium starts affecting the oxygen carrier behavior and performance of the ilmenite. Rutile, TiO_2 becomes unstable under the studied oxidizing conditions and the intervals in which the spinel and titania spinel are stable shift. With increasing concentration of Na₂O, slag-liquid phase stable over the whole oxygen partial pressure interval starts forming and ilmenite reacts with sodium and forms other stable compounds. This means that accumulation of sodium should affect the performance of the oxygen carrier.

When adding Cl to the system and constructing a phase diagram (not shown) it could be seen that Cl was stable as NaCl over the entire diagram. This indicates that the Na – Cl interactions are favored over Na – ilmenite when Cl is present in the system. As the concentration of sodium is low, Cl heavily impacts what phases are formed by the interactions between sodium and ilmenite.

As it is hard to distinguish the phases in the region around the sodium fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 14 below.



Figure 14. Phase diagram for system ilmenite $-Na_2O - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating interactions between Na_2O and ilmenite.

As can be seen in Figure 14, sodium forms $(Na_2O)(TiO_2)_3$ and $(Na_2O)(TiO_2)_6$ in the region based on the sample obtained from Händelö. If the sodium concentrations are similar in other units during operation, sodium is expected to mainly accumulate as the enumerated phases.

3.3.6. Interactions with major ash component K₂O (and K₂O/Cl)

The resulting phase diagram for the system ilmenite $-K_2O$ – oxygen can be seen in Figure 15 below. The green line indicates the potassium fraction (approximately 0.4 %) found in the sample obtained from Händelö.



Figure 15. Phase diagram for system ilmenite $-K_2O - O_2$ used for investigating interactions between K_2O and ilmenite. The green line indicates the K fraction (approximately 0.004) found in the sample obtained from Händelö. Note that the fraction based on the elemental analysis was divided by two as the compound contains two K atoms.

The phase diagram shows that K_2O forms compounds from interactions with ilmenite during almost all the studied oxygen partial pressures and concentrations. According to the phase diagram, K_2O is not stable under the studied conditions. This means that K_2O interacts readily with ilmenite when present. The main stable compounds formed are $K_2Ti_3O_7$ and $K_2Ti_6O_{13}$. The software also indicated that $K_8Ti_5O_{14}$ was stable in part of the diagram, but the area was too narrow to mark on the plot.

Already at low concentrations the potassium starts affecting the oxygen carrier behavior and performance of the ilmenite, in a similar way to sodium (both are alkali metals). Rutile, TiO_2 becomes unstable under all specified oxidizing conditions and the intervals in which the spinel and titania spinel are stable shift. At concentrations above roughly 30%, slag-liquid phase stable over the whole pressure interval starts forming. This indicates that the oxygen carrier performance of ilmenite is significantly affected if potassium accumulates on the surface of the particles and if it is present in significant concentrations in the combusted waste.

When adding Cl to the system (not shown), potassium behaves like sodium. Cl is stable as KCl over the entire diagram. This indicates that the K - Cl interactions are favored over K - ilmenite interactions as all existing Cl in the system binds with potassium.

Experimentally, potassium has been found as KTi_8O_{16} in ilmenite particles rather than as $K_2Ti_3O_7$ and $K_2Ti_6O_{13}$. Corcoran et al. (2018b) who received the same results proposed that this is due to the ilmenite particles not being fully saturated with potassium and thereby KTi_8O_{16} is formed as an intermediate. During the simulations in this project it was however discovered that data for KTi_8O_{16} is missing in the software. This is most likely the explanation for the inconsistent results between the simulations and the previous experimental findings. This highlights that although the software using thermodynamic calculations may give a good estimation of formed phases, physical and chemical limitations or compounds missing in the software databases can result in predictions of stable phases differing from the stable phases found in practice.

As it is hard to distinguish the phases in the region around the potassium fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 16 below.



Figure 16. Phase diagram for system ilmenite $-K_2O - O2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating interactions between K_2O and ilmenite.

As can be seen in the phase diagram (Figure 16), potassium forms $K_2Ti_3O_7$ and $K_2Ti_6O_{13}$ in the region indicated by the sample obtained from Händelö.

3.3.7. Interactions with major ash component MgO

The resulting phase diagram for the system ilmenite -MgO - oxygen can be seen in Figure 17 below. The green line indicates the magnesium fraction (approximately 3 %) found in the sample obtained from Händelö.



Figure 17. Phase diagram for system ilmenite – $MgO - O_2$ used for investigating interactions between MgO and ilmenite. The green line indicates the Mg fraction (approximately 0.03) found in the sample obtained from Händelö.

In the phase diagram, spinel and titania spinel denotes both the previously mentioned phases consisting of iron and titanium as well as phases formed mainly between iron and magnesium; which means that the magnesium interacts with the ilmenite. The major spinel phase containing magnesium and the major titania spinel both are $FeMg_2O_4$ (different structures). The software also indicated that $MgTiO_3$ was a stable phase in part of the phase diagram, but this area was too narrow to mark on the image.

At low concentrations of MgO, the structures formed in the different oxygen partial pressure intervals are similar to those formed when the system consist only of ilmenite and oxygen (see Figure 5) with an exception of pseudobrookite formed under highly oxidizing and reducing conditions within the studied interval. At the highly oxidizing conditions, the formed pseudobrookite consist mainly of MgTiO₅ and under the highly reducing conditions it is a solid solution of MgTi₂O₅, FeTi₂O₅ and Ti₃O₅ with the compounds enumerated according to the expected concentrations in descending order. As the compounds under the oxidizing conditions behave similarly to ilmenite with regards to uptake of oxygen, the oxidation of the ilmenite compounds should not be significantly affected by the interaction with magnesium. However, a significant amount of pseudobrookite is formed under the highly reducing conditions. The ratio between rutile and pseudobrookite is roughly 1:1 and the ratio of rutile and solid iron 1:3. The formation of pseudobrookite from titania spinel takes up oxygen rather than releasing it, thus possibly affecting the oxygen carrier performance under the highly reducing conditions. As these reducing conditions however correspond to the inner parts of the ilmenite particles, the magnesium would have to diffuse inward in the particles for this to occur which is unlikely to happen.

At higher concentrations of MgO, Fe_2O_3 and rutile become unstable and the ilmenite only displays reducing behavior, with spinel and titania spinel forming in different oxygen partial pressure intervals. This indicates that the oxygen carrier performance should be heavily affected as the ilmenite does not pick up and release as much oxygen as if the MgO was not present as a phase. As MgO is in excess, it becomes a stable phase (monoxide). One or more phases formed from interactions between magnesium and ilmenite are stable in all areas of the phase diagram, which means that magnesium should accumulate on the particles with time.

As it is hard to distinguish the phases in the region around the magnesium fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 18 below.



Figure 18. Phase diagram for system ilmenite – $MgO - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating interactions between MgO and ilmenite.

In the diagram the intervals in which magnesium forms spinel, titania spinel (both have the formula $FeMg_2O_4$) and Pseudobrookite as earlier described can be more easily seen.

3.3.8. Interactions with minor ash-component ZnO

The resulting phase diagram for the system ilmenite -ZnO - oxygen can be seen in Figure 19 below. The green line indicates the zinc fraction (approximately 2 %) found in the sample obtained from Händelö.



Figure 19. Phase diagram for system ilmenite – $ZnO - O_2$ used for investigating interactions between ZnO and ilmenite. The green line indicates the Zn fraction (approximately 0.02) found in the sample obtained from Händelö.

As zinc is a trace element/minor ash element, the leftmost part of the phase diagram is of greatest interest. As can be seen in the phase diagram, the formed phases and oxygen partial pressure intervals are similar to those of the system with only ilmenite and oxygen (Figure 5). Zinc however interacts with the ilmenite and forms spinel and $(ZnO)_2TiO_2$. The main spinel structure containing zinc is $ZnFe_2O_4$.

Possible reactions for interactions (also considering between levels) are given as Equation (15) - (20) below.

$$6 \operatorname{ZnO} + 3 \operatorname{FeTiO}_3 \rightarrow 3 (\operatorname{ZnO})_2 TiO_2 + \operatorname{Fe}_3 O_4 + 1\frac{1}{2} O_2$$
 (15)

$$ZnO + 2 FeTiO_3 + \frac{1}{2}O_2 \rightarrow ZnFe_2O_4 + 2 TiO_2$$
 (16)

$$5 \text{ ZnO} + 2 \text{ FeTiO}_3 + \frac{1}{2} \text{ O}_2 \rightarrow \text{ ZnFe}_2 \text{ O}_4 + 2 (\text{ZnO})_2 \text{TiO}_2$$
 (17)

$$3 \operatorname{ZnO} + 2 \operatorname{Fe}_3 O_4 + \frac{1}{2} O_2 \to 3 \operatorname{ZnFe}_2 O_4$$
 (18)

$$2 \operatorname{ZnO} + \operatorname{TiO}_2 \to (\operatorname{ZnO})_2 TiO_2 \tag{19}$$

$$ZnO + Fe_2TiO_4 + \frac{1}{2}O_2 \rightarrow ZnFe_2O_4 + TiO_2$$

$$\tag{20}$$

One or more phases formed from zinc and ilmenite interactions are stable over the entire oxygen partial pressure interval, indicating that zinc should accumulate on the ilmenite particles over time.

3.3.9. Interactions with minor ash-components CuO/Cu₂O

The resulting phase diagram for the system ilmenite – CuO – oxygen can be seen in Figure 20 below. The green line indicates the copper fraction (approximately 0.6 %) found in the sample obtained from Händelö which corresponds to the fraction CuO. The diagram can also be read for Cu₂O, for which the fraction corresponding to the sample instead would be 0.3 % (which is still at the very left end of the diagram and represented with the same line).



CuO/(FeTiO₃+CuO) (mol/mol)

Figure 20. Phase diagram for system ilmenite $- CuO/Cu_2O - O_2$ used for investigating interactions between CuO/Cu_2O and ilmenite. The green line indicates the Cu fraction (approximately 0.006) found in the sample obtained from Händelö which corresponds to the fraction CuO. The diagram can also be read for Cu₂O, for which the fraction corresponding to the sample instead would be 0.003.

As copper is a trace element/minor ash element, the leftmost part of the phase diagram is of greatest interest (lower concentrations of Cu). As can be seen in the phase diagram, the ilmenite oxidation/reduction behavior is unaffected by copper present in the system. Under oxidizing conditions, copper forms $(Cu_2O)(Fe_2O_3)$ (s2) and $(CuO)(Fe_2O_3)$ (s3) (where s2 and s3 refers to different solid structures possible for the same chemical formula) by interaction with ilmenite. Under reducing conditions, these phases are reduced to solid copper. This indicates that copper should still accumulate on the ilmenite particles over time as it first forms $(Cu_2O)(Fe_2O_3)$, is integrated into the ilmenite structure and then solidifies on the surface. Possible reactions for the interactions (also considering between level) are given as Equation (21) - (24) below.

$$6 \operatorname{Cu}0 + 2 \operatorname{Fe}_3 0_4 \to 3(\operatorname{Cu}_2 0)(\operatorname{Fe}_2 0_3)$$
 (21)

$$2 \text{ Cu0} + \text{Fe}_2 0_3 \rightarrow (\text{Cu}_2 0)(\text{Fe}_2 0_3) + \frac{1}{2} 0_2$$
(22)

$$3 Cu_2 0 + 2 Fe_3 0_4 + \frac{1}{2} 0_2 \to 3 (Cu_2 0) (Fe_2 0_3)$$
⁽²³⁾

$$Cu_2O + Fe_2O_3 \rightarrow (Cu_2O)(Fe_2O_3)$$
 (24)

3.4. Interactions between ilmenite and multiple ash components

3.4.1. Interactions with Zn and Cl

The resulting phase diagram for the system ilmenite -Zn - Cl - oxygen can be seen in Figure 21 below. The green line indicates the zinc fraction (approximately 2 %) found in the sample obtained from Händelö. A constant Cl fraction of 20 % was chosen as this was believed to be a high enough fraction to observe all possible phases of interaction but not be too high as to give unreasonable results. A decrease and increase to 5/10 and 30 % respectively give the same results (same stable phases) but somewhat shifted along the x-axis as the equilibrium concentrations are affected. The 20 % was chosen over the 5/10 % for the figure as the phases were easier to distinguish.



Figure 21. Phase diagram for system ilmenite $-Zn - Cl - O_2$ used for investigating favored interactions between Zn and ilmenite/Cl. The green line indicates the Zn fraction (approximately 0.02) found in the sample obtained from Händelö. The ideal gas is ZnCl₂ and the salt-liquid is FeCl₂.

As can be seen in the phase diagram, at low zinc fractions (close to the green line) the phases from interactions between zinc and ilmenite as found in Figure 19 are not stable when Cl is present in the system. Instead it forms ideal gas together with Cl, ZnCl₂. With an increase in concentration (to a Zn-fraction between 0.1 - 0.2), when half of the available Cl is bound to zinc, part of the gas becomes unstable and the Zn starts interacting with ilmenite and forms (ZnO)₂TiO₂. It is however very unlikely that zinc would reach these higher concentrations anywhere in the boiler, as it is a trace element and as indicated by the content in the sample obtained from Händelö. Above a zinc fraction of 0.2, (ZnO)₂TiO₂ forms as zinc and ilmenite are in excess to Cl.

As it is hard to distinguish the phases in the region around the zinc fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 22 below.



Figure 22. Phase diagram for system ilmenite $-Zn - Cl - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating favored interactions between Zn and ilmenite/Cl. The ideal gas is a composition of ZnCl₂, FeCl₃ and FeCl₂. The salt-liquid is FeCl₂.

As can be seen in Figure 22, the zinc is stable as gas, $ZnCl_2$, rather than $(ZnO)_2(TiO_2)$. This indicates that zinc will favor interactions with Cl over interactions with ilmenite under the conditions of low zinc concentrations in the boiler.
3.4.2. Interactions with Cu and Cl

The resulting phase diagram for the system ilmenite -Cu - Cl - oxygen can be seen in Figure 23 below. The green line indicates the copper fraction (approximately 0.6 %) found in the sample obtained from Händelö. A constant Cl fraction of 20 % was chosen as this was believed to be a high enough fraction to observe all possible phases of interaction but not be too high as to give unreasonable results (as for zinc). Increasing or decreasing the Cl content does not change the phases stable but shifts their intervals along the x-axis according to the new equilibrium concentrations.



Figure 23. Phase diagram for system ilmenite $-Cu - Cl - O_2$ for investigating favored interactions between Cu and ilmenite/Cl. The green line indicates the Cu fraction (approximately 0.006) found in the sample obtained from Händelö. The ideal gas consists of a majority (2/3) of Cu present as (CuCl)₃ with approximately a third of FeCl₂. The salt-liquid is FeCl₂.

As can be seen in the phase diagram, the copper behaves quite similar to zinc when Cl is present in the system. At low copper fractions (close to the green line) the phases from interactions between copper and ilmenite, as found in Figure 20, are not stable when Cl is present in the system. Instead it forms ideal gas, $(CuCl)_3$, together with Cl. Only when all Cl has reacted with copper (at a Cu-fraction above 0.2), the Cu interacts with ilmenite and forms (CuO)(Fe₂O₃) (s2) and (CuO)(Fe₂O₃) (s3) (where s2 and s3 refers to different solid structures possible for the same chemical formula). This behavior is different than that of zinc, seen in Figure 21, as zinc starts to interact with ilmenite at lower zinc concentrations (0.1) whereas copper starts to interact with ilmenite first after reaching Cu fraction 0.2 (which is the fraction of Cl in the entire system).

As it is hard to distinguish the phases in the region around the copper fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals

suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 24 below.



Cu/(FeTiO₃+Cu+Cl) (mol/mol)

Figure 24. Phase diagram for system ilmenite $-Cu - Cl - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating favored interactions between Cu and ilmenite/Cl. The ideal gas consists of a majority (2/3) of Cu present as (CuCl)₃ with approximately a third of FeCl₂. The salt-liquid is FeCl₂.

As can be seen in Figure 24, the copper is stable as ideal gas, $(CuCl)_3$ over a majority of the oxygen partial pressure interval rather than $(CuO)(Fe_2O_3)$ (s2) and $(CuO)(Fe_2O_3)$ (s3). Otherwise it is present as solid copper, Cu (s). This indicates that copper will favor interactions with Cl over interactions with ilmenite under the conditions of low copper concentrations in the boiler. Decreasing the Cl content does not change the phases stable.

3.4.3. Interactions with Zn and S

The resulting phase diagram for the system ilmenite -Zn - S - oxygen can be seen in Figure 25 below. The green line indicates the zinc fraction (approximately 2 %) found in the sample obtained from Händelö. A constant sulphur fraction of 10 % was chosen as this was believed to be a high enough fraction to observe all possible phases of interaction but not be too high as to give unreasonable results. Increasing or decreasing the sulphur content does not change the phases stable but shifts their intervals along the x-axis according to the new equilibrium concentrations. The elemental analysis on the sample obtained from Händelö indicated that approximately 1.7 % sulphur was present in the sample. However, it is important to keep in mind that this is the content of sulphur that has interacted with the ilmenite particles (and phases formed on them) and not necessarily representative for the surrounding system.



Figure 25. Phase diagram for system ilmenite $-Zn - S - O_2$ used for investigating favored interactions between Zn and ilmenite/S. The green line indicates the Zn fraction (approximately 0.02) found in the sample obtained from Händelö.

In the phase diagram for the system ilmenite $-Zn - S - O_2$, Figure 25, it can be seen that ZnS is formed under reducing conditions. Under oxidizing conditions, sulphur is stable as gas, SO₂. This indicates that interactions between zinc and sulphur are favored under reducing conditions, but interactions between zinc and ilmenite are favored under oxidizing conditions. This means that part of the available zinc should still accumulate on the ilmenite particles over time, but another part will form ZnS in the presence of sulphur. At very high concentrations of zinc (solid zinc pieces), ZnSO₄ can also be formed as a stable phase.

As it is hard to distinguish the phases in the region around the zinc fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals

suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 26 below.



Figure 26. Phase diagram for system ilmenite $-Zn - S - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating favored interactions between Zn and ilmenite/S.

In Figure 26, likewise as observed in Figure 25, ZnS is formed under reducing conditions. Under oxidizing conditions, the sulphur is stable as gas, SO₂. Decreasing the sulphur content does not change the phases stable.

3.4.4. Interactions with Zn and SiO₂

The resulting phase diagram for the system ilmenite $-Zn - SiO_2 - oxygen can be seen in Figure 25 below. The green line indicates the zinc fraction (approximately 2 %) found in the sample obtained from Händelö. A constant SiO₂ fraction of 34 % was chosen so that the stable phases of zinc could be observed when ilmenite, Zn and SiO₂ are in equal parts in the system (for investigating favored interactions between the compounds when they are in equal fractions) as well as for a low zinc fraction and high ilmenite and SiO₂ fractions. A lot of SiO₂ is present in the system; both as bed material and as an ash component. The elemental analysis on the sample obtained from Händelö indicated that approximately 18 % Si was present in the sample. However, this content does not only represent the Si that has interacted with the ilmenite particles (and phases formed on them) but the sample contains SiO₂ which was not successfully magnetically separated from the sample. The Si fraction present in only the ilmenite particles is lower. The sample fraction can however be used as an indication of an upper limit of Si. Looking at the figure, fractions below 18 % all result in the same stable phases formed.$



Zn/(FeTiO₃+Zn+SiO₂) (mol/mol)

Figure 27. Phase diagram for system ilmenite $-Zn - SiO_2 - O_2$ used for investigating favored interactions between Zn and ilmenite/SiO₂. The green line indicates the Zn fraction (approximately 0.02) found in the sample obtained from Händelö.

As it is hard to distinguish the phases in the region around the zinc fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals

suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 28 below.



Figure 28. Phase diagram for system ilmenite $-Zn - SiO_2 - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating favored interactions between Zn and ilmenite/SiO₂.

As can be seen in the phase diagram, zinc forms spinel, $ZnFe_2O_4$, under oxidizing conditions. Under reducing conditions it forms willemite, Zn_2SiO_4 , instead. Willemite is stable rather than the phase $(ZnO)_2(TiO_2)$ observed in Figure 19. This indicates that zinc favors interactions with ilmenite under oxidizing conditions, and interactions with SiO₂ under reducing conditions. Therefore, SiO₂ should lead to a decrease in zinc accumulation on the ilmenite particles when it is present in the system.

3.4.5. Interactions with Zn, H₂O and CO₂

The resulting phase diagram for the system ilmenite $-Zn - H_2O - CO_2 - oxygen can be seen in Figure 25 below. H₂O and CO₂ are the two compounds expected to together with Zn form hydrozincite (Zn₅(OH)₆(CO₃)₂), and therefore this system was chosen. The green line indicates the zinc fraction (approximately 2 %) found in the sample obtained from Händelö. A constant H₂O and CO₂ fraction of 25 % was chosen so that the stable phases of zinc could be observed when ilmenite, H₂O and CO₂ are in equal parts in the system as well as for a low zinc fraction and high ilmenite and H₂O/CO₂ fractions. This, since a lot of H₂O and CO₂ may be present in the system. The important compound hydrozincite (Zn₅(OH)₆(CO₃)₂), was found to be missing in the database, making the results inconclusive.$



Zn/(FeTiO₃+Zn+H₂O+CO₂) (mol/mol)

Figure 29. Phase diagram for system ilmenite $-Zn - H_2O - CO_2 - O_2$ used for investigating favored interactions between Zn and ilmenite/ H_2O/CO_2 . The green line indicates the Zn fraction (approximately 0.02) found in the sample obtained from Händelö.

As it is hard to distinguish the phases in the region around the zinc fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 30 below.



Zn/(FeTiO₃+Zn+H₂O+CO₂) (mol/mol)

Figure 30. Phase diagram for system ilmenite $-Zn - H_2O - CO_2 - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating favored interactions between Zn and ilmenite/ $H_2O - CO_2$.

As can be seen in the phase diagram, zinc is not stable as hydrozincite $(Zn_5(OH)_6(CO_3)_2)$, the compound expected from $Zn/H_2O/CO_2$ interactions. Instead, it is present as the same phases as in Figure 19 (spinel, $ZnFe_2O_4$ and $(ZnO)_2(TiO_2)$). However, it was found that the important compound hydrozincite $(Zn_5(OH)_6(CO_3)_2)$ was missing in the database, making the results inconclusive. Any conclusions regarding the favored interactions between zinc, ilmenite and H_2O/CO_2 (to form hydrozincite) could therefore not be drawn.

3.4.6. Interactions with Zn and Al_2O_3

The resulting phase diagram for the system ilmenite $-Zn - Al_2O_3 - oxygen$ can be seen in Figure 31 below. The green line indicates the zinc fraction (approximately 2 %) found in the sample obtained from Händelö. A constant Al_2O_3 fraction of 33 % was chosen so that the stable phases of zinc could be observed when ilmenite, Zn and Al_2O_3 are in equal parts in the system as well as for a low zinc fraction and high ilmenite and Al_2O_3 fractions.



Figure 31. Phase diagram for system ilmenite $-Zn - Al_2O_3 - O_2$ used for investigating favored interactions between Zn and ilmenite/ Al_2O_3/CO_2. M_2O_3(Corundum) corresponds to a majority of Fe_2O_3 with some Al_2O_3. M_2O_3(Corundum)#2 corresponds to a majority of Al_2O_3 with some Fe_2O_3. Spinel denotes FeAl_2O_4 together with ZnAl_2O_4, and spinel#2 Fe_3O_4 together with FeAl_2O_4. The green line indicates the Zn fraction (approximately 0.02) found in the sample obtained from Händelö.

As it is hard to distinguish the phases in the region around the zinc fraction found in the sample obtained from Händelö (green line), an additional phase diagram was constructed within the intervals suggested by the sample content (estimation with error margins) as the x-axis, thus enlarging the areas of particular interest of the same phase diagram. This diagram can be seen in Figure 32 below.



Zn/(FeTiO₃+Zn+Al₂O₃) (mol/mol)

Figure 32. Phase diagram for system ilmenite $-Zn - Al_2O_3 - O_2$ within the intervals suggested by the sample content (estimation with error margins) as the x-axis for investigating favored interactions between Zn and ilmenite/ Al_2O_3 .

In the phase diagram for the system ilmenite $-Zn - Al_2O_3 - O_2$, Figure 31, it can be seen that the compound $(ZnO)_2(TiO_2)$ seen in Figure 19 is no longer stable. Instead, the zinc forms M₂O₃ and spinel structures. The M₂O₃(Corundum) structure corresponds to a majority of Fe₂O₃, approximately 90 %, with 10 % Al₂O₃. M₂O₃(Corundum)#2 corresponds to a majority of Al₂O₃ with some Fe₂O₃ (approximately 90 and 10 % respectively). Spinel denotes FeAl₂O₄ together with ZnAl₂O₄, and spinel#2 Fe₃O₄ together with FeAl₂O₄. Over the entire diagram, the zinc is stable as ZnAl₂O₄. This indicates that interactions between zinc and Al₂O₃ should be favored over interactions between zinc and ilmenite.

4. Conclusions

This thesis has investigated how major ash components (Si, Al, Fe, Mg, Ca, K, Na and Cl) and the minor ash components Cu and Zn interact with ilmenite (FeTiO₃) during waste incineration, by simulating different boiler conditions and constructing phase diagrams using the software FactSage 7.2. The results obtained from the simulations are applicable for OCAC but could be used for understanding interactions in the CLC systems. Different phase formations depending on boiler conditions have been discussed throughout this thesis along with possible reaction paths for Cu and Zn. It was also discussed how the ilmenite oxygen carrier properties may be affected practically based on the theoretically calculated phases formed from interactions.

For the major ash components, simulations indicate that:

- Ilmenite interacts with Al₂O₃, CaO/CaCO₂, Na₂O, K₂O, MgO, ZnO and Cu/Cu₂O but does not interact with SiO₂.
- Interactions between ilmenite and aluminum oxide should form the titania spinel structure FeAl₂O₄.
- Calcium (CaO) should interact readily with ilmenite when it is present in the boiler and accumulate on the particles over time, mainly in the form of CaTiO₃ (a calcium rich ash-layer was observed on the ilmenite particles during SEM-EDX analysis). The interactions with calcium can be desirable, as calcium has been shown to sometimes increase the reactivity/catalytic ability of ilmenite.
- CaCO₃ behaves similar to CaO at temperatures above 893°C, but a temperature below 893°C results in stability of CaCO₃ in the oxidizing region and only interacting with ilmenite under reducing conditions, forming CaTiO₃.
- Sodium (Na₂O) should interact with ilmenite and form mainly (Na₂O)(TiO₂)₃ and (Na₂O)(TiO₂)₆.
- Potassium forms $K_2Ti_3O_7$ and $K_2Ti_6O_{13}$, which does not correspond to experimental findings, where potassium has been found as KTi_8O_{16} . The compound KTi_8O_{16} is missing in the software database, therefore giving inconclusive results not corresponding to experimental findings.
- Potassium displays behavior similar to sodium with increasing concentration. With increasing concentration, slag-liquid phase stable over the whole studied pressure interval starts forming. This indicates that the oxygen carrier performance of ilmenite is significantly affected if potassium and sodium accumulate on the surface of the particles and if they are present in significant concentrations in the combusted waste. These interactions are therefore especially undesirable.

For the minor ash components Cu and Zn, simulations indicate that:

- Zinc interacts with the ilmenite and forms spinel phase and (ZnO)₂TiO₂. The main spinel structure containing zinc in the simulations is ZnFe₂O₄.
- Under oxidizing conditions, copper should form (Cu₂O)(Fe₂O₃) (s2) and (CuO)(Fe₂O₃) (s3) by interaction with ilmenite.
- The Cu and Zn systems simulated with Cl in them indicate that both Cu and Zn favors interactions with Cl over ilmenite, forming gas, (CuCl)₃ and ZnCl₂.
- Interactions between zinc and sulphur are favored under reducing conditions, while interactions between zinc and ilmenite are favored under oxidizing conditions.
- Similarly, zinc favors interactions with ilmenite under oxidizing conditions but interactions with SiO₂ to form willemite (Zn₂SiO₄) under reducing conditions.
- Interactions between zinc and Al₂O₃, forming ZnAl₂O₄, should be favored over interactions between zinc and ilmenite.

• No conclusions regarding whether interactions between zinc and H₂O/CO₂, to form hydrozincite (Zn₅(OH)₆(CO₃)₂), are favored over interactions between zinc and ilmenite can be drawn as data for the compound hydrozincite was found to be missing in the software database.

Proposed reaction paths for Zn based on the stable phases indicated by the simulations are:

- $6 \text{ZnO} + 3 \text{FeTiO}_3 \rightarrow 3 (\text{ZnO})_2 TiO_2 + \text{Fe}_3O_4 + 1\frac{1}{2}O_2$
- $\operatorname{ZnO} + 2 \operatorname{FeTiO}_3 + \frac{1}{2} \operatorname{O}_2 \rightarrow \operatorname{ZnFe}_2 \operatorname{O}_4 + 2 \operatorname{TiO}_2$
- $5 \operatorname{ZnO} + 2 \operatorname{FeTiO}_3 + \frac{1}{2} \operatorname{O}_2 \rightarrow \operatorname{ZnFe}_2 \operatorname{O}_4 + 2 (\operatorname{ZnO})_2 \operatorname{TiO}_2$
- $3 \operatorname{ZnO} + 2 \operatorname{Fe}_3 \operatorname{O}_4 + \frac{1}{2} \operatorname{O}_2 \rightarrow 3 \operatorname{ZnFe}_2 \operatorname{O}_4$
- $2 \operatorname{ZnO} + \operatorname{TiO}_2 \rightarrow (\operatorname{ZnO})_2 TiO_2$
- $\operatorname{ZnO} + \operatorname{Fe}_2\operatorname{TiO}_4 + \frac{1}{2}\operatorname{O}_2 \rightarrow \operatorname{ZnFe}_2\operatorname{O}_4 + \operatorname{TiO}_2$

Proposed reaction paths for Cu based on the stable phases indicated by the simulations are:

- $6 \operatorname{CuO} + 2 \operatorname{Fe}_3 \operatorname{O}_4 \rightarrow 3(\operatorname{Cu}_2 \operatorname{O})(\operatorname{Fe}_2 \operatorname{O}_3)$
- $2 \text{ CuO} + \text{Fe}_2 \text{O}_3 \rightarrow (\text{Cu}_2 \text{O})(\text{Fe}_2 \text{O}_3) + \frac{1}{2} \text{O}_2$
- $3 \operatorname{Cu}_2 0 + 2 \operatorname{Fe}_3 0_4 + \frac{1}{2} 0_2 \rightarrow 3 (\operatorname{Cu}_2 0)(\operatorname{Fe}_2 0_3)$
- $\operatorname{Cu}_2 0 + \operatorname{Fe}_2 0_3 \rightarrow (\operatorname{Cu}_2 0)(\operatorname{Fe}_2 0_3)$

For further continuation of the work, it would be of interest to experimentally determine the compounds present in spent ilmenite (for example for the sample obtained from Händelö) and compare with the preliminary estimation in this report. This, to investigate how well the simulation results correspond to reality and whether some important compounds are missing in the software database. Copper pigments used for dying different products, which may interact with the ilmenite, have already been established to be missing in this project. The compound $\text{KTi}_8\text{O}_{16}$ that has been the main potassium phase found experimentally on used ilmenite particles is also missing from the database, as well as hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) which is expected from zinc interactions with H₂O and CO₂. If the results in this report are inconsistent with the experimental results with regards to which of the included stable phases should be most represented on the ilmenite particles, it would be interesting to look closer at the reaction rates and activation energies in the system. In addition to this, as mentioned in the introduction, the information obtained in this thesis could help for understanding how to best leach copper and zinc from spent ilmenite for recycling the valuable trace metals.

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Elin Borgman

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Appendix i - Elemental analysis

For the experimental investigation, a sample of approximately 2 dl rock ilmenite was provided by the company E.ON and their CHP plant in Handelö. The sample has been magnetically separated twice to separate the ilmenite from the bottom ash (iron is magnetic) and sifted to a size $<720 \,\mu$ m to separate metal pieces as well as to obtain a unified fraction and remove surface area as a factor for the experimentation. The sample has been determined to have a magnetic fraction of approximately 27%. In the boiler, the ilmenite is used together with silica sand and after the magnetic separation most of the silica sand is expected to have been separated.

To determine the total elemental composition of the sample, part of it was sent to the company AK-LAB, where it was prepared in a pulverizing mill and analyzed according to the Swedish standard SS 02 81 13-1. The analytical sample was dried at 50°C, and concentrations were corrected for dry matter (105°C) content. Digestion was carried out according to ASTM D3682: 2013 and ASTM D4503: 2008 (LiBO₂ fusion). Digestion was carried out with HNO3/HCl/HF according to SS EN 13656: 2003. The ICP-SFMS analyses were carried out according to SS EN ISO 17294-2: 2016 and EPA-method 200.8: 1994. The results from the elemental analysis of the sample can be seen in Table 2 below.

Compound	mg Compound/kg Sample	Uncertainty (±mg Compound/kg Sample)
Si	95 500	17 400
Al	24 900	4620
Са	90 300	15 300
Fe	162 000	33 300
К	4650	780
Mg	16 100	2930
Mn	2110	368
Na	12 100	2390
Р	2170	571
Ti	93 400	14 800
As	75.9	23.8
Ва	1350	315
Ве	<0.5	-
Cd	12.5	1.8
Со	183	34
Cr	677	122
Cu	3180	691
Hg	0.0102	0.0040
Мо	47.4	9.1
Nb	22.1	3.0
Ni	479	94
Pb	686	170
S	8990	1660
Sb	722	119
Sc	15.5	3.6
Sn	468	78
Sr	307	50
V	160	39
W	15.1	2.6
Y	11.7	1.6
Zn	8650	1570
Zr	92.5	20.2

Table 2. Results from the elemental analysis, also showing uncertainty of the results.

Appendix ii – Solids, gases and solution phases included in system simulations

System FeTiO₃ – O₂:

Ideal gases included: O(g), O2(g), O3(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel

System FeTiO3 – SiO2 – O2:

Ideal gases included: O(g), O2(g), O3(g), Si(g), Si2(g), Si3(g), SiO(g), SiO2(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-cPyrA	A-Clinopyroxene	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Si(s)	FactPS	solid
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
SiTi(s)	FactPS	SiTi
Si2Ti(s)	FactPS	Si2Ti
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeSi(s)	FactPS	FeSi
FeSi2(s)	FactPS	FeSi2_ <fesi2_l></fesi2_l>
Fe3Si(s)	FactPS	solid
Fe3Si7(s)	FactPS	Fe3Si7_ <fesi2_h></fesi2_h>
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
SiO2(s)	FToxid	Quartz(1)
SiO2(s2)	FToxid	Quartz(h)
SiO2(s3)	FToxid	Tridymite(1)
SiO2(s4)	FToxid	Tridymite(h)
SiO2(s5)	FToxid	Cristobalite(1)
SiO2(s6)	FToxid	Cristobalite(h)
SiO2(s7)	FToxid	coesite
SiO2(s8)	FToxid	stishovite
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid

FToxid	solid
FToxid	Higher_Magneli_phases_(composite)
FToxid	hematite
FToxid	High-Pressure-Hematite
FToxid	High-Pressure-Hematite
FToxid	Clino-ferrosilite(metastable)
FToxid	Fe-perovskite(metastable)
FToxid	Ortho-ferrosilite(metastable)
FToxid	fayalite
FToxid	beta-fayalite(fictive)
FToxid	gamma-fayalite(spinel)
FToxid	Ilmenite
FToxid	solid
FToxid	Pseudobrookite
FToxid	Ulvospinel
	FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid

System FeTiO3 – Al2O3 – O2:

Ideal gases included: O(g), O2(g), O3(g), Al(g), Al2(g), AlO(g), AlO2(g), Al2O(g), Al2O2(g), Al2O3(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Al(s)	FactPS	solid
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
TiAl(s)	FactPS	solid
TiAl3(s)	FactPS	solid
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeAl3(s)	FactPS	solid
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
Al2O3(s)	FToxid	gamma
Al2O3(s2)	FToxid	delta
Al2O3(s3)	FToxid	kappa
Al2O3(s4)	FToxid	corundum(alpha)
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B

Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
Al2TiO5(s)	FToxid	Tialite
Al4TiO8(s)	FToxid	solid
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
Al2Fe2O6(s)	FToxid	solid
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel

System FeTiO3 – CaO – O2:

Ideal gases included: O(g), O2(g), O3(g), Ca(g), Ca2(g), CaO(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	
FToxid-CaTi	Ca3Ti2O7-Ca3Ti2O6	
FToxid-PERO	Perovskite	

Species	Database	Phase
Ca(s)	FactPS	Solid_Alpha
Ca(s2)	FactPS	Solid_Beta
CaO2(s)	FactPS	solid
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid

CaO(s)	FToxid	Lime
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
CaTiO3(s)	FToxid	Perovskite-A
CaTiO3(s2)	FToxid	Perovskite-B
Ca2Ti2O5(s)	FToxid	solid
Ca2Ti2O5(s2)	FToxid	solid
Ca3Ti2O6(s)	FToxid	solid
Ca3Ti2O7(s)	FToxid	solid
Ca5Ti4O13(s)	FToxid	solid
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
CaFe2O4(s)	FToxid	solid
Ca2Fe2O5(s)	FToxid	solid
CaFe4O7(s)	FToxid	solid
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel

System FeTiO3 – CaCO3 – O2:

Ideal gases included: C(g), C2(g), C3(g), C4(g), C5(g), O(g), O2(g), O3(g), CO(g), C2O(g), CO2(g), C3O2(g), Ca(g), Ca2(g), CaO(g), Ti(g), TiO(g), TiO2(g), Fe(G), FeO(g), Fe(CO)5(g)

Solution phases		
Base-phase Full name		
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	
FToxid-CaTi	Ca3Ti2O7-Ca3Ti2O6	
FToxid-PERO	Perovskite	

Species	Database	Phase
C(s)	FactPS	Graphite
C(s2)	FactPS	diamond
Ca(s)	FactPS	Solid Alpha
Ca(s2)	FactPS	Solid Beta
CaC2(s)	FactPS	solid
CaC2(s2)	FactPS	solid
CaO ₂ (s)	FactPS	solid
CaCO3(s)	FactPS	Aragonite Pmcn
CaCO3(s2)	FactPS	Calcite R-3c
Ti(s)	FactPS	Solid Alpha
Ti(s2)	FactPS	Solid Beta
CTi(s)	FactPS	- 2TiC2
TiO(s)	FactPS	Solid Alpha
TiO(s2)	FactPS	Solid Beta
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
Fe3C(s)	FactPS	CEMENTITE
Fe3C(s2)	FactPS	KSI_CARBIDE
FeCO3(s)	FactPS	Siderite
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
CaO(s)	FToxid	Lime
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
CaTiO3(s)	FToxid	Perovskite-A
CaTiO3(s2)	FToxid	Perovskite-B
Ca2Ti2O5(s)	FToxid	solid
Ca2Ti2O5(s2)	FToxid	solid
Ca3T12O6(s)	Floxid	solid
Ca3112O/(s)	Floxid	solid
Ca5T14O13(s)	Floxid	solid
Fe2O3(s)	Floxid	hematite
Fe2O3(s2)	Floxid	High-Pressure-Hematite
Fe2O3(s3)	F I OXIO	High-Pressure-Hematite
$CaFe_2O_4(s)$	FIOXIC	solid
Ca2Fe2O3(s)	F I OXIU ETovid	solid
$(E_{PO})(T_{1}O_{2})(s)$	FIOXIU FTovid	SOIId Ilmonito
FeTi2O4(s)	FTovid	solid
FeTi2Of(s)	FTovid	Sonu Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Illvocninel
(100)2(1102)(5)	1 TOAIQ	Cryospiller

System FeTiO₃ – Na₂O – O₂:

Ideal gases included: O(g), O2(g), O3(g), Na(g), Na2(g), NaO(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Na(s)	FactPS	solid
NaO2(s)	FactPS	solid
Na2O2(s)	FactPS	solid
Na2O2(s2)	FactPS	Solid-2
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
Na2O(s)	FToxid	Solid-A
Na2O(s2)	FToxid	Solid-B
Na2O(s3)	FToxid	Solid-C
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
Na2TiO3(s)	FToxid	Solid-A
Na2TiO3(s2)	FToxid	Solid-B
Na4TiO4(s)	FToxid	solid
(Na2O)(TiO2)3(s)	FToxid	solid
Na8Ti5O14(s)	FToxid	solid
(Na2O)(TiO2)6(s)	FToxid	solid
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite

FToxid	beta
FToxid	gamma
FToxid	solid
FToxid	Ilmenite
FToxid	solid
FToxid	Pseudobrookite
FToxid	Ulvospinel
	FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid FToxid

System FeTiO₃ – K₂O – O₂:

Ideal gases included: O(g), O2(g), O3(g), K(g), K2(g), KO(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
K(s)	FactPS	solid
KO2(s)	FactPS	solid
K2O2(s)	FactPS	solid
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
K2O(s)	FToxid	solid
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid

Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
K2TiO3(s)	FToxid	solid
K4TiO4(s)	FToxid	solid
K2Ti2O5(s)	FToxid	solid
K2Ti3O7(s)	FToxid	solid
K8Ti5O14(s)	FToxid	solid
K2Ti6O13(s)	FToxid	solid
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel
		•

System FeTiO3 – MgO – O2:

Ideal gases included: O(g), O2(g), O3(g), Mg(g), Mg2(g), MgO(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Mg(s)	FactPS	solid
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
MgO(s)	FToxid	periclase
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid

Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
MgTiO3(s)	FToxid	Geikielite
Mg2TiO4(s)	FToxid	Tetragonal
Mg2TiO4(s2)	FToxid	Cubic_spinel
MgTi2O5(s)	FToxid	Karrooite
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel

System FeTiO3 – ZnO – O2:

Ideal gases included: O(g), O2(g), O3(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g), Zn(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
Ftoxid-ZNIT	Zincite	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
Zn(s)	FactPS	solid
(ZnO)2(TiO2)(s)	FactPS	solid
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid

Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel
ZnO(s)	FToxid	Zincite

System FeTiO3 – Zn – Cl – O2:

Ideal gases included: O(g), O2(g), O3(g), Cl(g), Cl2(g), ClO(g), ClO2(g), ClO3(g), Cl2O(g), Cl2O2(g), Cl2O2(g2), Cl2O2(g3), Ti(g), TiO(g), TiO2(g), TiCl2(g), TiCl2(g), TiCl3(g), TiCl4(g), Ti2Cl6(g), OTiCl(g), TiOCl2(g), Fe(g), FeO(g), FeCl2(g), FeCl3(g), (FeCl2)2(g), (FeCl3)2(g), Zn(g), ZnCl2(g), Zn2Cl4(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
Ftoxid-ZNIT	Zincite	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
TiCl2(s)	FactPS	solid
TiCl3(s)	FactPS	solid
TiCl4(s)	FactPS	solid
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeCl2(s)	FactPS	solid
FeCl3(s)	FactPS	Molysite
FeOCl(s)	FactPS	solid
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
FeCl2(s)	FactPS	solid
FeCl3(s)	FactPS	Molysite
FeOCl(s)	FactPS	solid
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
Zn(s)	FactPS	solid
ZnCl2(s)	FactPS	solid
(ZnO)2(TiO2)(s)	FactPS	solid
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase

Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel
ZnO(s)	FToxid	Zincite

System FeTiO3 – Zn – S – O2:

Ideal gases included: O(g), O2(g), O3(g), S(g), S2(g), S3(g), S4(g), S5(g), S6(g), S7(g), S8(g), SO(g), SO2(g), SO3(g), SSO(g), TiO(g), TiO2(g), TiS(g), Fe(g), FeO(g), FeS(g), Zn(g), ZnS(g)

Solution phases		
Base-phase Full name		
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
Ftoxid-ZNIT	Zincite	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
S(s)	FactPS	Orthorhombic
S(s2)	FactPS	Monoclinic
SO3(s)	FactPS	solid
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
TiS(s)	FactPS	solid
TiS2(s)	FactPS	solid
TiS3(s)	FactPS	solid
Ti2S(s)	FactPS	solid
Ti2S3(s)	FactPS	solid
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc

FeS(s) FactPS FeS(s2) FactPS FeS(s3) FactPS FeS2(s) FactPS 'Fe7S8'(s) FactPS Fe9S10(s) FactPS Fe10S11(s) FactPS FactPS Fe11S12(s) FeSO4(s) FactPS Fe2(SO4)3(s) FactPS FactPS FeTi(s) Fe2Ti(s) FactPS Zn(s) FactPS ZnS(s) FactPS FactPS ZnS(s2) ZnSO4(s) FactPS ZnSO4(s2) FactPS ZnSO4(s3) FactPS FactPS ZnO(ZnSO4)2(s) (ZnO)2(TiO2)(s) FactPS FToxid TiO₂(s) FToxid TiO2(s2) Ti2O3(s) FToxid Ti2O3(s2) FToxid Ti3O5(s) FToxid Ti3O5(s2) FToxid Ti4O7(s) FToxid FToxid Ti5O9(s) FToxid Ti6O11(s) FToxid Ti7O13(s) Ti8O15(s) FToxid Ti9O17(s) FToxid Ti10019(s) FToxid Ti20O39(s) FToxid FToxid Fe2O3(s) Fe2O3(s2) FToxid Fe2O3(s3) FToxid (FeO)(TiO2)(s) FToxid FeTi2O4(s) FToxid FToxid FeTi2O5(s) FToxid (FeO)2(TiO2)(s) FToxid ZnO(s)

solid solid solid Pyrite pyrrhotite-4C pyrrhotite-5C pyrrhotite-11C pyrrhotite-6C solid solid FeTi solid solid Sphalerite Wurtzite Solid_Alpha Solid_Alpha_prime Solid_Beta solid solid Rutile Anatase Solid-A Solid-B Solid-A Solid-B solid solid solid solid solid solid solid Higher_Magneli_phases_(composite) hematite High-Pressure-Hematite High-Pressure-Hematite Ilmenite solid Pseudobrookite Ulvospinel Zincite

System FeTiO3 – CuO / Cu2O – O2:

Ideal gases included: O(g), O2(g), O3(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g), Cu(g), Cu2(g), CuO(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
Cu(s)	FactPS	solid
CuFeO2(s)	FactPS	solid
CuFeO2(s2)	FactPS	solid
(CuO)(Fe2O3)(s)	FactPS	solid
(CuO)(Fe2O3)(s2)	FactPS	solid
(CuO)(Fe2O3)(s3)	FactPS	solid
(Cu2O)(Fe2O3)(s)	FactPS	Solid-A
(Cu2O)(Fe2O3)(s2)	FactPS	Solid-B
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel

CuO(s)	FToxid
Cu2O(s)	FToxid

Tenorite solid

System FeTiO3 - Cu - Cl - O2:

Ideal gases included: O(g), O2(g), O3(g), Cl(g), Cl2(g), ClO(g), ClO2(g), ClO3(g), Cl2O(g), Cl2O2(g), Cl2O2(g2), Cl2O2(g3), Ti(g), TiO(g), TiO2(g), TiCl(g), TiCl2(g), TiCl3(g), TiCl4(g), Ti2Cl6(g), OTiCl(g), TiOCl2(g), Fe(g), FeO(g), FeCl2(g), FeCl3(g), (FeCl2)2(g), (FeCl3)2(g), Cu(g), Cu2(g), CuO(g), CuCl(g), (CuCl)3(g)

Solution phases		
Base-phase Full name		
Ftoxid-SpinA	A-Spinel	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
TiCl2(s)	FactPS	solid
TiCl3(s)	FactPS	solid
TiCl4(s)	FactPS	solid
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeCl2(s)	FactPS	solid
FeCl3(s)	FactPS	Molysite
FeOCl(s)	FactPS	solid
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
Cu(s)	FactPS	solid
CuCl(s)	FactPS	solid
CuCl2(s)	FactPS	solid
CuFeO2(s)	FactPS	solid
CuFeO2(s2)	FactPS	solid
(CuO)(Fe2O3)(s)	FactPS	solid
(CuO)(Fe2O3)(s2)	FactPS	solid
(CuO)(Fe2O3)(s3)	FactPS	solid
(Cu2O)(Fe2O3)(s)	FactPS	Solid-A
(Cu2O)(Fe2O3)(s2)	FactPS	Solid-B
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid

Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite
(FeO)(TiO2)(s)	FToxid	Ilmenite
FeTi2O4(s)	FToxid	solid
FeTi2O5(s)	FToxid	Pseudobrookite
(FeO)2(TiO2)(s)	FToxid	Ulvospinel
CuO(s)	FToxid	Tenorite
Cu2O(s)	FToxid	solid

System FeTiO3 – Zn – H2O – CO2 – O2:

Ideal gases included: H(g), H2(g), C(g), C2(g), C3(g), C4(g), C5(g), CH(g), CH2(g), CH3(g), CH4(g), C2H(g), C2H2(g), C2H3(g), C2H4(g), C2H5(g), C2H6(g), O(g), O2(g), O3(g), OH(g), H2O(g), HOO(g), HOOH(g), CO(g), C2O(g), CO2(g), C3O2(g), HCO(g), H2CO(g), CH3O(g), CH3O(g2), CH3OH(g), CH2CO(g), C2H4O(g), C2H4O(g2), CH3CH2OH(g), CH3CH2OH(g2), COOH(g), HCOOH(g), CH3COOH(g), Ti(g), TiO(g), TiO2(g), Fe(G), FeO(g), Fe(OH)2(g), Fe(CO)5(g), Zn(g)

Solution phases		
Base-phase	Full name	
Ftoxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FT-oxid-CORU	M2O3 (corundum)	
FT-oxid-TiO2	Rutile	
Ftoxid-ZNIT	Zincite	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
C(s)	FactPS	Graphite
C(s2)	FactPS	diamond
H2O(s)	FactPS	Ice
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiH2(s)	FactPS	solid
CTi(s)	FactPS	2TiC2
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
Fe3C(s)	FactPS	CEMENTITE
Fe3C(s2)	FactPS	KSI_CARBIDE
Fe(OH)2(s)	FactPS	solid
Fe(OH)3(s)	FactPS	solid
Fe2O3(H2O)(s)	FactPS	solid
FeCO3(s)	FactPS	Siderite

$\mathbf{F}_{\mathbf{a}}$	solid
racips	50114
Zn(s) FactPS	solid
Zn(OH)2(s3) FactPS	Epsilon
ZnCO3(s) FactPS	Smithsonite
ZnC2O4(H2O)2(s) FactPS	solid
(ZnO)2(TiO2)(s) FactPS	solid
TiO2(s) FToxid	Rutile
TiO2(s2) FToxid	Anatase
Ti2O3(s) FToxid	Solid-A
Ti2O3(s2) FToxid	Solid-B
Ti3O5(s) FToxid	Solid-A
Ti3O5(s2) FToxid	Solid-B
Ti4O7(s) FToxid	solid
Ti5O9(s) FToxid	solid
Ti6O11(s) FToxid	solid
Ti7O13(s) FToxid	solid
Ti8O15(s) FToxid	solid
Ti9O17(s) FToxid	solid
Ti10O19(s) FToxid	solid
Ti20O39(s) FToxid	Higher_Magneli_phases_(composite)
Fe2O3(s) FToxid	hematite
Fe2O3(s2) FToxid	High-Pressure-Hematite
Fe2O3(s3) FToxid	High-Pressure-Hematite
(FeO)(TiO2)(s) FToxid	Ilmenite
FeTi2O4(s) FToxid	solid
FeTi2O5(s) FToxid	Pseudobrookite
(FeO)2(TiO2)(s) FToxid	Ulvospinel
ZnO(s) FToxid	Zincite

System FeTiO3 – Zn – SiO2 – O2:

Ideal gases included: O(g), O2(g), O3(g), Si(g), Si2(g), Si3(g), SiO(g), SiO2(g), Ti(g), TiO(g), TiO2(g), Fe(g), FeO(g), Zn(g)

Solution phases		
Base-phase	Full name	
FToxid-SpinA	A-Spinel	
FToxid-MeO_A	A-Monoxide	
FToxid-cPyrA	A-Clinopyroxene	
FToxid-OlivA	A-Olivine	
FT-oxid-CORU	M2O3 (corundum)	
FToxid-ZNIT	Zincite	
FToxid-WILL	Willemite	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

Species	Database	Phase
Si(s)	FactPS	solid
Ti(s)	FactPS	Solid Alpha
Ti(s2)	FactPS	Solid Beta
TiO(s)	FactPS	Solid Alpha
TiO(s2)	FactPS	Solid Beta
SiTi(s)	FactPS	SiTi
Si2Ti(s)	FactPS	Si2Ti
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeSi(s)	FactPS	FeSi
FeSi2(s)	FactPS	FeSi2_ <fesi2_l></fesi2_l>
Fe3Si(s)	FactPS	solid
Fe3Si7(s)	FactPS	Fe3Si7_ <fesi2_h></fesi2_h>
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
Zn(s)	FactPS	solid
(ZnO)2(TiO2)(s)	FactPS	solid
SiO2(s)	FToxid	Quartz(1)
SiO2(s2)	FToxid	Quartz(h)
SiO2(s3)	FToxid	Tridymite(l)
SiO2(s4)	FToxid	Tridymite(h)
SiO2(s5)	FToxid	Cristobalite(l)
SiO2(s6)	FToxid	Cristobalite(h)
SiO2(s7)	FToxid	coesite
SiO2(s8)	FToxid	stishovite
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
11/013(s)	Floxid	solid
Ti8O15(s)	Floxid	solid
Ti9O17(s)	Floxid	solid
1110019(s)	Floxid	Solid
1120039(s)	Floxid	Higher_Magneli_phases_(composite)
Fe2O3(s)	F I OX10	hematite
Fe2O3(s2)	FIOXID	High-Pressure-Hematite
Fe2O3(83)	FIOXID	High-Pressure-Hematite
FeSiO3(s)	FIOXID	Ea paravekita(metastable)
FeSiO3(s2)	FTOXIC	Ortho formacilita(matastable)
Festos(ss) Festos(ss)	FTOXIC	foundite
Fe2SiO4(s) $Fe2SiO4(s2)$	FToxid	layalite beta favalite(fictive)
Fe2SiO4(s2) Fe2SiO4(s2)	FToxid	gamma favalite(fictive)
$(E_{2}O)(T_{1}O_{2})(s)$	FToxid	gamma-rayante(spiner)
(100)(1102)(3) EeTi $204(s)$	FToxid	solid
FeTi205(s)	FToxid	SUIIU Pseudobrookite
$(\text{Fe}\Omega)^2(\text{Ti}\Omega^2)(s)$	FTovid	Illyospinal
ZnO(s)	FTovid	Zincite
Zn2SiO4(s)	FToxid	Willemite
	ΤΤΟΛΙΨ	winchilte

System FeTiO3 – Zn – Al2O3 – O2:

Ideal gases included: O(g), O2(g), O3(g), Al(g), Al2(g), AlO(g), AlO2(g), Al2O2(g), Al2O2(g), Al2O3(g), Ti(g), TiO(g), TiO2(g), FeO(g), FeO(g), Zn(g)

Solution phases*		
Base-phase	Full name	
FToxid-MeO_A	A-Monoxide	
FToxid-ZNIT	Zincite	
FT-oxid-TiO2	Rutile	
FToxid-ILMEA	A-ilmenite	
FToxid-PSEU	Pseudobrookite	
FToxid-TiSP	Titania_Spinel	

*Ftoxid-SpinA and FToxid-CORU had to be manually marked as immiscible as the concentrations of both iron and zinc were high

Species	Database	Phase
Al(s)	FactPS	solid
Ti(s)	FactPS	Solid_Alpha
Ti(s2)	FactPS	Solid_Beta
TiO(s)	FactPS	Solid_Alpha
TiO(s2)	FactPS	Solid_Beta
TiAl(s)	FactPS	solid
TiAl3(s)	FactPS	solid
Fe(s)	FactPS	bcc
Fe(s2)	FactPS	fcc
FeAl3(s)	FactPS	solid
FeTi(s)	FactPS	FeTi
Fe2Ti(s)	FactPS	solid
Zn(s)	FactPS	solid
(ZnO)2(TiO2)(s)	FactPS	solid
Al2O3(s)	FToxid	gamma
Al2O3(s2)	FToxid	delta
Al2O3(s3)	FToxid	kappa
Al2O3(s4)	FToxid	corundum(alpha)
TiO2(s)	FToxid	Rutile
TiO2(s2)	FToxid	Anatase
Ti2O3(s)	FToxid	Solid-A
Ti2O3(s2)	FToxid	Solid-B
Ti3O5(s)	FToxid	Solid-A
Ti3O5(s2)	FToxid	Solid-B
Ti4O7(s)	FToxid	solid
Ti5O9(s)	FToxid	solid
Ti6O11(s)	FToxid	solid
Ti7O13(s)	FToxid	solid
Ti8O15(s)	FToxid	solid
Ti9O17(s)	FToxid	solid
Ti10O19(s)	FToxid	solid
Ti20O39(s)	FToxid	Higher_Magneli_phases_(composite)
Al2TiO5(s)	FToxid	Tialite
Al4TiO8(s)	FToxid	solid
Fe2O3(s)	FToxid	hematite
Fe2O3(s2)	FToxid	High-Pressure-Hematite
Fe2O3(s3)	FToxid	High-Pressure-Hematite

Al2Fe2O6(s) (FeO)(TiO2)(s) FeTi2O4(s) FeTi2O5(s) (FeO)2(TiO2)(s) ZnO(s)

FToxid FToxid FToxid FToxid FToxid FToxid solid Ilmenite solid Pseudobrookite Ulvospinel Zincite
Appendix iii – Numbering of phases

Number	Phase
1	Ilmenite, FeTiO3, solid solution: FeTiO3-Ti2O3-MgTiO3-MnTiO3, dilute Al2O3
2	Rutile, TiO ₂
3	Spinel, AB ₂ O ₄ (Cubic) A,B= Al-Co-Cr-Fe-Mg-Mn-Ni-Zn
4	Titania Spinel (Mg,Fe,Mn)(Mg,Fe,Mn,Ti ³⁺ ,Ti ⁴⁺ ,Al ³⁺)
5	Fe (s)
6	M_2O_3 (Corundum) M = Al, Ti, V, Cr, Fe
7	SiO ₂ (s4), Tridymite
8	(FeO) ₂ (TiO ₂) (s), Ulvospinel
9	Al_2O_3 (s4)
10	Fe_2O_3 (s), Hematite
11	Monoxide, Rocksalt-str. Fe(2), Ca, Sr, Ba, Mg, Ni, Co, Mn(2); dilute Zn, Al, Cr, Fe(3),
	Mn(3), Cu, Zr, Na.
12	$Ca_2Fe_2O_5(s)$
13	$Ca_3Ti_2O_7(s)$
14	$Ca_5Ti_4O_{13}(s)$
15	$CaFe_2O_4(s)$
16	CaTiO ₃ (s), Perovskite-A
17	$CaCO_3(s2)$
18	Ca ₃ Ti ₂ O ₇ -Ca ₃ Ti ₂ O ₆ , solid solution
19	C (s), Graphite
20	$Fe_3C(s)$, Cementite
21	Ideal gas
22	Slag-liquid, oxide Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, Ge, K, Mg, Mn, Na, Ni, P, Pb, Si,
	Sn, Sr, Ti, Zn, Zr + dilute S
23	$(Na_2O)(TiO_2)_3(s)$
24	$(Na_2O)(TiO_2)_6(s)$
25	$Na_2O(s2)$
26	$Na_2O_2(s_2)$
27	$Na_2TiO_3(s2)$
28	$Na_3Fe_5O_9(s)$
29	Na ₄ TiO ₄ (s)
	$Na_8Fe_2O_7(s)$
31	$Na_8Ti_5O_{14}(s)$
32	NaFeO ₂ (s)
33	K_2O_2 (s)
34	$K_2T_{13}O_7(s)$
35	$K_2 Ti_6 O_{13} (s)$
36	$K_8 I_{15} O_{14} (s)$
37	
38	Pseudobrookite solid solution: $Fe I_{12}O_5 - I_{13}O_5 - Mg I_{12}O_5 - Mn I_{12}O_5$
39	$Mg_{11}O_{3}(s), Getktelite$
40	Zincite, ZnO; dilute CoO, FeO, Fe_2O_3 , MgO, MinO, NiO
41	$(ZnO)_2(11O_2)$ (s)
42	$(Cu_2O)(Fe_2O_3)(s_2)$
43	$(CuO)(Fe_2O_3)(S_3)$
44	
45	$Cu_2 O(s)$
40	CuO (S) Colt liquid L: No IZ DE Co Ma Co Co Do Al E- $(2, 2)$ Ma Co N: 7a DE La Co TE
4/	J Salt-Inquite LI, INA, K, KU, CS, INB, CA, SI, BA, AI, Fe[2+,5+], MIN, CO, NI, ZIN, FD, LA, Ce, IN, JJ[3+4+] Pu[3+4+] Cr[2+3+] Mo[5+1]/F Cl Rr I O(dilute) OH NO3 CO3 SO4
48	FeS (s) Fe^{-3}
49	ZnS (s). Sphalerite
50	$ZnSO_4$ (s3)
51	Willemite (Zn, Fe2+, Mg)[Zn, Fe2+, Mg]SiO4. Zn2SiO4-rich only

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