

The influence of coal-associated trace elements on sintering and agglomeration of a model coal mineral mixture

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Declaration

I, Marika Verita Nel, hereby declare that the work contained in this thesis is my own original study and has not previously been submitted at any university for a degree.



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Abstract

A series of experiments was conducted to investigate the potential influence of selected inorganic compounds on sintering and agglomeration of a model mineral mixture. The minerals and inorganic compounds were chosen based on the constituents found in coal. The study simulated ash formation processes in the temperature range of 500 °C to 1000 °C. The mineral mixture consisted of kaolinite, quartz, pyrite, siderite, calcite, TiO_2 and magnesite in a fixed ratio. The mixture was doped with 4% (by weight) of each trace or minor element species. Different analytical methods were employed to investigate the extent of sintering and agglomeration and to identify the possible interactions between the species. Compressive strength measurements, TG/DTA, SEM/EDS and XRD analysis were used to evaluate the interactions in oxidizing and inert atmospheres. The influence of the compounds on the reducing-atmosphere ash fusion temperatures of the mineral mixture was also investigated. The results indicated that NaCl , Na_2CO_3 , GeO_2 , Mn_2O_3 , Ni_3S_2 , SrCO_3 and PbS increased sintering in the mineral mixture in the oxidizing atmosphere. Sintering was increased by enhancing sulfation of limestone, and/or by affecting the characteristics of the aluminosilicate phases. Na_2CO_3 , GeO_2 and Mn_2O_3 increased sintering of the mineral mixture in the inert atmosphere by affecting the characteristics of the aluminosilicate phases. MoS_2 and PbMoO_4 decreased sintering of the mineral mixture in the oxidizing atmosphere, while Cu_2S , CuS , PbS and NaCl decreased sintering in the inert atmosphere. The results obtained in oxidizing and inert atmospheres indicated that the oxidation numbers of the cations and the anions associated with the different compounds affected the potential of the additives to influence sintering and agglomeration of the mineral mixture. The influence of the inorganic compounds on the mineral mixture at different ashing temperatures was investigated with the ash fusion temperature test. The results indicated that the ash fusion temperatures were decreased by the addition of GeS and PbCO_3 at an ashing temperature of 500 °C, decreased by SrCO_3 at an ashing temperature of 815 °C, and increased by CrO_3 at an ashing temperature of 500 °C. The results confirm that the addition of trace element compounds can result in the formation of species with lower melting points, and that the ashing temperature has an influence on the ash fusion temperatures.

Uittreksel

'n Reeks eksperimente is uitgevoer om te bepaal of anorganiese verbinding (toevoegings) 'n invloed het op sintering en agglomerasie van 'n model mineraal mengsel. Die minerale en anorganiese verbindings is geselekteer op grond van die verbindings wat in steenkool voorkom. Die studie is ontwerp om die forming van as te simuleer in die temperatuur gebied van 500 °C tot 1000 °C. Die mineraal mengsel het bestaan uit kaolinit, kwarts, piriet, sideriet, kalsiet, TiO_2 and magnesiet in 'n vaste verhouding. Die anorganiese stowwe is elk bygevoeg in 'n massa konsentrasie van 4%. Verskillende analitiese metodes is gebruik om die interaksies tussen die mineraal mengsel en toevoegings te bepaal. Breeksterkte meetings, TG/DTA, SEM/EDS en XRD analyses is uitgevoer in oksiderende en inerte atmosfeer. Die invloed van die anorganiese verbindings op as smelt punte is ook bepaal in 'n reduserende atmosfeer. Die resultate het aangedui dat NaCl , Na_2CO_3 , GeO_2 , Mn_2O_3 , Ni_3S_2 , SrCO_3 en PbS sintering in die mineraal mengsel verhoog het in die oksiderende atmosfeer. Sintering is verhoog deur 'n hydraende toename tot die vorming van kalsium sulfaat, of deur die karakteristieke van die aluminosilikate te beïnvloed. Na_2CO_3 , GeO_2 en Mn_2O_3 het die sintering in die mengsel verhoog in die inerte atmosfeer deur die karakteristieke van die aluminosilikate te beïnvloed. MoS_2 en PbMoO_4 het die sintering verlaag in die oksiderende atmosfeer, en Cu_2S , CuS , PbS en NaCl het die sintering verlaag in die inerte atmosfeer. Die resultate wat opgelewer is in die oksiderende en inerte atmosfeer het aangedui dat die oksidasie getal van die katione en die anione geassosieer met die anorganiese verbindings beïnvloed die potentiaal van die verbinding om sintering en agglomerasie van die mineral mengsel te beïnvloed. Die as smelting eksperimente het aangedui dat die verasingstemperatuur die as smeltpunte affekteer. Die as smeltpunte van die mengsel is verlaag deur die toevoeging van GeS en PbCO_3 veras teen 500 °C, is verlaag deur SrCO_3 veras teen 815 °C, en is verhoog deur CrO_3 veras teen 500 °C. Die resultate bevestig dat die toevoeging van anorganiese verbindings kan veroorsaak dat spesies vorm in die mengsel met laer smeltpunte, en dat die verasingstemperatuur die as smeltpunte beïnvloed.

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Chapter 1

Problem Statement and Hypothesis

1.1 Problem Statement and Substantiation

Most naturally occurring elements are found in coal, with the majority only in trace quantities [Clarke, 1993; Swaine, 1994]. The definition of trace elements in coal differs among research groups, but the consensus, as used in this study, is that trace elements have a concentration of below 1000 ppm (0.1%) by weight in dry coal [Gibbs et al., 2004; Liu et al., 2005b; Reed et al., 2001; Wagner and Hlatshwayo, 2005; Wang et al., 2007b; Yiwei et al., 2007]. Partitioning of trace elements is linked to the transformation and partitioning of common minerals in coal, because trace elements are closely associated with major and minor minerals, and ash particles scavenge vaporized species in the gas phase [Dai et al., 2009; Ratafia-Brown, 1994]. The speciation or mode of occurrence of the elements also affects their transformation and partitioning during coal consumption. The environmental fate and health impact of some trace elements are dependent on their various forms and oxidation states [Folgueras et al., 2007; Shah et al., 2009; Yiwei et al., 2008].

The most common classification system of trace elements is based on their volatility, i.e. their partitioning behaviour during combustion and gasification [Clarke, 1993; Galbreath et al., 2000]. During combustion and gasification processes trace element species can exit the reactor in one of three different routes, i.e. in the vapour phase (e.g. Hg and elemental Se), as part of the fly ash, or included in the coarse ash removed at the bottom of the reactor [Galbreath et al., 2000; Galbreath and Zygarlicke, 2004; Klein et al., 1975; Shah et al., 2009].

Coal ash can sinter and agglomerate when certain species occur at sufficiently high temperatures. Agglomeration and sintering in the reactor bed will result in an increase in the particle size of the bed material and ash. Sufficient particle growth and the formation of agglomerates may cause bed defluidization in fluidized beds, ensuing interruptions to operation. Tendencies to form agglomerates are governed by the swelling index of the fuel, ash chemistry and operation temperatures [Collot, 2006]. However, agglomeration of ash particles may also aid operation in

packed-bed reactors by providing favourable porosity to allow steam and oxygen through the ash bed [Van Dyk et al., 2009a].

Sintering and agglomeration are more problematic in the utilisation of low-rank coals due to the presence of significantly larger amounts of organically bound inorganic matter that are released at low temperatures [Bhattacharya and Harttig; Manzoori and Agarwal, 1992; Vuthaluru et al., 1999]. Of particular concern in low-rank coals are high amounts of alkali metals (sodium, potassium) [Dahlin et al., 2006; Manzoori and Agarwal, 1992; Vuthaluru et al., 1999; Vuthaluru and Zhang, 2001]. Several elements (mostly major and minor elements) have been identified in the necks between particles. Researchers have attempted to predict the eutectics and species responsible for neck formation [Lin and Wey, 2004; Yan et al., 2003]. Several authors reported that trace elements may form low melting point species in ash and contribute to sintering and agglomeration [Álvarez-Rodríguez et al., 2007; Conn, 1995; Reed et al., 2001].

There is limited literature available on the influence of individual trace elements with different speciation on coal ash chemistry and their tendency to form low melting point species and agglomerates [Conn, 1995; Folgueras et al., 2007; Reed et al., 2001]. Trace elements have been the focus of numerous studies. Studies involving trace elements are mostly focussed on: determination of concentrations in raw coal; distribution or partitioning of elements in the ash of different systems; speciation of elements in coarse ash and fly ash; speciation of selected hazardous elements and reactions that may cause their release into the environment; and characterizing the layers on ash particles and glass phases or slag. A study detailing the influence of different trace species on sintering and agglomeration in coal ash and the formation of low melting point species is still lacking in literature. Trace element species in coal have very low concentrations and may not play a significant role in most coal utilization processes. However, the information is important on a fundamental level, and some of the data may be useful to other industries.

1.2 Hypothesis

Trace element species interact with associated minerals in coal during ash formation. Solid-state interactions may contribute or inhibit sintering and

agglomeration processes in oxidizing and inert environments. Differences in trace element speciation (oxidation numbers and anions) will have different effects on these processes.

1.3 Aims and Objectives

Aims and objectives of this study include:

- Creating a mineral mixture representative of the most common minerals in coal to represent ash formation processes in an oxidizing environment during heat treatment.
- Selecting trace and minor species in coal with different oxidation numbers and anions to evaluate as additives.
- Determining the influence of the additives on sintering and agglomeration of the mineral mixture.
- Using different analytical techniques to evaluate the interactions most likely involved in sintering and agglomeration of the mineral mixture.
- Determining whether relevant trends exist concerning sintering and agglomeration, with respect to oxidation numbers, anions, or groups in the periodic table.

1.4 Outline of Study

Figure 1.1 is a diagram representing the outline of the study. The experiments were designed to simulate ash formation processes in an oxidising environment at temperatures associated with fluidized-bed reactors. Experiments were performed in the temperature range of 500 °C to 1000 °C. To eliminate the need of ashing to obtain the mineral fraction of coal, a synthetic mineral mixture comprised of common minerals in coal was made up and used throughout all the experiments. Trace element species were identified from literature that commonly occur in coal or are products in ash. These species were added to the mineral mixture in a concentration of 4% by weight to evaluate their influence on sintering and agglomeration. Trace species were selected with various anions and oxidation numbers of the metals. A total of 23 trace or minor species was selected, as well as NaCl and Na₂CO₃. Sodium is known for the

sintering and agglomerating effect it has on ash. The 25 species were added to the mineral mixture independently to determine their influence on the compressive strength of pressed pellets sintered in static air.

Sixteen species were chosen for further investigation by applying certain criteria to the compressive strength data. Additional experiments or analyses included: compressive strength tests in nitrogen; simultaneous thermogravimetric and differential thermal analysis (TG/DTA) in air and nitrogen; backscatter SEM/BDS analysis of compressive strength pellets sintered in air; and XRD on selected samples collected from the compressive strength experiments in air. These experiments and analyses were performed in order to determine whether chemical reactions or physical influences were responsible for the increase or decrease observed in the oxidizing compressive strength experiments. The influence of a series of additives on the reducing-atmosphere ash fusion temperatures of the mineral mixture was also determined.

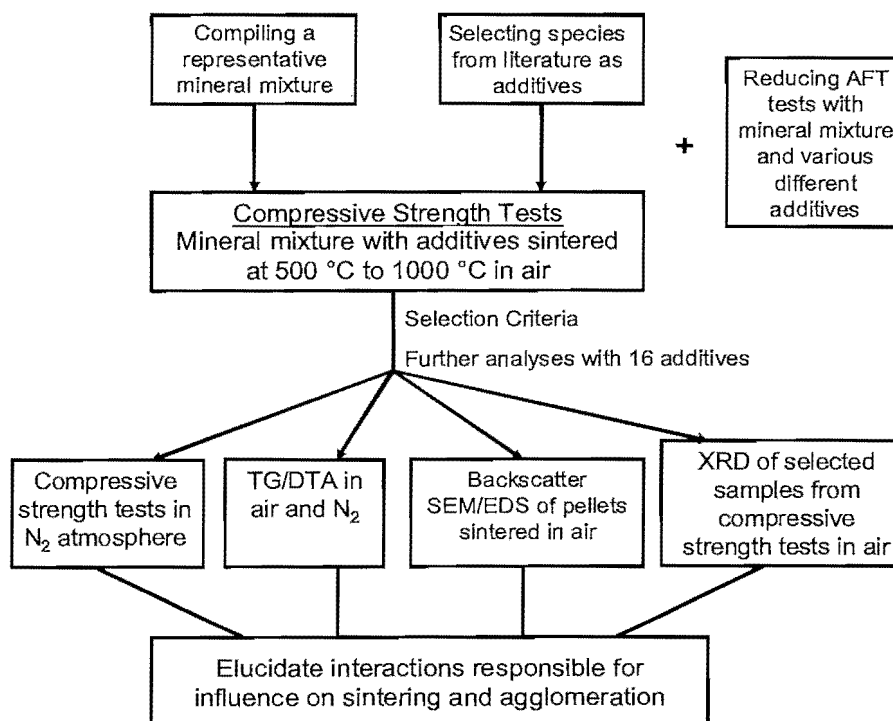


Figure 1.1 Outline of study

Chapter 2

Literature

The Formation of Ash from Coal: The Role of Major Minerals and the Importance of Trace Elements, Sintering and Agglomeration

A large amount of coal is used around the world each year in different industries, with power generation most likely the greatest consumer. China's coal consumption in 2005 was close to 2.19 billion tons and 2.72 billion tons in 2008 [Dai et al., 2009; Song et al., 2007]. Nelson [2007] commented that the USA has over 1300 coal-fired power plants. Coal can also be used to produce chemicals and fuels via gasification and liquefaction [Collot, 2006; Probststein and Hicks, 2006].

Coal consists of organic and inorganic matter in varying concentrations. The amount of inorganic matter found in coal is reported as the ash yield and expressed as a percentage of the coal on a weight basis. Depending on the technology, the resultant ash products from combustion and gasification systems exit the reactors either as dry ash or a slag. Different combustion and gasification technologies are designed to handle different amounts of ash. One such example is an entrained flow gasifier that uses a self-coating slag system [Collot, 2006]. Therefore, a minimum ash yield is required to cover the walls of the gasifier and reduce heat loss through the walls. Mineral matter in coal is not desired, but unavoidable. It is mined with the coal, but does not contribute to the coal's value [Ward, 2002].

Inorganic species occur in coal as mineral matter, or they can be organically bound. Organically bound inorganic species were part of the plant matter from which the coal seams originated, and are found incorporated into macerals. Mineral matter can enter the coal seam via different routes or processes. Initially, during the peat-forming process mineral matter can be deposited into the environment via sedimentation (e.g. from flooding) or blown in by the wind [Ward, 2002]. After the initial deposition, mineral matter and salts can also be introduced via water percolating through the seam. In this manner salts and mineral matter are precipitated in pores, cleats and fractures in the coal seam [Mukherjee and Srivastava, 2006; Snyman and Barclay, 1989; Swaine, 2000; Van Krevelen and Schuyer, 1957; Ward, 1989, 2002].

Coal hosts a variety of different mineral species. The concentrations and types of minerals are different in each coal source. The most common mineral species found in coal include quartz, kaolinite, illite, montmorillonite, gypsum, siderite, calcite, dolomite and feldspars [Conn and Austin, 1984; Estep et al., 1968; Franklin et al., 1981; Miller and Schobert, 1993; Ollila et al., 2006; Thiessen et al., 1936; Ward, 1989, 2002; Ward et al., 1999; Yu et al., 2007]. Apart from the common minerals, most naturally occurring elements are found in coal, with the majority only in trace quantities [Clarke, 1993; Swaine, 1994]. Clarkes (or Clarke values) refer to the average trace element concentrations in the black shales and coals of the world [Ketris and Yudovich, 2009]. Mineral matter and elements end up in different ash fractions during coal utilisation, and are removed from the reactor at intervals or continuously during operation.

This chapter reviews ash formation and distribution in fluidised beds; common minerals and trace elements in coal; their possible contribution to ash formation and the formation of low melting point species; definitions and mechanisms of sintering and agglomeration; and methods to evaluate sintering and agglomeration in ash. Possible reactions of minor and trace elements in ash are included in the results and discussion chapters under each element.

2.1 Fate of Ash in Fluidized-Bed Reactors

Fluidized-bed reactors require operation at temperatures well below the ash fusion temperature of the fuel, usually in the range of 800 °C to 1050 °C [Collot, 2006]. The velocity of the entering reactant gases allows the fuel, ash and initial bed material to stay fluidised, but is dependent on the required particle size distribution [Collot, 2006; Probstein and Hicks, 2006]. Ash formation constantly adds to the amount of bed material in the reactor. Coarse ash particles are removed from the bottom of the reactor. Finer ash particles or fly ash can leave the reactor with the gas and are collected with cyclones and other more efficient collection devices [Cooper and Alley, 2002; Probstein and Hicks, 2006].

Scala and Chirone [2006] described the fate of ash in a fluidized bed after formation. Figure 2.1 schematically represents the interactions between fuel ash and bed particles as compiled by Scala and Chirone [2006]. The fuel entering a fluidized

bed devolatilizes to form either coarse char or fine char particles. The ratio of fine to coarse char particles is determined by attrition, fragmentation and carbon consumption. The fine char can be elutriated from the bed. Both the coarse and fine char particles can collide with inert bed material. Ash transfer occurs if the ash or the bed material particles are sufficiently sticky. Attrition can cause the removal of ash particles adhered on the inert bed material and include them with the elutriable free char fines again. Some of the ash components may also be prone to vaporisation. The vapour phases can condense on the inert bed material or exit the bed with the gas and condense downstream.

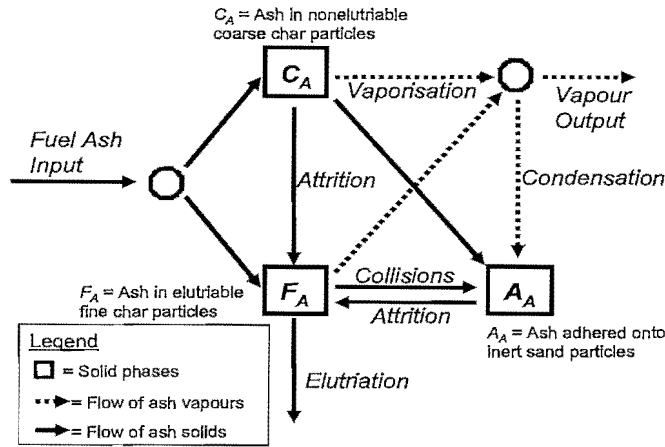


Figure 2.1 The fate of ash in a fluidized bed reactor. Adapted from Scala and Chirone [2006]

Components in a fluidized bed are thoroughly mixed due to constant turbulent circulation. Good heat exchange between interacting phases also results in a more uniform bed temperature than in packed beds [Probstein and Hicks, 2006]. Ash particles inside the bed are in constant collision with each other, the reactant gases and the incoming fuel particles. Some of the interactions may be responsible for the formation of agglomerates. Agglomeration and sintering mechanisms are described in Section 2.8. Agglomeration and sintering in the bed will result in an increase in the particle size of the bed material and ash. Sufficient particle growth and the formation of agglomerates may cause bed defluidization and therefore interruptions to operation. Tendencies to form agglomerates are governed by the swelling index of the fuel, ash chemistry and operation temperatures [Collot, 2006]. Many interactions between specific minerals participating in the formation of ash are discussed in Section 2.3.

2.2 Common Minerals in Coal

2.2.1 Common Mineral Species in Coal

Ward [1989, 2002] used various sources to compile lists of common minerals found in coal, including the minerals identified using low-temperature ashing (ashing by means of a low-temperature (<300 °C) oxygen plasma) as a preparation method for analysis. Table 2.1 is a selection of the common minerals in coal adapted from Ward [1989, 2002]. Table 2.2 lists the most abundant of the common minerals in coal, with examples of relatively high values reported for specific coal sources in comparison to other coal sources (not given). The values obtained from raw coals and ash are reported as weight percentages on a mineral basis. Other coal sources not included in these resources may have higher values for specific minerals.

Table 2.1 Common minerals in coal [Jones, 2007; Ward, 1989, 2002]

Silicates Quartz – SiO_2 Chalcedony – SiO_2 Kaolinite – $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ Illite – $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ Montmorillonite – $\text{Na}(\text{AlMg})\text{Si}_4\text{O}_{10}(\text{OH})_2$ Chlorite – $(\text{Fe,Mg,Mn,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH},\text{O})_8$ Feldspar – KAlSi_3O_8 ; $\text{NaAlSi}_3\text{O}_8$; $\text{CaAl}_2\text{Si}_2\text{O}_8$ Zircon – ZrSiO_4 Interstratified clay minerals	Sulfides Pyrite – FeS_2 Marcasite – FeS_2 Sphalerite – ZnS Galena – PbS Chalcopyrite – CuFeS_2 Millerite – NiS
Sulfates Gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ Bassanite – $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ Anhydrite – CaSO_4 Barite – BaSO_4 Szomolnokite – $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ Thenardite – Na_2SO_4 Natrojarosite – $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ Coquimbite – $\text{Fe}_2(\text{SO}_4)_3$ Celestite – SrSO_4 Hexahydrate – $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	Carbonates Calcite – CaCO_3 Aragonite – CaCO_3 Siderite – FeCO_3 Dolomite – $\text{CaMg}(\text{CO}_3)_2$ Ankerite – $\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$ Dawsonite – $\text{NaAlCO}_3(\text{OH})_2$ Strontianite – SrCO_3 Witherite – BaCO_3
Phosphates Apatite – $\text{Ca}_5\text{F}(\text{PO}_4)_3$ Goyazite – $\text{SrAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot 5\text{H}_2\text{O}$ Gorceixite – $\text{BaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$	Other Minerals Anatase – TiO_2 Rutile – TiO_2 Boehmite – $\text{AlO}(\text{OH})$ Goethite – $\text{Fe}(\text{OH})_3$ Crocoite – PbCrO_4 Chromite – $(\text{Fe,Mg})\text{Cr}_2\text{O}_4$ Haematite – Fe_2O_3 Clausthalite – PbSe

Table 2.2 Examples of the abundant minerals in coal and coal ash with reported high values found in specific coal sources

Minerals	High reported values (wt% on mineral basis)	Coal Type or Location	References
Silicates			
Quartz – SiO_2	78	Ulan Coal	Gupta et al. [1998a]
Kaolinite – $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	81	Australian Bituminous	Grigore et al. [2008]
Illite – $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	40	Keystone Coal	Conn and Austin [1984]
Montmorillonite – $\text{Na}(\text{AlMg})\text{Si}_4\text{O}_{10}(\text{OH})_2$	25	Pittsburgh No. 8 Bituminous	Ollila et al. [2006]
Interstratified clay minerals	28	Colombian Coal	Carmona and Ward [2007]
Sulfates			
Gypsum – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	10	Illinois No. 6	McCollor et al. [1993]
Bassanite – $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	43	Indonesian Coal	Vuthaluru and French [2008a]
Anhydrite – CaSO_4	20	Texas Lignite	Conn and Austin [1984]
Sulfides			
Pyrite – FeS_2	45	Pittsburgh No. 8 Bituminous	Franklin et al. [1981]
Carbonates			
Calcite – CaCO_3	46	Gholson Coal	Huffman et al. [1981]
Siderite – FeCO_3	19	Gholson Coal	Huffman et al. [1981]
Dolomite – $\text{CaMg}(\text{CO}_3)_2$	20	Gunnedah Basin	Ward et al. [1999]
Ankerite – $\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$	12	Colombian Coal	Carmona and Ward [2007]
Other Minerals			
Anatase – TiO_2	2	Coking Coal	Sakurovs et al. [2007]
Rutile – TiO_2	4	Coal bank sample	Liu et al. [2005]
Phosphates			
Apatite – $\text{Ca}_5\text{F}(\text{PO}_4)_3$	9	Australian Bituminous	Grigore et al. [2008]

2.2.2 Included and Excluded Minerals

The discrete mineral grains that are closely associated with the organic matter or macerals in coal are referred to as inherent or included minerals [Liu et al., 2007a; McLennan et al., 2000a; Ward, 2002]. These mineral particles are encased by the organic matrix and cannot be removed by beneficiation or coal preparation techniques [Ward, 2002]. Mineral matter that is completely liberated from the coal organic matrix or has negligible association with the organic matter is referred to as extraneous or excluded mineral matter [Bailey et al., 1998; Liu et al., 2007a; McLennan et al., 2000a; Ward, 2002]. Excluded mineral matter may be liberated from the organic matrix during coal preparation, or can be included in the coal during mining operations [Bailey et al., 1998; Fernandez-Turiel et al., 2004; Ward 2002]. The

deposition and sedimentation processes involved in coalification result in the formation of coal seams interlaid with bands of geological material [Fernandez-Turiel et al., 2004]. During mining activities the bands of non-coal material are co-excavated with the coal and incorporated as excluded mineral matter [Fernandez-Turiel et al., 2004; Ward 2002]. Beneficiation plants may be used to attempt the removal of the additional mineral matter. However, beneficiation processes may not be economically viable and are unable to remove all the mineral matter from coal [Ward, 2002]. Therefore, significant amounts of mineral matter are present during coal utilisation.

Differences in local temperature, atmosphere, heating rates and other minerals in close proximity cause included and excluded minerals to react differently during coal consumption [Liu et al., 2005, 2007a]. Included minerals tend to coalesce with associated minerals in the char structure as the char is consumed [Liu et al., 2005; McLennan et al., 2000a; Wu et al., 1999]. Included minerals are the major source of glass phases in ash [Van Dyk et al., 2009a, 2009b]. The organic association of the included minerals is responsible for creating local reducing conditions in combustion and gasification [McLennan et al., 2000a]. The reduction of included minerals produces species more prone to volatilisation (e.g. metal vapours) compared to excluded minerals not subjected to a reducing environment [Kitsuka et al., 2007; McLennan et al., 2000a; Zhang et al., 2007].

McLennan and co-workers [2000a] investigated the transformations of included and excluded pyrite and siderite during pulverized fuel combustion in reducing conditions. The study illustrated the importance of associated minerals during ash formation. They reported that included siderite and pyrite behaved similarly to excluded siderite and pyrite, except when the included iron species were associated with aluminosilicates. In the presence of aluminosilicates the siderite and pyrite formed iron aluminosilicate glass particles. Excluded pyrite and included pyrite in the absence of aluminosilicate species produced FeO–FeS melt phases, magnetite and hematite, depending on the level of oxidation [Bailey et al., 1998; Bool et al., 1995; McLennan et al., 2000a]. Excluded siderite and included siderite in the absence of aluminosilicate species produced wustite under reducing conditions, but the wustite oxidized to magnetite under oxidizing conditions [McLennan et al., 2000a].

Excluded minerals generally experience fragmentation [Wang et al., 2007, 2009; Wu et al., 1999; Yan et al., 2001c]. Fragmentation is a result of several mechanisms, including thermal shock, mechanical breakage, rapid gas release and

inorganic reactions [Wu et al., 1999; Yan et al., 2001c]. McLennan and co-workers [2000a] and Yan and co-workers [2001c] stated that excluded minerals have limited interaction during combustion due to a low probability of colliding. However, Wang and co-workers [2007, 2009] concluded that the proposed limited interaction is inconsistent when considering the fluxing promotion caused by calcium/iron-rich additives in high-temperature gasification. It is suggested that the excluded additive particles partly scavenge the inherent aluminosilicate species [Wang et al., 2007, 2009]. Kuramoto and co-workers [2004] also found that included minerals reacted with added Ca-based CO₂ sorbents during the study of a novel steam gasification process.

Exothermic reactions in an inorganic particle may raise its temperature above the gas temperature [McLennan et al., 2000a]. Excluded minerals often consist of a mixture of minerals in a single grain [Liu et al., 2007a]. Potential mineral-mineral interactions may influence ash formation [Wang et al., 2007]. A study by Liu and co-workers [2007a] on Australian coals revealed that illite associated with kaolinite tends to swell and form cenospherical ash particles.

The transformations of excluded mineral matter not only affect ash formation, but also have an influence on the particle size distribution (PSD) of the resultant ash [Ninomiya et al., 2009; Wang et al., 2007; Yan et al., 2001c]. Zhang and co-workers [2007] reported that excluded minerals barely contribute to particulate matter with a diameter less than 1 μm (PM₁). PM₁₀ (particulate matter with a diameter less than 10 μm) is mostly a result of inherent or included minerals in the coal [Wang et al., 2007; Zhang et al., 2007].

2.2.3 Analysis Methods to Determine Coal Mineralogy

The two most popular methods used in coal science to analyze the mineralogy in coal or low-temperature ash (LTA) are X-ray diffraction (XRD) [Beale and Sankar, 2006; Carmona and Ward, 2007; Erol et al., 2008; González et al., 2005; Gupta, 2007; Huggins, 2002; Hurley and Schobert, 1992; Matjie and Van Alphen, 2008; Mukherjee and Srivastava, 2006; Van Alphen, 2007; Vassilev and Tascón, 2003; Ward, 2002; Zhao et al., 2006] and computer-controlled scanning electron microscopy (CCSEM) [Gupta et al., 1998a; Gupta, 2007; Huggins, 2002; Matsuoka et al., 2006; McLennan et al., 2000a, 2000b; Van Alphen, 2007; Vassilev and Tascón, 2003; Ward, 2002; Yu et al., 2007]. Both XRD and CCSEM give qualitative and

quantitative information regarding the common mineral species in coal [Gupta, 2007; Huggins, 2002; Ward, 2002].

2.2.3.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is based on the existence of a unique X-ray powder diffraction pattern for each crystalline substance [Skoog et al., 1998]. The crystal lattice spacings of the unknown samples are compared to authentic or pure known samples and are calibrated accordingly. However, XRD analyses on raw coal samples are semi-quantitative. To improve quantification the use of LTA is suggested [Huggins, 2002; Ward, 2002]. The amorphous carbon in raw coal samples gives rise to three very broad peaks with low intensities superimposed on the sharper mineral peaks. The influence of amorphous carbon and non-crystalline mineral species can be subtracted to quantify the mineral species [Huggins, 2002; Vassilev and Tascón, 2003; Wertz, 1990]. A drawback is that the method is limited to the evaluations of about six of the main minerals in the sample and should preferably be performed on LTA [Huggins, 2002].

Some methods have been developed to improve the XRD analysis on raw coal and LTA. One such method is called the Rietveld method of analysis [Huggins, 2002]. The Rietveld technique uses a formula with which the intensity of any point in the diffraction trace of a single mineral can be determined without the use of integrated neutron powder intensities [Rietveld, 1969; Ward, 2002]. SIROQUANT is a software package developed based on the Rietveld XRD analysis technique [Ward et al., 1999; Ward, 2002]. It allows the determination of 25 different minerals in a mixture with conventional powder XRD [Ward, 2002]. The SIROQUANT software has a function that can be used to remove the background attributed to organic matter and other amorphous materials from raw coal XRD traces [Sakurovs et al., 2007; Ward, 2002]. Sakurovs and co-workers [2007] used XRD with the SIROQUANT software package to successfully analyze the mineral matter in the LTA of several cokes and their parent coals.

2.2.3.2 Computer-Controlled Scanning Electron Microscopy (CCSEM)

Computer-controlled scanning electron microscopy (CCSEM) is a technique combining both scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) technologies. The relative elemental concentrations determined

by EDS are used to identify different mineral categories or species. The back-scattered electron intensities are used to identify the mineral particles [Gupta, 2007]. SEM morphology analysis determines the average diameter, perimeter and aspect ratio of individual particles. Therefore, CCSEM gives information regarding the distribution of the mineral categories in different particle size fractions and the relative elemental composition on a weight percent basis of each mineral category [Matsuoka et al., 2006]. CCSEM can scan many particles in an hour. However, the limitations of the technique include the fact that it is a surface analysis technique. CCSEM is also unable to identify all the mineral grains and species. A percentage of the mineral matter is reported as unclassified or undefined. This restriction is caused by measurements at overlapping particles and particles covered by a thin film of another mineral. It is also not possible to analyze particles smaller than 1 μm [Matsuoka et al., 2006; Van Dyk et al., 2009b; Vassilev and Tascón, 2003]. These include finely dispersed inorganic matter associated with the organic matter [Matsuoka et al., 2006].

QEMSCAN or QEM*SEM (quantitative evaluation of materials by scanning electron microscopy) is a variant of CCSEM and the name refers to the software used in the technique [Creelman and Ward, 1996; Galbreath et al., 1996; Grigore et al., 2008; Liu et al., 2005; Van Alphen, 2007; Ward, 2002]. The backscattered electrons combined with EDS are used to produce an image of individual coal particles as well as their chemical associations [Liu et al., 2005; Ward, 2002]. The images of the particles are built up pixel by pixel by identifying the chemical species corresponding to each pixel [Gupta, 2007; Liu et al., 2005; Ward, 2002]. This method is useful to directly determine mineral matter–organic matter or mineral matter–mineral matter associations without further image processing, as well as giving the distribution or abundance of the mineral species [Gupta, 2007; Liu et al., 2005]. In an international study by six laboratories comparing different CCSEM techniques or configurations it was determined that the QEM*SEM system produced the most precise results [Galbreath et al., 1996; Van Alphen; 2007; Ward, 2002].

2.2.3.3 *Mössbauer Spectroscopy*

Mössbauer spectroscopy is a method mostly used to characterize the iron-bearing minerals in coal (^{57}Fe -Mössbauer spectroscopy) [Medina et al., 2006; Ram et al., 1995; Taneja and Jones, 1984]. Common iron-bearing minerals in coal include pyrite, marcosite, illite, jarosite and siderite [Taneja and Jones, 1984]. Mössbauer

spectroscopy can be performed in either absorption or transmission mode [Kolker and Huggins, 2007; Ram et al., 2007]. The samples are bombarded by γ -radiation from a source, most commonly ^{57}Co [Carmona and Ward, 2007; Kolker and Huggins, 2007; Pusz et al., 1997; Ram et al., 1995; Taneja and Jones, 1984]. The absorption or transmission values of the iron in the samples are compared to values obtained for a calibration standard, e.g. crystalline hematite or natural iron film [Carmona and Ward, 2007; Huffman and Huggins, 1978; Ram et al., 1995]. Spectral parameters are recorded based on the calibration standard, i.e. isomer shift (δ), quadrupole splitting (Δ) and hyperfine magnetic field (H). Each mineral species has a specific set of Mössbauer parameters derived from a characteristic Mössbauer spectrum, with which they can be identified [Kolker and Huggins, 2007; Ram et al., 1995]. Mössbauer spectroscopy can be very time-consuming. Herod and co-workers [1996] and Richaud and co-workers [2000a] reported analysis times of several days or weeks due to low absorption. Due to the low absorption obtained, Richaud and co-workers [2000a] were unable to obtain spectra for small samples and/or samples with iron concentrations of less than 500 ppm.

2.2.4 A Classification System

Vassilev and Vassileva [2009] compiled a chemical and mineral classification system for inorganic matter in coal based on 37 samples with different ranks, ash yields, age, and chemical and mineral compositions. The chemical classification was based on (1) the sum of Si, Al, K, and Ti oxides; (2) sum of Ca, Mg, S, and Na oxides; and (3) Fe oxides. Four chemical coal ash types were derived, i.e. sialic, calsialic, ferrisialic and ferricalsialic. Based on the sum of Si, Al, K, and Ti oxides the groups were subdivided into subtypes with high, medium and low acid tendencies. The mineral classification system was derived based on (1) silicates + oxyhydroxides; (2) carbonates; and (3) sulfides + sulfates + phosphates. Four mineral coal types were derived, i.e. silicate, silicate-carbonate, silicate-sulfide and silicate-sulfide-carbonate or mixed. Based on the sum of silicates and oxyhydroxides the groups were subdivided into subtypes with high, medium, and low detrital tendencies. The new classification systems have scientific and industrial applications, including prospecting and recovery; mining, preparation and processing; predictions of slagging,

fouling, composition of combustion residues, corrosion problems and environmental and health concerns [Vassilev et al., 2009].

2.3 Transformation of Common Mineral Species during Ash Formation

2.3.1 Silicates

2.3.1.1 Kaolinite

Kaolinite is the main clay mineral in kaolin and in most coal sources [Klein, 2002; Salmang, 1961; Vassileva and Vassilev, 2005, 2006; Yu et al., 2007]. The transformations of kaolinite during heat treatment have been studied extensively [Castelein et al., 2001; Frost et al., 2003; Mayoral et al., 2001; McLennan et al., 2000a; O’Gorman and Walker, 1973; Querol et al., 1994; Reifenstein et al., 1999]. McLennan and co-workers [2000a] reported that the ash formation behaviour of excluded kaolinite was unaffected by the atmosphere (reducing or oxidising).

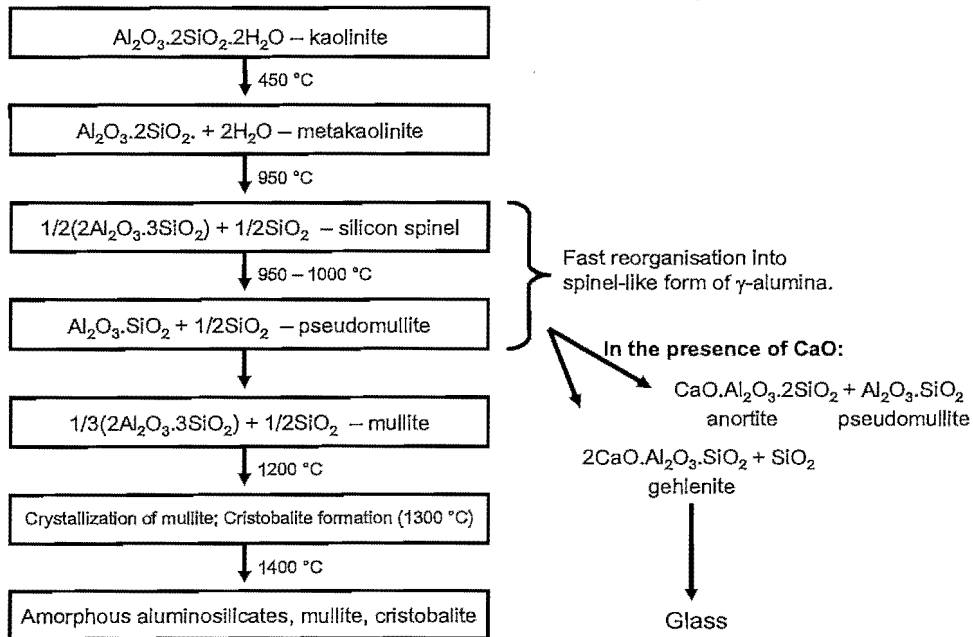


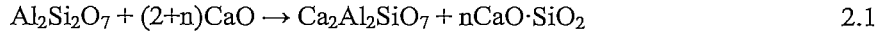
Figure 2.2 Major mineral transformations of kaolinite during combustion conditions and reactions with calcium oxide [Mayoral et al., 2001; Querol et al., 1994]

Figure 2.2 is a diagram of the phase transitions of kaolinite as presented by Mayoral and co-workers [2001]. Initially, kaolinite loses adsorbed water at 100 °C to 120 °C (see Figure 2.2) [Frost et al., 2003; O’Gorman and Walker, 1973]. From 400 °C to 600 °C kaolinite loses lattice water through endothermic dehydroxylation. The amorphous product formed is known as metakaolinite [Frost et al., 2003; Matsuoka et al., 2006; Mayoral et al., 2001; O’Gorman and Walker, 1973; Öhman and Nordin, 2000; Qiao et al., 2008; Reifenstein et al., 1999; Traoré et al., 2006]. It remains unaltered up to 950 °C. The metakaolinite undergoes an exothermic transformation from 950 °C to 1000 °C [O’Gorman and Walker, 1973; Traoré et al., 2006]. The products from the transformation are silicon spinel (950 – 980 °C), or a fast rearrangement results in the formation of a spinel-like form of γ -alumina [Frost et al., 2003; Mayoral et al., 2001; O’Gorman and Walker, 1973]. A further increase in temperature changes the silicon spinel and spinel-like form of γ -alumina into mullite [Frost et al., 2003; Mayoral et al., 2001; O’Gorman and Walker, 1973; Reifenstein et al., 1999]. Above 1200 °C, cristobalite (a tetragonal modification of silica) starts to form with the mullite [Frost et al., 2003; Mayoral et al., 2001; Traoré et al., 2006]. At temperatures between 1200 °C and 1500 °C cristobalite and mullite co-exist [Hlatshwayo et al., 2009; Mayoral et al., 2001; O’Gorman and Walker, 1973; Reifenstein et al., 1999; Traoré et al., 2006]. However, O’Gorman and Walker [1973] and Reifenstein and co-workers [1999] stated that at temperatures above 1500 °C, cristobalite is substituted into mullite. The mullite persists and is the only stable phase at higher temperatures.

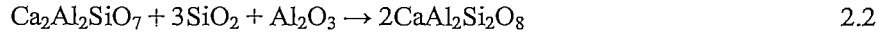
Kaolinite in the form of metakaolinite can react with various minerals in coal during combustion and gasification. A study by Matsuoka and co-workers [2006] determined that metakaolinite can interact with other minerals and species at temperatures below 800 °C. Kaolinite at 800 °C is more reactive than quartz and corundum [Matsuoka et al., 2006; Vassileva and Vassilev, 2005]. Matjie et al. [2007] stated that a mixture of kaolinite with pyrite or calcite forms a molten solution at 750 °C to 760 °C.

The reaction of kaolinite with CaO primarily forms gehlenite and anorthite [Mayoral et al., 2001; Traoré et al., 2003]. The reaction of CaO with kaolinite is summarized in Equations 2.1 and 2.2. Gehlenite and anorthite fuse at temperatures between 1400 °C and 1500 °C [Matjie et al., 2007].

Formation of gehlenite [Traoré et al., 2003]:



Formation of anorthite from gehlenite [Traoré et al., 2003]:



Reactions of CaO with kaolinite and/or metakaolinite can also result in the formation of boehmite (Ca_2SiO_4), corundum (Ca_2SiO_4) and grossular ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$) [Marinov et al., 1992]. The reaction of metakaolinite with NaCl and water results in the formation of nepheline, as presented by Equation 2.3 [Bhattacharya and Harttig, 2003]. Nepheline ($\text{NaAlSi}_3\text{O}_8$) has a melting point higher than 1250 °C [Bhattacharya and Harttig, 2003].



Other products formed from the reactions of kaolinite with minerals in coal, apart from the ones mentioned above, include Ca-Mg silicates, wollastonite (α - CaSiO_3), larnite (β - Ca_2SiO_4), rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$), melilite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$), spinel, glass, kalsilite (KAlSiO_4), leucite (KAlSi_2O_6) and albite ($\text{NaAlSi}_3\text{O}_8$) [Klein, 2002; McLennan et al., 2000a; Öhman and Nordin, 2000; Vassileva and Vassilev, 2005, 2006].

2.3.1.2 Quartz

Quartz is a major component of the mineral matter in coal [Reifenstein et al., 1999; Vassileva and Vassilev, 2006; Yu et al., 2007]. The concentration varies significantly with different coal sources [Yu et al., 2007]. A study by McLennan and co-workers [2000a] concluded that the ash formation behaviour of excluded quartz was unaffected by the atmosphere (reducing or oxidising). The transformations of excluded quartz are mostly not influenced by other minerals due to the low probability of collision and interaction [McLennan et al., 2000a; Sheng and Li, 2008; Yan et al., 2001a]. The transformations of excluded quartz are given in Figure 2.3.

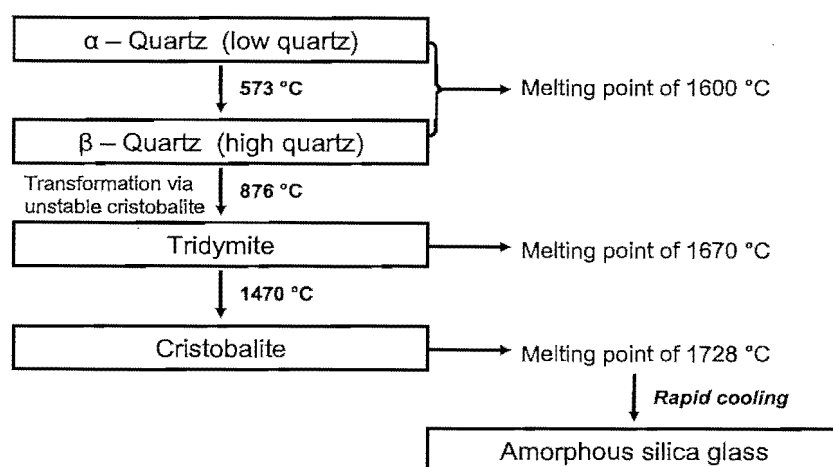


Figure 2.3 Transformations of excluded quartz. Schematic compiled from information in Klein [2002], Nankervis and Furlong [1980], O’Gorman and Walker [1973], Reifenstein et al. [1999] and Salmang [1961]

Low quartz (or α -quartz) transforms to high quartz (or β -quartz) at 573 °C (see Figure 2.3) [Klein, 2002; Nankervis and Furlong, 1980; O’Gorman and Walker, 1973; Reifenstein et al., 1999]. The transformation comprises small structural changes without bond breakage and is slightly endothermic [Klein, 2002; O’Gorman and Walker, 1973]. The β -quartz is stable up to 876 °C and indirectly transforms at this temperature to tridymite [Matjie et al., 2007; Reifenstein et al., 1999; Salmang, 1961]. The lattice breaks first and unstable cristobalite is formed. The cristobalite then changes into tridymite [Salmang, 1961]. This is due to Ostwald’s rule of stages [Salmang, 1961]. The tridymite is only stable up to 1470 °C, where it converts to cristobalite. Rapid heating and short retention times can prevent conversion of silica into other polymorphs [Reifenstein et al., 1999; Salmang, 1961]. Vuthaluru and French [2008a, 2008b] examined the ash of ten coal samples from drop-tube furnace and pilot-scale tests. In the ash from the drop-tube tests, quartz was the dominant polymorph present in all the samples and cristobalite and tridymite were only minor phases (maximum ashing temperature 1400 °C) [Vuthaluru and French, 2008a]. However, the furnace ash from the pilot-scale tests had more cristobalite in the ash than quartz [Vuthaluru and French, 2008b]. Reifenstein and co-workers [1999] stated that tridymite forms slowly. This may explain the large amount of quartz not converted into other polymorphs. Quartz has a melting point of 1600 °C and tridymite

melts at 1670 °C [McLennan et al., 2000a; Salmang, 1961]. Cristobalite has the highest melting point of the three polymorphs, i.e. at 1728 °C at atmospheric pressure [Klein, 2002; Salmang, 1961]. Rapid cooling of molten cristobalite below its melting point forms amorphous silica glass [Salmang, 1961].

Included quartz and quartz associated with other minerals react to form silicates and aluminosilicate compounds. Liu and co-workers [2007a] stated that it is very common to find quartz embedded within kaolinite and siderite. Vassileva and Vassilev [2006] reported softening of quartz particles at temperatures as low as 1200 °C. A study by Qiu and co-workers [1999] on blended ashes found amorphous quartz starting to form at 1300 °C. Mitchell and Gluskoter [1976] noted that amorphous glass compounds are formed from the reaction of quartz with other compounds. Quartz reacts readily with Ca, Mg and Al to form compounds similar to the products from kaolinite reactions, but quartz is less reactive than kaolinite [Matsuoka et al., 2006]. Compounds include anorthite, mullite, Ca-silicates, Ca-Mg silicates, feldspars and glass (see Section 2.3.1.1) [Marinov et al., 1992; Matjie et al., 2007; Matsuoka et al., 2006; Vassileva and Vassileva, 2005, 2006]. When quartz is associated with iron species (pyrite or siderite), iron silicates are formed (Liu et al., 2007). Iron silicates often have low melting points and may form molten species at low operating temperatures [Al-Otoom et al., 2005; Liu et al., 2007; Mason, 1992; Steenari et al., 1997]. Quartz also readily reacts with alkali species to form low melting point eutectics and feldspars [Dahlin et al., 2006; Klein, 2002; Steenari et al., 1998].

2.3.1.3 Illite

Illite is an alkali-deficient micaceous clay [Klein, 2002; Salmang, 1961]. The composition is similar to muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$); however, it has less Al substituted for Si and contains more water [Carrol et al., 2005; Klein, 2002]. Half of the K is also substituted by Ca and Mg [Klein, 2002; Salmang, 1961]. The general formula for illite is given as $\text{K}_{1.5}\text{Al}_4(\text{Si}_{6.5}\text{Al}_{1.5})\text{O}_{20}(\text{OH})_4$ [Carrol et al., 2005]. Mg, Ca, Ti and Fe are commonly substituted into the crystal lattice [Zhao et al., 2006]. Illite is a major iron-containing clay in coal due to the frequent inclusion of Fe^{2+} [Taneja and Jones, 1984]. It is also the main source of potassium in bituminous coals [Huffman et al., 1990]. The transformations of illite upon heating are given in Figure 2.4.

Illite loses adsorbed and interlayered moisture from 50 °C to 400 °C (see Figure 2.4) [Carroll et al., 2005; Jiang et al., 2007; O’Gorman and Walker, 1973; Reifenstein et al., 1999]. Dehydroxylation occurs from 400 °C to 700 °C [Carroll et al., 2005; Jiang et al., 2007; O’Gorman and Walker, 1973; Reifenstein et al., 1999]. After dehydroxylation the layered lattice framework is still intact [Jiang et al., 2007]. The clay structure is irreversibly destroyed in the temperature range of 850 °C to 1100 °C [Jiang et al., 2007; O’Gorman and Walker, 1973]. Melt phases of silica-rich glass already start to form at 950 °C [Carroll et al., 2005; O’Gorman and Walker, 1973; Srinivasachar et al., 1990a]. The crystallisation of different compounds can also occur, depending on the illite composition [Carroll et al., 2005; Jiang et al., 2007]. Mullite is formed at temperatures above 1050 °C [Jiang et al., 2007; O’Gorman and Walker, 1973; Reifenstein et al., 1999]. All the mullite is destroyed again above 1400 °C and incorporated into the aluminosilicate glass [O’Gorman and Walker, 1973; Reifenstein et al., 1999]. The presence of MgO stabilises the formation of spinel at temperatures above 900 °C [Carroll et al., 2005; Reifenstein et al., 1999]. The amount and particle size increase with the temperature [Carroll et al., 2005]. All the spinel is destroyed above 1300 °C and incorporated into the silica-rich glass [O’Gorman and Walker, 1973; Reifenstein et al., 1999].

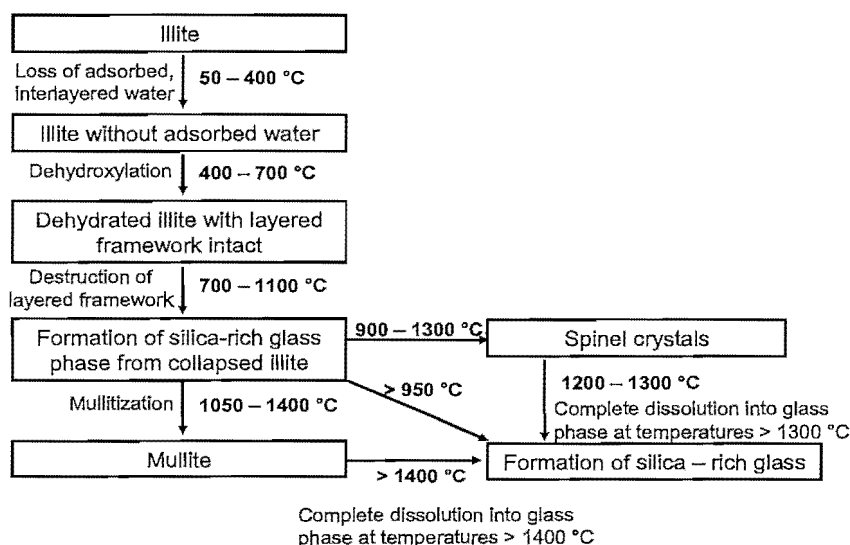


Figure 2.4 Transformations of illite. Compiled from information by Carrol et al. [2005], Jiang et al. [2007], O’Gorman and Walker [1973], Reifenstein et al. [1999] and Srinivasachar et al. [1990a]

Illite can be associated with other minerals in the same particle. Liu and co-workers [2007a] found the inclusion of illite in kaolinite particles. Illite can also react with other mineral species during coal consumption [Srinivasachar et al., 1990a]. Interactions of illite with other minerals may form low melting point species. Matjie et al. [2007] stated that an illite mixture with pyrite or calcite forms a molten solution at 600 °C to 650 °C. Illite has been identified as a fluxing agent [Vassileva and Vassilev, 2005]. Liu and co-workers [2007a] established that illite associated with kaolinite forms molten slag from which gases are released. The released gases contribute to the formation of cenosphical ash particles. Iron-containing illite generally forms Fe^{3+} - silica glass in oxidizing conditions due to the oxidation of Fe^{2+} to Fe^{3+} [McLennan et al., 2000a; Ram et al., 1995; Sheng and Li, 2008; Taneja and Jones, 1984]. Fe^{2+} - silica glass persists in reducing atmospheres [McLennan et al., 2000a; Sheng and Li, 2008].

The potassium in illite may contribute to the formation of low melting point eutectics and feldspars [Huffman et al., 1981; 1990]. Aras [2004] investigated illite/sericite-rich mixtures. The author observed that high potassium contents were related to large amounts of melt phases, which inhibited the formation of cristobalite. Srinivasachar and co-workers [1990a] did not find any volatilizing potassium species from included and excluded illite particles during combustion. The main product from illite in coal is potassium aluminosilicate glass [Carroll et al., 2005].

2.3.1.4 Montmorillonite

Montmorillonite is a monoclinic clay with the general formula of $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_8\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ [Klein, 2002; Marinov et al., 1992; Ward, 2002]. The clay loses adsorbed water from 50 °C to 150 °C. Lattice water is removed from 600 °C to 730 °C [O’Gorman and Walker, 1973]. The lattice structure is destroyed from 800 °C to 1100 °C [Grim and Kulbicki, 1961; Vassileva and Vassilev, 2005, 2006]. Heat transformations of montmorillonite are similar to the transformations of illite from 1000 °C to 1300 °C [O’Gorman and Walker, 1973]. In this temperature range the clay forms silicate glasses and some crystallisation occurs [Qui et al., 1999]. The crystallisation products include quartz, cristobalite, corundum, cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$), enstatite (MgSiO_3), mullite, spinel and Ca and Ca-Mg silicates [Grim and Kulbicki, 1961; O’Gorman and Walker, 1973; Vassileva and Vassilev, 2005, 2006]. Mullite, cordierite and cristobalite are more abundant at the

higher temperatures in the range [O’Gorman and Walker, 1973]. Montmorillonite is included in slag and agglomerates as amorphous matter or glass phases [Marinov et al., 1992; Qui et al., 1999]. Montmorillonite is also known as a fluxing agent due to the formation of phases melting in the range of 1000 to 1300 °C [Vassileva and Vassilev, 2005].

2.3.2 Sulfides

2.3.2.1 Pyrite

Many researchers have investigated the transformation of pyrite in coal under both oxidizing and reducing conditions [Bool et al., 1995; Groves et al., 1987; Jensen and Austin, 1977; Marinov et al., 1992; Mason, 1992; McLennan et al., 2000a, 2000b; Ram et al., 1995; Srinivasachar and Boni, 1989; Srinivasachar et al., 1990b; Taneja and Jones, 1984; Ten Brink et al., 1996a]. Ash usually starts to melt at lower temperatures under reducing conditions than under oxidizing conditions [Huffman et al., 1981; McLennan et al., 2000b]. Wu and co-workers [2009] reported that the most important reason for differences in ash melting behaviours under oxidizing and reducing conditions is the different states of iron. Figure 2.5 is a schematic representation of the transformations of included and excluded pyrite under both oxidizing and reducing conditions. The environment determines the final product.

Excluded pyrite (pathway A) decomposes to pyrrhotite at relatively low temperatures (330 – 630 °C) (see Figure 2.5) [Bool et al., 1995; Groves et al., 1987; O’Gorman and Walker, 1973; Srinivasachar and Boni, 1989]. The sulfur released during decomposition can be oxidized to SO_x or reduced to H₂S, depending on the atmosphere [Jensen and Austin, 1977]. Oxygen diffusion causes the oxidation of the pyrrhotite from the surface inward and results in a FeO shell with a FeS core [Bool et al., 1995; McLennan et al., 2000a, 2000b; Srinivasachar and Boni, 1989]. The FeO-FeS eutectic has a melting point of 920 °C to 940 °C [Laursen and Frandsen, 1998; Marinov et al., 1992]. Further oxidation forms a FeO melt. However, under reducing conditions the FeO-FeS tends to persist [McLennan et al., 2000a, 2000b]. The FeO melt crystallizes to magnetite (Fe₃O₄) when sufficient oxygen is available and changes to hematite (Fe₂O₃) after further oxidation [Bool et al., 1995; Jensen and Austin, 1977; McLennan et al., 2000a, 2000b; Srinivasachar and Boni, 1989]. Oxidation of the pyrrhotite does not go to completion under reducing conditions [Bool et al., 1995; McLennan et al., 2000a, 2000b]. Wustite and pyrrhotite phases are the

dominant species under reducing conditions and magnetite is dominant under oxidizing conditions [Marinov et al., 1992; McLennan et al., 2000a, 2000b]. No hematite forms under reducing conditions [McLennan et al., 2000a, 2000b]. The existence of the FeO-FeS eutectic and wustite were observed in combustion studies under reducing conditions, steam-air gasification and steam-oxygen gasification [Marinov et al., 1992; Mason, 1992; McLennan et al., 2000a].

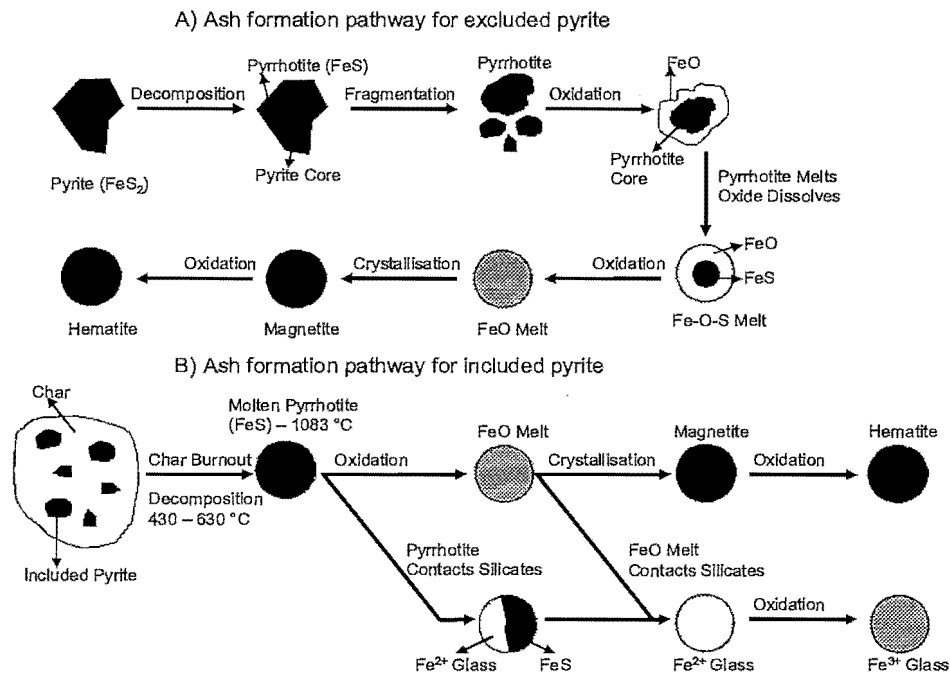


Figure 2.5 Ash formation pathways of excluded (A) and included (B) pyrite in coal. Adapted from Bool et al. [1995], McLennan et al. [2000a, 2000b] and Srinivasachar and Boni [1989]

Included pyrite (pathway B) behaves similarly to excluded pyrite, except when the included pyrite comes into contact with aluminosilicates (see Figure 2.5) [Bool et al., 1995; Mason, 1992; McLennan et al., 2000a, 2000b]. The carbonaceous char forms a locally reducing environment during both oxidizing and reducing conditions. Oxidation of the pyrrhotite will only proceed once the char structure is completely consumed [Bool et al., 1995; Srinivasachar and Boni, 1989]. Therefore, char consumption delays oxidation [McLennan et al., 2000a]. After complete char combustion or gasification, the transformation of pyrrhotite will proceed as described

for excluded pyrite with consideration of the gas environment (oxidizing or reducing). However, the lower branch of pathway B is followed when the pyrite decomposition products encounter quartz or clays [Bool et al., 1995; McLennan et al., 2000a, 2000b; Ten Brink et al., 1996a]. Both pyrrhotite and the FeO melt oxidation product can react with silicates and aluminosilicates [McLennan et al., 2000a, Ten Brink et al., 1996a]. Iron-containing glass does not form directly, due to the low solubility of pyrrhotite [McLennan et al., 2000a, Ten Brink et al., 1996a]. A two-phase particle consisting of clearly separated FeS and Fe-glass forms first and coalesces with the aluminosilicate glass after oxidation of FeS to FeO [Groves et al., 1987; Mason, 1992; McLennan et al., 2000a]. The iron in the glass is most probably Fe^{2+} , due to the locally reducing environment created by the char [McLennan et al., 2000a; Ten Brink et al., 1996a]. Fe^{2+} in the glass may oxidize to Fe^{3+} in the presence of sufficient oxygen after complete consumption of the char; however, under a reducing atmosphere the Fe^{2+} will persist [Bool et al., 1995; McLennan et al., 2000a, 2000b; Ram et al., 1995]. The iron aluminosilicates formed from included pyrite and other silicates and aluminosilicates partially melt at significantly lower temperatures under reducing conditions compared to oxidizing conditions [Bool et al., 1995; McLennan et al., 2000b; Ram et al., 1995]. McLennan and co-workers [2000c] predicted that sticky particles or melt phases from pyrite under reducing conditions may occur at temperatures as low as 1000 °C compared to 1400 °C for oxidizing conditions.

Reports indicate that pyrite/pyrrhotite can be reduced to elemental iron and sulfur during gasification. Jensen and Austin [1977] studied the reactions of iron in coal under steam gasification conditions in a fluidized-bed reactor. The recovered iron species in the solid reactor product was magnetic in nature, suggesting the formation of either elemental iron or magnetite. The species was identified as elemental iron through metallographic analysis and microscopy. The magnetism of the slag was greatly reduced under specific conditions (CO_2 concentration in reactor greater than 10% or continued water feed beyond maximum H_2S production), indicating transformation to either FeO or hematite. Jensen and Austin [1977] deduced that hydrogen was most probably responsible for the reduction of iron, because H_2S was the only significant sulfur-containing gaseous product. The reaction is represented by Equation 2.4. Other possible reactions are represented by Equations 2.5 and 2.6. Any CS or CS_2 formed would immediately react with H_2 or CO to form H_2S or COS

[Jensen and Austin, 1977]. These authors only found small quantities of COS in the product gas.



2.3.3 Carbonates

2.3.3.1 Calcite

Calcite or limestone (CaCO_3) is one of the major calcium-containing minerals in coal. It is also an important additive for sulfur capturing and a fluxing agent [Bryant et al., 1998; Jung and Schobert, 1992; Li et al., 2006]. A study by McLennan and co-workers [2000a] indicated that the decomposition and transformation of excluded calcite is independent of the atmosphere in the system. Calcite generally decomposes in the temperature range of 600 °C to 950 °C [Liu et al., 2007a; Nankervis and Furlong, 1980; O’Gorman and Walker, 1973; Reifenstein et al., 1999; Vassileva and Vassilev, 2006]. Reifenstein and co-workers [1999] reported that calcite heated to 800 °C transforms to other polymorphs and partially decomposes to lime (CaO). Metastable polymorphs of calcite (trigonal) include aragonite (orthorhombic) and vaterite [Attar and Dupuis, 1979; Reifenstein et al., 1999]. The decomposition of calcite is represented by Equation 2.7 [Attar and Dupuis, 1979; Katalambula et al., 2001; Kuramoto et al., 2004; Li et al., 2006]. The final products from the decomposition of calcite are lime and CO_2 [Vassileva and Vassilev, 2005, 2006]. Lime has a melting point in the vicinity of 2570 °C [Liu et al., 2007a].



Limestone is a sulfur-capturing additive used during both combustion and gasification [Katalambula et al., 2001; Li et al., 2006]. The reactions of CaO with gaseous sulfur compounds yield different products under oxidizing and reducing conditions. The major gaseous sulfur species are H_2S (reducing conditions) and SO_2 (oxidizing conditions) [Attar and Dupuis, 1979; Katalambula et al., 2001]. The reaction of lime with gaseous sulfur species yields CaS under reducing conditions, and CaSO_4 under oxidizing conditions [Huffman et al., 1981]. The reactions are

represented by Equations 2.8 and 2.9, respectively [Attar and Dupuis, 1979; Huffman et al., 1990; Katalambula et al., 2001; Li et al., 2006].



Lime is very reactive and readily reacts with a wide range of species. Reaction with water yields portlandite (Ca(OH)_2) [Kuramoto et al., 2004; Reifenstein et al., 1999; Ward, 2002]. The reactions of lime with clays and quartz have been described earlier (see Section 2.3.1), and the products are Ca-based aluminosilicates [Van Dyk et al., 2009b]. Anorthite and gehlenite (m.p. 1590 °C) are the most common species formed [Ishom et al., 2004; Mayoral et al., 2001; Mitchell and Gluskoter, 1976; Nankervis and Furlong, 1980; Van Dyk et al., 2009b]. Matjie and co-workers [2007] stated that the reactions of clays with calcite and pyrite yield liquid species in the temperature range of 600 °C to 760 °C. Therefore, calcite in a system can be a major contributor to the formation of low melting point species.

2.3.3.2 Siderite

Reports show that siderite is one of the most common forms of iron in southern hemisphere coals, whereas pyrite and marcasite are most common in northern hemisphere coals [Laursen and Frandsen, 1998]. McLennan and co-workers [2000a, 2000b] conducted an extensive study on the transformation of siderite when heated under reducing and oxidizing combustion conditions. Figure 2.6 was adapted from their work. Wu and co-workers [2009] reported that the most important reason for differences in ash melting behaviours under oxidizing and reducing conditions is the different states of iron.

Excluded siderite decomposes endothermically to wustite (FeO) and CO_2 at 400 °C to 800 °C (see Figure 2.6) [Bailey et al., 1998; Liu et al., 2007a; McLennan et al., 2000a; O’Gorman and Walker, 1973; Ten Brink et al., 1996b; Vassileva and Vassilev, 2005, 2006]. Wustite has a melting point of 1370 °C to 1380 °C [Bailey et al., 1998; McLennan et al., 2000a]. Under oxidizing conditions, wustite oxidizes to magnetite and then hematite [Liu et al., 2007a; McLennan et al., 2000a, 2000b, 2000c; O’Gorman and Walker, 1973; Ram et al., 1995; Sheng and Li, 2008]. Magnetite is more stable at temperatures greater than 1388 °C than hematite [Ram et al., 1995]. It

is the dominant species occurring under oxidizing conditions [McLennan et al., 2000a, 2000b]. Magnetite melts at 1590 °C and hematite at 1565 °C [Bailey et al., 1998; Liu et al., 2007a]. Wustite persists under reducing conditions [McLennan et al., 2000a, 2000b, 2000c]. Therefore, reducing conditions result in the onset of melting at lower temperatures [Bailey et al., 1998]. Bailey and co-workers [1998] reported that siderite will most likely not form sticky or molten particles at 1600 °C under combustion conditions, unless $\text{MgO} < 5 \text{ wt\%}$, $\text{CaO} < 37.5 \text{ wt\%}$ and $(\text{MnO} + \text{FeO}_n) > 60 \text{ wt\%}$.

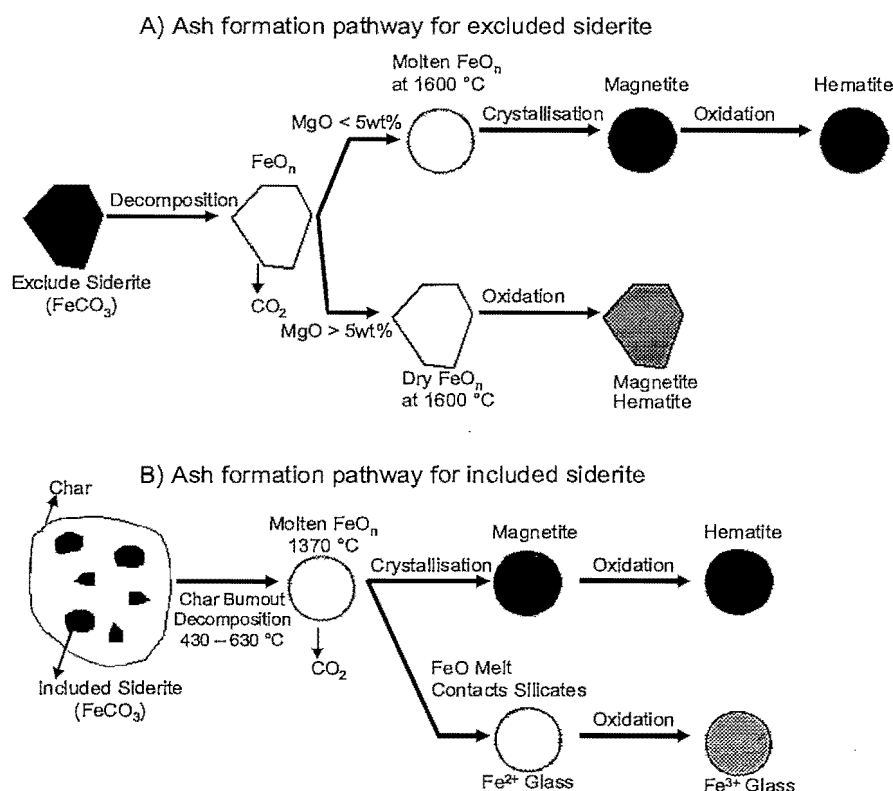


Figure 2.6 Ash formation pathways of excluded (A) and included (B) siderite in coal. Adapted from McLennan et al. [2000a, 2000b]

Included siderite reacts similarly to excluded siderite, except in the presence of silicates and aluminosilicates [McLennan et al., 2000a; Zhao et al., 2006]. The char surrounding included siderite provides a reducing atmosphere [McLennan et al., 2000a, 2000b; Ten Brink et al., 1996a]. Oxidation of FeO can only begin after complete char consumption. Thus, as for included pyrrhotite, oxidation will be delayed [McLennan et al., 2000a]. Siderite decomposes directly to FeO, unlike the

decomposition of pyrite, with iron in a Fe^{2+} state [McLennan et al., 2000a; Ram et al., 1995]. FeO can immediately coalesce with the silicate and aluminosilicates species to form iron aluminosilicate glasses [McLennan et al., 2000a; Sheng and Li, 2008; Ten Brink et al., 1996b]. The fast incorporation of FeO into glass yields sufficient residence time for the oxidation of Fe^{2+} species to Fe^{3+} [McLennan et al., 2000a; Ram et al., 1995]. The Fe^{2+} aluminosilicate glass will persist under reducing conditions [McLennan et al., 2000a]. McLennan and co-workers [2000c] predicted that sticky particles or melt phases from siderite under reducing conditions may occur at temperatures as low as 1100 °C, compared to 1400 °C for oxidizing conditions.

2.3.3.3 Dolomite and Ankerite

Dolomite ($\text{CaMg}(\text{CO}_3)_2$) and ankerite ($\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$) are carbonate minerals with similar structures [Bailey et al., 1998; Liu et al., 2007a]. Dolomite consists of 40 – 50% magnesium normalised as MgO, and the balance consists of CaO [Liu et al., 2007a]. Ankerite is an isotype of dolomite with up to 60% of the magnesium substituted by iron in the dolomite lattice [Bailey et al., 1998; Liu et al., 2007]. The decomposition of dolomite proceeds as for a mixture of two separate carbonates and is therefore a two-stage process [O’Gorman and Walker, 1973; Salmang, 1961; Vassileva and Vassilev, 2006]. MgCO_3 decomposes to MgO at 700 °C to 800 °C [Salmang, 1961]. CaCO_3 decomposes to CaO at 800 °C to 900 °C [Reifenstein et al., 1999; Salmang, 1961]. Decomposition temperatures of 400 °C to 900 °C have been reported for dolomite and 560 °C to 800 °C for ankerite [Vassileva and Vassilev, 2006]. As with all carbonates, CO_2 is released during decomposition [Vassileva and Vassilev, 2006]. Periclase (MgO) has a melting point of 2800 °C and lime has a melting point of 2570 °C [Liu et al., 2007a].

MgO, CaO and FeO contribute to the formation of Ca/Mg/Fe-containing aluminosilicates and act as fluxing agents [Jung and Schobert, 1992; Matjie et al., 2007]. The products from the reactions of dolomite and ankerite with clays are similar to the products from the reactions of calcite and siderite with clays. A major compound in ash produced from ankerite is magnesioferrite (MgFe_2O_4) [Huffman et al., 1981; Ram et al., 1995; Taneja and Jones, 1984]. MgO and CaO can also react with amorphous silica to produce diopside ($\text{CaMgSi}_2\text{O}_6$) [Matjie et al., 2007].

2.3.4 Other Common Minerals

2.3.4.1 Gypsum

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is another major source of calcium in coal [Mitchell and Gluskoter, 1976]. Gypsum can occur in raw coal, but the dehydration products can also be formed via other routes during coal consumption, e.g. anhydrite (CaSO_4) is formed by the reaction of CaO with SO_2 (see Equation 2.9) [Li et al., 2006 Vassileva and Vassilev, 2005, 2006]. The reactions and transformations of gypsum are shown in Figure 2.7.

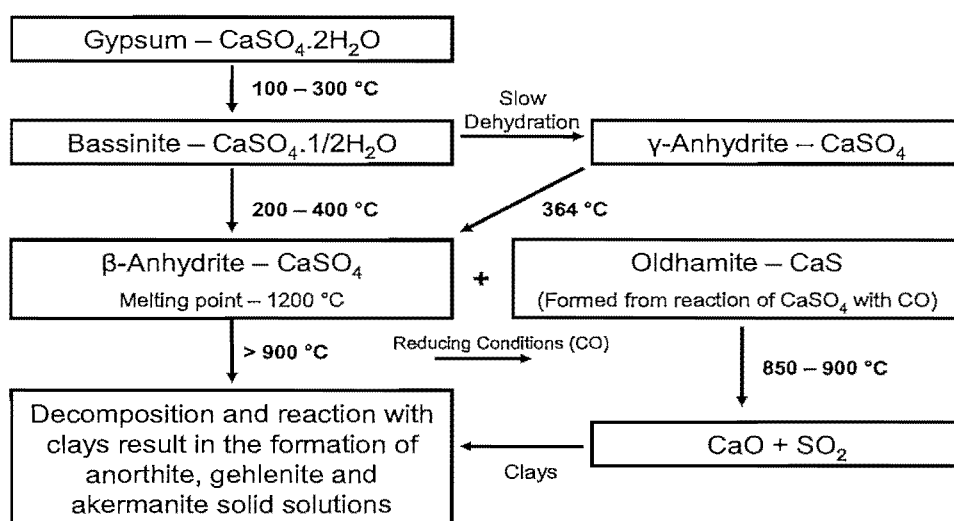


Figure 2.7 The transformations and reactions of gypsum. Compiled from information by Klein [2002], Mitchell and Gluskoter [1976], Nankervis and Furlong [1980], O’Gorman and Walker [1973] and Vassileva and Vassilev [2005, 2006]

The dehydration of gypsum occurs in two stages (see Figure 2.7) [O’Gorman and Walker, 1973]. In the first stage (100 – 300 °C) gypsum loses part of its water molecules to form bassinite [O’Gorman and Walker, 1973; Vassileva and Vassilev, 2005, 2006]. The water associated with bassinite is lost at 200 °C to 400 °C, and anhydrite is formed [Mitchell and Gluskoter, 1976; Nankervis and Furlong, 1980; Vassileva and Vassilev, 2005, 2006]. If the dehydration occurs slowly, bassinite is first transformed to γ -anhydrite and then to β -anhydrite above 364 °C [Klein, 2002; O’Gorman and Walker, 1973]. Anhydrite has a melting point of 1200 °C [Nankervis and Furlong, 1980; Vassileva and Vassilev, 2005]. Anhydrite decomposes to lime and

SO_x above 900 °C and can react with clay minerals [Vassileva and Vassilev, 2005, 2006]. Anorthite, gehlenite and akermanite solid solutions are formed from the reactions [Mitchell and Gluskoter, 1976; Nankervis and Furlong, 1980]. The initial decomposition temperature of anhydrite is lowered to 780 °C in a reducing atmosphere [O’Gorman and Walker, 1973]. O’Gorman and Walker [1973] determined that both lime and CaS occur in reducing conditions, because the decomposition of anhydrite in the presence of CO is a two-stage process (see Equations 2.10 and 2.11).



Anhydrite can react with oldhamite (CaS) (under reducing conditions) at 850 °C to 900 °C to produce lime and SO₂ (see Figure 2.7) [Vassileva and Vassilev, 2005]. Lime reacts with clays to form Ca-containing and Ca-Mg-containing aluminosilicates, as discussed for calcite (see Section 2.3.3.1).

Anhydrite has been identified as a contributor to the formation of low melting point eutectics. Steenari and co-workers [1998] investigated sintering and deposition in fluidized-bed combustion. They concluded that a mixture of CaSO₄ and CaS was responsible for neck-forming between particles when using specific coal sources. The presence of alkali metals lowered the melting temperature further. A eutectic of CaSO₄ and Na₂SO₄ melts at 917 °C, a NaCl-CaSO₄ eutectic at 721 °C and a K₂SO₄-CaSO₄ eutectic at 866 °C [Iribarne et al., 2003; Manzoori and Agarwal, 1993]. In another fluidized-bed combustion study, Ishom and co-workers [2004] observed that CaSO₄ derived from CaO was responsible for the formation of agglomerates.

2.3.4.2 *Titanium Dioxide*

Titanium in coal occurs as TiO₂ polymorphs or incorporated into the aluminosilicate structure of clay minerals, especially kaolinite [Ward et al., 1999; Yu et al., 2007]. There are three common polymorphs of TiO₂, i.e. rutile, anatase and brookite [Heald and Weiss, 1972; Riyas and Das, 2004]. Rutile is the stable form, and anatase and brookite are metastable [Riyas and Das, 2004]. Only anatase and rutile are commonly found in coal [Liu et al., 2005; Matjie et al., 2007; Sakurovs et al. 2007; Ward, 1989, 2002; Yu et al., 2007].

Anatase and brookite are irreversibly transformed to rutile upon heating [Riyas and Das, 2004]. The transformation of anatase to rutile occurs between 600 °C and 1100 °C, depending on the impurities present [Heald and Weiss, 1972]. Grigore and co-workers [2008] stated that anatase transforms to brookite at 800 °C and to rutile at 1040 °C. Pure anatase transforms to rutile at 900 °C to 1000 °C [Riyas and Das, 2004; Salmang, 1962]. The presence of Cr^{3+} , Cu^{2+} , Fe^{2+} , hematite and reducing conditions lower the transformation temperature [Heald and Weiss, 1972; Riyas and Das, 2004]. Rutile and anatase often contain iron as an impurity [Zhao et al., 2006]. Anions such as sulfates and phosphates raise the temperature and retard the transformation process [Heald and Weiss, 1972; Riyas and Das, 2004]. The rate of transformation is also dependent on the time, temperature and particle size [Riyas and Das, 2004].

TiO_2 in coal ash is characterised as an acidic component [Van Dyk, 2006]. The existence of TiO_2 in coal ash tends to increase the ash fusion temperature [Van Dyk, 2006; Vassileva and Vassilev, 2006]. A study by Zhao and co-workers [2006] on iron species in Chinese coal ash identified ilmenite (FeTiO_3) and ulvospinel (TiFe_2O_4) as titanium-containing iron species in the fly ash. O’Gorman and Walker [1973] detected rutile as a distinct phase in the ash of Pennsylvania anthracite up to 1200 °C.

2.3.4.3 *Apatite*

Apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$) is one of the major sources of phosphorus in coal [Sakurovs et al., 2007]. Other phosphorus-containing minerals in coal include goyazite and gorceixite [Matjie et al., 2007; Sakurovs et al., 2007]. Phosphorus is also associated with kaolinite and other clays [López and Ward, 2007; Yu et al., 2007]. Reifenstein and co-workers [1999] observed that apatite is relatively inert and remains unchanged when heated to 1600 °C. The phosphorus included in clays is incorporated in glass at high temperatures. Matjie and co-workers [2007] detected apatite and gorceixite in gasification feed coal. However, analyses of the ash and clinkers from the reactor suggested that all the phosphorus was incorporated in amorphous aluminosilicate glass phases or Al-phosphates.

2.4 Trace Elements in Coal

Most naturally occurring elements are found in coal, with the majority only in trace quantities [Clarke, 1993; Swaine, 1994]. The definition of trace elements in coal differs among research groups. Most researchers define trace elements as having a concentration below 1000 ppm (0.1%) by weight in dry coal [Gibbs et al., 2004; Liu et al., 2005b; Reed et al., 2001; Wagner and Hlatshwayo, 2005; Wang et al., 2007b; Yiwei et al., 2007]. However, some researchers define trace elements in coal as species with concentrations below 100 ppm (0.01%) by weight in dry coal [Bool and Helble, 1995; Xu et al., 2003; Yi et al., 2008]. For this study the concentration of trace elements in coal was used as below 1000 ppm by weight, which seems to be the consensus.

Elements are emitted into the environment from both natural and anthropogenic sources [Galbreath and Zygarlicke, 2004; Swaine, 2000]. Natural sources include volcanoes, weathering of rocks, sedimentation, vegetation, and forest fires [Nelson, 2007; Swaine, 1994, 2000]. Anthropogenic sources include mining, combustion of coal and biofuels, smelting, agriculture, waste disposal and industrial operations [Swaine, 2000]. Naturally occurring elements were included in coal in trace quantities during the coalification process. These elements and their compounds are liberated from the carbon matrix during utilisation of coal. The major interest in trace elements can be ascribed to their potential harmful effects on the environment and health of animals and humans [Galbreath and Zygarlicke, 2004; Swaine, 2000]. A few examples include mercury, selenium, chromium, vanadium, and nickel.

Mercury can react with other species in the atmosphere to form toxic substances, such as methyl mercury [Shah et al., 2008]. Mercury is infamous for bioaccumulation in the environment, especially in fish. People are advised not to eat the fish from certain lakes around the world, because they contain high concentrations of mercury [Zhang et al., 2007c]. Mercury has been linked with neurological defects, and holds considerable risk to the development of unborn foetuses [Zahir et al., 2005]. Selenium is also enriched in fish found in some of the lakes in Australia. Nobbs and co-workers [1997] reported selenium values in fish from Lake Macquarie at 12 times higher than the recommended level for human consumption. The mode of occurrence of chromium species is of utmost importance [Shah et al., 2009]. Trivalent chromium

(Cr³⁺) is essential for metabolic processes, but hexavalent chromium (Cr⁶⁺) is a toxic carcinogen [Narukawa et al., 2007]. Vanadium may cause cardiovascular disease, bronchitis and lung carcinoma, and nickel has been established as a human carcinogen [Lee and Wu, 2002; Profumo et al., 2003].

The amounts of trace elements in coal appear to be small, but the accumulated amount released into the environment is significant. Enormous amounts of coal are consumed across the world every year. China's coal output in 2005 was close to 2.19 billion tons and 2.72 billion tons in 2008 [Dai et al., 2009; Song et al., 2007]. Yudovich and Ketris [2005] reported that the United States of America emits 40 tons of mercury (Hg) into the atmosphere in a year, and China even more. According to Nelson [2007] the USA releases 48 tons of mercury annually from 1300 coal-fired power plants. Government organisations have realized the need to identify and regulate hazardous pollutants [Clarke, 1993]. Many countries have implemented emission standards and regulations to limit the trace elements emitted from anthropogenic sources. One such legislation in the USA is the Clean Air Amendment Act (CAAA) of 1990 [Cooper and Alley, 2002; Linak and Wendt, 1994]. The CAAA monitors and/or regulates the emission of 189 organic and metallic hazardous air pollutants (HAPs) [Cooper and Alley, 2002; Bool and Helble, 1995; Galbreath and Zygarlicke, 2004]. Of these 189 species, 16 are elements occurring in coal [Galbreath et al., 2000]. These include antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), chlorine (Cl), cobalt (Co), fluorine (F), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se), thallium (Th) and uranium (U) [Galbreath et al., 2000; Linak and Wendt, 1994; Wagner and Hlatshwayo, 2005]. Australia has included arsenic, mercury, lead, hexavalent chromium, cadmium, nickel, and compounds of these elements in their "Air Toxics" program [Shah et al., 2008, 2009]. The regulation and monitoring of hazardous species may become even more stringent in the future [Hower et al., 2008].

Swaine [1994] classified As, Cd, Cr, F, Hg, Ni, Pb and Se as elements of "prime environmental interest". Several other elements are also considered to have interest to the environment [Swaine, 1994]. During combustion and gasification processes these species can exit the reactor in one of three different routes, i.e. in the vapour phase (e.g. Hg and elemental Se), as part of the fly ash, or included in the coarse ash removed at the bottom of the reactor [Galbreath et al., 2000; Galbreath and Zygarlicke, 2004; Klein et al., 1975; Shah et al., 2009]. Species in the vapour phase

and fly ash enter the environment and aquatic systems through deposition [Klein et al., 1975]. Toxic species can also be leached from the ash storage dams, or finer particles can be dispersed by the wind [Haynes, 2009].

Atmospheric fine particulates originate from similar natural and anthropogenic sources as element emissions [Nelson, 2007]. During coal consumption, volatile trace element species can condense on the surface of existing ash particles or absorb onto minerals, especially clays [Galbreath et al., 2000; Quann et al., 1982]. Vapour deposition models indicate that elemental concentrations of many species are inversely proportional to particle diameter (d_p) [Galbreath et al., 2000]. Elemental concentrations to particle size distribution trends characterized by both $1/d_p$ and $1/d_p^2$ dependences are indications of vapour deposition and film condensation reactions, respectively [Galbreath et al., 2000; Linak and Wendt, 1994].

Many countries have also implemented emission standards for particulate matter smaller than $10\text{ }\mu\text{m}$ (PM_{10}) and $2.5\text{ }\mu\text{m}$ ($\text{PM}_{2.5}$), since they are prone to inhalation [Galbreath et al., 2000; Nelson, 2007; Ninomiya et al., 2009; Ratafia-Brown, 1994; Yi et al., 2008]. Studies have shown that exposure to fine particles ($1 - 2\text{ }\mu\text{m}$) has short-term and long-term health risks, and increases the risk for lung cancer and cardiopulmonary mortality [Nelson, 2007]. $\text{PM}_{2.5}$ can readily penetrate the lungs, and any toxic substances included in the particulates are subsequently introduced to the body [Wang et al., 2005]. Particulates released from coal-firing sources are enriched with trace elements, including toxic elements such as As, Sb, Se, Ni, Zn, Pb and Cr [Galbreath et al., 2000; Quann et al., 1982]. Due to their carcinogenic and toxic nature, the inhalation of As, Cr and Ni pose the greatest health risks [Galbreath et al., 2000; Galbreath and Zygarlicke, 2004]. Lee and co-workers [2003] measured the chemical composition of $\text{PM}_{2.5}$ in Toronto, Canada, for a year to identify the contribution of different emission sources to the total $\text{PM}_{2.5}$ levels. Many of the sources emitting particulate matter were identified based on their clear trace element signatures. They found that the trace elements occurring in particulate matter from secondary coal sources included As, Cr, Ni and Se. Linak and co-workers [2007] also reported trace element enrichment in coal fly ash particles. Results indicated that ultrafine particles (diameters less than $0.5\text{ }\mu\text{m}$) were enriched with chromium and thiophenic sulfur.

Apart from the environmental and health concerns associated with trace elements, interest in certain elements can also be ascribed to their potential economic

value. These elements can be concentrated in the ash from coal utilisation. One example is germanium. Font et al. [2005a] reported that the price for a kilogram of germanium at €1000 justified further research into metal extraction from ash. Both the positive and negative attributes of trace elements necessitate the determination of the concentrations and mode of occurrence of these elements to evaluate the value and risks associated with coal utilisation. Swaine [2000, 1994] stressed the importance of evaluating the circumstances and concentration of trace elements instead of labelling their toxicity per se. The mode of occurrence of these trace elements and their reactions with other species are important factors to evaluate the health risks related with emission [Bool and Helble, 1995; Helble, 1994; Meij and Te Winkel, [2009]; Shah et al., 2008, 2009].

2.5 Classification of Trace Elements in Coal

Trace elements are classified in various ways based on the purpose of the information. Swaine [1994] grouped trace elements according to their environmental importance. Swaine [1994] reported two different trace elements groups. The elements As, Cd, Cr, F, Hg, Ni, Pb, and Se were included in a group labelled as elements with “prime environmental interest”; and the elements B, Ba, Be, Cl, Co, Co, Mn, Mo, Sb, Sn, Th, Tl, U, V, and W were grouped together as elements with “environmental interest”.

Xu and co-workers [2003] reviewed the concentrations of different elements in more than 1500 coal samples and grouped different trace elements together according to abundance. The researchers stated that concentrations varied greatly between different coal samples, but four main groups could be identified. The four concentration groups identified were: >50 ppm (Ba, B, F, Mn, P, Sr, Ti, Zn); 10 to 50 ppm (As, Br, Ce, Cl, Cr, Cu, Li, Ni, Pb, Rb, V, Zr); 1 to 10 ppm (Be, Cd, Co, Cs, Ga, Ge, I, La, Mo, Nb, Sb, Sc, Se, Th, Tl, U); and < 1 ppm (Ag, Hg, Ta).

Yiwei and co-workers [2007] grouped 44 trace elements into four groups by considering transformation behaviours, and chemical and thermal features under pyrolysis conditions. They grouped Li and Be as “light elements”; B, P, As and Se as “non-metal elements”; 24 were grouped together as “heavy metal elements”; and 14 as

“rare earth elements”. The “rare earth elements” demonstrated the lowest release rates from the coal during different pyrolysis temperatures.

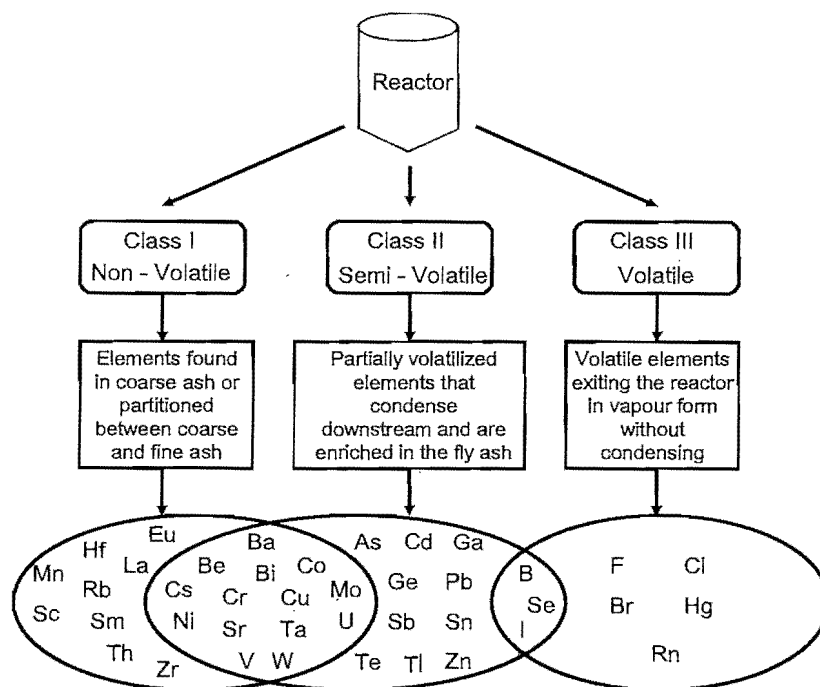


Figure 2.8 Classification of trace elements according to their volatilities. Adapted from Bunt and Waanders [2008], Clarke [1993] and Ratafia-Brown [1994]

The most common classification system is based on the volatility of trace elements during combustion and gasification [Clarke, 1993; Galbreath et al., 2000]. The elements are divided into three different groups according to their partitioning behaviour [Bunt and Waanders, 2008; Clarke, 1993; Ratafia-Brown, 1994; Sekine et al., 2008]. Figure 2.8 is a schematic representation of the three groups. Group 1 consists of elements that are found in the coarse ash, or are partitioned between the coarse ash and the fine ash. The elements in group 2 tend to partition between the fly ash and the gaseous phase. Elements that become volatile may condense again downstream and are enriched on the finer ash particles. The elements in group 3 are the most volatile elements and generally exit the reactor in the vapour phase, without condensing onto ash particles.

The classification of elements into the three groups is not precise. Many elements demonstrate volatility characteristics that can be classified into more than one group under different operating conditions [Bunt and Waanders, 2008; Clarke, 1993; Galbreath et al., 2000]. Figure 2.8 also shows the overlapping of groups and elements that generally fall into these categories. The volatility of the elements is affected by temperature, coal type, atmosphere in the reactor, interactions with ash, affinities, and modes of occurrence [Galbreath et al., 2000; Sekine et al., 2008; Wang and Tomita, 2003].

2.6 Methods to Analyze Trace Elements in Coal

The methods used to analyze trace elements in coal can be divided into two main groups, i.e. methods to determine elemental concentrations, and methods to determine trace element speciation. The analysis of trace elements requires sensitive methods and, in most cases, tedious sample preparation, such as digestion, to remove all organic matter. Due to instrument limitations, it is improbable to use only one technique to analyze all the trace elements in coal [Wagner and Hlatswayo, 2005]. Therefore, the use of a combination of techniques to analyze the different trace elements in a single source is commonly found in literature. Huggins [2002] published an overview of the methods used to analyze inorganic constituents in coal. The paper contains more techniques and variations of techniques than discussed in this section, as well as in depth details regarding elemental analysis methods and methods to determine mode of occurrence. Only the most common methods are discussed below.

2.6.1 Methods to Determine Elemental Concentrations

2.6.1.1 Spectroscopic Methods

Inductively coupled plasma (ICP) – atomic emission spectroscopy (AES) and ICP – mass spectroscopy (MS) are the most widely used spectroscopic methods to determine element concentrations in coal [Bunt and Waanders, 2008; Liu et al., 2005b; Piispanen et al., 2009; Reed et al., 2001; Richaud et al., 2000b; Sekine et al., 2008; Wagner and Hlatswayo, 2005; Wang and Tomita, 2003]. ICP is a very powerful tool used to atomize the elements in an inert argon environment before entering a detector. The chemically inert atmosphere associated with the argon plasma ensures

an extended lifetime for the analytes [Skoog et al., 1996]. Other advantages include the assurance of low detection limits for most elements. Table 2.3 is a summary of some of the detection limits for ICP-AES, as presented in Skoog et al. [1996, 1998].

Table 2.3 ICP-AES detection limits for some elements as presented in Skoog et al. [1996, 1998]

Element	Detection Limit (ng/mL)	Element	Detection Limit (ng/mL)
Al	2	Mn	0.06
As	40	Mo	0.2
Ca	0.02	Na	0.2
Cd	2	Ni	0.4
Cr	0.3	Pb	2
Cu	0.1	Sn	30
Fe	0.3	V	0.2
Hg	1	Zn	2
Mg	0.05		

ICP has the disadvantage that solid samples cannot be analyzed directly. Digestion of solid samples is necessary to solubilise the species before analysis. The most common methods for digestion are acid digestion and microwave-assisted acid digestion [Richaud et al., 2000b; 2004]. However, digestion can adversely affect the coal sample, and therefore give inaccurate results. Some species are not quantitatively dissolved, and the use of sequential extraction can result in the dissolution of unwanted phases [Laban and Atkin, 1999; Wang et al., 2004]. One of the major disadvantages of acid digestion is interactions that can occur between the coal samples and the acid, especially when halogenated acids are used. Chlorine atoms from HCl cause the formation of polyatomic cations, e.g. $^{75}\text{AsCl}^+$, which interferes with ICP-MS analysis. The use of HF can result in the formation of insoluble fluorides, especially with Al and Mg [Wang et al., 2004]. Wang and co-workers [2004, 2006] attempted to develop a HF-free microwave digestion method using $\text{HNO}_3/\text{H}_2\text{O}_2$ or HNO_3 instead. The methods yielded good recoveries, but elevated temperatures and pressures were required to extensively decompose the organic matrix and clays. However, some minerals in coal are resistant to HNO_3 [Wang et al., 2004]. Richaud and co-workers

[2000b] compared different digestion techniques and reported various shortcomings for these methods. Richaud and co-workers [2000b] found that microwave digestion in HNO_3 gave accurate results for As, Be, Co, Cr, Cu, Mn, Mo, Ni and Pb when analyzed with ICP-MS; but all the digestion methods resulted in the loss of mercury from the coal samples [Richaud et al., 2000b; Wang et al., 2006]. Wagner and Hlatshwayo [2005] reported that microwave digestion appears to be the most common digestion technique currently in use, which is attributed to rapid dissolution, reduced contamination and enhanced safety of laboratory personal.

Several sample introduction methods have been developed to overcome the limitations of ICP and digestion methods. One such method allows the direct analysis of solid samples, i.e. laser ablation (LA)-ICP-MS. Laser ablation is a sample introduction technique that uses a high-intensity, focussed laser beam to vaporize the species in a few square micrometers [Booth et al., 1999; Piispanen et al., 2009; Skoog et al., 1998; Spears, 2004]. The vapours and particulate matter are swept into the ICP and detection follows with the mass spectrometer [Booth et al., 1999].

Advantages of this sample introduction technique include minimal sample preparation, and the analysis of small, specific areas [Piispanen et al., 2009; Skoog et al., 1998]. Mercury can also be determined with LA-ICP-MS and has a detection limit of parts per billion [Spears, 2004]. Laser ablation reduces the possible adverse effects that acid digestion may have on the samples, e.g. overestimation of the ^{75}As isotope due to the formation of $^{75}\text{AsCl}^+$ when using HCl as acid [Booth et al., 1999; Wang et al., 2004]. Booth and co-workers [1999] stated that disadvantages of the laser ablation sample introduction technique are mostly ascribed to calibration difficulties, especially when wet and dry aerosols are compared. It is necessary for the system to remove the same mass of the sample and carry it into the system at a constant efficiency for proper calibration. This is difficult when working with heterogeneous samples and samples with different matrices [Booth et al., 1999; Piispanen et al., 2009].

Sample preparation of powders for LA-ICP-MS is similar to the method used for X-ray fluorescence, i.e. a 35 mm pellet is pressed from the powders mixed with binder [Booth et al., 1999]. Spears [2004] compared two different methods for data acquisition from fly ash particles. He reported that the analysis of individual fly ash particles in a pressed pellet was not successful. The reasons included difficulties with identifying individual particles, and the necessity to use a narrower laser beam which

compromised the sensitivity to analyze key elements. The data acquisition method recommended by Spears [2004] is the analysis of “transects”. Particles are scattered onto a microscope slide and scanned along a traverse with the laser.

Other sample introduction or preparation methods have also been developed and coupled with ICP-AES or ICP-MS for specific applications. The hydride generation method (HG-ICP-AES) is used to introduce As, Sb, Sn, Se, Bi and Pb into the ICP atomizer as a gas [Bunt and Waanders, 2008; Sekine et al., 2008; Skoog et al., 1998]. These metals react with a sodium borohydride solution in a closed vessel to form the volatile hydride. Shah and co-workers [2008] used ion chromatography combined with ICP-MS (IC-ICP-MS) to determine the speciation of arsenic and selenium in coal combustion products. Fluorination-assisted electrothermal vaporization (FETV)-ICP-MS is a useful method to study trace rare earth elements such as Y, La, Ce, Pr, Nd and Sm in coal fly ash [Zhang et al., 2007b]. Wang and co-workers [2008] stated that flow injection (FI)-ICP-MS has a lower quantification limit than the common ICP-MS method and can be used to determine ultra-trace elements in coal.

Other spectroscopic methods, i.e. atomic absorption spectroscopy (AAS) and atomic fluorescence spectroscopy (AFS) are not commonly used to analyze the majority of trace elements in coal. Some researchers have used these methods, but they are mostly optimized for the analysis of specific elements, e.g. Song and co-workers [2007] analyzed Cd in coal with graphite furnace-AAS. Atomic absorption techniques commonly used in coal analysis are cold-vapour atomic absorption spectroscopy (CVAAS) and cold-vapour atomic fluorescence spectroscopy (CVAFS) [Bunt and Waanders, 2008; Ingle and Crouch, 1988; Shah et al., 2008; Wagner and Hlatswayo, 2005; Zhang et al., 2007c]. These methods apply solely to the determination of mercury. Mercury in the sample is initially converted to Hg^{2+} with acid treatment, followed by reduction to the metal (Hg) with SnCl_2 or NaBH_4 [Ingle and Crouch, 1988; Skoog et al., 1998]. The elemental mercury is swept into an absorption tube with an inert carrier gas. Absorption is measured at 253.7 nm (CVAAS), and the elemental mercury is excited by the 254 nm line from a Hg arc lamp in the fluorescence method (CVAFS) [Ingle and Crouch, 1988; Shah et al., 2008]. Automated instrumentation for the determination of mercury incorporates these methods [Skoog et al., 1998].

2.6.1.2 Instrumental Neutron Activation Analysis (INAA)

Instrumental neutron activation analysis (INAA or NAA) can be used to analyze or detect 69 different elements, and 40 elements can be determined simultaneously [Huggins, 2002; Skoog et al., 1998]. Quann and co-workers [1982] stated that INAA is the preferred method to analyze major, minor and trace elements in coal. The reasons they gave include high sensitivity for small samples, the method is less tedious than wet chemical techniques, and it minimizes sample handling and contamination. Ashing of coal prior to analysis is not required and the influence from matrix effects is less critical than with some of the other techniques [Huggins, 2002]. INAA is a non-destructive technique and easy to calibrate [Huggins, 2002; Skoog et al., 1998].

Samples are irradiated with high energy neutrons in a reactor, which in turn induces radioactivity in the sample components [Skoog et al., 1998]. The resulting γ -rays are counted with a high-resolution germanium detector and compared to a standard [Quann et al., 1982; Skoog et al., 1998]. Detection limits for most elements are in the range of 10^{-3} to $10 \mu\text{g}$ [Skoog et al., 1998]. Markowski and Filby [1985] reported that the INAA sensitivity for Sc is very high.

INAA requires the use of expensive and large equipment, therefore equipment is only available at certain institutions [Benson and Holm, 1985; Skoog et al., 1998; Song et al., 2007]. Special facilities are also needed for handling and disposal of the radioactive materials. Experimental times vary according to which radionuclides are used; in some instances analyses can be very time-consuming [Skoog et al., 1998]. In a study by Markowski and Filby [1985], brittle samples made it impossible to reanalyze for the short half-lived elements, i.e. Ti, V, Ca, Al and Mn. Bool and Helble [1995] reported that the large errors associated with measurements of Se in the coal samples they investigated were probably due to interference from other elements. Helble [1994] reported good accuracy and sensitivity for INAA as determined with standard reference materials. Standard deviations of up to $\pm 20\%$ are regarded as acceptable [Helble, 1994; Bool and Helble, 1995].

2.6.1.3 X-ray Methods

X-ray methods for determining elemental concentrations include X-ray fluorescence (XRF), particle/proton-induced X-ray emission (PIXE) and electron microprobe (EMP or EPMA).

X-ray fluorescence is widely used for the quantitative and semi-quantitative determination of elements with atomic numbers greater than 8, i.e. heavier than oxygen (O) [Skoog et al., 1998]. Solid, liquid or powder samples are bombarded with X-ray radiation. If the energy absorbed is sufficient to eject an inner shell electron, an electron from the outer shell falls into the unoccupied orbital to re-establish stability in the atom [Huggins, 2002]. X-rays with characteristic energies are emitted during the transition of the electron from the outer shell to the inner shell, and the X-rays can be measured with a fluorescence detector [Skoog et al., 1998]. Concentrations of the elements occurring in the sample are determined by the intensity of the X-rays. Intensities are compared with standards of known composition for quantitative measurements [Skoog et al., 1998].

The identity and concentrations of the elements found in the sample can be determined using either wavelengths or energies of emitted X-rays. Consequently, two main types of spectrometers exist: wavelength dispersive spectrometers (WD-XRF) and energy dispersive spectrometers (ED-XRF) [Skoog et al., 1998; Suarez-Fernandez et al., 2001]. In wavelength dispersive spectrometers, the wavelengths of individual X-rays are separated by a crystal with specific lattice spacing, based on Bragg diffraction (X-ray diffraction by crystalline solids) [Ingle and Crouch, 1988; Suarez-Fernandez et al., 2001]. The crystal then focuses the specific wavelengths on the detector. The entire spectrum can be collected by rotating the crystal [Skoog et al., 1998]. In energy dispersive spectrometers, the detector distinguishes between the energies of the incident X-rays as they are detected [Huggins, 2002; Skoog et al., 1998].

X-ray fluorescence is a non-destructive technique and sample preparation includes polishing of solid chunks, pelletizing, or casting fusion disks [Bartoňová et al., 2007; Koukouzas et al., 2007; Skoog et al., 1998]. A study by Demir and co-workers [2006] showed that correct sample preparation for XRF analysis is very important to eliminate large errors. Analyses can be performed on very small and very large samples within minutes [Demir et al., 2006; Skoog et al., 1998]. Scattering has a negative effect on the determination. Both coal and ash samples can be analyzed, but coal samples need more extensive calibration due to matrix effects [Suarez-Fernandez et al., 2001]. Concentrations in the parts per million (ppm) or sub-ppm range can be measured [Skoog et al., 1998]. Concentrations in the sub-ppm levels can be detected, depending on whether WD-XRF or ED-XRF is used. ED-XRF is cheaper than WD-XRF, but has a lower resolution and higher detection limit [Skoog et al., 1998;

Suarez-Fernandez et al., 2001]. WD-XRF has very high resolution and a very low detection limit due to the separation of the wavelengths before detection. A major limitation of the XRF system is that low X-ray yields of lighter elements make it difficult to quantify elements lighter than sodium ($Z = 11$). Wang and co-workers [2008] stated that many trace elements are not detectable with ED-XRF due to insufficient sensitivity. Booth and co-workers [1999] reported that elements cannot be determined with ED-XRF unless their concentrations are above 1 mg/kg.

Proton/particle-induced X-ray emission (PIXE) is a non-destructive nuclear method that can be used to analyze up to 75 elements simultaneously [Huggins, 2002; Nayak et al., 2004; Nayak and Vijayan, 2006]. PIXE can simultaneously detect all elements heavier than sodium and is well suited to small sample sizes [Huggins, 2002; Cerada et al., 1996]. Nayak and co-workers [2004, 2006] reported that this method is especially suited to analyze elements with atomic numbers in the middle mass region ($Z = 19$ to $Z = 31$). It has been used as a complementary technique to XRF, which has good sensitivity for high atomic number elements [Nayak et al., 2004; Nayak and Vijayan, 2006]. The sensitivity of PIXE is 1 to 10 ppm, but below ppm levels for several elements [Cerada et al., 1996; Nayak and Vijayan, 2006]. Matrix effects and interference from elements could lower the detection limit, especially with thick samples [Huggins, 2002; Nayak et al., 2004]. Chen and co-workers [1981] used PIXE to compare the elemental concentrations in vitrinite, exinite and inertinite of three different coals.

Electron probe microanalysis (EPMA) determines surface elemental compositions by using a narrowly focussed electron beam [Palmer et al., 1997; Skoog et al., 1998]. This method can be used to analyze micron-sized particles [Palmer et al., 1997; Spears, 2004]. The electron beam is produced by an accelerating anode and heated tungsten cathode [Skoog et al., 1998]. The X-rays emitted can be analyzed with either a wavelength or energy dispersive spectrometer, as in XRF [Skoog et al., 1998]. Nayak and Vijayan [2006] stated that EPMA can only be used to detect elements with a concentration higher than 200 ppm due to the interference of generated bremsstrahlung X-rays. Spears [2004] commented that EPMA is more suited to major and minor element analysis due to a detection limit of greater than 100 ppm. Palmer and co-workers [1997] also assumed a detection limit of 100 ppm for the analysis of trace elements in different pyrite morphologies in several coals.

Electron probe microanalysis combined with backscattered electron imaging can also be used to determine mode of occurrence or the association of different elements, similar to computer-controlled scanning electron microscopy [Hlatshwayo et al., 2009; Huggins, 2002; Van Dyk et al., 2009b].

2.6.2 Methods to Determine Mode of Occurrence

2.6.2.1 X-ray Absorption Fine Structure Spectroscopy (XAFS)

X-ray absorption fine structure spectroscopy (XAFS) is a non-destructive, direct technique used to investigate the local bonding, valence states and molecular structure of specific elements [Huggins et al., 1993; Shah et al., 2009; Shoji et al., 2002]. Samples are bombarded with synchrotron radiation with energies corresponding to the elements of interest, and absorption data are recorded [Huggins et al., 1993; Shah et al., 2008]. The k-edge XAFS spectra are collected with a germanium X-ray detector [Galbreath and Zygarlicke, 2004; Riley et al., 2007]. The XAFS spectra can be divided into two distinct regions for analysis, i.e. the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) [Galbreath et al., 2000; Galbreath and Zygarlicke, 2004; Huggins et al., 1993; Shah et al., 2007]. The EXAFS region is mathematically manipulated to create the radial structure function (RSF) [Galbreath et al., 2000; Galbreath and Zygarlicke, 2004]. The RSF spectrum describes the local structure around the elements of interest. Information obtained from the RSF spectrum include average interatomic distances, chemical identities, and number of atoms in a 5 Å radius from the absorbing elements of interest [Galbreath et al., 2000; Galbreath and Zygarlicke, 2004]. The XANES spectra are very difficult to interpret, but give information regarding coordination chemistry, band structure, molecular orbits, and multiple scattering [Shah et al., 2007]. The XANES spectra are spectral “fingerprints” pertaining to specific chemical species [Huggins et al., 1993; Shah et al., 2007].

XAFS has a detection limit as low as 0.2 ppm, but is only a semi-quantitative method [Linak et al., 2007; Shah et al., 2008; Wang et al., 2008]. It is not a routine analysis, because specialized equipment is needed [Galbreath et al., 2000; Galbreath and Zygarlicke, 2004; Huggins et al., 1993; Wang et al., 2008]. XAFS can be used to determine only the elements of interest, but other elements can cause interference [Huggins, 2002]. Galbreath and co-workers [2000, 2004] reported that they were unable to gather information from the k-edge EXAFS spectra for Cr and Ni due to the

interference of abundant vanadium and iron in the samples. Huggins and co-workers [1993] used vanadium and germanium filters in their study of chromium and arsenic in coal to reduce background noise.

2.6.2.2 Secondary Ion Mass Spectroscopy (SIMS)

Secondary ion mass spectrometry (SIMS) is a destructive surface analysis technique used to determine elemental composition [Skoog et al., 1998]. Shah and co-workers [2008] used secondary ion mass spectrometry (SIMS) to determine the speciation of selected trace elements in coal by calibrating the instrument with various reference compounds. The surface of the sample is bombarded with a stream of high-energy ions [Skoog et al., 1998]. Resulting ions, atoms and molecules are swept into a secondary-ion mass analyser. Extensive sample preparation may be needed for SIMS. Sample preparation used by Shah and co-workers [2008] included mounting on resin, polishing, gold coating and outgassing for at least 24 hours before analysis. SIMS is not as common and informative as XAFS to determine mode of occurrence. The sensitivity of SIMS can be 10^{-15} g or better [Skoog et al., 1998]. Shah and co-workers [2008] reported that the method was successful to qualitatively determine the speciation of chromium and arsenic, but not selenium.

2.7 Speciation and Partitioning of Trace Elements during Ash Formation

Condensation and volatilisation of trace elements are dependent on ash chemistry, e.g. the occurrence of chlorine compounds greatly enhances the volatility of some species [Bool and Helble, 1995; Cousins et al., 2008; Folgueras et al., 2007; Sekine et al., 2008]. Partitioning of trace elements is linked to the transformation and partitioning of common minerals in coal, since trace elements are closely associated with major and minor minerals, and ash particles scavenge vaporized species in the gas phase [Dai et al., 2009; Ratafia-Brown, 1994]. The speciation or mode of occurrence of the elements also affects their transformation and partitioning during coal consumption [Folgueras et al., 2007; Yiwei et al., 2008]. Several physicochemical interactions determine trace element partitioning. These include: condensation, absorption and adsorption, coalescence, chemical reactions among trace elements, gas constituents and ash, and vaporization [Ratafia-Brown, 1994]. Folgueras

and co-workers [2007] reported that a higher Si content in coal during combustion results in a higher retention of Cd and Pb in ash. They also found that Ca can retain As in ash and decrease the volatility of Se.

Chemical reactions may result in the formation of crystalline phases incorporating trace elements, or trace elements can be included in the glass phases. Font and co-workers [2005a] analyzed the fly ash and deposition on a gas cooling system of an IGCC power plant to determine crystalline phases that may occur. Some of the species they found include PbS, ZnS, NiAs, GeO_2 , GeS, GeS_2 , GeSnS_3 , $\text{Ni}_3(\text{As}_2\text{O}_7)\text{O}$, and VO_2 . Vanadium, Cr, Cu and Zn are commonly found in glass phases [Spears, 2004]. Arsenic vapour can react with calcium species in the ash above 500 °C to form calcium arsenates ($\text{Ca}_3(\text{AsO}_4)_2$) [Bool and Helble, 1995; Galbreath et al., 2000; Galbreath and Zygarlicke, 2004; Ratafia-Brown, 1994; Shoji et al., 2002; Sterling and Helble, 2003]. Bool and Helble [1995] reported that Zn and Cr associated with silicates and oxides reacted with other minerals in coal without prior vaporization during pulverized coal combustion. Many research groups have used thermodynamic calculations to predict the speciation of trace elements in ash [Bunt and Waanders, 2008, 2009a, 2009b; Díaz-Somoano et al., 2006; Lee and Wu, 2002; Linak and Wendt, 1994; Sandelin and Backman, 2001; Wang and Tomita, 2003; Yan et al., 2001b]. Theoretical equilibrium calculations performed by Sandelin and Backman [2001] for pulverized-coal-fired power stations predicted that As, Ni, Zn, and Pb are likely to dissolve in the molten ash.

Several authors reported that trace elements may form low melting point species in ash and contribute to sintering and agglomeration. Reed and co-workers [2001] studied the distribution of trace elements in the output stream of a pilot-scale gasifier. They observed that Pb was associated with the aluminosilicate fraction in the fly ash. The Pb-silicate products agglomerated and made the removal of Pb with filtration possible. Álvarez-Rodríguez and co-workers [2007] stated that PbS oxidized to PbO (m.p. 886 °C) can react with silicates to form PbSiO_3 (m.p. 764 °C) and Pb_2SiO_4 (m.p. 743 °C). Conn [1995] reported that even a 0.8% V_2O_5 content in the ash can cause other constituents to interact with the vanadium and form species with melting points of less than 900 °C, e.g. $\text{CaO}\cdot\text{V}_2\text{O}_5$ (m.p. 780 °C) and $\text{Fe}_2\text{O}_3\cdot\text{V}_2\text{O}_5$ (m.p. 860 °C). Ni and Ca can also form low melting eutectics with vanadium [Conn, 1995]. Germanium species in fly ash include GeS (m.p. 615 °C), GeS_2 (m.p. 530 °C) and GeO_2 (m.p. 1116 °C) [Font et al., 2005b]. Ni, V and P together with Al, Fe, K,

Na, S and Si have been associated with sintering or clinker bridges in waste incineration [Lin and Wey, 2004; Yan et al., 2003].

2.8 Sintering and Agglomeration

2.8.1 Definitions of Sintering and Agglomeration

Many literature sources describe the relationship between sintering and agglomeration without properly defining the two terms. In some cases the two terms are used interchangeably. Therefore, many contradicting ideas are given to define agglomeration and sintering. Skrifvars and co-workers [1994] defined sintering as a term describing particle-to-particle agglomeration that starts off with bridges forming between particles. Teleki and co-workers [2008] commented that TiO_2 agglomerate formation starts at the end of sintering. Tangsathitkulchai and Tangsathitkulchai [2001] stated that rapid sintering can lead to severe agglomeration, but also that sintering and other reactions may strengthen agglomerates after their formation. It is therefore necessary to define both sintering and agglomeration as they will be applied throughout this study:

- **Sintering** is the process during which adjacent particles are bonded together in the attempt to lower excess surface tension [Al-Otoom et al., 2000a, 2000b; German, 1996]. German [1996] defined sintering as: *"Sintering is a thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events that often occur on the atomic scale. The bonding leads to improved strength and a lower system energy"*. Sintering starts with neck formation between the particles. The sintering temperature is an inherent quality of the particle composition [Basu and Sarka, 1983; Tardos and Pfeffer, 1995]. Two adjacent particles interact with each other or form a solution at surface level due to e.g. initial melting on the surface, and fuse into a larger particle [Manzoori and Agarwal, 1994; Nowok et al., 1990; Skrifvars et al., 1994]. Sintering is characterised by densification and grain growth [Kang, 2005].
- **Agglomeration** on the other hand is a process in which the particles are adhered together on the surface by a substance that does not necessarily originate from the composition of the particles [Nuutinen et al., 2004; Öhman

and Nordin, 2000; Öhman et al., 2000, 2005]. The coating on a particle can melt to form the glue to hold two particles together [Bhattacharya and Harttig, 2003; Nuutinen et al., 2004; Öhman and Nordin, 2000; Öhman et al., 2000, 2005; Olofsson et al., 2002; Vuthaluru and Zhang, 2001]. Agglomeration per se does not result in grain growth, but rather in the increase in the size of particle clusters [Arastoopour et al., 1988].

Therefore, the melt phase on the surface of sintered particles can act as glue to adhere other particles [Basu and Sarka, 1983]. Likewise, agglomerated particles can undergo sintering at elevated temperatures [Arastoopour et al., 1988]. Both processes result in larger particle sizes, either through grain growth or adhesion, and may cause defluidization of fluidized beds, and instability and operation difficulties in combustors and gasifiers [Al-Otoom et al., 2000b; Basu and Sarka, 1983; Lin and Wey, 2004; Manzoori and Agarwal, 1994; Skrifvars et al., 1994; Van Dyk et al., 2009a]. However, agglomeration of ash particles may also aid operation in fixed-bed reactors by providing favourable porosity to allow steam and oxygen through the ash bed [Van Dyk et al., 2009a].

2.8.2 Sintering Mechanisms

Various sintering mechanisms exist based on differences in mass transport mechanisms, and they can largely be grouped into two categories, i.e. solid-state sintering and liquid phase sintering [Kang, 2005]. General characteristics of sintering processes in these two groups are discussed in Sections 2.8.2.1 and 2.8.2.2. Kingery and Berg [1955] stated that it is very difficult to unambiguously distinguish between different sintering mechanisms when combined effects are possible.

The most common sintering mechanism found in coal ash is reported to be the viscous flow mechanism, during which mass transfer occurs via viscous flow [Al-Otoom et al., 2000b; Benson, 1986; Jung and Schobert, 1991]. The viscous flow mechanism was proposed by Frenkel [Frenkel, 1945; Kang, 2005]. Viscous flow sintering can be grouped under liquid-phase sintering and solid-state sintering, depending on the viscosity and abundance of liquid or melt phases present in the ash [Frenkel, 1945; German, 1996; Kang, 2005]. Nowok and co-workers [1990] investigated the viscous flow sintering of coal ashes. Their results indicated that viscous sintering proceeds via neck formation, the development and shrinkage of closed pores, and/or the diffusion of slag or liquid phases along grain boundaries or

surfaces. Ash particles can adhere to the slag and dissolve into it [Song et al., 2009]. Nowok and co-workers [1990] noted that viscous flow sintering is dependent on temperature, atmosphere and ash composition.

During pressure-assisted sintering, as in the case of most conventional combustors and gasifiers, glass and amorphous material sinter via viscous flow [German, 1996; Skrifvars et al., 1994]. Liquid phases densify under shear stress and the densification is in proportion to the applied pressure [German, 1996].

2.8.2.1 Liquid-Phase Sintering

Liquid-phase sintering is common in mixtures where the temperature is higher than the solidus temperature of some of the components in the mixture [Kang, 2005]. Material transport is fast through the liquid phase [German, 1996; Kang, 2005]. Liquid-phase sintering occurs in several stages [German, 1996; Nowok et al., 1990]. Chemical forces on the surface tend to pull particles together (e.g. due to capillary pressures) in an attempt to lower surface tension when a liquid phase is formed between the particles [German, 1996; Kang, 2005; Nowok et al., 1990]. Particle rearrangement may occur under suitable conditions, resulting in the formation of closed pores and voids [Al-Otoom et al., 2000b; Conn and Austin, 1984; Kang, 2005; Nowok et al., 1990]. Neck formation begins when the particles are positioned favourably with regard to each other [Conn and Austin, 1984]. The rate of neck growth between particles is dependent on the liquid volume, liquid viscosity and surface tension [Conn and Austin, 1984; German, 1996; Kang, 2005]. The various stages of liquid phase sintering in consecutive order are: mixed powders forming non-reactive liquids, particle rearrangement, solution-reprecipitation with associated grain growth, and final densification [German, 1996].

2.8.2.2 Solid-State Sintering

Solid-state sintering consists of three overlapping stages, i.e. the initial, intermediate, and final stages [German, 1996; Kang, 2005]. Neck growth between particles is an important aspect of the initial stage of solid-state sintering [Conn and Austin, 1984; German, 1996; Kang, 2005]. Neck formation requires mass transfer. Mass transfer mechanisms for solid-state sintering include lattice, surface, volume or grain-boundary diffusion, viscous and plastic flow, and vapour phase diffusion from solid surfaces [Conn and Austin, 1984; German, 1996; Kang, 2005]. The intermediate

stage is characterised by densification of up to 92% or shrinkage of the porosity to around 8% with associated grain growth [German, 1996; Kang, 2005]. The final stage involves shrinkage to a total porosity of less than 8% and final densification [Frenkel, 1945; German, 1996].

2.8.3 Agglomeration Routes

Agglomeration proceeds via two different routes, i.e. “melt-induced” agglomeration and “coating-induced” agglomeration [Nuutinen et al., 2004; Öhman et al., 2005]. The “coating-induced” agglomeration route appears to be the most common [Bhattacharya and Harttig, 2003; Manzoori and Agarwal, 1992, 1993, 1994; Nuutinen et al., 2004; Öhman and Nordin, 2000; Öhman et al., 2000, 2005].

“Coating-induced” agglomeration describes the agglomeration processes where the original bed-material or fuel particles are covered with a coating [Nuutinen et al., 2004; Öhman et al., 2005]. The coatings may contain low-melting point species that can cause agglomeration under the right conditions, since the coatings produce the melt phases responsible for binding the particles together [Manzoori and Agarwal, 1992, 1993, 1994; Öhman and Nordin, 2000; Öhman et al., 2000]. “Melt-induced” agglomeration describes the agglomeration process where particles are bonded or glued together with a melt phase derived from ash [Nuutinen et al., 2004; Öhman et al., 2005]. The melt phase forms independently due to high local temperatures [Nuutinen et al., 2004].

2.8.4 Major Contributors to Sintering and Agglomeration during Coal Utilisation

Sintering and agglomeration are more problematic in the utilisation of low-rank coals due to the presence of significantly larger amounts of organically bound inorganic matter that are released at low temperatures [Bhattacharya and Harttig; Manzoori and Agarwal, 1992; Vuthaluru et al., 1999]. Of particular concern in low-rank coals are high amounts of alkali metals (sodium, potassium) [Dahlin et al., 2006; Manzoori and Agarwal, 1992; Vuthaluru et al., 1999; Vuthaluru and Zhang, 2001]. Other elements that can have a detrimental effect on sintering and agglomeration include calcium, sulfur, iron, silicon, aluminium, chlorine and magnesium [Al-Otoom et al., 2005; Bhattacharya and Harttig, 2003; Manzoori and Agarwal, 1992, 1993, 1994]. In most cases these elements become problematic when they are associated

with other elements in the group. An example is CaSO_4 that has a melting point of 1400 °C on its own, but in association with other inorganic species the melting point of the eutectics can drop to below 800 °C [Bhattacharya and Harttig, 2003]. However, the addition of Ca- and Mg-based additives to coal in a combustion study improved the ash fusibility and reduced the emissions of particulate matter with diameters less than 2.5 μm (combustion temperatures 1200 °C and higher) [Ninomiya et al., 2009]. Ash analysis of the coals before combustion showed concentrations of 5.5% to 9% for MgO and CaO after addition of the additives.

Vuthaluru and co-workers [2000] identified that the type of coal has a very significant role in agglomeration. They determined that different levels of sulfur and sodium together with varying ash contents in the coals were mainly responsible for differences in agglomeration and deposition characteristics of low-rank coals. Bhattacharya and Harttig [2003] and Manzoori and Agarwal [1992, 1993] studied agglomeration and defluidization of high alkali and high sulfur low-rank coals in fluidized-bed combustion. They found that the agglomeration in the systems was mostly caused by alkali, magnesium and calcium sulfates. Alkali, magnesium and calcium sulfates form a ternary system [Manzoori and Agarwal, 1993; Steenari et al., 1998]. Eutectics can form in the ternary system with melting points in the range of 650 °C to 940 °C [Manzoori and Agarwal, 1993; Steenari et al., 1998]. The sodium sulfate – calcium sulfate eutectic melts at 899 °C [Marinov et al., 1992].

Manzoori and Agarwal [1993, 1994] added NaCl to coal samples during agglomeration and defluidization tests with low-rank coals. Defluidization of the bed occurred after only 30 minutes of operation at 800 °C. The closest defluidization time of the other tests was 3.5 hours at 850 °C. Most of the tests did not show defluidization with operation between 9 and 24 hours. Steenari and co-workers [1998] stated that the addition of sodium and chlorine to the potassium, calcium and magnesium sulfates ternary system may result in the formation of eutectics with melting points as low as 600 °C. Dahlin and co-workers [2009] investigated different additives to minimize agglomeration in a circulating fluidized bed reactor during high-sodium lignite gasification. They found that the addition of metakaolin reduced agglomeration by capturing sodium and forming solid nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

Various silicates and aluminosilicates also contribute to sintering and agglomeration at temperatures below 1000 °C [Dahlin et al., 2006; Jung and Schobert, 1991; Marinov et al., 1992; Steenari et al., 1998; Tangsathitkulchai and

Tangsathitkulchai, 2001]. The phase diagram for the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ system indicates that the compound $\text{Na}_2\text{O}-\text{SiO}_2$ melts at 874°C [Dahlin et al., 2006]. Tests performed by Jung and Schobert [1991] and Arvelakis and co-workers [2006] suggested that anhydrite (CaSO_4) reacts with clays and quartz in ash to form low-melting calcium aluminosilicate species. Calcium species, magnesium species and iron species (especially FeS and FeCO_3) may act as fluxing agents and produce silicates and aluminosilicates with melting points between 900°C and 1200°C [Laursen and Frandsen, 1998; Matjie et al., 2007; McLennan et al., 2000b]. Some of the silicates and aluminosilicate species identified in studies of fly ash and coatings include anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), melilite ($\text{NaCaAlSi}_2\text{O}_7$), albite ($\text{NaAlSi}_3\text{O}_8$), sodium melilite ($\text{NaCaAlSi}_2\text{O}_7$), merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$), wollastonite (CaSiO_3) and nosean ($\text{Na}_8(\text{Si}_6\text{Al}_6)\text{O}_{24}(\text{SO}_4)$) [Bhattacharya and Harttig, 2003; Erol et al., 2008; Hlatshwayo et al., 2009; Ishom et al., 2004; Jung and Schobert, 1991].

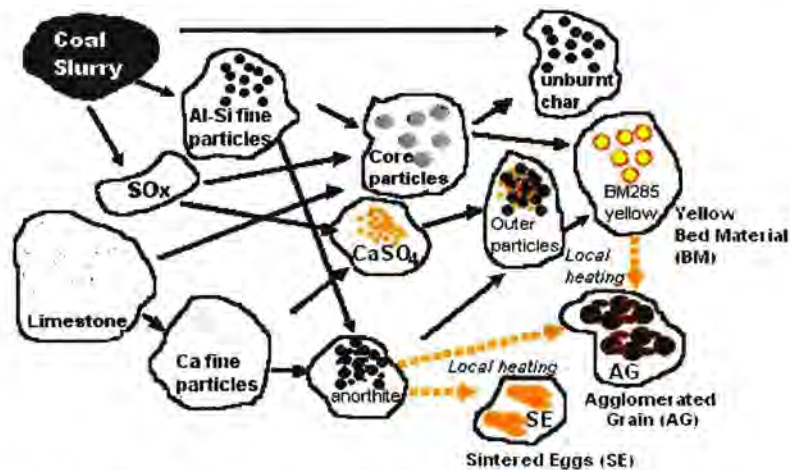


Figure 2.9 Outline for the mechanism of bed material formation in a PFBC at 285 MW output. Adapted from Ishom et al. [2004]

Ishom and co-workers [2004] investigated the bed material from a pressurized fluidized-bed combustion (PFBC) boiler running under different loads (270 MW and 285 MW). Blair Athol coal was used as fuel and limestone was added for in-bed desulfurisation. Figure 2.9 gives a schematic outline for the mechanism of bed material formation compiled from results obtained at 285 MW output. The

schematic shows how the aluminosilicate fine particles from the coal, SO_x and limestone reacted to form a variety of different bed material particles. Included in the bed material particles were yellow particles, grey particles, sintered eggs (SE), agglomerated grains (AG) and unburnt char. CaCO_3 calcined to CaO and reacted extensively with aluminosilicates, especially at higher local temperatures. The products had low melting points that resorted in the formation of the sintered eggs and agglomerated grains. The yellow particles were covered with a layer of calcium aluminosilicate. The layers on the yellow particles were softened by local heating, which caused the particles to adhere together and form the larger agglomerated grains. Iron species may play a significant role in sintering and agglomeration, especially during reducing conditions [Bailey et al., 1998; Mason, 1992; Steenari et al., 1998]. Pyrite particles become sticky around 1080 °C [Bailey et al., 1998]. Under reducing conditions the pyrite (FeS_2) transforms to pyrrhotite (FeS). Various researchers [Marinov et al., 1992; Matjie et al., 2007; McLennan et al., 2000a, 2000b; Steenari et al., 1998] have identified the role of FeS in the formation of low melting point eutectics. Matjie et al., [2007] identified the presence of FeS in gasification clinkers. FeS can form a eutectic with wustite (FeO) that has a melting point of 924 °C [Marinov et al., 1992]. Iron oxides and FeS can also react with clays and quartz to form species with melting points in the range of 900 °C to 1000 °C [Steenari et al., 1998].

2.9 Methods to Detect and Predict Agglomeration and Sintering

Several methods are available to predict the tendency of ash from a fuel source to agglomerate and sinter in gasification and combustion processes. The influence of additives can also be investigated; e.g. Li and co-workers [2008] used Fourier transform infrared spectroscopy (FTIR) to determine ash melting temperatures and study the influence of Fe_2O_3 as fluxing agent on the melting (method not included in section below). The information required from an investigation dictates which analysis methods will be best suited. The most accurate and ideal method to determine the influence of a fuel source on a reactor will be to test it in the reactor itself. Cost implications of unscheduled shutdowns and damage to the reactor usually do not permit direct testing, and therefore various methods have been developed to predict

how a fuel source will perform in a specific reactor, especially with reference to ash behaviour [Skrifvars et al., 1999; Gupta, 2007].

2.9.1 Ash Fusion Temperature (AFT)

The standard ash fusion temperature (AFT) test gives an indication of the slagging and fouling properties of ash samples and the influence of the ash on clinker formation and deposition. The test can also give information regarding the suitability of coal sources for combustion and gasification. The AFT test is still the most accepted or widely used method to assess the slagging properties of coal, even though the method has well-documented shortcomings [Gupta, 2007; Van Dyk and Waanders, 2007; Van Dyk et al., 2009a; Wall et al., 1999].

In the AFT test, a cone or pyramid of the ash sample is prepared and placed in a furnace. The ash sample is then heated at approximately 5 to 10 °C/min from 1000 °C to 1600 °C, or the temperatures expected in a furnace or reactor [Wall et al., 1998, 1999]. Based on the operator's observation, four different temperatures are noted [Gupta et al., 1998b; Seggiani, 1999; Van Dyk et al., 2005; Wall et al., 1998, 1999]:

- **Initial deformation temperature (IDT or DT)** – temperature where the tip of the cone or pyramid rounds, denoted as the first sign of the ash softening and becoming sticky.
- **Spherical or softening temperature (ST)** – temperature where the height of the cone or pyramid and width of the base are equal.
- **Hemispherical temperature (HT)** – temperature where the cone or pyramid height is equal to half of the cone's width, and thus forming a hemispherical-shaped droplet.
- **Flow or fluid temperature (FT)** – temperature where the cone height is approximately 1.5 mm or a sixteenth of the width, and thus where the ash is a free-flowing fluid.

The determination of AFTs has many advantages and uses. The IDT has important implications for the design of furnaces and the marketing thereof [Gupta et al., 1998b]. The IDT is used to select the temperature for the exit gas of a furnace [Wall et al., 1999]. Ash fusion temperatures have been correlated with the composition of coal ash and give important information regarding the behaviour of inorganic matter in fuel sources at high temperatures [Gupta, 2007]. Van Dyk and

Waanders [2007] used the standard AFT test to show the influence of silica (SiO_2), alumina (Al_2O_3) and titania (TiO_2) additions to ash in an attempt to increase the AFT and allow the operation of gasifiers at higher temperatures.

The AFT method has many disadvantages and they have inspired researchers to develop new or improved methods in an attempt to eliminate the AFT method's shortcomings. One of the greatest objections to this method is the fact that it is not a measurement, but an observation subject to the best efforts of the operator, even though the method has been improved by the use of optical and other auxiliary devices [Wall et al., 1998, 1999]. This subjective method has poor repeatability compared to other methods used to obtain similar results, e.g. the ceramic tile method developed by Kahraman et al. [1998] has a repeatability of $\pm 10^\circ\text{C}$. Gupta and co-workers [1998] and Wall and co-workers [1998] submitted several ash samples for analysis to different laboratories. The variation in IDT estimations showed differences of up to 400°C . Kahraman and co-workers [1998] indicated that the repeatability limits for the IDT determined with standard ash fusion tests are between 30°C and 50°C when the same operator and instrument is used, and between 80°C and 150°C when a different operator and instrument is used. Özbayoğlu and Özbayoğlu [2006] stated that the reproducibility of AFTs for a particular coal sample analyzed by different laboratories may differ by as much as 20 to 100°C . Gupta [2007] listed various reasons for the poor predictive behaviour of the standard AFT test. These include: boiler design and operation are not taken into account when the fusion temperatures are determined; the heating rate allows for measurements over a short period of time, but deposits accumulate over a long period; fusion behaviour changes when samples stand for periods at given temperatures; and the composition of deposits is not necessarily the same as the composition of the ash. The AFT test gives average bulk ash melting temperatures, and does not detect the temperature where melting starts [Van Dyk et al., 2009a]. Wu and co-workers [2009] stated that initial melting of ash starts as much as 200°C to 300°C below the IDT.

Skrifvars and co-workers [1999] compared three different methods to predict bed agglomeration tendencies, of which the AFT test was one. The study was conducted to see how well the AFT test and the compressive strength test could predict the bed agglomeration temperature, compared to a laboratory-scale fluidized-bed combustion test. The results indicated that the IDT as predicted by the AFT test was higher in all cases than the temperature found in the bed of the fluidized-bed

combustor. In all the cases the AFT test failed to predict the bed agglomeration temperature and was noted as giving very little useful data to predict bed agglomeration.

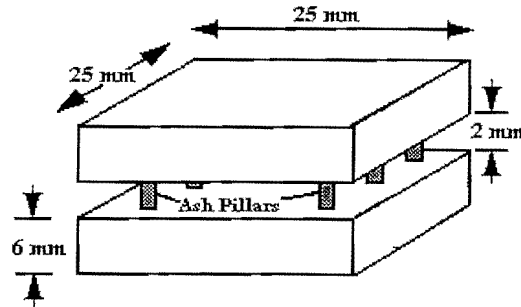


Figure 2.10 Schematic of the arrangement of ash cylinders and ceramic tiles in an improved method to determine the ash fusion temperature [Kahraman et al., 1998]

Due to the numerous shortcomings of the AFT test, researchers have attempted to improve the method or to find alternative means to predict the ash fusion temperatures. Kahraman and co-workers [1998] devised a method that eliminates the subjectivity introduced by the operator. The method they described involves two standard ash fusion ceramic tiles, six cylinders of ash, and a standard ash fusion furnace. The tiles with the ash cylinders or pillars are placed in the furnace and heated at $5^{\circ}\text{C}/\text{min}$. Photographs are taken every 10°C and the distance between the two tiles is measured from the negatives with the help of a transmitted light microscope at 25 times magnification. A primary graph is plotted using the percentage separation between the tiles versus temperature. The derivative of the plot gives the ash fusion temperature with a good repeatability and reproducibility of $\pm 10^{\circ}\text{C}$, limited by the measuring frequency. Currently available digital photography instrumentation may be able to reduce the limitation introduced by measuring frequency. Figure 2.10 is a schematic of the arrangement of the ash cylinders and ceramic tiles in this alternative method to predict ash fusion temperatures.

Mathematical models have also been used to predict the ash fusion temperatures [Özbayoğlu and Özbayoğlu 2006; Seggiani, 1999]. Examples of mathematical models using linear and non-linear correlations and regression analysis to calculate the ash fusion temperatures are discussed in Section 2.9.8.

2.9.2 Compressive Strength Test

The compressive strength method is based on measurements of the mechanical strength that develops in the ash as sintering occurs [Al-Otoom et al., 2000a; Jung and Schobert, 1991; Skrifvars et al., 1992, 1999]. This is the most common technique to determine the sintering temperature in coal ash [Al-Otoom et al., 2000a].

Sample preparation includes the manufacturing of compressed ash pellets [Al-Otoom et al., 2000a; Conn, 1995; Jung and Schobert, 1991; Nowak et al., 1990; Skrifvars et al., 1999; Tangsathitkulchai and Tangsathitkulchai, 2001]. The compacted ash pellets are heat-treated inside a furnace at heating rates varying from 6 to 10 °C/min and held at the desired temperature for a certain length of time. Sintering tests with temperatures as high as 1500 °C have been reported and hold times of up to 4 hours in different gas environments [Nowok et al., 1990; Skrifvars et al., 1992, 1999; Tangsathitkulchai and Tangsathitkulchai, 2001]. The cooled ash pellets are crushed using standard strength-testing devices. The compressive strength is usually calculated as the maximum force where the ash pellet breaks divided by the top area of the pellet (measured as N/mm^2 or N/m^2), or it is noted as the pressure applied when the pellet breaks. The compressive strength is plotted against heat treatment temperature. The temperature where sintering begins is noted as the temperature where the ash pellets start to develop measurable mechanical strength [Conn, 1995; Tangsathitkulchai and Tangsathitkulchai, 2001].

When it is difficult to get an ash pellet suitable for the conventional compressive strength technique, the compressive strength of the sample can be measured using the instrumentation for thermomechanical analysis (TMA) (see Section 2.9.7). Al-Otoom and co-workers [2003] determined the compressive strength of unsintered ash and samples from ash bridges with TMA. They used this method because it was difficult to prepare ash pellets with the desired density for conventional compressive strength measurements. Compressive strength was determined by increasing the load of the ram in increments of 0.5 g/min. As breakage of the pellet occurred, the displacement of the ram was significantly higher than the displacement of the previous loads.

Compressive strength tests are more sensitive than the standard ash fusion temperature (AFT) test [Skrifvars et al., 1999]. Skrifvars and co-workers [1999] compared three different techniques to predict agglomeration and sintering tendencies

in biomass combustion fuels. Laboratory-scale fluidized-bed combustion tests were used as a basis, and agglomeration temperatures predicted by AFT tests and compressive strength tests were compared to the laboratory-scale tests. They reported that the compressive strength tests were a better prediction method than AFT tests. To predict the interactions of ash with bed material in fluidized-bed reactors, the bed material must be added to the ash pellets before compressive strength tests.

It has been reported that researchers have no agreed standard procedure for compressive strength tests, even though the method is widely used [Al-Otoom et al., 2000a]. Al-Otoom and co-workers [2000a] reported accuracies for determining sintering temperatures with the compressive strength test as ± 50 °C and stated that compressive strength measurements overestimated the initial sintering temperature. However, in their experimental design the temperatures were increased by increments of 100 °C, which decreased the sensitivity of the technique. Smaller intervals may improve the accuracy. Conn [1995] used a Buehler metallurgical press to determine compressive strength. He reported that the accuracy of the strengths yielded by the instrument was ± 25 psi. Triplicate samples were crushed to obtain the average compressive strength.

Compressive strength tests have been criticized because measurements are made in temperature increments and not continuously. It is also a cold or ambient temperature crushing method [Al-Otoom et al., 2000a]. The method therefore does not give the strength of ash pellets at actual combustion temperatures. The influence of “hot” versus “cold” crushing was illustrated in work by Conn and Austin [1984]. They reported compressive strength measurements for ash pellets heat-treated at various temperatures between 850 °C and 1200 °C. The initial sinter point for Keystone coal was determined as 950°C. Cold crushing and crushing at 900 °C (of pellets sintered at higher temperatures) gave similar compressive strength values, with the predicted tendency of increased compressive strength with increase in heat treatment temperature. However, strength values obtained from crushing pellets at the heat-treatment temperature gave much lower compressive strength values than crushing at ambient conditions, and it was difficult to observe a precise fracture point due to plastic deformation. Compressive strength values also peaked at 1100 °C and had a significantly lower value at 1200 °C. However, the same sinter point was determined from crushing at 25 °C and at the heat treatment temperature.

Tangsathitkulchai and Tangsathitkulchai [2001] used the compressive strength method to compare initial sintering temperatures of four different Thai coal ashes and the influence of additives on their sintering. They reported an initial sinter temperature as low as 650 °C for coal from the Maemoh seam that contained relatively high percentages of clays and anhydrite. Their results revealed a possible inverse relationship between initial sinter temperature and sintered strength. The lower initial sinter point ashes gave higher sintered strength in the coal ashes they investigated.

2.9.3 *Differential Scanning Calorimetry (DSC) and Simultaneous Thermal Analysis (STA)*

Differential scanning calorimetry (DSC) is a widely used thermal method that measures energy differences as physical or chemical processes occur [Skoog et al., 1998]. DSC can be used to detect phase transitions or changes by monitoring the heat flow needed or released to maintain the sample cell or pan at the same temperature as an inert reference cell [Gupta, 2007]. The temperature of the sample cell is usually increased or decreased linearly in order to measure the difference in heat flow between the sample cell and reference cell [Skoog et al., 1998]. Cells or pans are usually made from aluminium, platinum or alumina. The analytes and temperature program dictate which is more suitable, e.g. Mayoral and co-workers [2001] used platinum pans instead of alumina pans in a study of aluminosilicates, since alumina pans are damaged by calcite included in some of the experiments.

Two types of methods or systems are commonly used that provide the same information, but the instrumentation differs significantly [Skoog et al., 1998]. One of these systems is power-compensated DSC in which the sample and reference cells are heated separately with identical furnaces. The power input to the furnaces is varied to keep the temperatures equal, and the power or energy is a measure of the difference in enthalpy between the two cells. The other system is heat-flux DSC in which the two cells are connected via a heat flow path and the difference in temperature between the two cells is an indication of the difference in enthalpy. The sample and reference cells are heated simultaneously by a single furnace or electrically heated constantan thermoelectric disk [Gupta, 2007; Skoog et al., 1998].

DSC has been used to monitor the interaction and kinetics of coal reacting with gasses and to detect glass-transition temperatures [Opaprakasit and Painter, 2004;

Yu et al., 2005]. Yu and co-workers [2005] determined the influence of particle size on the proximate composition and combustion properties of coal with DSC, and Opaprakasit and Painter [2004] determined the glass-transition temperatures of a pyridine-soluble coal extract. Mayoral and co-workers [2001] used this technique to study aluminosilicate mineral transformations. They investigated the behaviour of quartz, kaolinite and calcite as the main components of coal mineral matter. Transformations of aluminosilicates and crystallization of spinel were determined at different sintering times. From this study they concluded that solid-state reactions at temperatures below mineral transformations have an impact on the degree of crystallisation of mineral species and slagging in combustion systems. Crystallisation causes densification processes to occur at higher temperatures [Nowak et al., 1990].

DSC has the advantage that small changes can be detected and energy changes can be quantified. However, in some cases transitions overlap or small transitions are masked by larger transitions if they fall in the same temperature range. In these cases indirect methods or other analytical methods may be necessary to determine the information required [Opaprakasit and Painter, 2004]. The analysis of complex systems may also be difficult to interpret due to overlapping transitions.

Hansen and co-workers [1999] used simultaneous thermal analysis (STA), which involves simultaneous TG and DSC measurements, to quantify ash fusion; similar to thermogravimetry combined with differential thermal analysis (TG/DTA) [Skoog et al., 1998]. Therefore, the weight of the sample and calorimetric changes are measured continuously and simultaneously as a function of temperature. Melting in the sample is identified as an endothermic reaction during which the sample shows no weight loss. They reported that the repeatability of the method was good, with accuracies within 10 °C. However, this method requires the identity of the ash constituents and knowledge pertaining to their chemistry to be able to convert the STA curves to a melt curve. Melt curves are formed by subtracting energies not related to melting, e.g. evaporation, from the DSC signals. The melting curves therefore only depict energies related to melting. With the STA method the total energy used for ash melting in a certain temperature range can be calculated, as well as the fraction of the ash that melted. The authors demonstrated this technique by generating melt curves for simple binary salt mixtures, salt-rich straw ashes, and silicate-rich coal ashes. Melting temperatures for the ashes were found to be 40 °C to 110 °C below the onset temperatures determined with AFT. De Casa and co-workers [2007] used STA to

evaluate the thermal behaviour of municipal incinerator fly ash in an attempt to use sintering as a method of manufacturing improved ceramic materials from incinerated municipal waste.

2.9.4 *Electrical Resistance and Thermal Conductivity Analysis (TCA)*

The electrical resistance method for determining sinter point is based on the theory that the logarithm of electrical resistance decreases linearly as the absolute temperature increases (plotted as $\log R$ vs $1/T$) [Conn and Austin, 1984; Jung and Schobert, 1991]. At the onset of sintering the resistance is reduced due to inter-particle bonding and increased ionic conductance. A reduction in resistance is indicated by an increase in the slope. The temperature at the change in slope is referred to as the electrical sinter point [Conn, 1995; Conn and Austin, 1984; Jung and Schobert, 1991].

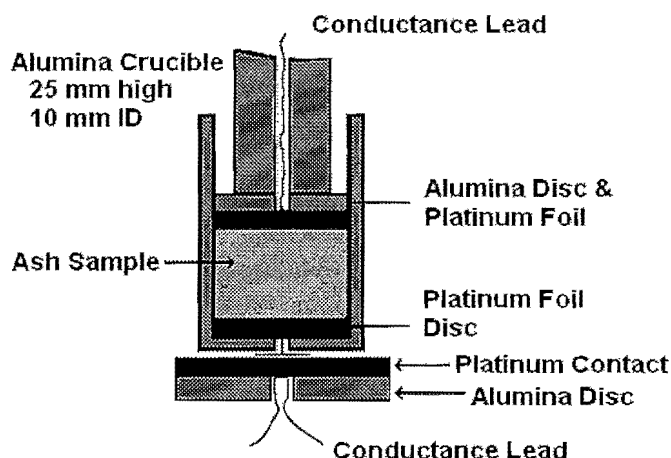


Figure 2.11 An illustration of the alumina crucible with ash sample used to determine the electrical resistance. The crucible is heated in a furnace. The platinum foils are connected to a resistor and power source [Conn and Austin, 1984; Jung and Schobert, 1991]

Figure 2.11 is a schematic of the apparatus used to determine the sinter point via electrical resistance. The alumina crucible with ash sample is placed inside a tube furnace to control the temperature. The platinum foils are connected to a resistor with a potentiometer across it to measure the electrical resistance. The method of measuring the change in electrical resistance to determine sintering temperatures is a very sensitive technique. Unlike the standard ash fusion temperature test, the electrical

resistance method can detect small amounts of melt phases and sintering at temperatures below the initial deformation temperature [Conn, 1995; Jung and Schobert, 1991]. This attribute is useful for many applications. The samples can also be collected after resistance determinations and submitted for further analyses, e.g. SEM.

From electrical resistance measurements Jung and Schobert [1991] determined that the sinter point decreases as particle size decreases due to an increase in the surface area to volume ratio. However, the rate of sintering increases as the particle size decreases due to an increase in surface energy.

Conn [1995] investigated the influence of vanadium compounds on the agglomeration potential of petroleum coke fired in a circulating fluidized-bed combustor. The electrical resistance of loop seal ash was measured. Electrical resistance measurements showed traces of melting on particle surfaces starting at temperatures as low as 700 °C (1300 °F). The author noted that this temperature corresponded to the melting temperature of V_2O_5 , but could also have been due to ash eutectics of nickel and calcium with vanadium. Electrical resistance measurements of a cyclone deposit enriched in vanadium indicated that the onset of sintering was lowered to 680 °C (1250 °F) compared to the loop seal ash.

Conn and Austin [1984] evaluated the Raask shrinkage – electrical resistance method. This method is a combination of shrinkage measurements and electrical resistance determinations. A cathetometer was connected to the alumina tube resting on the alumina disk and platinum foil to follow the expansion and shrinking of the ash pellet. The temperature at which the expansion deviated from linearity was called the “shrinkage sinter point”. Results indicated that electrical resistance was more sensitive than shrinkage measurements for a soda glass system. The authors determined that particle size distribution, bulk density, contact pressure and temperature affected resistance measurements. The two methods were not closely reproducible, but both the sinter points decreased with particle size for soda glass as reference or model substance. For finer particle sizes both the shrinkage and electrical sinter points were the same for soda glass. The authors determined that both the sinter points could be estimated within ± 25 °C.

Thermal conductivity analysis (TCA) is a similar method to the electrical resistance technique, except that the thermal conductance is measured instead of the electrical resistance. An ash pellet is prepared and placed between two nickel plates

connected to thermocouples [Al-Otoom et al., 2000a; Rezaei et al., 2000]. The ratio of height to diameter of the ash pellet should be very low to minimize radial heat loss. Reference layers of Pyrex and Vycor, which have known thermal conductivities, are used in the set-up to calculate the heat flux at different temperatures. Al-Otoom and co-workers [2000a] continuously recorded the temperature of an ash pellet in 50 °C intervals. Figure 2.12 is a schematic representation of the TCA set-up and an example of the output obtained from TCA [Al-Otoom et al., 2000a]. The thermal conductivity of ash increases with temperature. When sintering occurs the thermal conductivity shows a marked increase. The T_s value in Figure 2.12(B) signifies the sinter point temperature of the ash sample.

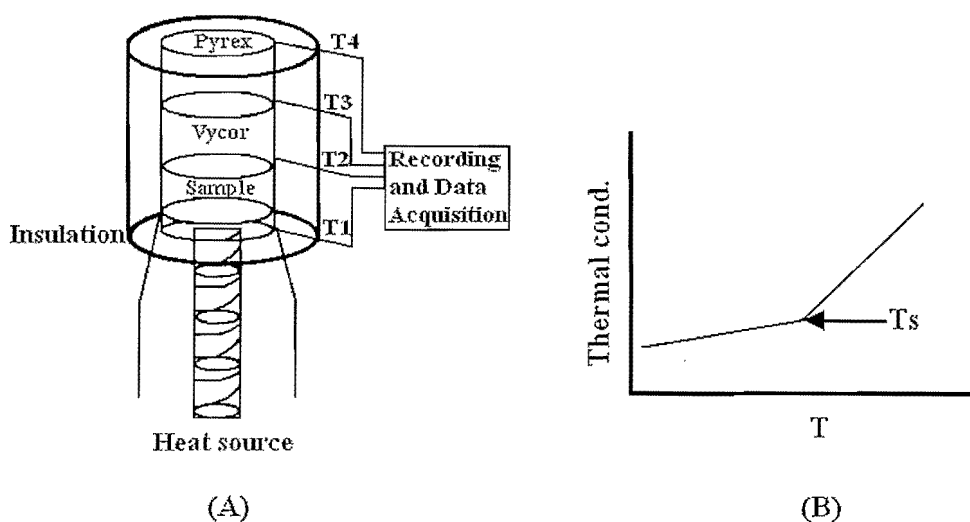


Figure 2.12 A) Schematic of thermal conductivity analysis set-up. B) Example of output obtained from thermal conductivity analysis [Al-Otoom et al., 2000a]

2.9.5 Pressure-Drop Technique

The pressure-drop technique was published by Al-Otoom and co-workers in 2000 [Al-Otoom et al., 2000a, 2000b]. The technique can be used to determine sintering temperature, rate of porosity change, and its kinetic parameters. The pressure-drop technique is based on measuring the pressure-drop of the airflow through a pellet of ash.

Sintering is driven by a reduction of free surface energy, which can occur through changes in porosity. Sintering conditions are usually accompanied by pore growth. Figure 2.13 illustrates the mechanism of sintering according to Al-Otoom and co-workers [2000b]. As sintering starts the size of small pores decreases, but the size of open pores increases and the total porosity is kept approximately constant.

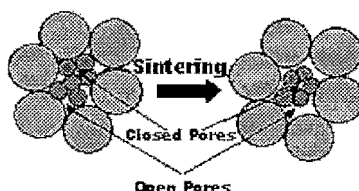


Figure 2.13 Illustration of the mechanism of sintering obtained from Al-Otoom et al. [2000b]

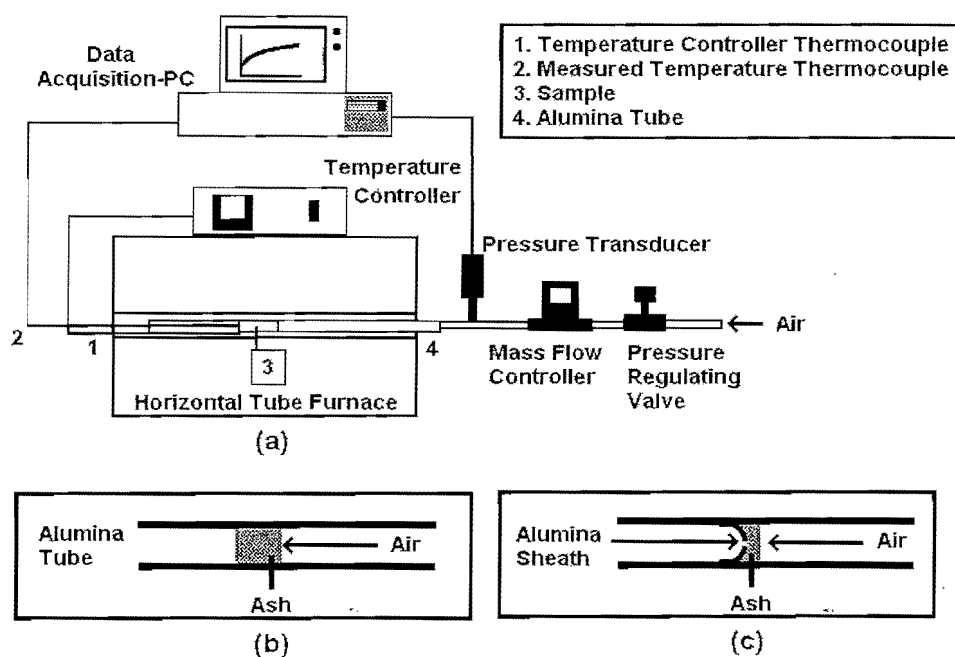


Figure 2.14 Apparatus used by Al-Otoom and co-workers [2000a] to measure the pressure drop across a pellet of ash to determine the sintering temperature and kinetics. (a) is the experimental set-up, and (b) and (c) are the suggested sample arrangements. The authors suggested (c) as the sample arrangement to determine sintering kinetics

The open pores are accessible to external airflows. The open pore volume increases as a result of sintering. In an instrument with an external airflow over the

porous substance, the pressure-drop of the gas across the pellet decreases when the open pore volume increases. The data can be used to determine sintering kinetics. As sintering causes the pellet to shrink and the dimensions of the pellet to change, it pulls away from the tube wall and more air can pass the pellet [Al-Otoom et al., 2000a, 2003]. The data from the decrease in pressure drop across the pellet can be used to determine the sintering temperature. The instrument set-up used by Al-Otoom and co-workers [2000a, 2000b] is shown in Figure 2.14. Both the pressure drop across the pellet and the temperature are monitored and recorded continuously as the ash pellet is heated. The sintering temperature is designated as the temperature where the pressure drop reaches a maximum [Al-Otoom et al., 2000a, 2003]. The kinetic parameters can be extracted from the pressure-drop technique with the use of appropriate equations [Al-Otoom et al., 2000b].

The pressure-drop technique has many advantages and can be used for multiple applications. The reported reproducibility for the technique yields sintering temperatures of $\pm 10^\circ\text{C}$ [Al-Otoom et al., 2000a]. It is both a sensitive and fast technique. Sintering temperatures can be determined in one to two hours. The authors suggest that this technique can be used to simulate conditions in fluidized beds, with sintering temperatures determined to be as low as 610°C . The atmosphere and temperature can be controlled. Different gas mixtures can be used to simulate different stages in combustion or gasification, and the pressure drop observed with the method will represent the pressure drops encountered in fluidized beds, and possibly also fixed beds. Al-Otoom and co-workers [2005] used the pressure-drop technique to determine the agglomeration tendency of five Australian black coals for use in a pressurized fluidized-bed combustor (PFCB). The pressure drop observed during the operation of the PFCB showed similar behaviour to that seen in the laboratory pressure-drop tests. Sample sizes required for this technique are between 0.5 and 1.0 g of ash. The samples can be salvaged and subjected to other analysis techniques, e.g. SEM.

This technique also has limitations. One such limitation is that the gas velocity must be low enough to prevent the ash sample from moving in the tube due to pressure build-up. A binder is also needed to pelletize the ash if the particles show poor compactability. Al-Otoom and co-workers [2000a] stated that the use of a binder had no influence on the sintering temperature as it decomposed completely at 300°C . The specific binder they used was not mentioned.

2.9.6 Scanning Electron Microscopy (SEM)

SEM is an imaging technique that uses a high-energy electron beam to produce secondary electrons as the beam hits the sample. The secondary electrons are collected and processed to display an image. In the study of ash chemistry, SEM is used to visually determine or follow the extent of agglomeration and sintering in samples prepared with other techniques or methods. SEM instrumentation can be fitted with different detectors to yield combined analysis techniques. The most common is SEM combined with energy-dispersive X-ray spectroscopy (EDS). Literature contains many examples of researchers using SEM and combined techniques (EDS or backscattered electrons) to study sintering/agglomeration and identify the elements involved in the transformations [Iribarne et al., 2003; Jung and Schobert, 1992; Li and Whitty, 2009; Lin and Wey, 2004; Manzoori and Agarwal, 1993; Nuutinen et al., 2004; Öhman and Nordin, 2000; Nowok et al., 1990; Olofsson et al., 2002; Skrifvars et al., 1994; Steenari et al., 1998; Tangsathitkulchai and Tangsathitkulchai, 2001; Yan et al., 2003; Zevenhoven-Onderwater et al., 2006].

SEM is operated under vacuum and the high-energy electron beam is focused on the sample via a series of magnetic lenses [Skoog et al., 1998]. Scanning coils allow the electron beam to move over a rectangular area of the sample in a raster or grid pattern. As the electrons hit the surface of the sample, interactions occur and secondary electrons are released. The secondary electrons are collected by an electron detector and the image is displayed with a cathode-ray tube. The interaction of the electron beam with the surface of the sample will also produce characteristic X-rays, similar to X-ray fluorescence spectroscopy (XRF). These X-rays can be detected by SEM instruments equipped with energy-dispersive (EDS) spectroscopy or wavelength dispersive X-ray spectroscopy to determine the elemental composition of the scanned area. Elements from Na to U can be detected and quantified if their concentrations are greater than 0.1 to 0.5% [Vassilev and Tascón, 2003]. Grains with diameters greater than 0.5 to 1 μm can be observed and analyzed. SEM systems can also be equipped with backscatter electron detectors. Backscatter electrons give information regarding surface topography and elemental distribution [Vassilev and Tascón, 2003]. This mode is used for CCSEM analyses (see Section 2.2.1.3) [Benson et al., 1993; Vassilev and Tascón, 2003].

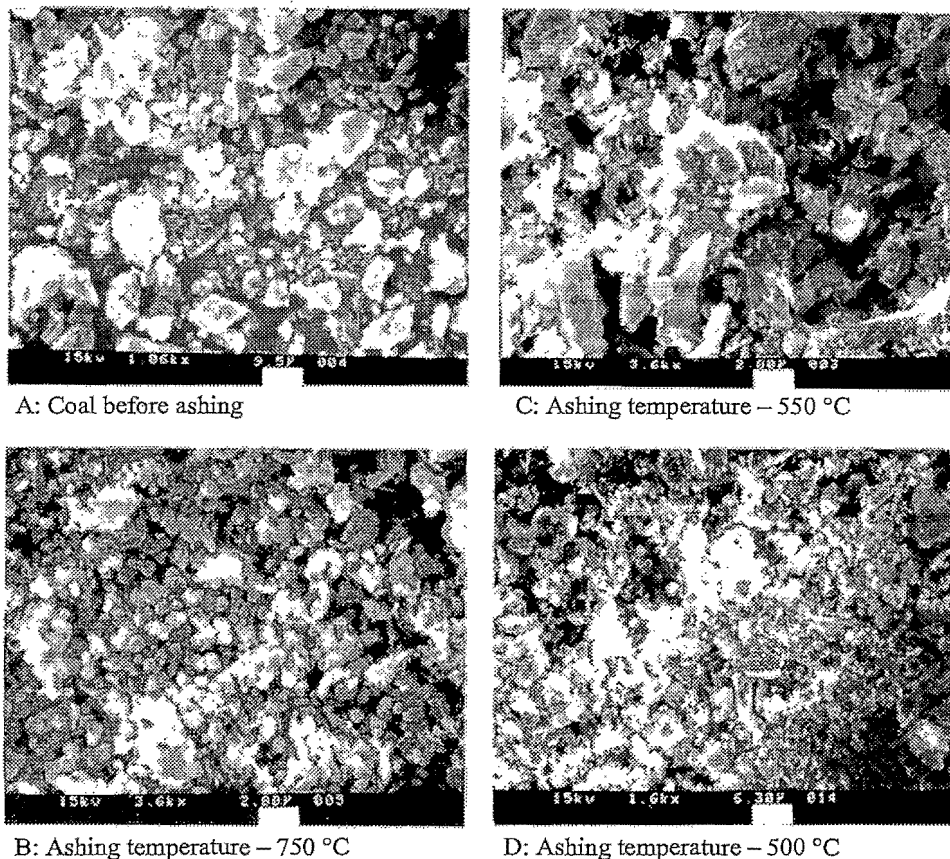


Figure 2.15 SEM micrographs of Elk Creek bituminous coal ashed at different temperatures to determine the highest ashing temperature where no sintering was observed [Jung and Schobert, 1992]

Jung and Schobert [1992] performed an empirical determination of ash samples using SEM micrographs to determine the highest possible ashing temperature where unwanted sintering did not occur. Figure 2.15 presents an example from their study illustrating visual comparisons of coal samples ashed at different temperatures. Sintering of the coal ash was confirmed by the presence of spherical-shaped particles. The spherical form of the particles was due to surface tension resulting from heat treatment. The transformation rate was governed by viscous flow. They determined that the highest ashing temperature they could use without unwanted sintering in Elk Creek bituminous coal was 500 °C (see Figure 2.15).

Lin and Wey [2004] used SEM/EDS to analyze the influence of sodium, magnesium and calcium on agglomeration and defluidization during waste

incineration. Defluidization in the reactor was noted when a rapid pressure drop was detected through the bed. The SEM/EDS results presented in Figure 2.16 indicated that Na, Si, Mg and Ca were involved in bridge formation between particles. The authors determined that the eutectics in the bridges were not crystalline and were too thin to be detected by X-ray diffraction (XRD). However, SEM/EDS was able to qualitatively identify the elements present.

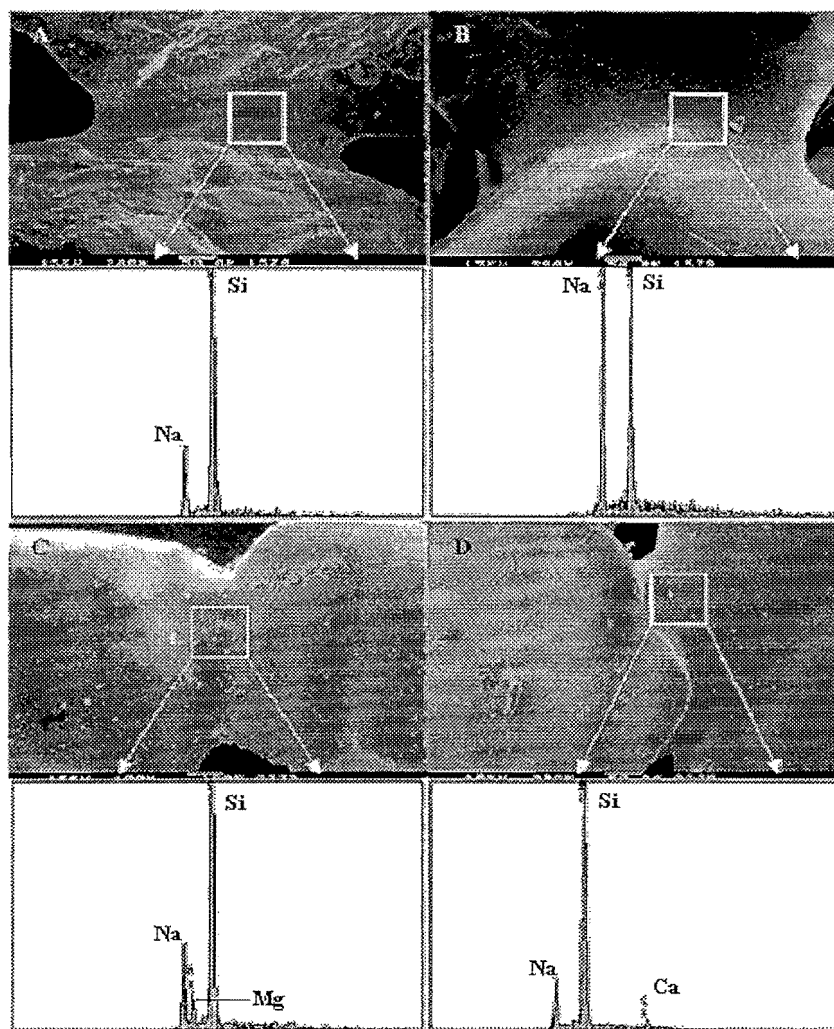


Figure 2.16 SEM/EDS results for particles from a bubble fluidized-bed incinerator. The incinerator temperature was 800 °C with the following conditions: (A) 0.8 wt% Na, (B) 1.5 wt% Na, (C) 1.2 wt% Na + 0.8 wt% Mg, (D) 1.2 wt% Na + 0.8 wt% Ca [Lin and Wey, 2004]

2.9.7 Thermomechanical Analysis (TMA) / Shrinkage Analysis

Thermomechanical analysis (TMA) is a technique used to derive temperatures corresponding to phase changes in ash by measuring the penetration of a ram into the sample during heat treatment. The method was developed in Australia as an alternative method to characterize fusibility of laboratory ashes and slag [Bryant, et al., 1998; Bryant et al., 2000; Liu et al., 2007b]. TMA measurements are based on the percentage penetration of a ram into the sample as a function of temperature as it is heated under load [Gupta, 2007]. The penetration corresponds to the shrinkage of the ash. Characteristic temperatures corresponding to phase changes can be determined from the first derivative of the penetration measurements as well as the rate of shrinkage of the ash pellet [Bryant et al., 1998; Gupta, 2007]. Figure 2.17 is a simplified diagram illustrating the TMA technique, also referred to as the CSIRO Test [Gupta et al., 1998b; Wall et al., 1998].

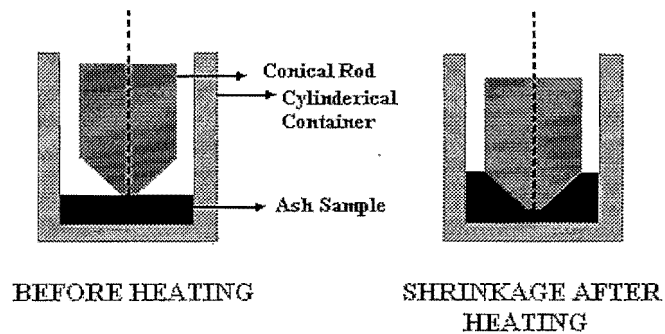


Figure 2.17 Illustration of the ash sample shrinkage in the thermomechanical analysis technique / CSIRO test [Gupta et al., 1998b; Wall et al., 1998]

For the TMA technique 35 to 100 mg loose ash is compacted into a flat-bottomed crucible with 260 to 350 kPa pressure [Al-Otoom et al., 2000a; Bryant et al., 2000; Gupta et al., 1998b; Wall et al., 1998; Wall et al., 1999]. The penetrating ram is inserted into the crucible on the sample surface with a load of 100 g (≈ 140 kPa pressure applied to the sample). The whole system is purged with argon for 15 minutes. After argon purging, the ash sample is heated from room temperature to the desired temperature (1000 – 1600 °C) at 5 to 10 °C/min. As the sample is heated, the ram sinks into the ash sample. The ram reaches the bottom of the crucible as the ash fully melts and fills the annular gap between the ram and the crucible. Output from this technique is a displacement value corresponding to a specific temperature. The

displacement is expressed as the percentage penetration based on the original height of the sample at a specific temperature. Alternatively, the reduction in the distance between the ram bottom and the bottom of the crucible indicates the shrinkage of the ash as temperature increases. The first derivative of the displacement values indicates the rate of shrinkage and peaks in the derivative curve represent the temperatures corresponding to phase changes [Al-Otoom et al., 2000a; Bryant et al., 1998; Gupta, 2007; Liu et al., 2007b]. Figure 2.18 is a schematic of the SETARAM TMA 92 Thermo Mechanical Analyzer that has been used in various TMA studies [Bryant et al., 2000; Liu et al., 2007b].

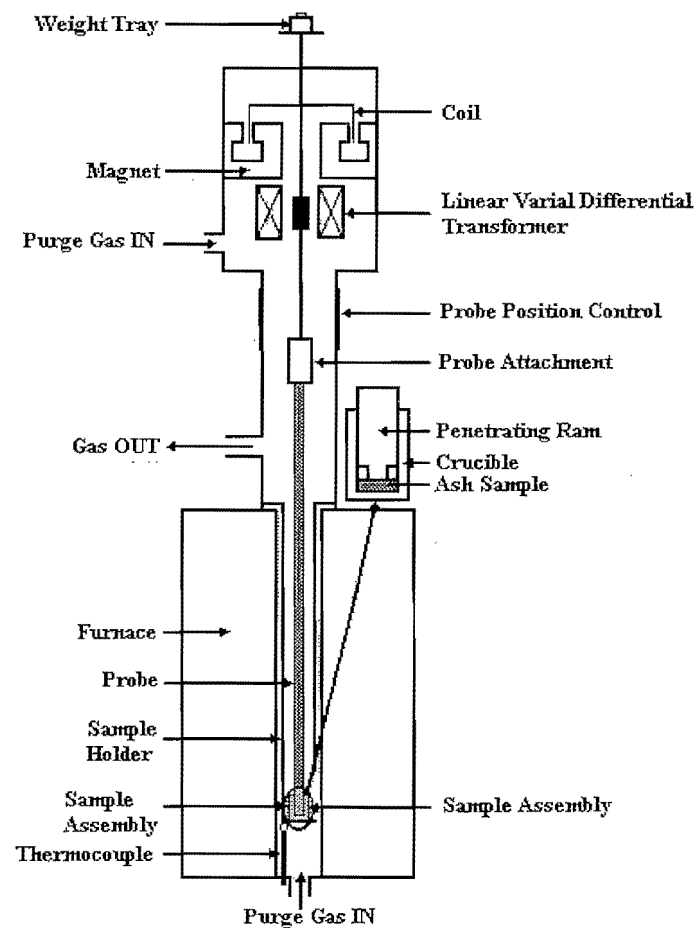


Figure 2.18 Schematic of the SETARAM TMA 92 Thermo Mechanical Analyzer and ash sample assembly before heat treatment [Bryant et al., 2000; Liu et al., 2007b]

The TMA technique has many advantages. Bryant and co-workers [2000] indicated that the technique yields reproducible results with accuracies of ± 10 °C. However, Al-Otoom and co-workers [2000a] reported accuracies of ± 20 °C for TMA. The method is cost-effective and relatively simple to perform without extensive training [Buhre et al., 2005]. Measurements can be completed for a sample in less than three hours [Buhre et al., 2005]. Small sample amounts are needed for the analysis (35 – 100 mg) [Al-Otoom et al., 2000a; Bryant et al., 2000; Gupta et al., 1998b; Wall et al., 1998; Wall et al., 1999]. The technique is very sensitive to changes in the ash composition and chemistry [Al-Otoom et al., 2000a; Liu et al., 2007b].

Liu and co-workers [2007b] obtained TMA measurements of ash from coal samples collected at different times from a power station. The coal samples were ashed at 815 °C. The ash samples contained different amounts of iron expressed as Fe_2O_3 . Some of the samples analyzed also contained additions of quartz, kaolinite and bauxite. The researchers reported that the TMA measurements were very sensitive to the varying amounts of iron in the ash samples. They proposed that TMA measurements can be used to compare and predict slagging related to iron in pf-boilers based on their results.

The TMA technique also has numerous disadvantages. Al-Otoom and co-workers [2000a] found that the TMA readings contained fluctuations or noise which made it difficult to identify the onset of phase changes. They also stated that TMA is limited in that the gas environment does not allow studies under reducing conditions. The material of the sample assembly also influences the TMA measurements. Bryant and co-workers [2000] studied the influence of the sample assembly material on TMA measurements. In the study they used sample assemblies constructed of graphite (C), zirconia (ZrO_2), alumina (Al_2O_3), molybdenum (Mo), platinum (Pt) and boron nitride (BN). They used the platinum assembly as reference due to its stability and inertness. Results indicated that graphite assemblies react with iron oxide in ash. It was proposed that the carbon reduced the Fe^{3+} to Fe^{2+} and Fe^0 at temperatures above 1150 °C. The authors stated that the graphite assemblies caused stronger reducing conditions than the standard reducing AFT test. Graphite, BN and Al_2O_3 assemblies were found to be unsuited for TMA measurements due to adverse reactions with the hot ash. Pt, ZrO_2 and Mo assemblies were the most suitable for TMA as they showed little interactions with the ash or only interacted at very high temperatures. However, Mo is not stable in an oxidising atmosphere above 770 °C due to possible evaporation as MoO_3 .

TMA measurements have been used in various studies. These include using TMA as a method to derive viscosity values for slag compared to rotating bob viscometer measurements [Bryant et al., 1998; Buhre et al., 2005]. Results indicated that TMA has good potential to quantify the effect of flux additions to slagging gasifiers. TMA may also be a fast, cost-effective alternative to techniques currently used to determine the viscosity of high-temperature ash samples.

Al-Otoom and co-workers [2000a] used four different techniques, including TMA, to determine the sintering onset temperature of coal ash. They concluded that both TMA and the pressure-drop technique (see Section 2.9.5) gave accurate indications of the onset of sintering. Sintering was found to start in the temperature range of 600 °C to 1000 °C for a wide range of sub-bituminous and bituminous coal ashes.

Lawrence and co-workers [2008] derived a novel technique based on shrinkage measurements with TMA to assess the slagging propensity of coal ash in pf boilers. Significant shrinkage was observed at temperature above 900 °C. They combined data from shrinkage measurements, proximate analysis and calorific values to calculate a slagging index. Ash with an index of more than 80 is an indication of possible slagging in the boiler. The index is calculated as the maximum rate of shrinkage divided by the temperature corresponding to the maximum rate, multiplied by the weight of ash in kg per million kcal. Results correlated well with data compiled in boiler field tests.

2.9.8 *Thermodynamic and Mathematical Modelling*

Different thermodynamic and mathematical models or software packages have been developed and used by various research groups to predict ash fusion temperatures or confirm the presence of liquid phases and slags that may contribute to agglomeration and sintering [Costen et al., 2000; Jak et al., 1998; Jak, 2002; Kosminski et al., 2006a; Özbayoğlu and Özbayoğlu, 2006; Seggiani, 1999; Van Dyk and Waanders, 2007; Wang and Harb, 1997; Yan et al., 2003]. Modelling has many limitations. Assumptions have to be made in order to set up a model [Costen et al., 2000]. Models also focus on limited systems with many interactions and species not accounted for [Gibbs et al., 2004]. With thermodynamic modelling equilibrium is assumed, but in reality the interactions may be kinetically controlled or not all of the reactions may go to completion [Erickson et al., 1991]. However, even with all these

limitation and gaps in thermodynamic data, modelling can still yield significant information [Argent and Thompson, 2002; Bale et al., 2002; Gibbs et al., 2004].

Thermodynamic packages include GEMINI, FactSage, F*A*C*T/FACTwin, ChemSage/SOLGASMIX, CHEMIX, MTDATA, STANJAN, MINGTSYS and NASA-CET89 [Argent and Thompson, 2002; Bale et al., 2002; Erickson et al., 1991; Gibbs et al., 2004, 2008; Jak et al., 1998; Jak, 2002; Kosminski et al., 2006a; Lee and Wu, 2002; Sandelin and Backman, 2001; Song et al., 2009; Thompson and Argent, 2002; Van Dyk, 2006; Van Dyk and Waanders, 2007; Yan et al., 2001a; Yan et al., 2001b; Yan et al., 2003]. In general, thermodynamic equilibrium calculations are based on the minimization of Gibbs free energy in order to predict the concentration and speciation of products when specified elements or compounds react to reach chemical equilibrium [Bale et al., 2006; Jak et al., 1998; Lee and Wu, 2002]. The thermodynamic data of the species are accessed through the use of extensive chemical databases.

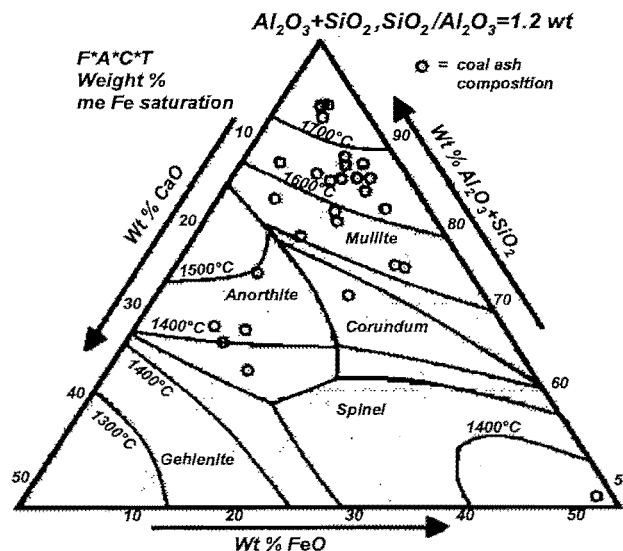


Figure 2.19 Liquidus surface in the five-component Al-Ca-Fe-O-Si system with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.2 in equilibrium with metallic iron. The bulk compositions of the coal ashes were simplified to the five-component system [Jak, 2002]

Jak [2002] used the F*A*C*T thermodynamic computer package to predict the coal ash fusion temperatures of 23 different samples from a coal seam. A five-component system, Al-Ca-Fe-O-Si, was used. The calculations were performed for

both reducing and oxidising atmospheres. Figure 2.19 is a pseudo-ternary phase diagram calculated by F*A*C*T with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.2 and in reducing conditions (metallic iron saturation) [Jak, 2002]. The results predicted liquidus temperatures from 1278 °C to 1744 °C in reducing conditions, and 1404 °C to 1742 °C in oxidising conditions by evaluating the compositions of the ash samples. The author concluded that excellent agreement was obtained between the measured AFT values of the coal samples and the values predicted with the F*A*C*T equilibrium calculations using the five-component system. Song and co-workers [2009] presented a similar study by using FactSage and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.79.

Van Dyk and co-workers [2009] used FactSage combined with Urbain viscosity predictions to determine temperatures where species start to melt in gasification ash. AFT results gave the initial deformation temperature as 1300 °C, but FactSage and viscosity predictions indicated that slag formation already started at 1000 °C. They concluded that FactSage combined with viscosity predictions gave better understanding of the ash and slag properties at specific temperatures.

Kosminski and co-workers [2006a] used the CSIRO CHEMIX thermodynamic equilibrium program to evaluate the influence of different gas environments on the reaction between sodium and silicon minerals. Thermodynamic calculations were performed to predict the formation of potential liquid phases in fluidized-bed gasification of high-sulfur low-rank coal. Calculations were focussed on determining sodium speciation in the resultant products. Results indicated that the distribution or speciation of sodium depends on the forms of sodium and silicon present in the coal, as well as the gas environment. In a carbon dioxide environment the calculations predicted the formation of liquid sodium sulfate and sodium sulfide at temperatures above 800 °C when sodium was included in the calculations as carboxylated sodium. Results also indicated that gasification of coal in steam lowers the melting point of sodium carbonate to 800 °C compared to 851 °C in air. This agreed with experimental results. Calculations with NaCl and kaolin in a carbon monoxide environment predicted liquid albite ($\text{NaAlSi}_3\text{O}_8$) formation at temperatures above 650 °C with 30% of the total sodium in this form. Different gas environments, sodium species and silicon species resulted in different liquid phases forming at various temperatures. These liquid phases occurring at relatively low temperatures may act as glue during fluidized bed gasification and cause bed agglomeration [Kosminski et al., 2006a; Yan et al., 2003].

Yan and co-workers [2003] performed thermodynamic equilibrium calculations using the GEMINI code and its COACH database to evaluate potential low-melting point species that may form during fluidized multi-waste incineration. The feed consisted of 62% carbon soot, 20% bio-sludge and 18% fuel oil. Low-melting point species identified with the calculations that may contribute to sintering and agglomeration in fluidized beds included: $\text{Al}_2(\text{SO}_4)_3$ (770 °C), $\text{Fe}_2(\text{SO}_4)_3$ (480 °C), CoSO_4 (880 °C), CuSO_4 (600 °C), MnSO_4 (700 °C), MnCl_2 (650 °C), MnO_2 (>230 °C), Na_2SO_4 (884 °C), NaCl (800 °C), NaSiO_3 (635 – 815 °C), Ni_2O_3 (400 °C) and V_2O_5 (800 °C). Melting points are given in brackets. They determined that $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, Na_2SO_4 , NaCl , Na_2SiO_3 and V_2O_5 were probably the main contributors to bed agglomeration due to their stability, low melting points and relatively high contents in the system.

Different approaches can be followed to determine fusion temperatures and fouling tendencies via mathematical means. Seggiani [1999] developed a method to calculate the ash fusion temperatures and the critical viscosity of ash with a good level of accuracy using empirical correlations derived by statistical means. Regression analysis was performed based on the chemical compositions of 295 samples by using 49 different parameters. The parameters included the standard nine oxides in the ash composition normalized and SO_3 -free on a molar basis, various combinations of these values (e.g. cross product and sum), as well as the silica value and base, acid and dolomite ratios. The computer program derived empirical equations with which to calculate the four standard ash fusion temperatures and the temperature of critical viscosity with standard deviations for the temperatures in the range of 45 °C to 80 °C.

Özbayoğlu and Özbayoğlu [2006] developed a technique based on non-linear correlations derived by regression analysis to predict the ash fusion temperatures. They used the eight oxides (P_2O_5 was excluded) from the chemical composition of the ash and coal parameters such as ash contents, specific gravity, Hardgrove grindability index (HGI) and mineral matter contents to estimate the ash fusion temperatures. The regression analysis was based on the chemical composition and physical parameters measured for thirty different Turkish lignites. The calculations included 16 different variables. The statistical program STATISTICA[®] was used with an iterative approach to find solutions for the equation parameters. They found that non-linear regression analyses are more accurate than linear regression analyses and the method estimated

the softening, melting and fluid temperatures with a difference of less than 40 °C in 80% of the samples.

Several of the methods discussed in the section above were used to investigate the influence of trace species on the model mineral mixture in this study. The compressive strength test was chosen as a key analytical technique, and was also used to limit the number of trace species subjected to further investigation. Some of the other methods used include TG/DTA, SEM/EDS and XRD. In the following chapter the experimental methodology, selected inorganic species, and mineral mixture chosen for the study will be discussed.

Chapter 3

Experimental

This study focussed mainly on ash formation in an oxidizing environment, but some reducing-atmosphere experiments were also performed. In order to evaluate the influence of trace and minor species on ash behaviour it is important to limit the variables in the system, especially variations in the chemical composition. Secondly, to investigate ash formation processes the starting materials must consist of minerals found in coal. To satisfy both criteria, experiments were performed on a model mineral mixture representing the major minerals found in coal.

Experiments were performed in a temperature range conducive to sintering in the mineral mixture, as well as temperatures required for the operation of fluidized-bed reactors. Several inorganic species were selected as additives based on trace and minor species found in coal and coal ash. Methods used to investigate the influence of these additives on sintering and agglomeration in the model mineral mixture included: compressive strength tests; simultaneous thermogravimetric and differential thermal analysis (TG/DTA); scanning electron microscopy (SEM); X-ray diffraction (XRD); and reducing-atmosphere ash fusion temperature tests (AFT).

3.1 Materials

3.1.1 *Model Mineral Mixture*

The common minerals in coal were determined from literature (see Section 2.2). A model mineral mixture was prepared by mixing the main minerals in a fixed ratio. The mineral mixture consisted of 25% kaolin clay, 20% quartz (SiO_2), 20% pyrite (FeS_2), 15% calcite (CaCO_3), 8% siderite (FeCO_3), 8% hydromagnesite (MgCO_3 , basic), and 4% anatase (TiO_2) by weight percentages. Table 3.1 lists the chemical compounds representing the minerals included in the mixture. Characterization of the chemical compounds or minerals will be discussed in Chapter 4. The mixture is not representative of a specific coal, but an attempt was made to incorporate the most relevant minerals. A portion of the calcite together with the hydromagnesite represented dolomite. It is seldom that the concentration of TiO_2 is as

high as 4% in coal mineral matter. However, the concentration was chosen to meet the detection limitations of analytical techniques.

Table 3.1 Chemical compounds representing minerals included in the model mineral mixture

Name	Formula	Purity	Ratio (wt %)	Supplier and/or CAS Number
Kaolin clay (heavy)	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Ph. Eur. Bp	25	Riedel-de Haën; 1332-58-7
Quartz	SiO_2	Purum p.a. sand	20	Fluka; 14808-60-7
Iron disulfide	FeS_2	95 %	20	Strem Chemicals; 12068-85-8
Calcium carbonate	$\text{CaCO}_3 \cdot n\text{H}_2\text{O}$	98.0 – 100.5 %	15	Merck
Ferrous carbonate	$\text{FeCO}_3 \cdot n\text{H}_2\text{O}$	Laboratory reagent	8	Qualikems; 60676-86-0
Magnesium carbonate, basic	$\text{MgCO}_3 \cdot n\text{H}_2\text{O}$	Meets USP testing specifications	8	Sigma; 546-93-0
Titanium (iv) oxide	TiO_2	–	4	Sigma; 1317-70-0

The minerals (as received) were mixed in the appropriate ratios and dried overnight at approximately 100 °C. An attempt was made to size the mixture to - 212 µm to meet the specifications stipulated in the South African National Standard ashing procedure (SABS ISO 1171:1997 or SANS 131:1997). However, the characteristics of the mixture made sieving to the - 212 µm size range very time-consuming. The mixture was sized to - 355 µm instead. Weighing of the mineral mixture before and after drying at 100 °C yielded mass losses associated with moisture of between 1% and 2%.

3.1.2 Additives

Several minor and trace elements were selected from literature to serve as additives to the mineral mixture. Inorganic compounds found in both raw coal and ash products were considered due to the homogenous nature of fluidized beds. The mode of occurrence of trace and minor elements affects their transformation and partitioning during coal consumption [Folgueras et al., 2007; Shah et al., 2009; Yiwei et al., 2008]. Therefore, the oxidation numbers of the elements, as well as the anions, were

intentionally varied to investigate and compare sintering and agglomeration trends among the different inorganic compounds.

Table 3.2 Compounds selected as additives to the mineral mixture based on trace and minor elements in coal

Inorganic Compounds	Formula	Particle Size	CAS Number	Justification for Inclusion
Arsenic (III) oxide	As ₂ O ₃		1327-53-3	Orpiment. Bunt and Waanders [2008]
Chromium(III) sulfate hydrate	Cr ₂ (SO ₄) ₃ .nH ₂ O		15244-38-9	Linak and Wendt [1994]
Chromium (VI) oxide	CrO ₃		1333-82-0	Linak and Wendt [1994]
Cobalt (II) sulfate heptahydrate	CoSO ₄ .7H ₂ O		10026-24-1	Folgueras et al. [2007]
Copper (I) sulfide	Cu ₂ S	- 44 µm	22205-45-4	Chalcocite. Laban and Atkin [1999]
Copper (II) sulfide powder	CuS	-150 µm	317-40-4	Covellite. Laban and Atkin [1999]
Germanium (II) sulfide	GeS		16812-54-7	Font et al. [2005]
Germanium(IV) oxide	GeO ₂		1310-53-8	Font et al. [2005]
Lead (II) carbonate, basic	C ₂ H ₂ O ₈ Pb ₃	- 44 µm	1319-46-6	Cerussite. Clarke [1993]
Lead (II) molybdate	PbMoO ₄		10190-55-3	Wulfenite. Klein [2002]
Lead (II) sulfate	PbSO ₄		7446-14-2	Anglesite. Font et al. [2005]; Shah et al. [2009]
Lead (II) sulfide	PbS		1314-87-0	Galena. Font et al. [2005]; Shah et al. [2009]
Manganese (II) carbonate	MnCO ₃		598-62-9	Rhodochrosite. Clarke [1993]
Manganese (II) oxide	MnO	- 250 µm	1344-43-0	Folgueras et al. [2007]
Manganese (III) oxide	Mn ₂ O ₃	- 44 µm	1317-34-6	Manganite. Folgueras et al. [2007]
Manganese (IV) oxide	MnO ₂	-250 µm + 63 µm	1313-13-9	Pyrolusite. Folgueras et al. [2007]
Mercury (II) sulfide, red	HgS		1344-48-5	Cinnibar. Yudovich and Ketris [2005]
Molybdenum (IV) sulfide	MoS ₂	- 40 µm	1317-33-5	Molybdenite. Klein [2002]
Nickel carbonate, basic hydrate	CH ₄ Ni ₃ O ₇		39380-74-0	Shah et al. [2009]
Nickel sulphide	Ni ₃ S ₂	-105 µm	12035-72-2	Galbreath et al. [2000]
Strontium carbonate	SrCO ₃		1633-05-2	Strontianite. Laban and Atkin [1999]
Strontium sulphate	SrSO ₄		7759-02-6	Celestite. Laban and Atkin [1999]
Vanadium (III) oxide	V ₂ O ₃		1314-34-7	Font et al. [2005b]
Vanadium (V) oxide	V ₂ O ₅		1314-62-1	Folgueras et al. [2007]
Zinc sulfide	ZnS	- 10 µm	1314-98-3	Sphalerite or wurtzite. Font et al. [2005b]
Additional Additives				
Sodium Chloride	NaCl			Halite. Yudovich and Ketris [2006]
Sodium Carbonate	Na ₂ CO ₃			Kosminski et al. [2006b]
Coal	Bituminous	- 75 µm		Liu et al. [2007a]; Ward [2002]

Table 3.2 lists the compounds chosen as additives based on trace and minor elements in coal, as well as the justification for their inclusion. Sodium compounds were included since they can cause agglomeration in fluidized-bed reactors [Dahlin et al., 2006, 2009]. Coal was selected as an additive, due to the close association of coal with mineral particles [Liu et al., 2007a; McLennan et al., 2000a; Ward, 2002]. The results of proximate and ash analyses of the South African bituminous coal blend selected as additive are given in Chapter 5, Section 5.2.

Inorganic compounds were selected based on availability, and by no means represent a complete list of elements and inorganic species found in coal. Due to the toxic, carcinogenic and/or irritant nature of most of the additives, they were not dried

and sized before addition to the mineral mixture, but were used as received. In some instances the compounds were ground to smaller sizes. Where available, the particle sizes of the compounds used are given in Table 3.2.

Some of the species have considerable health risks, especially those that yield volatile products when heated. Due to a lack of proper ventilation for some of the instruments, V_2O_3 , V_2O_5 and As_2O_3 were excluded from the oxidizing experiments as a safety precaution. It was also not viable to prepare pellets with CrO_3 as additive, since chromium (VI) oxide (CrO_3) is very reactive in the presence of water (see Section 3.2.1). However, these compounds were included in the reducing-atmosphere ash fusion temperature tests (see Section 3.4).

3.1.3 Concentration of Additives in the Mineral Mixture

Trace elements have a concentration of below 1000 ppm (0.1%) in dry coal (elemental concentration, weight percent basis). A hypothetical coal source with an ash yield of 25% was considered. A trace element concentration of 0.1% in the dry coal equates to a trace element concentration of 0.4% in the ash, assuming no losses occurred due to volatilization. To overemphasize the influence of the particular species and to account for detection limits of analytical techniques, the concentration was increased by a factor of 10, yielding a concentration of 4%. Consequently, 40 milligrams of additive was added for every gram of mineral mixture (weight percentage, as received). The higher concentration is justified as the study was aimed at qualitatively identifying chemical interactions, and not necessarily deducing the influences on reactor operation.

3.2 Compressive Strength Tests

Compressive strength tests of pellets sintered in air were used as the initial method to evaluate the influence of the inorganic compounds on sintering in the mineral mixture (see Section 2.9.2 for a detailed discussion of the method). The compressive strength test results were used to: (1) reduce the number of additive/mineral mixture blends subjected to additional analytical techniques, (2) determine the sintering temperature of the mineral mixture, and (3) to investigate the influence of ashing (heat-treating) the mineral mixture before analysis. Compressive

strength tests of pellets sintered under nitrogen were also performed for a reduced number of additives. Section 3.2.5 contains the selection criteria applied to decrease the number of additives for further investigation, as well as a list of the selected additives.

3.2.1 *Pelletizing Method*

Compressive strength tests were performed on cylindrical pellets. Several different pelletizing procedures were investigated in order to prepare pellets with good integrity, and to limit cracking during heat treatment. Neat (without additives) mineral mixture pellets were prepared from 1 gram of the mineral mixture. Pellets with additives comprised of a well blended mixture of 1 gram mineral mixture and 40 milligrams of additive. At least six pellets were prepared for each sample to be heat-treated at each temperature. In isolated cases only four pellets were prepared due to limited reagents.



Figure 3.1 Photograph of the Ametek Lloyd Instruments LRXplus strength tester

Pellets with 10 mm diameters were prepared for compressive strength tests. Die sets were obtained from Specac. Drops of water were added to the mixture in the die set at intervals. The addition of water improved compression and prevented crumbling of pellet edges. The pellets were pressed by applying a force of 1500 N for three minutes on the die set, which was placed between compression plates. The force

was applied with an Ametek Lloyd Instruments LRXplus strength tester equipped with a 5 kN loadcell, as shown in Figure 3.1. A force of 1500 N provided pellets with the desired integrity. Experiments indicated that applying the force for less than three minutes resulted in more cracking during heat treatment.

3.2.2 Sintering Methods

3.2.2.1 Oxidizing Atmosphere Compressive Strength Tests (Sintered in Air)

The pellets for oxidizing compressive strength tests were sintered in static air at 500 °C to 1000 °C (in 100 °C increments) and kept at the desired temperatures for 2.5 hours. A Lenton muffle furnace equipped with a TOHO 300 micro-processor was used. The furnace was heated at 5 °C/min to the desired temperature. After completion of the temperature program, the pellets were left in the furnace to cool down to below 60 °C before removal. In order to determine the initial sintering temperature of the mineral mixture (without additives), pellets were also sintered at 100 °C to 400 °C in 100 °C increments, and at 1100 °C.

3.2.2.2 Inert Atmosphere Compressive Strength Tests (Sintered in N₂)

The additives selected based on the results obtained in oxidizing compressive strength tests (see Section 3.2.5) were subjected to inert compressive strength tests. Pelletizing, data acquisition and data representation of the inert compressive strength tests were identical to the oxidizing compressive strength tests.

Pellets were sintered under nitrogen in a Lenton ceramic tube furnace (model TSH15/75/610). Ceramic heat shields were inserted at both ends of the tube furnace to improve the stable temperature working area of the furnace. The ends of the tube furnace were enclosed by stainless steel caps with a gas inlet or outlet. The tube furnace with pellets was flushed with nitrogen for at least 15 minutes at a flow rate of approximately 1 L/min before each experiment. A nitrogen flow of approximately 500 ml/min was maintained for the duration of the experiments and the cooling period.

The pellets for inert compressive strength tests were sintered at 500 °C to 1000 °C (in 100 °C increments); similar to the oxidizing experiments. The pellets were heated at 5 °C/min and kept at the desired temperatures for 2.5 hours. After completion of the temperature program, the pellets were left in the furnace to cool down to below 60 °C before removal. In order to determine the initial sintering

temperature of the mineral mixture (without additives) under nitrogen, pellets were also sintered at 100 °C to 400 °C in 100 °C increments, and at 1100 °C.

3.2.3 *Crushing Procedure and Data Acquisition*

The pellets, sintered in air or nitrogen, were crushed at ambient conditions to record their compressive strengths. The Ametek Lloyd Instruments LRXplus strength tester used to prepare the pellets was also used to crush and record the compressive strength of each pellet (see Figure 3.1). The speed of the compression plates was maintained at 10 mm/min during crushing to apply an increasing force on the pellets. The maximum force applied to incur breakage was recorded for each pellet.

3.2.4 *Data Representation*

Each batch of pellets in the furnaces contained neat mineral mixture pellets to serve as baseline for comparison with the pellets with additives. The average compression strength values were calculated for each experiment sintered at the different temperatures. Averages were calculated from four to seven compressive strength values. The average values for the neat mineral mixture experiments were subtracted from the values for the experiments with additives. The differences were expressed as a percentage of the average values for the neat mineral mixtures pellets. The formula is given in equation 3.1.

$$\% \text{ deviation} = (\text{Average}_{\text{Additive}} - \text{Average}_{\text{Mixture}}) / \text{Average}_{\text{Mixture}} \times 100 \quad (3.1)$$

The graphs depicting the compressive strength results for the experiments with additives contain the neat mineral mixture results as the baseline or zero line, and the percentage deviations from the zero line for the experiments with additives. The graphs are included in the results discussed in Chapters 5 to 8. The data points are connected with a line to enhance visualisation, and may not necessarily represent statistical trends. The error bars associated with each average value represent 95% confidence limits. Confidence limits account for the number of data points, and the uncertainty associated with the standard deviation by using the *t* function [Anderson, 1987].

The compressive strength results for the neat mineral mixture experiments depicting characteristics of the mixture, as well as determining the reproducibility of

the method, are expressed as the maximum force divided by the area, or N/mm² (results included in Chapter 4). The results represent the maximum pressure that was necessary to incur breakage of the pellets.

3.2.5 *Selection Criteria for Further Analysis*

Based on the results from the oxidising compressive strength tests, sixteen additives were selected for more detailed investigation. Only these sixteen additives were included in inert compressive strength tests and other analytical methods.

All additives eligible for inclusion in further analyses required:

- Firstly, an average at one or all of the applicable sintering temperatures differing from the mineral mixture baselines by more than 14%, since the maximum error (confidence interval) calculated for the neat mineral mixture experiments sintered in air was 14%.
- Secondly, average values for the additives with their confidence limits differing significantly from their mineral mixture baselines, i.e. confidence limits or error bars were not allowed to overlap.

Inorganic compounds satisfying both criteria, and therefore included in further investigations, are listed in Table 3.3. All other additives were limited to oxidizing compressive strength tests, unless stated otherwise.

Table 3.3 Species selected for inclusion in additional experiments

NaCl	SrCO ₃	NiCO ₃	GeO ₂
Na ₂ CO ₃	MoS ₂	Ni ₃ S ₂	Cu ₂ S
Mn ₂ O ₃	PbMoO ₄	Cr ₂ (SO ₄) ₃	CuS
MnCO ₃	PbS	ZnS	Coal

3.3 Characterisation and Chemical Transformations

The inorganic compounds listed in Table 3.3 were used in additional experiments to investigate different aspects of the mineral transformations during heat treatment. The mineral mixture with additives were subjected to compressive strength tests with pellets sintered under nitrogen, as mentioned in Section 3.2.2.2. The other experiments measured different parameters, including mass loss and thermal

transformations (determined by TG/DTA); precipitation of crystalline species (determined by XRD); and visual determination of sintering and element associations in the pellets via SEM/EDS analysis. Characterisation of the mineral mixture also included thermomechanical analysis (TMA) that recorded dimension changes in the pellets during heat treatment.

3.3.1 *X-ray Fluorescence Spectroscopy*

Major, minor and trace elements of the minerals in the mixture were determined by X-ray fluorescence spectroscopy (XRF). Analyses of major elements were performed on a ThermoARL Model 9800XP, simultaneous/sequential XRF instrument, using either pressed pellets or ignited material fused with lithium borate. Trace analyses were performed with a ThermoARL Model Advant 'XP instrument on pressed pellets.

3.3.2 *Thermomechanical Analysis*

Thermomechanical analysis (TMA) was used to investigate the shrinkage and expansion of the mineral mixture during heat treatment to determine the onset of chemical reactions. Only the mineral mixture was analyzed by TMA due to the release of corrosive gasses from the mixture during heat treatment that damaged the instrument. The TMA analysis was performed on a SII Technology TMA/SS6100 instrument equipped with an EXSTAR6000 station. The mineral mixture was pelletized as described in Section 3.2.1, except that no water was added, and the pellet was pressed at 2000 N for 3 minutes. Experiments determined that this pelletizing method gave the best results for TMA. The pellet was analyzed in static air and heated from room temperature to 1000 °C at 5 °C/min. A constant force of 50 mN was maintained on the pellet to detect changes.

3.3.3 *Thermogravimetric (TG) and Differential Thermal Analysis (DTA)*

Mass loss of the minerals, mineral mixture and mineral mixture with additives (listed in Table 3.3) was measured with a Mettler Toledo TGA/SDTA 851° system. The DTA curve for each sample was also determined. The TG curves were used to determine mass loss on ignition according to the South African National Standard method, SANS 6298:2006. Approximately 20 to 80 mg of sample was

heated from 30 °C to 1000 °C at 5 °C/min in a gas flow of 120 ml/min of either air or nitrogen, depending on the experiment.

3.3.4 X-ray Diffraction

X-ray diffraction (XRD) was used to characterize the minerals, as well as analyze the crushed pellets from compressive strength tests to determine which crystalline phases persisted, formed during heating, or precipitated during cooling. Semi-qualitative XRD analysis of the minerals in the mixture was performed on a PANalytical X-PERT PRO instrument equipped with a Cu anode. The powders were scanned at 2θ angles from 2 ° to 100 °. The instrument was operated at 40 kV and 45 mA at ambient conditions.

Selected pellets were subjected to qualitative XRD analysis. Analyses were performed on a Thermo-Fischer ARL X'tra instrument equipped with a Cu anode. The instrument was operated at 45 kV and 44 mA at ambient conditions. The 2θ angles of the finely pulverised material were measured from 2 ° to 75 °. The samples were selected based on significant differences observed in the oxidizing compressive strength results.

3.3.5 Scanning Electron Microscopy (SEM)

A selection of samples, based on the results for oxidizing compressive strength tests, was analyzed with scanning electron microscopy. A few samples from the inert compressive strength tests were also included for comparison. SEM analyses were performed on a FEA Quanta 200 ESEM instrument equipped with an Oxford INCA X-Sight 400 EDS (energy-dispersive spectrometry) system and operated with a 15 kV electron beam.

Mineral mixture samples were coated with a layer of gold-palladium for visual assessment of sintering at a 10,000 times magnification. Backscattered electrons combined with EDS were used to determine the elemental composition in different areas of the pellets, viewed at a 200 times magnification. Bulk analysis of the pellet surfaces was also performed at a 400 times magnification with backscattered electrons. Elements with higher atomic numbers appear lighter in colour than elements with lower atomic numbers on a backscattered image. Large areas consisting of glass phases tend to glow white on a backscattered image.

The composition of deposits collected from the heat shield in the tube furnace during some of the inert compressive strength tests were also determined using SEM/EDS. The results were helpful to determine the chemical transformations of some of the additives in the inert atmosphere.

3.4 Reducing-Atmosphere Ash Fusion Temperature (AFT) Tests

Reducing-atmosphere ash fusion temperature (AFT) tests were used as an alternative, faster method than the compressive strength test to investigate the influence of additives on ash formation under reducing conditions. However, a detailed study of ash interactions under reducing conditions lay outside the scope of this study.

3.4.1 Method

Reducing-atmosphere ash fusion temperature (AFT) tests were performed according to the SABS ISO 540:1995 (SANS 43) standard method. Samples were sized and ashed (heat-treated) before ash fusion temperature determination according to the SABS ISO 1171:1997 (SANS 131:1997) standard method. A detailed description of the method is available in Section 2.9.1.

The standard ashing method used to prepare the samples stipulates a two-stage temperature program, i.e. initial heating to 500 °C, maintained for 30 minutes, followed by further heating to 815 °C. Research has shown that sintering can occur at temperatures below the standard ashing temperature [Jung and Schobert, 1992]. To investigate the influence of different ashing temperatures on the ash fusion temperatures, a portion of the samples consisting of the mineral mixture with 4% additives was ashed at 500 °C, whilst the rest was ashed according to the standard method. Ash fusion temperatures were recorded in triplicate for samples ashed at both temperatures. Results for the neat mineral mixtures and a few of the additives include more than three measurements due to the inclusion of duplicate samples as internal checks. Results from duplicate samples were well within permitted ranges.

3.4.2 *Data Representation*

Ash fusion temperature results obtained for the mineral mixture and mixture with additives are represented by bar graphs, and compare ash fusion temperatures of the neat mineral mixture to the mixture with additives at different ashing (heat-treating) temperatures. Ashing temperatures are given in parentheses. The results are included in Chapters 4 to 8 in the sections allocated to the results and discussion of the neat mineral mixture or the relevant additive.

Averages were calculated from the multiple determinations. According to the standard method, ash fusion temperatures are reported as rounded to the nearest 10 °C. The averages were also rounded to the nearest 10 °C following rounding rules. The error bars for the neat mineral mixture represent the characteristic error of ± 30 °C associated with AFT tests (thick error bars). Error bars associated with the results for the mixture with additives represent 95% confidence limits (thin error bars). Where error bars appear to be absent the results in triplicate gave the same temperature, and the standard deviation was therefore zero.

3.4.3 *Interpretation*

Ash fusion temperatures of the mixture with additives were deemed significantly different from the neat mineral mixture when the averages for the mixtures with additives and their 95% confidence limits fell outside the ± 30 °C error range for the neat mineral mixture ashed at the corresponding temperature.

The results obtained using the methods and analyses described in this chapter are discussed in the following chapters. Chapter 4 contains the characterization of the minerals and mineral mixture, as well as the repeatability and suitability of the methods.

Chapter 4

Results and Discussion

Characterisation and Evaluation of Minerals, Mineral Mixture and Methods

Associated minerals can react with one another when heated to appropriate temperatures. Characterization of the minerals can assist in elucidating possible chemical reactions that occur. This chapter includes the evaluation of methods used in the study, characterisation of chemicals in the mixture, and an investigation into the chemical interactions occurring in the mixture during heat treatment.

4.1 Characterisation of Chemicals in the Mixture

Kaolin clay, SiO_2 , FeS_2 , CaCO_3 , basic MgCO_3 , FeCO_3 , and TiO_2 were added to the mixture in fixed ratios. They represented the minerals kaolinite, quartz, pyrite, dolomite, calcite, siderite and anatase. The major, minor and trace constituents in each compound were evaluated with X-ray fluorescence (XRF). XRF results were reported on a weight basis, and are presented in Table 4.1.

The anticipated major elements in the compounds were confirmed by the XRF results. The compounds contained minor and trace impurities. The majority of minor elements occurred in concentrations lower than 0.1% (1000 ppm by weight, reported as oxides). Some of the minor elements were detected as having concentrations between 0.1% and 1%. However, sodium in FeCO_3 and potassium in kaolin clay (reported as Na_2O and K_2O , respectively) occurred in concentrations of more than 1%. XRF results of the major and minor constituents suggested that the compounds were of high purity. Fe in FeS_2 was not reported as an oxide, but as Fe instead. The amount of gaseous species released during decomposition of the compounds, e.g. CO_2 , H_2O and SO_x , were combined and reported as the loss on ignition (LOI). LOI values are presented in Table 4.2.

The majority of trace elements were detected as having very low concentrations in the compounds (less than 100 ppm). However, some exceptions existed, e.g. FeS_2 contained As, Cu, Zn and Ba in concentrations of more than 300

ppm. Barium in FeS₂ had a concentration of 0.3%. It was not possible to determine the Ba concentration in TiO₂ due to overlapping signals. High concentrations of Co and W were found in SiO₂. The laboratory reported that the high concentrations could be due to contamination from the mortar used to prepare the sample for analysis.

Table 4.1 Major, minor and trace elemental analysis of chemicals added to the mixture as determined by XRF (on a weight basis)

Major and Minor Elements (weight %, oxide basis)													
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	K ₂ O	MnO	Cr ₂ O ₃	V ₂ O ₃	P ₂ O ₅	S
Kaolin	46.7	36.6	0.6	0.1	0.4	<0.1	<0.1	1.2	<0.1	<0.1	<0.1	0.1	<0.1
SiO ₂	99.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CaCO ₃	<0.1	<0.1	<0.1	56.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
MgCO ₃	<0.1	<0.1	<0.1	0.5	41.5	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
FeCO ₃	0.3	<0.1	71.2	0.1	<0.1	<0.1	1.2	<0.1	0.4	<0.1	<0.1	<0.1	0.6
TiO ₂	<0.1	<0.1	0.5	0.1	<0.1	98.5	<0.1	0.2	<0.1	<0.1	<0.1	0.3	<0.1
FeS ₂	0.4	<0.1	46.6 as Fe	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	53.0
Trace Elements (ppm)													
	As	Bi	Co	Cu	Nb	Ni	Mo	Pb	Rb	Se	Sr	Ta	U ₃ O ₈
Kaolin	22	20	<3	19	17	<2	<4	19	130	<3	116	<18	20
SiO ₂	<3	<2	218*	<4	<3	<2	<4	<3	<4	<3	3	<18	<7
CaCO ₃	17	5	<3	<4	<3	2	<4	10	<4	<3	173	<18	<7
MgCO ₃	8	3	<3	<4	<3	<2	<4	<3	<4	<3	11	<18	<7
FeCO ₃	3	18	68	25	<3	7	<4	170	<4	<3	7	<18	<7
TiO ₂	11	3	<3	9	70	13	<4	22	<4	<3	3	18	<7
FeS ₂	397	<2	64	566	<3	37	<4	63	<4	23	21	<18	<7
Trace Element (ppm) continued													
	W	Y	Yb	Zn	Zr	Ag	Cd	Sb	Sn	Ba	La	Ce	Eu
Kaolin	20	33	<8	26	72	<4	<10	<10	<10	175	47	94	<2
SiO ₂	1480*	<3	13	<4	19	<4	<10	<10	<10	<4	44	21	<2
CaCO ₃	<10	<3	<8	9	<3	<4	29	11	<10	<4	44	13	<2
MgCO ₃	10	5	<8	4	<3	<4	<10	23	<10	<4	46	<5	<2
FeCO ₃	37	4	<8	22	<3	9	181	23	<10	<4	36	7	22
TiO ₂	20	<3	<8	5	137	<4	110	38	<10	**	<2	46	<2
FeS ₂	127	<3	<8	1111	<3	6	186	29	<10	2877	38	21	<2

* Possible contamination due to mortar

** Unable to analyze due to overlap

Table 4.2 X-ray diffraction and loss on ignition results of the compounds

	Kaolin	SiO ₂	FeS ₂	CaCO ₃	MgCO ₃	FeCO ₃	TiO ₂
Semi-qualitative XRD results	Kaolinite	α-Quartz	Pyrite	Calcite	Hydro-magnesite	Inconclusive	98% Anatase 2% Rutile
LOI based on XRF results	13.7%	0.1%	27.1%	44.0%	57.8%	26.0%	0.5%
LOI based on TG results (in air)	12.5%	-0.2%	34.6%	44.7%	58.7%	17.8%	-0.3%

X-ray diffraction (XRD) analysis was performed on the compounds to determine which crystalline phases were present. The XRD results, as well as loss on ignition values obtained from XRF and thermogravimetry (TG) are presented in

Table 4.2. The XRD results indicated that the mineral phases constituting the different compounds were kaolinite, α -quartz, pyrite, calcite, hydromagnesite, anatase and rutile. The basic MgCO_3 occurred as hydromagnesite. Results for FeCO_3 were inconclusive.

Loss on ignition values obtained from XRF and TG measurements were comparable, except for FeS_2 and FeCO_3 . In most cases the values differed by less than 1%. TG experiments with SiO_2 and TiO_2 recorded a slight weight gain during heating in air (less than 0.5%). The negative LOI values for SiO_2 and TiO_2 in Table 4.2 represent the amount of weight gained. The implications of the LOI values will be discussed together with the TG and differential thermal analysis (DTA) results obtained for each compound (see Section 4.2.1). TG experiments in N_2 also provided weight loss values for the compounds in an inert atmosphere.

4.2 Mineral Interactions in the Mixture During Heating

Several different analytical techniques were employed to investigate the chemical transformations occurring in the individual mineral compounds and the mixture during heat treatment. Experiments were conducted in air and in N_2 . Simultaneous TG and DTA (TG/DTA) analyses were performed to evaluate the weight loss and phase changes in the mineral compounds and the mixture. Loss on ignition values represent the weight loss at 1000 °C. DTA results indicated that heating of the compounds in N_2 were generally more exothermic over the total heating range than compounds heated in air. Weight loss information, XRD analyses and scanning electron microscopy (SEM) were used to identify the formation of species during heat treatment. Qualitative XRD analyses were performed on pellets obtained from compressive strength tests sintered in air at the relevant temperatures.

4.2.1 Chemical Transformations in the Mineral Compounds

4.2.1.1 Oxides: SiO_2 and TiO_2

The TG and DTA results of SiO_2 and TiO_2 are presented in Figures 4.1 and 4.2. The results are similar for both compounds. No significant weight loss was recorded for SiO_2 heated in N_2 (<0.05%). TiO_2 heated in N_2 had a weight loss of 0.3%. However, SiO_2 gained 0.2% and TiO_2 gained 0.3% weight during heating in air. The

weight gain is probably due to adsorption of oxygen on the surface of the particles [Arasa et al., 2008; Ménétrey et al., 2007; Uner et al., 2003].

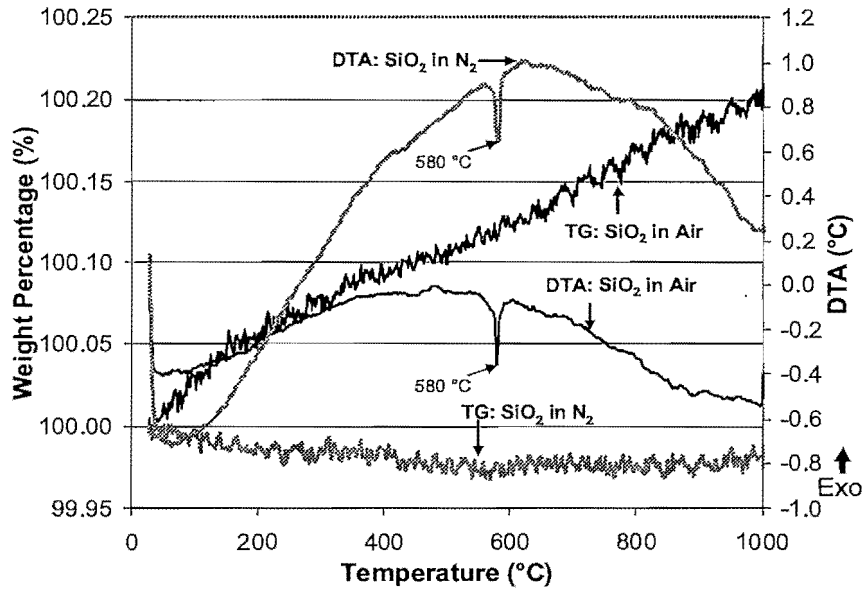


Figure 4.1 TG/DTA results of SiO_2 heated in air and N_2

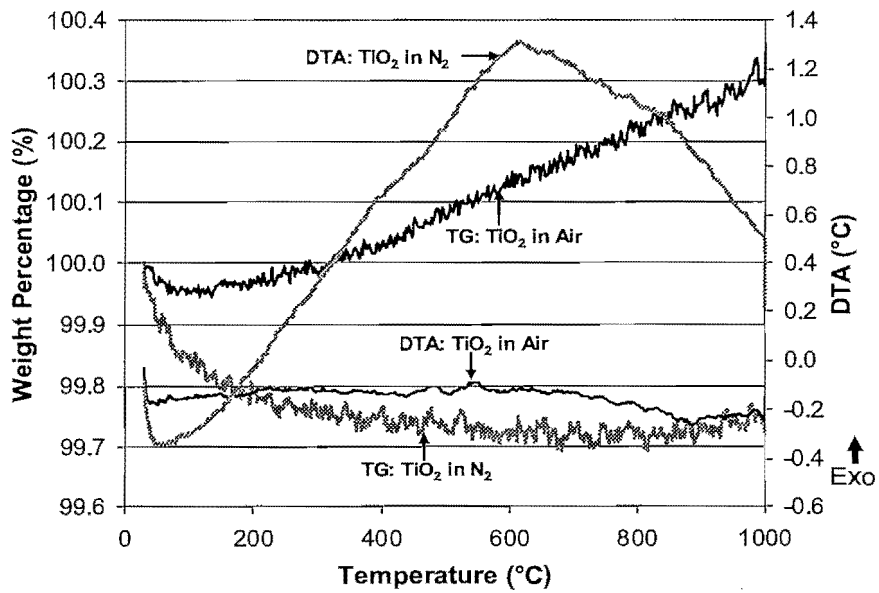


Figure 4.2 TG/DTA results of TiO_2 heated in air and N_2

The DTA curves of SiO₂ heated in air and N₂ indicate a small endothermic peak at 580 °C not associated with weight loss. The peaks represent the structural changes associated with the transformation of α -quartz (low quartz) to β -quartz (high quartz) [Klein, 2002; Nankervis and Furlong, 1980; O’Gorman and Walker, 1973; Reifenstein et al., 1999].

Researchers have indicated that β -quartz transforms into tridymite at 876 °C [Matjie et al., 2007; Reifenstein et al., 1999; Salmang, 1961]. However, the DTA results do not suggest that the transformation occurred in the SiO₂ sample under the specific experimental conditions. XRD analysis confirmed that SiO₂ occurred as quartz in the mineral mixture sintered at 1000 °C in air. The existence of SiO₂ as quartz at high temperatures is not uncommon. Vuthaluru and French [2008a] reported the persistence of SiO₂ as quartz in drop-tube furnace experiments heated to 1400 °C.

Pure anatase transforms irreversibly to rutile between 900 °C and 1000 °C, depending on impurities, time, temperature and particle size [Heald and Weiss, 1972; Riyas and Das, 2004]. However, the DTA results of TiO₂ indicate that the transformation did not occur under these specific experimental conditions. The presence of hematite lowers the transformation temperature, whereas sulfates and phosphates raise the temperature [Heald and Weiss, 1972; Riyas and Das, 2004]. According to the XRF results (Table 4.1), TiO₂ contained Fe and P species as impurities that could have contributed to a shift in the transformation temperature. XRD analysis confirmed the occurrence of TiO₂ as anatase in the mineral mixture sintered at 1000 °C in air.

4.2.1.2 Kaolinite

The TG/DTA results of kaolin clay are presented in Figure 4.3. The weight loss patterns of kaolin clay heated in air and N₂ are similar. The transformation of kaolinite (Al₂O₃·2SiO₂·2H₂O) into amorphous metakaolinite (Al₂O₃·2SiO₂) through dehydration occurred from 420 °C to 620 °C, based on the endothermic peaks in the DTA curves. The transformation of pure kaolinite into metakaolinite is associated with a weight loss of approximately 16%. Loss on ignition values obtained in both these atmospheres were comparable at approximately 13%. XRD analysis of the mineral mixture sintered at 500 °C in air indicated that kaolinite was transformed to amorphous phases under the experimental conditions. Metakaolinite can interact with

other compounds at temperatures below 800 °C to form complex aluminosilicates [Matsuoka et al., 2006].

Small exothermic peaks, not associated with weight loss, occurred at approximately 990 °C. Exothermic transformations at 990 °C represent the formation of silicon spinel or a spinel-like form of γ -alumina [Frost et al., 2003; Mayoral et al., 2001; Reifenstein et al., 1999].

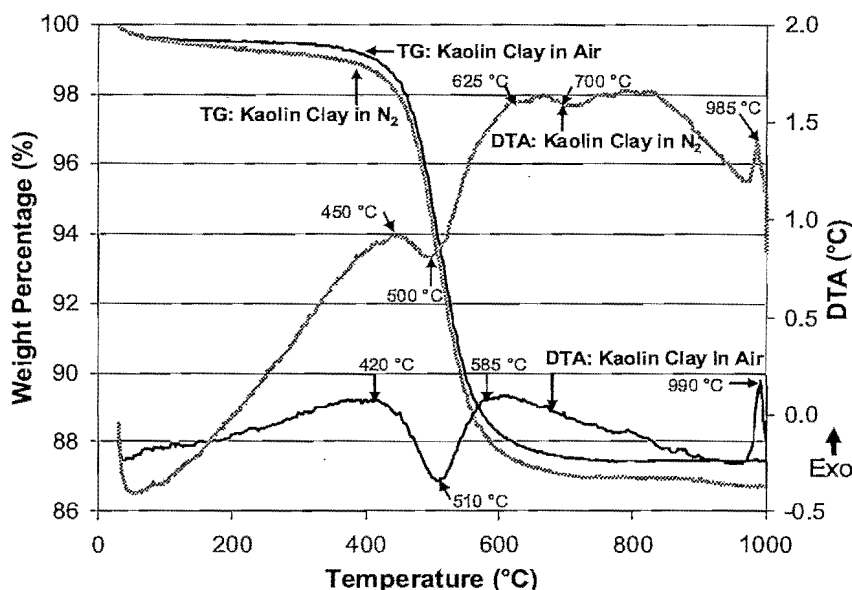


Figure 4.3 TG/DTA results of kaolin clay heated in air and N_2

4.2.1.3 Carbonates: $CaCO_3$, $MgCO_3$ and $FeCO_3$

Carbonates decompose to yield metal oxides and CO_2 . The TG/DTA results of $CaCO_3$ are presented in Figure 4.4. The endothermic decomposition of $CaCO_3$ occurred from 560 °C to 780 °C. Decomposition of $CaCO_3$ was similar in air and N_2 . The observed weight loss is characteristic of the complete decomposition of $CaCO_3$ to CaO (56%) and CO_2 (44%). $CaCO_3$ did not transform to other polymorphs.

The TG/DTA results of basic $MgCO_3$ heated in air and N_2 are presented in Figure 4.5. XRD analysis indicated that basic $MgCO_3$ occurred as hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$). Results of hydromagnesite heated in air and N_2 were similar. The endothermic peaks from 150 °C to 350 °C, associated with weight loss of approximately 15%, represent loss of the lattice water. Endothermic decomposition of the dehydrated product occurred from 370 °C to 500 °C. The observed weight loss is

characteristic of the complete decomposition of hydromagnesite to MgO , CO_2 and H_2O .

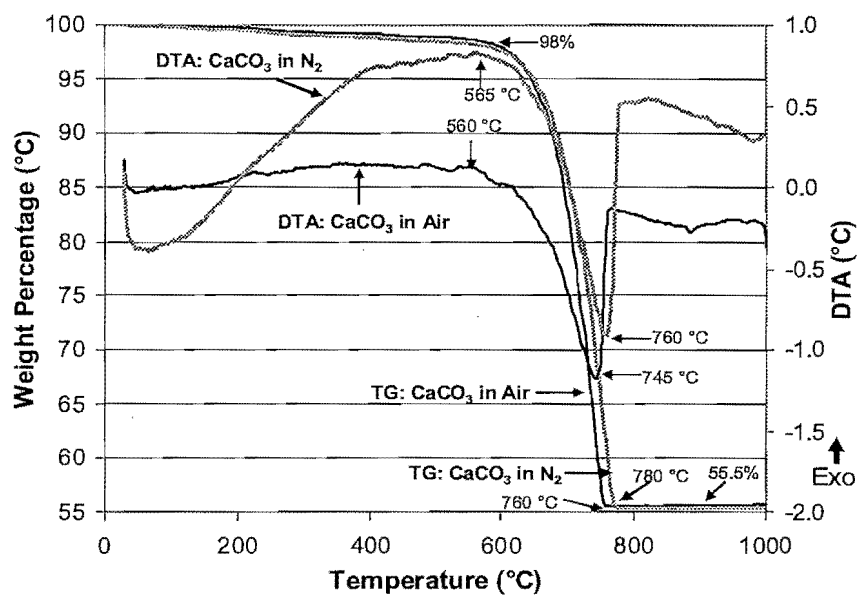


Figure 4.4 TG/DTA results of CaCO_3 heated in air and N_2

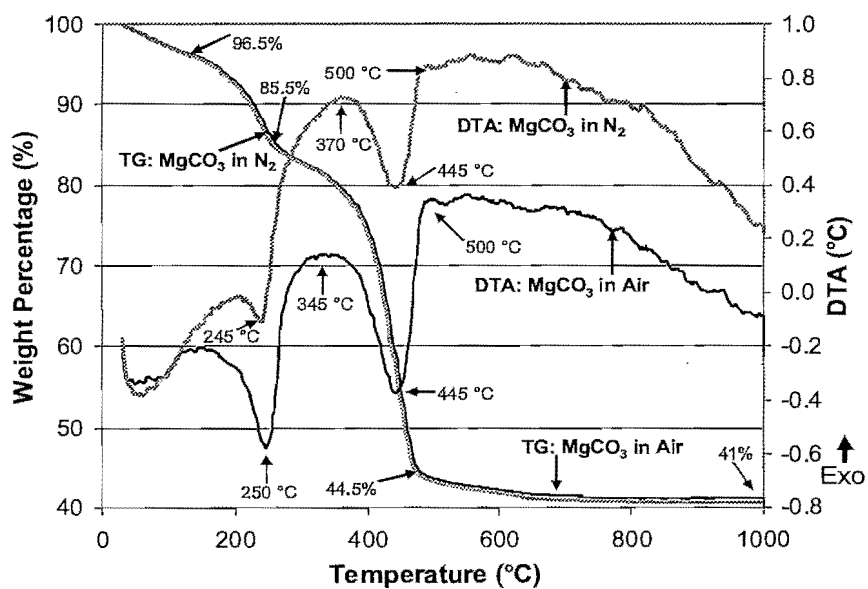


Figure 4.5 TG/DTA results of basic MgCO_3 heated in air and N_2

The TG/DTA results of FeCO_3 heated in air and N_2 are presented in Figure 4.6. XRD analysis was inconclusive regarding the crystal structure of the as received compound before heating. The results of FeCO_3 heated in air and N_2 were similar. The weight loss observed from 30 °C to 150 °C was most likely due to drying. The decomposition of pure FeCO_3 to FeO and CO_2 is associated by a weight loss of 37%. However, the weight loss observed in the TG experiments was only approximately 12%. XRF results for FeCO_3 (Table 4.1) indicate that the substance consisted of a high iron concentration (reported as an oxide), and contained low amounts of impurities. The possibility exists that the substance consisted of a mixture of FeCO_3 and FeO or Fe_2O_3 , instead of being pure FeCO_3 . However, the FeCO_3 is completely decomposed to FeO at the temperature range of interest to the compressive strength tests (500 °C to 1000 °C).

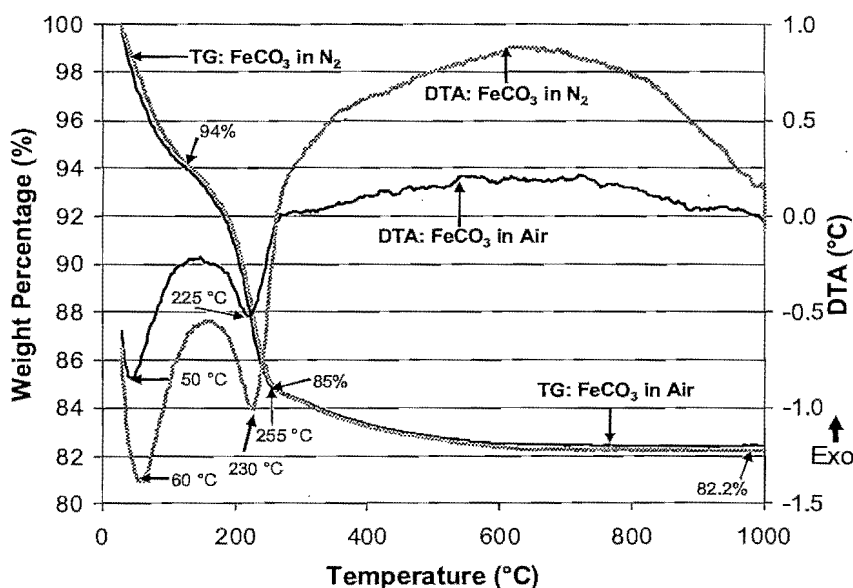


Figure 4.6 TG/DTA results of FeCO_3 heated in air and N_2

4.2.1.4 Pyrite

The TG/DTA results of pyrite (FeS_2) differed significantly in air and N_2 . The results for pyrite heated in air are presented in Figure 4.7. Decomposition of pyrite in air occurred mainly from 370 °C to 665 °C. The DTA curve indicates that heating did not cause a single transformation. FeS_2 decomposes to pyrrhotite (FeS), which in turn oxidizes to FeO in an oxidizing atmosphere [Bool et al., 1995; McLennan et al.,

2000a, 2000b]. Oxidation of pyrite is an exothermic process [Zodrow, 2005]. The weight loss pattern and DTA curve support the complete decomposition and oxidation of FeS_2 to Fe_2O_3 (hematite) and SO_x . XRD analyses confirmed the presence of hematite in mineral mixture pellets sintered at 500 °C to 1000 °C in air.

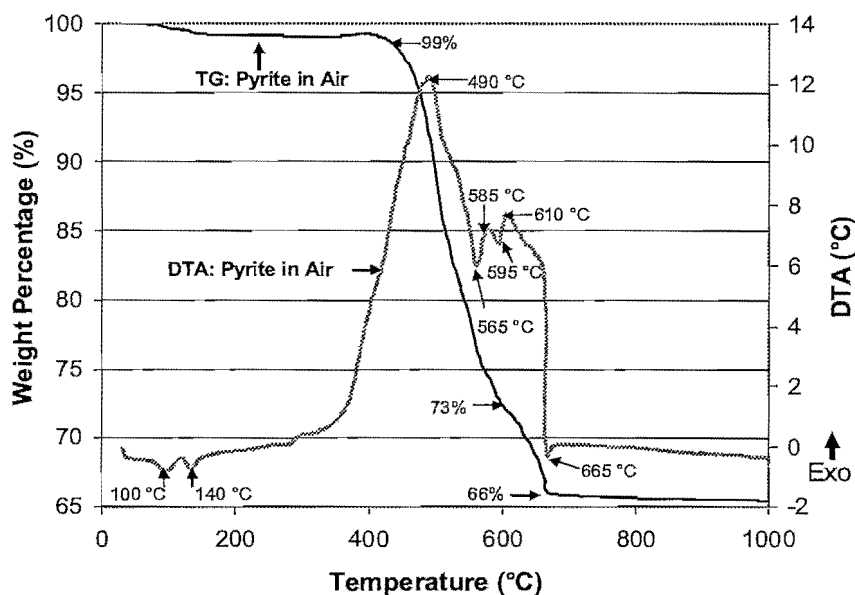


Figure 4.7 TG/DTA results of pyrite heated in air

The TG/DTA results of pyrite heated in N_2 are presented in Figure 4.8. The results differ considerably from the experiment performed in air. The transformation of pyrite in N_2 was mostly endothermic as opposed to the exothermic oxidation of pyrite in air.

The cause of the endothermic peaks, associated with 3% weight loss, observed from 480 °C to 570 °C in the DTA curve is unclear. It may represent transformations of impurities in the pyrite, or the decomposition of marcasite (FeS_2) to FeS , if any was present. Marcasite is dimorphous with pyrite and metastable relative to pyrite above 157 °C [Klein, 2002]. The transformations from 480 °C to 570 °C are not visible in the DTA curve of pyrite heated in air, because if they occurred, they were masked by the large exothermic peak associated with the decomposition and oxidation of pyrite.

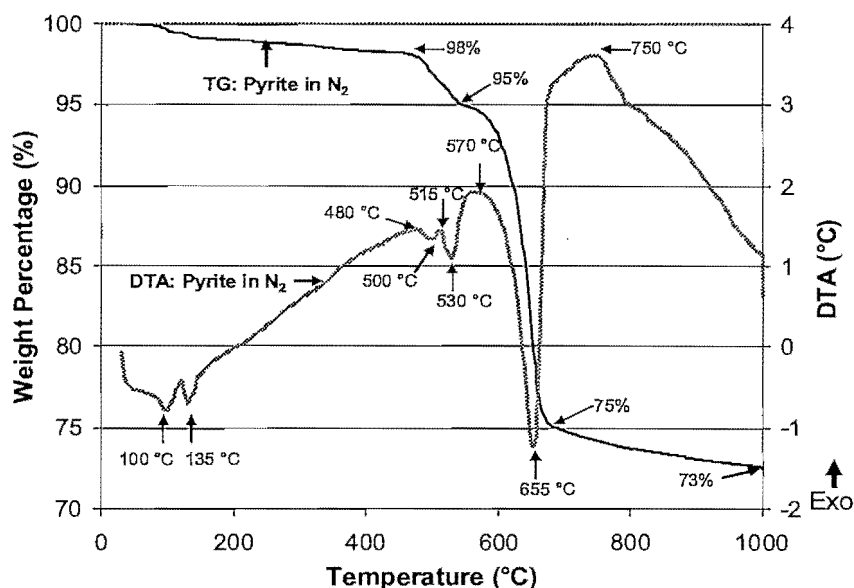


Figure 4.8 TG/DTA results of pyrite heated in N_2

In the absence of oxygen, FeS_2 decomposes to FeS , which is stable under inert conditions [Bool et al., 1995; McLennan et al., 2000a]. This transformation occurred from 570 °C to 700 °C in the pyrite sample heated in N_2 . The total weight loss of 27% signifies the decomposition of FeS_2 to FeS .

Figure 4.9 presents SEM images of iron species detected in mineral mixture pellets sintered at 1000 °C in air and at 900 °C in N_2 . Energy-dispersive spectrometry (EDS) analyses confirmed the occurrence of Fe and O in the molten phase shown in image A (sintered in air), and Fe and S in the crystalline species sintered in N_2 (image B). The Fe and O in the molten phase in image A probably represent FeO from the decomposition and oxidation of pyrite. FeO has a melting point of 1370 °C, but a eutectic of FeS and FeO melts at 920 °C to 940 °C [Laursen and Frandsen, 1998; Marinov et al., 1992]. Further oxidation of the FeS - FeO eutectic yields an FeO -melt (see Section 2.3.2.1) [Bool et al., 1995; Jensen and Austin, 1977; McLennan et al., 2000a, 2000b]. In the absence of sufficient oxygen (perhaps in the centre of the pellets), oxidation of FeO to magnetite and hematite will not occur. Cooling at an adequate rate will inhibit crystallisation. In N_2 (image B), Fe and S occurred as discrete crystals at 900 °C, and probably represent FeS . FeS has a hexagonal crystal structure and melts at approximately 1080 °C [Klein, 2002; McLennan et al., 2000a].

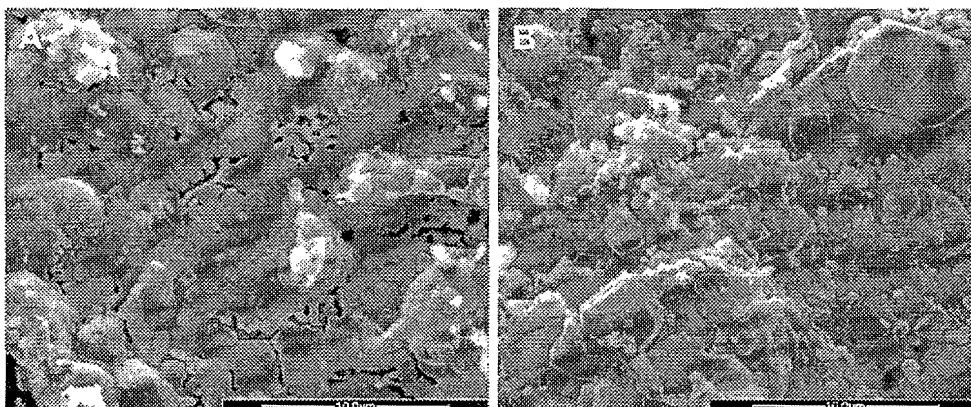


Figure 4.9 SEM images of FeO detected in mineral mixture pellets sintered at 1000 °C in air (A), and FeS in pellets sintered at 900 °C in N₂ (B)

4.2.2 Chemical Interactions in the Mineral Mixture

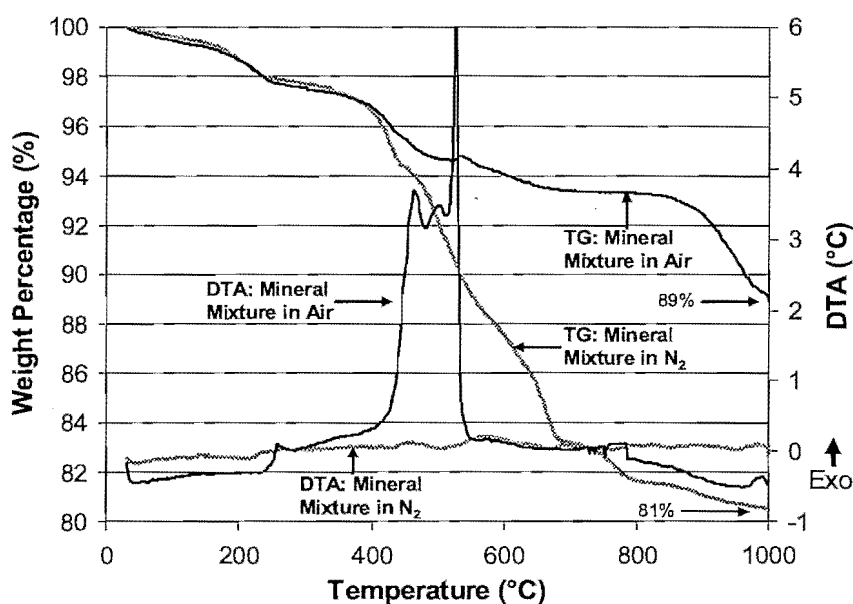


Figure 4.10 TG/DTA results of the mineral mixture heated in air and N₂

Figure 4.10 presents the TG/DTA results obtained for the mineral mixture heated in air and N₂. The mineral mixture heated in air had a smaller weight loss (11%) than the mixture heated in N₂ (19%). The difference can be explained by the oxidation of pyrite to hematite in air resulting in oxygen uptake together with decomposition. It is difficult to distinguish peaks in the DTA curve of the mineral

mixture heated in N₂ in Figure 4.10, due to the large exothermic peak in the DTA curve of the mineral mixture heated in air. Therefore, the results are also presented in separate graphs below. The results of repeated samples are also shown to determine the repeatability of the method.

Figure 4.11 presents the TG/DTA results obtained for four experiments of the mineral mixture heated in air. Experiments 1, 2 and 3 were performed with samples from the same batch of mineral mixture. Experiment 4 was performed at a different time and the sample was from a different batch of the mineral mixture. The results of the different experiments were comparable. Weight loss results varied by $\pm 1\%$. The DTA curve of experiment 4 indicates an exothermic peak at 465 °C, but this peak is only visible as a slight shoulder in experiments 1, 2 and 3. The values of the DTA curves differ by up to 2 °C. The DTA experiments were only intended as qualitative analyses.

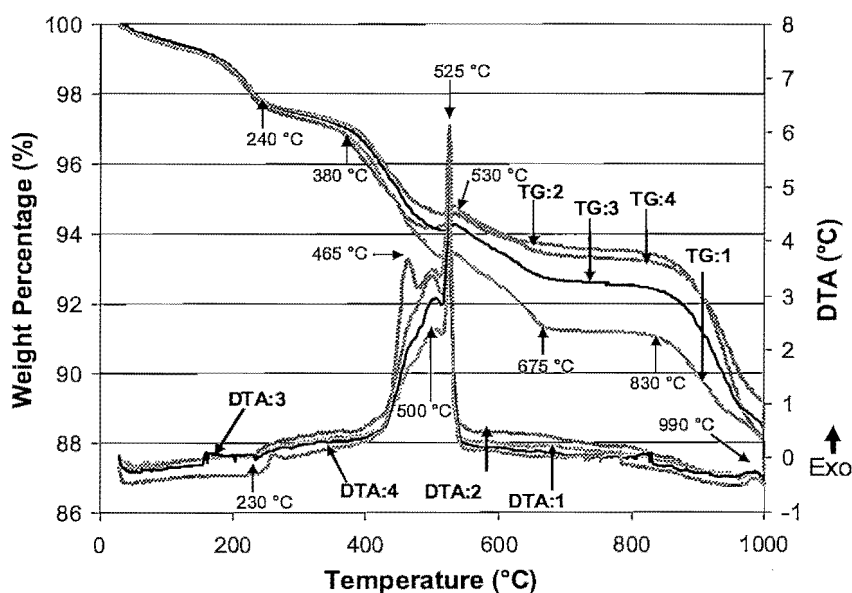


Figure 4.11 TG/DTA results of the mineral mixture heated in air

XRD analyses indicated that the major crystalline phases in the mineral mixture pellets sintered in air at intervals from 500 °C to 1000 °C were quartz (SiO₂), hematite (Fe₂O₃), anhydrite (CaSO₄), anatase (TiO₂), and magnesium sulphate

(MgSO_4) (only 500 – 800°C). Kaolinite was almost completely amorphous in the 500 °C sample.

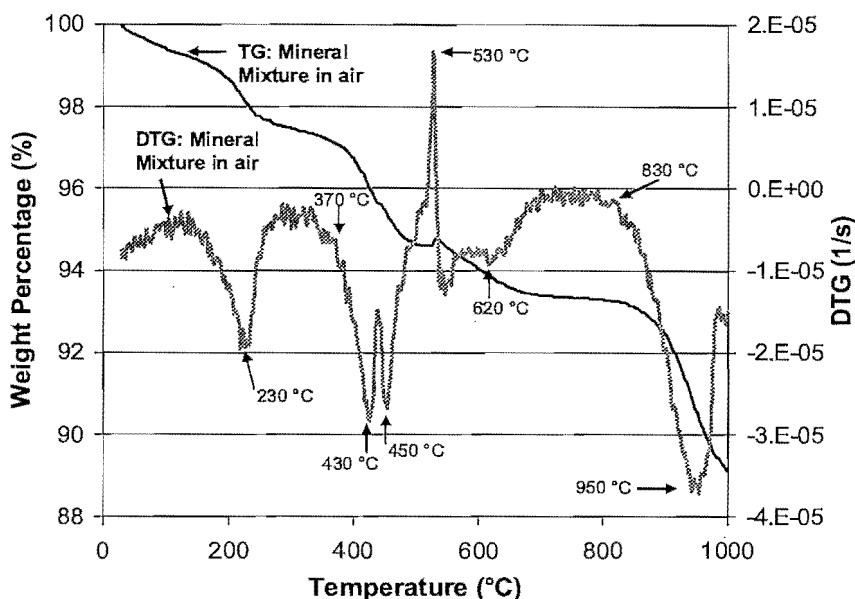


Figure 4.12 First derivative (DTG) of the TG curve of the mineral mixture heated in air (Experiment 4)

Figure 4.12 presents the first derivative of the TG curve of the mineral mixture heated in air. The first derivative of the TG curve indicates the weight loss or gain associated with different temperature intervals. The DTG peak at 230 °C and endothermic peaks at 230 °C in the DTA curves correspond to a weight loss of approximately 2%, and represent the dehydration of hydromagnesite and decomposition of FeCO_3 .

XRD analyses indicated that some of the SiO_2 and TiO_2 remained unchanged throughout heating of the mineral mixture in air. However, parts may have been incorporated into glass phases, especially the SiO_2 . Groen and co-workers [1998] reported that the presence of TiO_2 caused a reduction in melting points of calcium aluminosilicate glass phases in reducing conditions.

The weight loss occurring from 370 °C include the weight loss associated with the dehydration of kaolinite and decomposition of MgCO_3 . The exothermic peak in the DTA curve at 990 °C most probably signifies the formation of silicon spinel or a spinel-like form of γ -alumina [Frost et al., 2003; Mayoral et al., 2001; Reifenstein et

al., 1999]. However, qualitative XRD analysis was not able to detect the occurrence of these phases. FeO (from the decomposition of FeCO_3) can also react with silicates and aluminosilicates to form iron aluminosilicate glasses [McLennan et al., 2000a; Sheng and Li, 2008]. The large exothermic peak in the DTA curve most probably masks the existence of other transformations.

The DTA curves in Figure 4.11 and the DTG curve in Figure 4.12 show that the exothermic decomposition and oxidation of pyrite to hematite occurred from 370 °C to 550 °C. The TG/DTA results of pyrite heated in air (Figure 4.7) indicated that the most exothermic interactions occurred at approximately 490 °C. However, in the mineral mixture heated in air, the most exothermic interaction occurred at approximately 520 °C to 530 °C. The transformation at this temperature is associated with an increase in the weight of the sample, as indicated in Figure 4.12. XRD analyses confirmed the occurrence of CaSO_4 in pellets sintered at 500 °C. The exothermic decomposition and oxidation of pyrite may have caused the CaCO_3 in the mixture to decompose at a lower temperature than indicated in Figure 4.4 (560 – 780 °C). Sulphur released during the decomposition of pyrite in air is oxidised to SO_x [Jensen and Austin, 1977]. Lime (CaO) is a common sulphur-capturing additive used in both combustion and gasification [Katalambula et al., 2001; Li et al., 2006]. XRD results indicate that CaO in the mixture captured or reacted with SO_x released from the decomposition of pyrite to form CaSO_4 (anhydrite).

Weight loss in the mineral mixture remained stable from 675 °C to 830 °C, followed by further weight loss of approximately 4%. In oxidizing conditions, CaSO_4 decomposes to lime and SO_x at temperatures above 900 °C, and the lime can react with clay minerals [Vassileva and Vassilev, 2005, 2006]. The decomposition temperature is lowered depending on the conditions [O’Gorman and Walker, 1973]. The 4% weight loss from 830 °C to 1000 °C was therefore most probably due to the decomposition of CaSO_4 and CaO interacting with amorphous clay phases. Jung and Schobert [1991] reported a depletion of anhydrite and subsequent increase in calcium-containing aluminosilicates with an increase in sintering temperature. XRD analysis indicated that the CaSO_4 was not completely decomposed at 1000 °C. Quantitative XRD could be helpful to map the changes in CaSO_4 concentration in the mineral mixture sintered at temperatures above 800 °C.

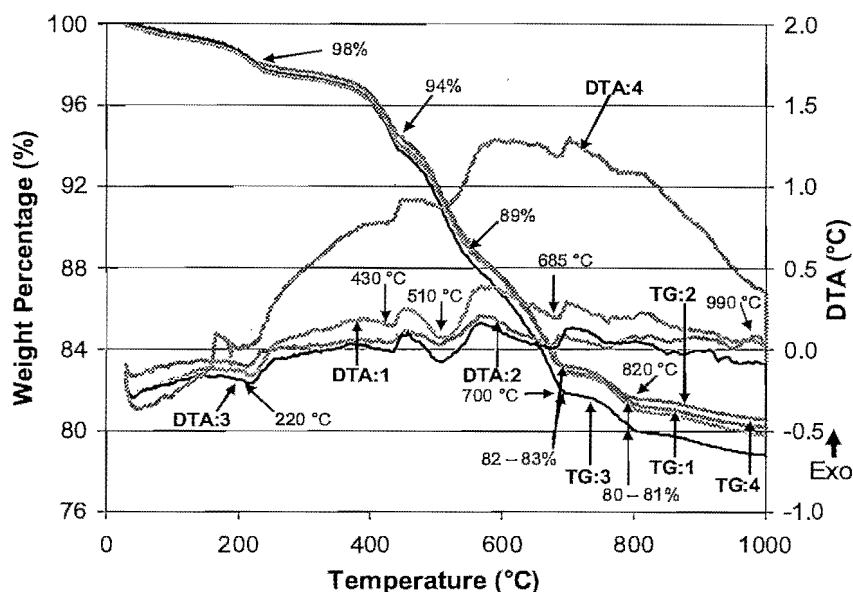


Figure 4.13 TG/DTA results of the mineral mixture heated in N₂

Figure 4.13 presents the TG/DTA results obtained for four experiments of the mineral mixture heated in N₂. Experiments 1, 2 and 3 were performed with samples from the same batch of mineral mixture. Experiment 4 was performed at a different time with a sample obtained from a different batch of the mineral mixture. The results for the different experiments were comparable. Weight loss results varied by $\pm 1\%$, similar to the experiments in air. The values of the DTA results in experiment 4 differ by approximately 1 °C from the other experiments, thus well within the DTA reproducibility limits.

Figure 4.14 presents the first derivative of the TG curve of the mineral mixture heated in N₂. The DTA and DTG results indicate that most of the interactions occurring in the mineral mixture heated in N₂ signify the decomposition as determined for the individual minerals, and interactions in the amorphous clay phases. In the inert atmosphere FeS₂ did not decompose and oxidize to form SO_x. The absence of the exothermic interactions seen in the experiments in air is an indication thereof. Therefore, SO_x was not available to react with CaO and form anhydrite (CaSO₄). SEM/EDS analysis identified the occurrence of hexagonal pyrrhotite crystals in the mineral mixture heated to 900 °C in N₂ (see Figure 4.9). SEM/EDS analysis also confirmed the deposition of elemental (yellow) sulphur on the inside of the tube furnace used for sintering experiments in N₂.

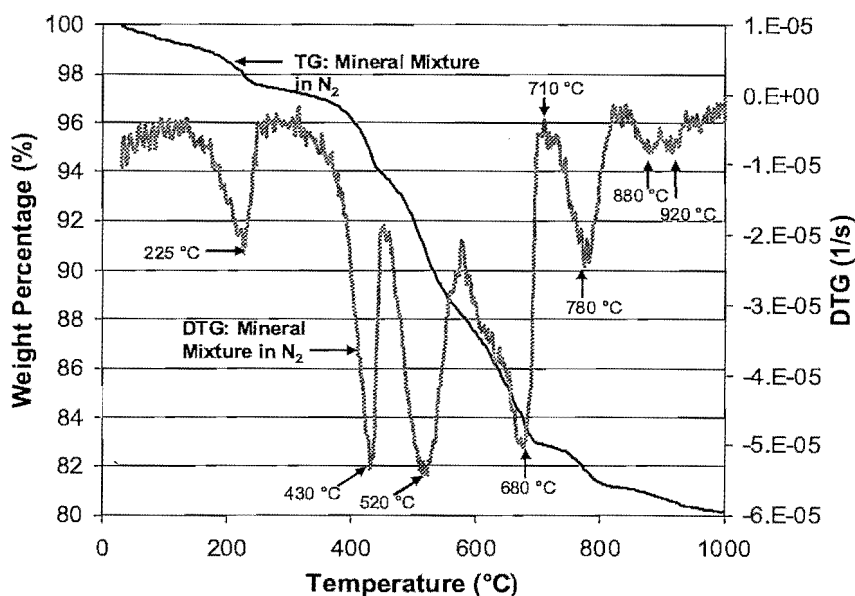


Figure 4.14 First derivative (DTG) of the TG curve of the mineral mixture heated in N_2 (Experiment 4)

Initial weight loss, associated with endothermic peaks at 220 °C in the DTA curves, and 225 °C in the DTG curve of the mineral mixture heated in N_2 , corresponds to the dehydration of hydromagnesite and decomposition of $FeCO_3$. The weight loss from 370 °C incorporates the decomposition of $MgCO_3$ and dehydration of kaolinite to metakaolinite. The transformations are represented by the DTG peaks at 430 °C ($MgCO_3$) and 520 °C (kaolinite). TG/DTA results of pyrite in N_2 (Figure 4.8) indicated that pyrite decomposed to pyrrhotite from approximately 570 °C to 700 °C. The transformation of pyrite in the mixture is represented by the DTG peak at 680 °C. The weight loss from 710 °C to 830 °C signifies the decomposition of $CaCO_3$ to CaO and CO_2 , and is represented by the DTG peak at 780 °C. CaO and MgO react with clays and amorphous silica to form Ca and Ca-Mg aluminosilicates, as described in Section 2.3. FeO can also react with silicates and aluminosilicates to form iron aluminosilicate glasses [McLennan et al., 2000a; Sheng and Li, 2008]. These interactions with the clay phases are evident in the small peaks in the DTA curves from 800 °C to 1000 °C. Weight losses associated with these interactions are presented by the DTG peaks at 880 °C and 920 °C. The DTA peak at 990 °C signifies the possible formation of silicon spinel or a spinel-like form of γ -alumina.

4.3 Evaluation of Sintering in the Mineral Mixture

In the previous section, TG/DTA, SEM/EDS and XRD analyses were used to evaluate the chemical interactions occurring in the mineral mixture during heating. It is also important to determine the influence of the chemical interactions on sintering and agglomeration of the mineral mixture. Compressive strength tests, SEM and thermomechanical analysis (TMA) were used to evaluate the extent of sintering and/or agglomeration in the mixture. The TG/DTA analyses were performed on loose powders and not on compressed pellets. It is not known whether the oxygen availability due to gas flow in and out of the pellets had an effect on mineral interactions. It was assumed that the gas flow was the same for all pellets during compressive strength experiments, and the interactions in the pellets were comparable to the results obtained with TG/DTA.

The compressive strength test is the most common technique to evaluate or determine sintering in coal ash [Al-Otoom et al., 2000a]. Compressive strength measurements were made at room temperature. Crushing of pellets at the sintering temperature will yield different compressive strength values [Conn and Austin, 1984]. However, crushing at the sintering temperature has several difficulties. Therefore, compressive strength tests at room temperature may not be completely representative of reactions in the reactor in all circumstances, but is a very convenient way to evaluate ash characteristics.

SEM is a qualitative technique with which sintering and agglomeration can be evaluated visually. TMA measurements in this application represent bulk characteristics of the mineral mixture. Dimension changes can be caused by sintering and/or melting.

4.3.1 *Compressive Strength Tests*

Figure 4.15 represents the results of five compressive strength experiments in air. The data points represent averages calculated for four to seven mineral mixture pellets. The results include values obtained with the same and different batches of mineral mixture. The same is true of the results for the mineral mixture pellets sintered in N₂, as presented in Figure 4.16.

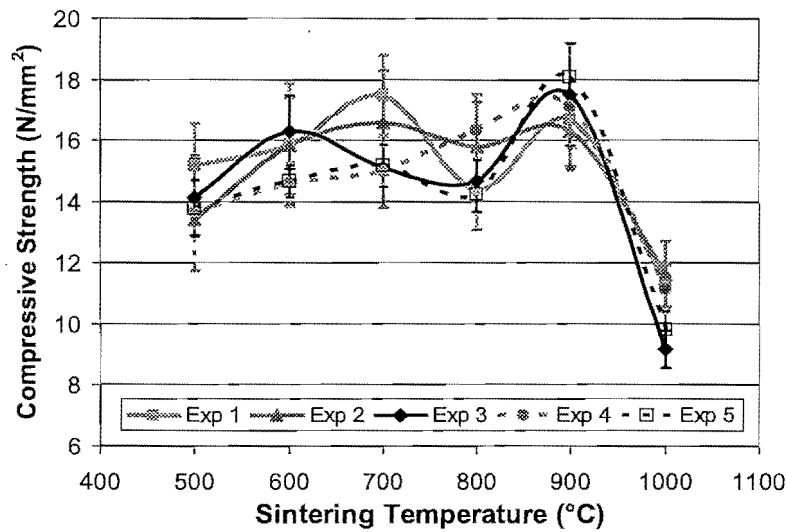


Figure 4.15 Compressive strength results of the mineral mixture sintered in air

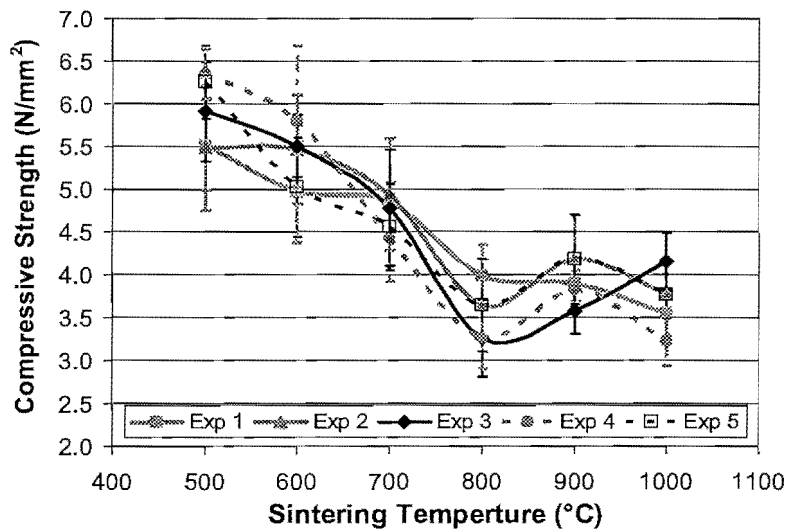


Figure 4.16 Compressive strength results of the mineral mixture sintered in N₂

The repeatability of the compressive strength test is very important, because it was used as a comparative technique. Application of the Cochran test [Anderson, 1987] to the variances obtained for the values in each experiment indicated that the variances were homogeneous for each atmosphere. It was therefore possible to pool the variances. The statistical values representing the repeatability of the methods are summarized in Table 4.3. The repeatability of the method was satisfactory. The

average and pooled standard deviations and coefficients of variance were comparable. The coefficient of variance of the method for pellets sintered in air and N_2 was less than 10%.

Table 4.3 Statistical values depicting the repeatability obtained for the compressive strength method

	Maximum Standard Deviation (N/mm ²)	Minimum Standard Deviation (N/mm ²)	Average Standard Deviation (N/mm ²)	Pooled Standard Deviation (N/mm ²)
Sintered in Air	2.0 (DF = 6)	0.4 (DF = 4)	1.1 (DF = 5)	1.2 (DF = 156)
Sintered in N_2	0.8 (DF = 5)	0.2 (DF = 5)	0.4 (DF = 5)	0.5 (DF = 148)
	Maximum Coefficient of Variance (%)	Minimum Coefficient of Variance (%)	Average Coefficient of Variance (%)	Pooled Coefficient of Variance (%)
Sintered in Air	13.0 (DF = 5)	2.9 (DF = 4)	7.6 (DF = 5)	7.9 (DF = 156)
Sintered in N_2	15.6 (DF = 4)	4.3 (DF = 5)	9.5 (DF = 5)	9.9 (DF = 148)

DF = degrees of freedom

4.3.2 Mineral Mixture Sintered in Air and N_2

Figure 4.17 compares the results of the mineral mixture pellets sintered in air and N_2 . The data points from 500 °C to 1000 °C are the averages of the different values shown in Figures 4.15 and 4.16 at the corresponding temperature. The 95% confidence limits were calculated based on the averages for the different experiments.

Compressive strengths were determined for mineral mixture pellets sintered in air and N_2 from 100 °C to 1100 °C, in order to determine the sintering temperature of the mixture. The sintering temperature is noted as the temperature where the pellets develop a significant increase in mechanical strength [Conn, 1995; Tangsathitkulchai and Tangsathitkulchai, 2001]. The results indicate that sintering commenced between 400 °C and 500 °C in the mineral mixture pellets sintered in air. The temperature range incorporated the decomposition and oxidation of pyrite and the subsequent formation of $CaSO_4$ (see Section 4.2.3), the dehydration of kaolinite to metakaolinite, and the decomposition of $MgCO_3$ to MgO . XRD analysis indicated that most of the kaolinite transformed to amorphous metakaolinite at 500 °C.

Compressive strengths significantly decreased at sintering temperatures above 900 °C in air. Nowak and co-workers [1990] also reported a decrease in compressive strengths for cylinders prepared from coal ash and sintered from 900 °C to 1100 °C in air. The compressive strength increased again at a sintering temperature

of 1200 °C in their experiments. They attributed the reduction in strength to the opening of closed pores and breakage of connections between particles.

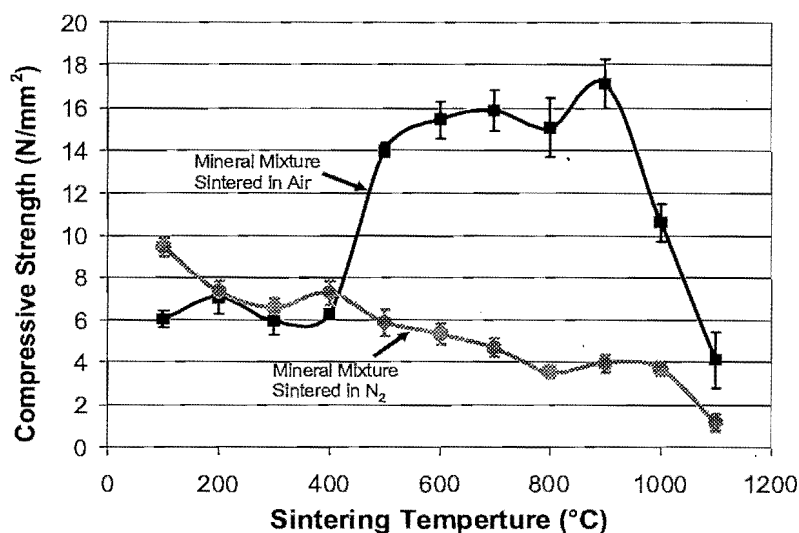


Figure 4.17 Compressive strength results of mineral mixture pellets sintered in air and N₂ from 100 °C to 1100 °C

The strongest pellets (see Figure 4.17) were obtained at a sintering temperature of 900 °C, but values for the pellets sintered from 500 °C to 900 °C were in the same range. TG/DTA results indicated that weight loss occurred in the mineral mixture at temperatures above 900 °C in air (Figure 4.11). The temperature interval corresponds to the decomposition of CaSO₄ to CaO and SO_x. CaO reacts with clays to form Ca-based aluminosilicates.

No significant increase in mechanical strength was observed over the temperature range for mineral mixture pellets sintered in N₂. Therefore, based on the compressive strength test results, the mineral mixture did not sinter in N₂. TG/DTA results indicated that CaSO₄ did not form in the inert atmosphere, and pyrite decomposed to pyrrhotite (Figures 4.8 and 4.13). However, kaolinite still transformed to metakaolinite and MgCO₃ decomposed to MgO. The decomposition of CaCO₃ formed CaO that readily reacts with clays to form Ca-based aluminosilicates.

Based on the compressive strength data and elucidation of chemical interactions it appears that CaSO₄ contributed significantly to strength formation in the pellets sintered in air. Several studies have shown that CaSO₄ contributes to

sintering and agglomeration and the formation of low melting eutectics [Ishom et al., 2004; Steenari et al., 1998]. Iribarne and co-workers [2003] studied agglomeration in petroleum coke-fired fluidized-bed boilers. They determined that the cohesion and strength observed in deposits were caused by an open framework of sintered CaSO_4 particles. Ishom and co-workers [2004] determined that CaSO_4 derived from CaO was the main adhesive in agglomerated grains found in pressurized fluidized-bed combustion of coal operating with limestone as desulfurizing bed material.

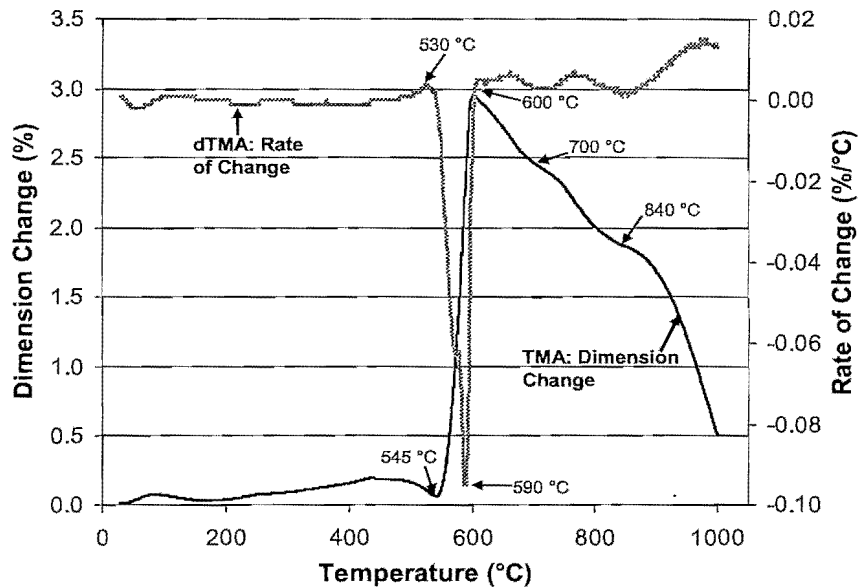


Figure 4.18 Dimension changes in a mineral mixture pellet heated in static air

Sintering and melting can be evaluated by dimension changes in the pellets. Figure 4.18 represents the dimension changes in a mineral mixture pellet sintered in static air. Dimension changes were measured with thermomechanical analysis (TMA), and the analysis was performed on a pellet prepared without water (see Section 3.3.2). Sintering causes the pellet to shrink and the dimensions of the pellet to change [Al-Otoom et al., 2000a, 2003]. The pellet height increased significantly from 530 °C to 600 °C. Shrinkage occurred from 600 °C to 1000 °C. The rate of change increased rapidly at temperatures above 900 °C. Sintering in this temperature range corresponds to weakening in the mineral mixture pellets, contrary to the expected relationship between sintering and mechanical strength.

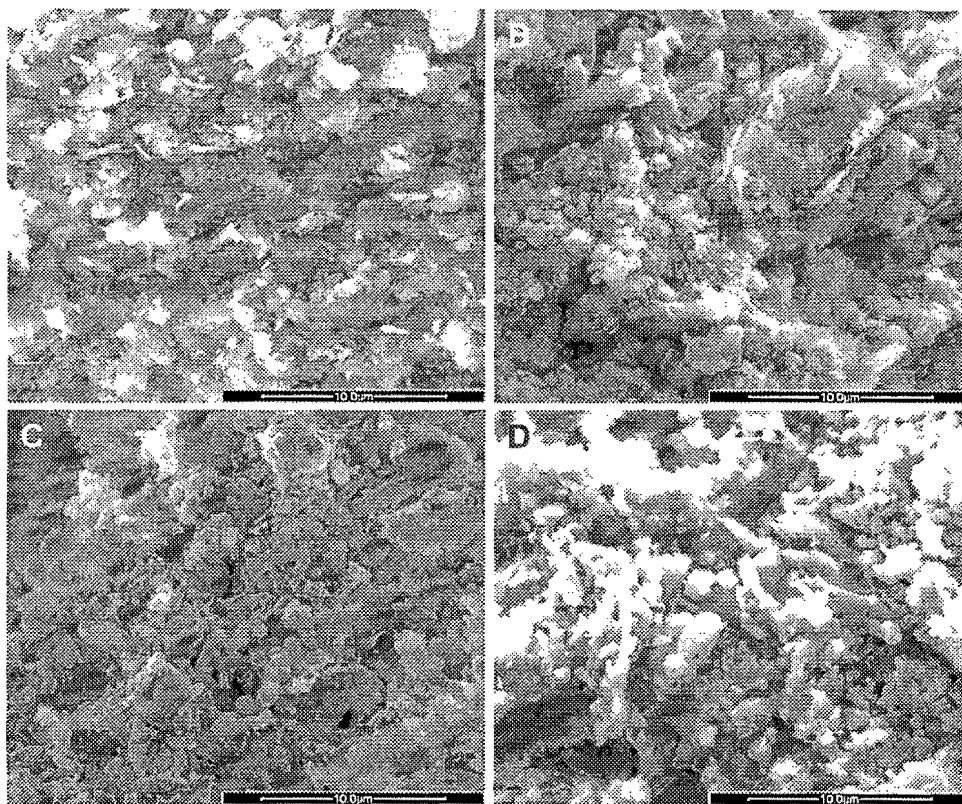


Figure 4.19 SEM images of mineral mixture pellets sintered in air at 400 °C (A), 700 °C (B), 900 °C (C) and 1000 °C (D)

Figure 4.19 presents SEM images of mineral mixture pellets sintered at 400 °C (image A), 700 °C (image B), 900 °C (image C) and 1000 °C (image D) in air. Sintering and agglomeration can be identified by the presence of spherical-shaped particles and rounding of edges. The spherical form is due to a reduction in surface tension [Jung and Schobert, 1992]. Agglomeration is associated with particle growth.

In the image of mineral mixture pellets sintered in air at 400 °C (image A), many sharp edges and needle-shaped particles are visible. Compressive strength results indicated that significant sintering only occurred at temperatures higher than 400 °C. Pellets sintered at 700 °C (image B) still show some sharp-edged particles, but less than at 400 °C. Spherical particles are visible to the left of the image. Particles sintered at 900 °C (image C) have rounded edges. Considerable sintering and particle growth are also visible. Extensive sintering and agglomeration occurred in the mineral mixture pellets sintered at 1000 °C (image D). SEM/EDS analysis identified the main components in the sintered areas of the 1000 °C pellets as Si, Al, Ca, Mg, Fe, S and O,

which constitute Fe/Ca/Mg-containing aluminosilicates and sulfates. However, compressive strength results indicated that the pellets did not strengthen due to the sintering at 1000 °C. Perhaps sintering as defined by an increase in mechanical strength is therefore more applicable to an oxidizing environment. SEM images suggest that a sintered matrix existed that covered and surrounded other discrete particles not involved in the sintered. Therefore, a Fe/Ca/Mg-containing aluminosilicate and CaSO₄ matrix existed derived from clay phases and CaCO₃ that covered and surrounded SiO₂, TiO₂ and hematite particles.

Figure 4.20 presents SEM images of mineral mixture pellets sintered in N₂ at 900 °C (image A) and 1000 °C (image B). Both images indicate that sintering and agglomeration occurred, especially at 1000 °C. The mineral mixture did not show an increase in mechanical strength associated with sintering over the temperature range. Therefore, even though SEM images confirm that sintering occurred, sintering did not result in strengthening of the pellets.

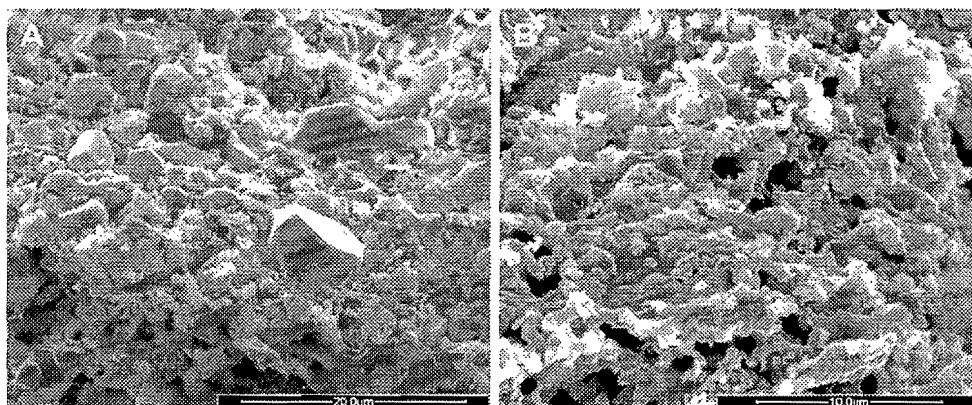


Figure 4.20 SEM images of mineral mixture pellets sintered in N₂ at 900 °C (A) and 1000 °C (B)

4.3.3 *Possible Explanations for the Decrease in Compressive Strength at High Temperatures (in Air) and in N₂*

Many factors should be considered to attempt an explanation for the decrease or lack of mechanical strength in the pellets at higher temperatures and in N₂, even though sintering was confirmed with SEM and TMA analyses. These include: extent and distribution of microcracks, cracks, pores and flaws; grain coarsening; heterogeneity in the system; non-uniform densification; stability of bridges between particles; decrease in elasticity; and friability of aluminosilicate phases [Blanco et al.,

2006; Dai and Lu, 1998; Novak et al., 1990, 1993, 1998; Schmücker et al., 1996; Yoshida et al., 2004].

Large pores and cracks were observed in the pellets with SEM. The increase in porosity and formation of cracks in the pellets are most likely due to sintering processes. Sintering conditions are usually accompanied by pore growth [Al-Otoom et al., 2000b]. Sintering and agglomeration are also associated by grain or particle growth. Grain coarsening reduces mechanical strength, due to the introduction of brittleness and/or friability into the material [Schmücker et al., 1996, Novak et al., 1998]. Apart from sintering, pores can also be formed by decomposition and volatilization of species.

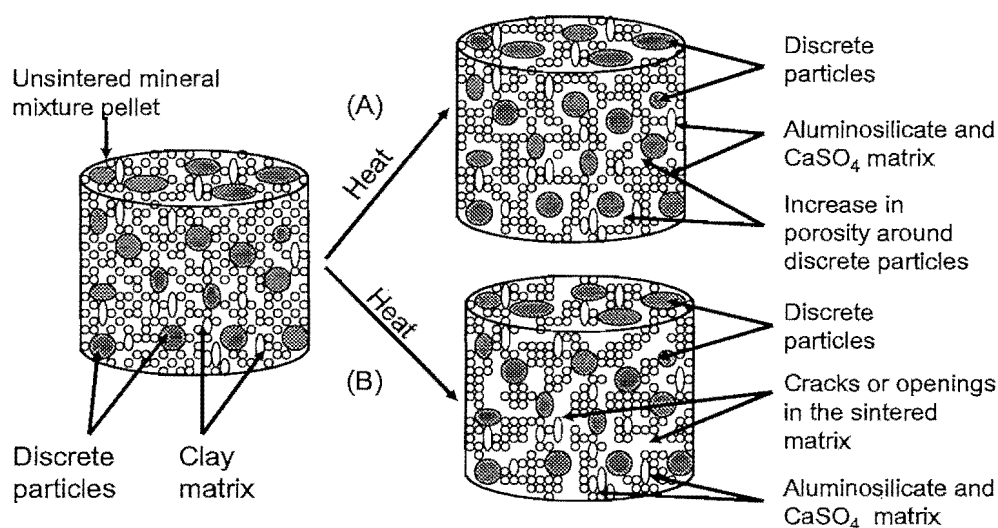


Figure 4.21 Illustration of possible sintering mechanisms responsible for increased porosity in the pellets

Figure 4.21 illustrates the possible mechanisms responsible for increased porosity in the pellets due to sintering and non-uniform densification. If the sintering matrix (Fe/Ca/Mg-containing silicates, aluminosilicates and CaSO₄) do not have a strong affinity to the discrete particles (SiO₂, TiO₂ and hematite) in the pellets, sintering would cause the sintering matrix to pull away from the discrete particles and increase large pores (Path A). However, non-uniform densification in the heterogeneous pellets could also increase the porosity in the pellets due to the formation of cracks or openings in the sintering matrix (Path B). Results indicated that

considerable sintering occurred at temperatures between 900 °C and 1000 °C in the pellets, which would result in pore formation. An increase in porosity reduces mechanical resistance [Blanco et al., 2006]. Pores also enable easier crack propagation when a force is applied and affects elastic constants [Oliveira and Ferreira, 2003]. A decrease in the pellet's ability to deform ensures easy crack initiation [Yoshida et al., 2004].

TG/DTA results of the mineral mixture in air indicated a weight loss of 4% from 830 °C to 1000 °C, most likely associated with the decomposition of CaSO_4 (see Figures 4.11 and 4.12). The decomposition of CaSO_4 and subsequent incorporation of CaO into the sintering matrix could affect: a) the stability of liquid bridges between particles; b) the continuity and distribution of the sintered matrix; and c) the friability of the aluminosilicate phases. The stability of the bridges between sintered or agglomerated particles is important to mechanical strength [Dai and Lu, 1998]. The composition determines the stickiness of particles. Decomposition of CaSO_4 could result in a reduced amount of sticky phases, and/or the formation of phases with less sticky properties. These changes could negatively impact bridge formation between particles, and also the compressive strength.

Iribarne and co-workers [2003] determined that the cohesion and strength observed in deposits were caused by an open framework of sintered CaSO_4 particles. If such a CaSO_4 framework existed in the pellets, decomposition of CaSO_4 would cause disintegration of the framework, and subsequently reduce the compressive strength of the pellet.

Yoshida and co-workers [2004] stated that crack formation in glass is dependent on its composition. Due to the heterogeneity in the pellets, particles in the pellets melt at different temperatures. Nowok and co-workers [1998] stated that coal ash deposits have similar mechanical properties to glass ceramics, and they tend to be friable at temperatures below the glass-transition temperature. Therefore, some of the species in the pellets at temperatures between 900 °C and 1000 °C could have friable characteristics, or the incorporation of CaO into the silicate and aluminosilicate phases could result in the formation of friable phases.

Friableness in the sintering matrix and a reduction in particle stickiness could also be due to transformations and crystallization in the aluminosilicate matrix, independent of the decomposition of CaSO_4 . Zeng and co-workers [2009] determined that the oxidation of Fe^{2+} to Fe^{3+} in glassy particles reduced the particle stickiness.

The lack of mechanical strength in pellets sintered in N_2 was most probably due to the absence of a sintered $CaSO_4$ network. The reduction in mechanical strength observed in Figure 4.17 from 1000 °C to 1100 °C can be explained by possible changes in porosity and the characteristics of aluminosilicate phases.

4.4 Influence of Mineral Mixture Ashing (Pre-Heating) on Compressive Strength Tests

Most sintering experiments are conducted on ash, unless low-temperature ashing is used. Ashing is the most convenient way to liberate the mineral matter from coal. However, during ashing the minerals undergo transformations. As described previously, most of the transformations in the mineral mixture occurred at temperatures below the standard ashing temperature of 815 °C. An experiment was conducted to determine the influence of ashing (heat-treating) the mineral mixture before preparing pellets for compressive strength tests. Results of the ashing experiment are presented in Figure 4.22. Compressive strengths of the ash are lower than for the mineral mixture. At a sintering temperature of 500 °C the results were comparable, but at higher sintering temperatures, the ashed mixture yielded lower compressive strength values. Similar to the mineral mixture, but unlike reports in literature, the mechanical strength of the sintered ash pellets did not increase with sintering temperature. Jung and Schobert [1991] reported that the strength of sintered ash increased with sintering temperature over the range of 750 °C to 950 °C.

The same chemical transformations occurred in the mixture during ashing, as well as during sintering of the unashed mineral mixture pellets below 815 °C. The association of particles is important to form a sintered matrix or network during heat treatment. The most important chemical transformations responsible for strength formation in pellets occurred at temperatures below 815 °C. The pelletizing process is necessary to ensure particles are closely associated before transformations occur. Therefore, ash and minerals yield different results in the compressive strength test. Hu and co-workers [2007] also determined that the thermal history of limestone affects its conversion rate to $CaSO_4$. It is thus advised to use low-temperature ashing to liberate minerals from coal for compressive strength tests to prevent transformations that could affect the results.

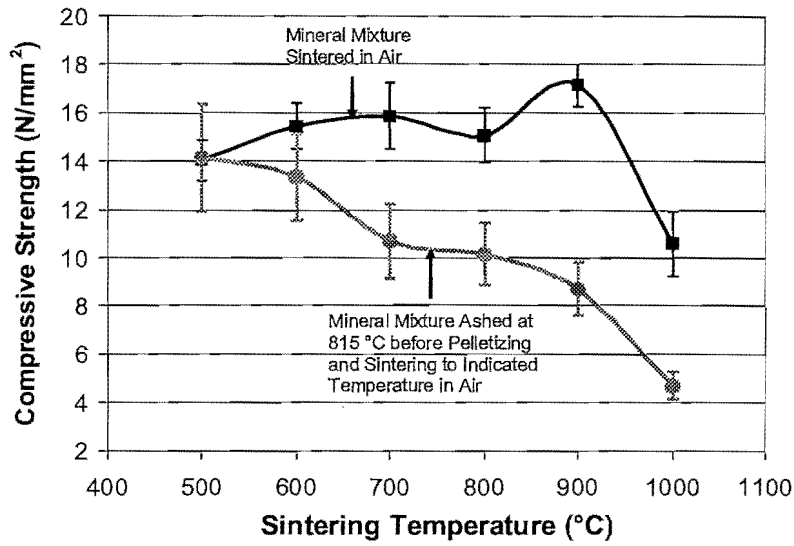


Figure 4.22 Compressive strength results of mineral mixture ashed before pelletizing and sintering, compared to unashed, sintered, mineral mixture pellets

4.5 Melting Characteristic of the Mineral Mixture in a Reducing Atmosphere

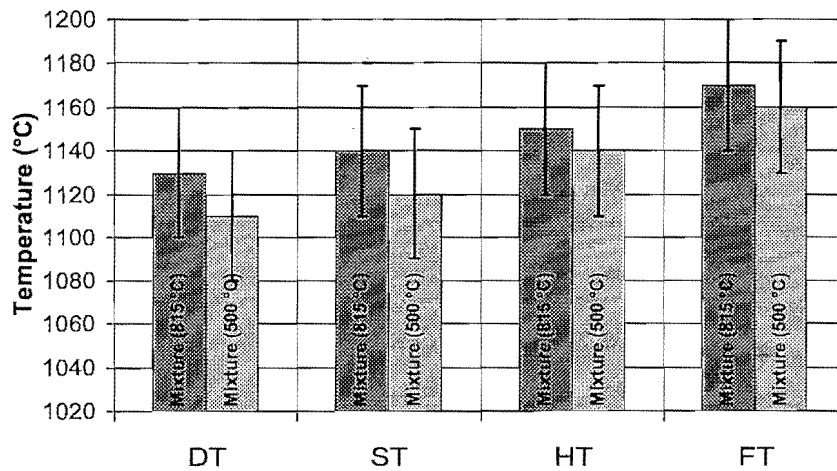


Figure 4.23 Comparison of the ash fusion temperatures for the neat mineral mixture ashed at 815 °C and the neat mineral mixture ashed at 500 °C

Figure 4.23 represents the reducing-atmosphere ash fusion temperatures obtained for the mineral mixture ashed at different temperatures, as described in Section 3.4. The ashing temperatures are given in parentheses.

The ash fusion temperatures are not significantly different for the different ashing temperatures. This is an indication that the ashing temperature did not affect the ash fusion temperatures of the neat mineral mixture. Initial melting commenced at approximately 1110 °C according to the ash fusion temperature values. The mixture was a free-flowing fluid at approximately 1160 °C.

This chapter described the interactions and sintering and/or agglomeration observed in the mineral mixture without additives. The results obtained for the neat mineral mixture will be used as the bases to evaluate and compare results obtained for the mineral mixture with additives. The results obtained for the addition of sodium species and coal to the mineral mixture are discussed in Chapter 5, followed by the results for the other additives in Chapters 6 to 8. The additives were divided alphabetically between the chapters to obtain three chapters of approximately the same length.

Chapter 5

Results and Discussion

Sodium Chloride, Sodium Carbonate and Coal

Sodium is generally regarded as a minor element in coal. Some coal sources, especially lignites, contain significant amounts of sodium [Nowok et al., 1993; Vuthaluru and Zhang, 2001; Wan et al., 2009]. Sodium compounds were included as additives, since they are known causes of agglomeration in fluidized-bed reactors [Dahlin et al., 2006, 2009; Manzoori and Agarwal, 1994]. However, sodium chloride and sodium carbonate do not occur in trace quantities in coal. Sodium-containing minerals in coal include montmorillonite, feldspar, thenardite, natrojarosite and dawsonite (see Table 2.1, Section 2.2.1). Coal was selected as an additive, since coal and mineral particles are often closely associated [Liu et al., 2007a; McLennan et al., 2000a; Ward, 2002]. Included minerals are also enclosed by a coal matrix [McLennan et al., 2000a; Ten Brink et al., 1996]. For these reasons, sodium species and coal as additives are discussed separately from the other additives.

5.1 Sodium Compounds

5.1.1 Sodium Chloride

Sodium chloride (NaCl) is chemically representative of the mineral halite. Halite or rock salt is a sedimentary mineral with a cubic crystal structure [Jones, 2007; Miessler and Tarr, 1999]. Kosminski and co-workers [2006b] stated that approximately half of the sodium found in a South Australian lignite was in the form of NaCl. High concentrations of NaCl are found in “saline” coals, e.g. some coals from the UK, Russia, Ukraine, USA and a few others [Yudovich and Ketris, 2006]. Saline coals were formed from the epigenetic inclusion of brine. Kyi and Chadwick [1999] reported that NaCl is the primary sodium species released in the gas phase from coal during combustion. NaCl has a melting point of 801 °C [Vuthaluru and Zhang, 2001].

Figure 5.1 presents the compressive strength results of mineral mixture pellets with NaCl as additive sintered in air and N₂. The addition of NaCl increased

the compressive strengths of pellets by approximately 60% at a sintering temperature of 500 °C, compared to the neat mineral mixture in air. The compressive strengths were also increased at sintering temperatures of 600 °C to 800 °C, with the influence at 700 °C slightly less than at 600 °C and 800 °C. The effect of NaCl addition on the compressive strengths decreased by approximately 20% with each consecutive sintering temperature from 500 °C to 700 °C. The results were comparable to the neat mineral mixture values at sintering temperatures of 900 °C and 1000 °C.

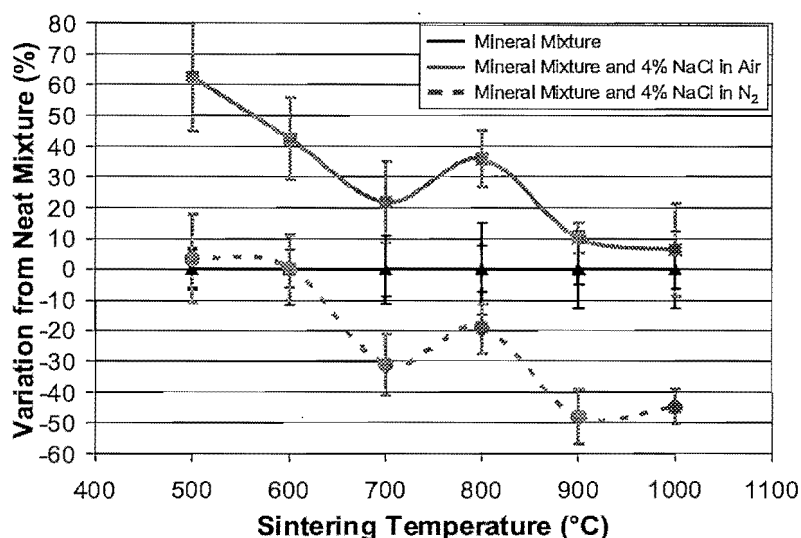


Figure 5.1 Compressive strength results of mineral mixture pellets with NaCl as additive

Results of the mineral mixture with NaCl as additive sintered in N₂ at 500 °C and 600 °C were comparable to the neat mineral mixture values. The addition of NaCl reduced the compressive strength values by 20 – 50% at sintering temperatures ranging between 700 °C to 1000 °C. The compressive strength trends in air and N₂ were similar over the temperature range, but the influence of NaCl in N₂ was 40 – 60% lower than the influence in air, with relation to each experiment's baseline.

Figure 5.2 presents the TG/DTA results of the mineral mixture with NaCl as additive heated in air. Weight loss and DTA peaks were similar from 30 °C to 500 °C. At 500 °C to 650 °C the mixture with NaCl either gained more weight than the neat mineral mixture and/or lost weight at a slower rate. Weight loss in the sample with NaCl was approximately 1.5% more than in the neat mineral mixture sample.

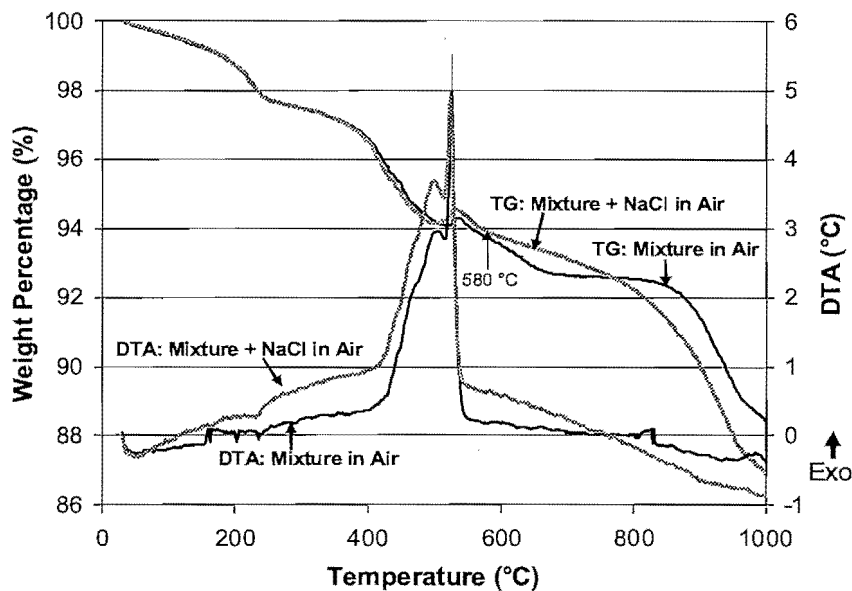


Figure 5.2 TG/DTA results of the mineral mixture with NaCl as additive heated in air

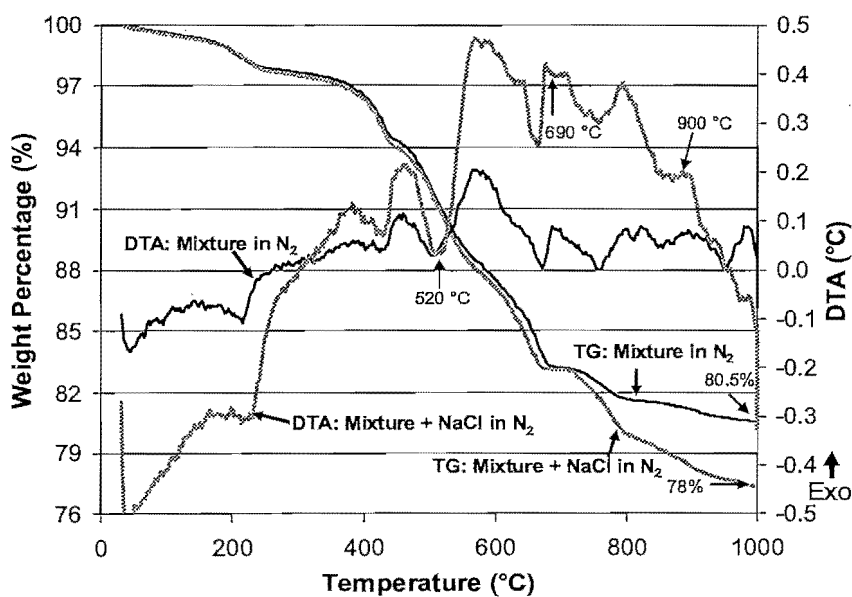


Figure 5.3 TG/DTA results of the mineral mixture with NaCl as additive heated in N_2

Figure 5.3 presents the TG/DTA results of the mineral mixture with NaCl as additive heated in N_2 . The weight loss in both samples was similar from 30 °C to

700 °C. At 700 °C the weight of the sample containing NaCl decreased more rapidly than the weight of the neat mineral mixture sample. Weight loss in the sample with NaCl was 2.5% more than for the neat mineral mixture.

SEM/EDS analyses were performed on pellets obtained from the compressive strength experiments sintered at 500 °C, 800 °C and 1000 °C in air. Bulk chemical analyses indicated the presence of 1.8% chlorine (elemental basis, wt %) in the pellets sintered at 500 °C, but chlorine was absent from pellets sintered at 800 °C and 1000 °C. The sodium concentration increased from 1.0% in pellets sintered at 500 °C and 800 °C to 1.5% in the pellets sintered at 1000 °C, due to the volatilisation of other elements (e.g. C, Cl, S) and normalisation of the results to 100%.

Figure 5.4 presents SEM images of mineral mixture pellets with NaCl as additive sintered in air at 500 °C. EDS analysis of sintered areas in image A indicated the occurrence of Cl (2.5%) and Na (1.3%) (elemental basis, wt %), suggesting the presence of NaCl. The weight ratio of Cl to Na is higher than expected for pure NaCl (1.9 instead of 1.5). The enrichment of chlorine in the analysed areas may indicate that some of the NaCl reacted with minerals in the mixture. The formation of CaCl_2 and MgCl_2 as chlorine-containing compounds could have resulted in chlorine enrichment.

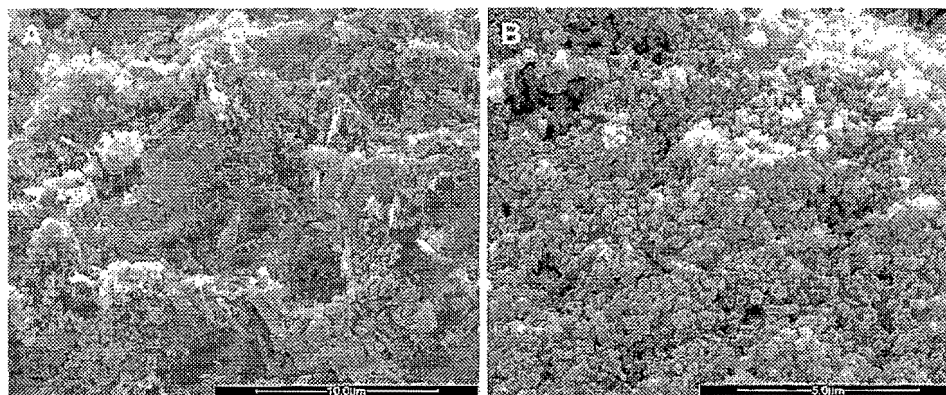


Figure 5.4 SEM images of mineral mixture pellets with NaCl as additive sintered in air at 500 °C

Compressive strength results in Figure 5.1 indicated that NaCl as additive had the greatest influence on the compressive strength at 500 °C in air. Sulfation of limestone is of great importance to the strength development in the mineral mixture pellets. As determined in Chapter 4 (see Section 4.3.2), the sulfation of limestone, and subsequent formation of CaSO_4 , was most probably responsible for the additional

strength in the pellets sintered in air, compared to the pellets sintered in N₂. Research indicated that the addition of alkali salts to desulfurization systems enhanced the sulfation of limestone [Chen et al., 2009; Hu et al., 2006, 2007]. Direct sulfation of limestone is presented by Equation 5.1.



Hu and co-workers [2007] investigated the potential of several alkali metal salts to enhance direct sulfation of limestone. They reported that NaCl enhanced the sulfation of limestone by increasing the surface reactivity and mobility of limestone (reagent) and anhydrite (product) by incorporating the ions (Na⁺ and/or Cl⁻) into the crystal lattices, and causing more extrinsic point defects. They also noted that the increased mobility and surface reactivity created deformed anhydrite crystals due to non-orientated nucleation, and the crystals tended to coalesce when they touched each other. Therefore, the enhanced sulfation of limestone due to the addition of NaCl to the pellets would produce a more continuous sintered CaSO₄ network with better stability to resist breaking under an applied force.

Competing reactions exist to the enhanced sulfation of limestone by NaCl, e.g. the chlorination of limestone and the reaction of NaCl with silicates [Hu et al., 2007; Wei et al., 2002]. Analysis of the particles observed in image B (Figure 5.4) indicated that they contained a large amount of Ti (39.1%) (elemental wt%). TG/DTA and XRD analyses indicated that TiO₂ remained mostly unchanged in the mixture during heat treatment (see Sections 4.2.1.1 and 4.2.2), and therefore the particles were most likely TiO₂. The chlorine concentration was detected as 1.7% (elemental wt%), but no sodium was detected. The particles also contained Ca (1.7%) and Mg (0.6%). These elements could indicate the formation of small amounts of CaCl₂ or MgCl₂. However, the ratio of CaCl₂ to MgCl₂ can not be determined, since some of the Ca and Mg could also have occurred in the oxide form.

Several interactions of NaCl with the minerals in the mixture are possible to explain the decrease in compressive strength observed for pellets sintered in air at 500 °C to 700 °C. Firstly, NaCl can react with silicates, aluminosilicates and water to form sodium aluminosilicates and HCl [Kyi and Chadwick, 1999; Wei et al., 2002]. An example of such a reaction between NaCl and aluminosilicates is presented by Equation 5.2 [Kyi and Chadwick, 1999]:

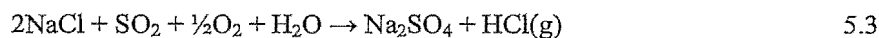


The majority of reactions between NaCl and silicates or aluminosilicates require water. No steam was added during the sintering experiments, but water was released during the dehydration of kaolinite to metakaolinite in the temperature range of 450 °C to 625 °C (see Figure 4.3) [Kyi and Chadwick, 1999]. The TG/DTA results obtained for kaolin clay (see Section 4.2.1.2) indicated that dehydration of the kaolin used in the mixture to form metakaolin resulted in a weight loss of approximately 12%. This translated into a weight loss of 3% in the mineral mixture during heating (mixture contained 25% kaolin clay). Stoichiometrically, the dehydration of kaolin clay in the mixture resulted in a concentration of H₂O in the pellets of more than four times the required amount necessary for the added 4% NaCl to react with aluminosilicates.

Bulk analysis of the sample sintered at 800 °C indicated the presence of sodium, but not of chlorine. The volatilisation of chlorine as HCl from the reaction of NaCl with aluminosilicates would remove the chlorine from the pellets. The loss of chlorine would decrease the effect of NaCl on the sulfation of limestone. The subsequent incorporation of sodium into aluminosilicates would also render the sodium unavailable to participate in sulfation reactions.

NaCl can form a eutectic with CaSO₄. The eutectic has a melting point of 721 °C [Manzoori and Agarwal, 1993; Vuthaluru and Zhang, 2001]. The incorporation of CaSO₄ into melt phases could cause partial disintegration of the solid, sintered CaSO₄ network, and reduce the compressive strength in the pellets. The decomposition and volatilisation of NaCl could also increase the porosity in the pellets, causing more instability in the sintered matrix and reducing the compressive strength compared to the pellets prepared from the neat mineral mixture.

Secondly, Na₂SO₄ can be formed from the sulfation of NaCl. Sodium sulfate can form from the reaction of NaCl or Na₂O with oxygen and SO₂, as shown in Equations 5.3 and 5.4 [Erickson et al., 1991; Huffman et al., 1990, Nankervis and Furlong, 1980]. Coda and co-workers [2001] suggested that the presence of limestone stimulate a shift from alkali chlorides to alkali sulfates [Coda et al., 2001; Wei et al., 2002]. Erickson and co-workers [1991] stated that sodium sulphate formation inhibits the formation of sodium silicates below 1030 °C.



The formation of Na_2SO_4 probably only occurred at temperatures above 500 °C, based on the weight loss results in Figure 5.2. The sample with NaCl as additive gained slightly more weight from 500 °C to 580 °C compared to the neat mineral mixture, and the weight loss of the sample with NaCl was smaller than the neat mineral mixture up to 780 °C. This weight loss pattern can possibly be explained by the incorporation of additional SO_2 into the pellets through the formation of Na_2SO_4 .

Na_2SO_4 also enhances the sulfation of limestone, according to Hu and co-workers [2007]. However, NaCl has a greater effect than Na_2SO_4 . During the formation of Na_2SO_4 from NaCl, chlorine is released as HCl. The loss of chlorine would decrease the enhanced effect on the sulfation of limestone and negatively influence the formation of the sintered CaSO_4 network; thereby lowering the compressive strength.

Sodium sulfate can form low-melting eutectics with various species, e.g with MgSO_4 (m.p. 670 °C), CaSO_4 (m.p. 900 °C), and NaCl (m.p. 623 °C). A eutectic of CaSO_4 , MgSO_4 and Na_2SO_4 melts at 650 °C [Manzoori and Agarwal, 1993; Vuthaluru and Zhang, 2001]. However, the formation of low-melting point species may lead to greater sintering, but as described in Section 4.3.2, an increase in sintering does not necessarily contribute to greater strength formation in the pellets. The incorporation of CaSO_4 into melt phases could cause partial disintegration of the solid, sintered CaSO_4 network and reduce the compressive strength in the pellets.

The formation of Na_2SO_4 in the pellets sintered in air can be deduced by comparing the TG/DTA results of the samples with NaCl in air and N_2 . Significant differences in weight loss compared to the neat mineral mixture started from 700 °C in N_2 , most probably due to the formation and/or volatilisation of HCl or NaCl. Witthohn and co-workers [1998] reported that NaCl was released in the gas phase from lignites ashes at temperatures between 600 °C and 900 °C in N_2 . The rate of weight loss of the samples with NaCl deviated from the neat mineral mixture in air at temperatures higher than 500 °C. Water and aluminosilicates were present in pellets sintered in both atmospheres, from the dehydration of kaolinite. Metakaolinite can react with NaCl in

the presence of water. However, the lack of oxygen and the subsequent decomposition and oxidation of pyrite to form SO_2 was the major difference in the two samples. Total weight loss in the sample with additive was 1.5% less than the neat mineral mixture in air, and 2.5% less than the neat mineral mixture in N_2 . Due to the lack of SO_2 in N_2 , CaS most probably formed instead of CaSO_4 , and the formation of Na_2SO_4 in N_2 was also unlikely. Therefore, the differences in the weight loss curves obtained in air (sample with NaCl compared to neat mineral mixture) are most probably due to the formation of Na_2SO_4 . The occurrence of Na_2SO_4 was not confirmed by XRD, because only the major phases in the pellets were identified in the XRD analyses.

The compressive strength results in Figure 5.1 indicated a decrease at a sintering temperature of 700 °C in N_2 . Witthohn and co-workers [1998] reported that NaCl was released in the gas phase from lignite ashes at temperatures between 600 °C and 900 °C in N_2 . They measured almost complete volatilization of chlorine at 850 °C in N_2 . Theoretically, the complete reaction of 4% NaCl with water to form Na_2O and HCl would translate into a weight loss of 2.1% in the mineral mixture. However, in N_2 the additional weight loss of the sample with additive (compared to the neat mineral mixture) was 2.5%. This indicates that the weight loss was most probably not only due to the formation of HCl, but some of the sodium was also volatilized as NaCl.

The volatilisation of NaCl and/or HCl would cause an increase in the porosity, causing more instability in the sintered matrix, and reducing the compressive strength of the pellets compared to the pellets prepared from the neat mineral mixture. Nowok and co-workers [1990] reported that the strength of sintered pellets prepared from Beulah coal ash was dependent on the porosity variations and instability of the crystalline structure. Kosminski and co-workers [2006b] reported that the release of sodium and chlorine from NaCl in coal is disproportionate due to the incorporation of sodium into aluminosilicates. The incorporation of sodium into aluminosilicates can result in the formation of friable aluminosilicate phases (compared to the aluminosilicate phases in the mineral mixture pellets without additive) that could also have decreased the compressive strength of the pellets. The friability is influenced by the characteristics of the phases between particles (stability of bridges).

The compressive strength results of pellets containing NaCl decreased considerably from a sintering temperature of 800 °C to 900 °C in both air and N_2 . The results were comparable to the neat mineral mixture at sintering temperatures of 900 °C and 1000 °C in air. Nankervis and Furlong [1980] reported that Na_2SO_4

(m.p. 884 °C) decomposes to Na_2O and SO_3 . Na_2O is incorporated into sodium aluminosilicates. The decomposition of Na_2SO_4 and/or volatilisation of NaCl or HCl would explain the continued weight loss from 650 °C to 850 °C in the TG/DTA results in air (Figure 5.2) compared to the constant weight of the neat mineral mixture within the same temperature interval. At 700 °C, the weight of the sample containing NaCl also decreased more rapidly than the neat mineral mixture in N_2 . The weight loss signifies the volatilisation of NaCl and/or HCl , with subsequent incorporation of sodium into sodium aluminosilicates. The results are too limited to consider the formation of Na_2S in N_2 .

The similar compressive strength trends in both atmospheres for sintering temperatures from 600 °C to 1000 °C (excluding the increase due to enhanced sulfation in air) implies that the characteristics of the sodium aluminosilicate species played a significant role, and was most probably responsible for the decrease in compressive strengths from 800 °C to 900 °C, together with the volatilisation of species (NaCl and/or HCl). The incorporation of sodium into aluminosilicates can result in the formation of aluminosilicate phases that are more friable than the aluminosilicate phases that formed in the neat mineral mixture pellets.

The enhanced sintering at lower temperatures (due to the additive) could also have caused a considerable increase in the porosity compared to the neat mineral mixture. An increase in porosity may decrease the compressive strength. Even though sintering can result in the formation of a denser framework, bear in mind that the pellets are heterogeneous. Therefore, a non-continuous sintered framework, as well as non-uniform densification most probably occurred (see Figure 4.21, path B). An increase in porosity result in better crack propagation through the heterogeneous system, and cracks can also form along grain boundaries. Increased crack propagation would also have resulted in more brittle pellets [Yoshida et al., 2004].

Figure 5.5 presents images obtained from mineral mixture pellets containing NaCl sintered at 1000 °C in air. The occurrence of melted phases and sintering is clearly visible in image A, and also the formation of pores. The formation of cracks and pores as described in Section 4.3.3 is also clearly visible in image B. SEM/EDS analysis of the discrete crystals in image B indicated that they consisted mostly of Fe and O. The crystals are probably Fe_2O_3 (hematite) crystals, based on XRD results and the lack of melting (compare to Figure 4.9, see Section 4.2.1.4). The weight ratio of Fe to O as determined by EDS (ratio of 2.1) is also closest to the ratio of Fe to O in Fe_2O_3

(ratio of 2.3), compared to FeO (ratio of 3.5) and Fe_3O_4 (ratio of 2.6). As sintering occurred, the crystals were drawn in different directions, resulting in cracks and an increase in porosity. An increase in porosity and crack formation add instability, friability and brittleness to the pellets.

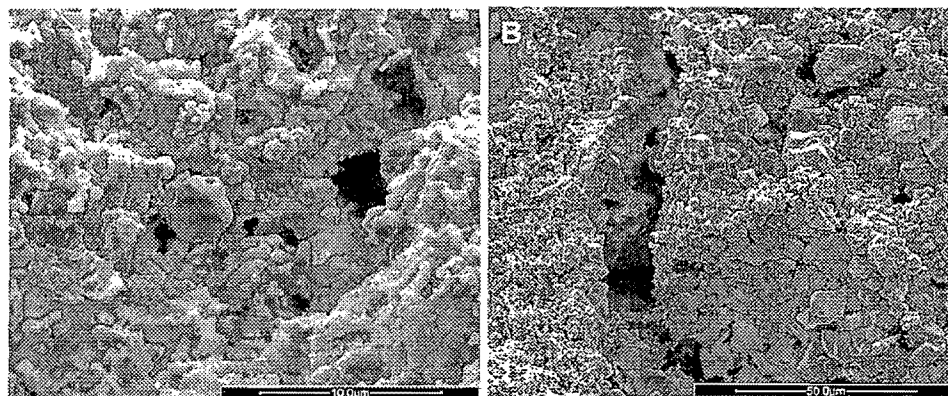


Figure 5.5 SEM images of mineral mixture pellets with NaCl as additive sintered in air at 1000 °C

5.1.2 Sodium Carbonate

Sodium carbonate (Na_2CO_3) occurs in nature as part of Trona deposits. Na_2CO_3 is obtained from heating Trona ore ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) [Kotz and Treichel, 1999; Lee, 1996]. The products are Na_2CO_3 , CO_2 and water. Sodium carbonate is commonly used to make glass and silicates [Kotz and Treichel, 1999; Lee, 1996]. Kosminski and co-workers [2006b] reported that Na_2CO_3 formed as the principal form of sodium from carboxylate sodium during pyrolysis and gasification of coal. Na_2CO_3 has a melting point of 851 °C in air, but the melting point is dependent on the atmosphere [Kosminski et al., 2006b; Skoog et al., 1996].

Figure 5.6 presents the compressive strength results of the mineral mixture pellets containing Na_2CO_3 as additive, sintered in air and N_2 . The addition of Na_2CO_3 to the mineral mixture increased the compressive strengths at sintering temperatures from 500 °C to 800 °C in air. The compressive strengths were increased by 25 to 80%. The largest influence, of approximately 80%, was observed at a sintering temperature of 800 °C. Compressive strengths in air at sintering temperatures of 900 °C and 1000 °C (17.4 N/mm² and 9.8 N/mm², respectively) were comparable to the neat mineral mixture pellets (17.1 N/mm² and 10.6 N/mm², respectively).

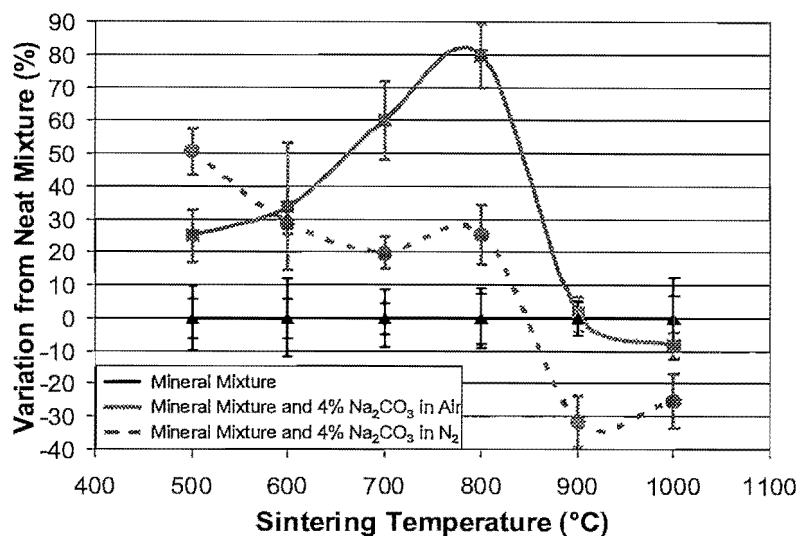


Figure 5.6 Compressive strength results of mineral mixture pellets with Na₂CO₃ as additive

The addition of Na₂CO₃ to the mineral mixture also increased the compressive strengths in N₂ at sintering temperatures of 500 °C to 800 °C. However, the influence was not as large as in air. The largest increase (50%) was observed at a sintering temperature of 500 °C. The addition of Na₂CO₃ decreased the compressive strengths at sintering temperatures of 900 °C and 1000 °C, compared to the compressive strength at 800 °C. Similar results were observed in air. The compressive strengths in N₂ at sintering temperatures of 900 °C and 1000 °C (2.7 N/mm² and 2.7 N/mm², respectively) were 25 – 30% lower than for the neat mineral mixture (3.9 N/mm² and 3.7 N/mm², respectively).

Figure 5.7 presents the TG/DTA results of the mineral mixture with Na₂CO₃ as additive heated in air. Weight loss of the sample with additive and the neat mineral mixture were similar over the total temperature range. Slight differences in weight loss may have occurred from 450 °C to 650 °C and at temperatures above 950 °C, but it could also be due to the repeatability of the method (see Figure 4.11). In both intervals the weight loss of the sample with additive occurred at a slower rate than for the neat mineral mixture. The DTA curves of both samples were also very similar, except that the exothermic transformation in the DTA curve of the sample with Na₂CO₃ occurred from 930 °C, compared to 965 °C in the neat mineral mixture.

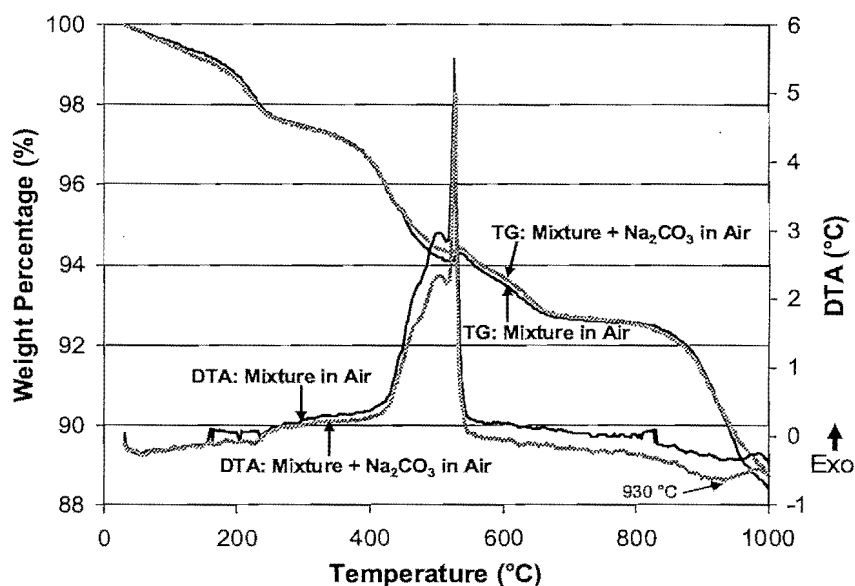


Figure 5.7 TG/DTA results of the mineral mixture with Na_2CO_3 as additive heated in air

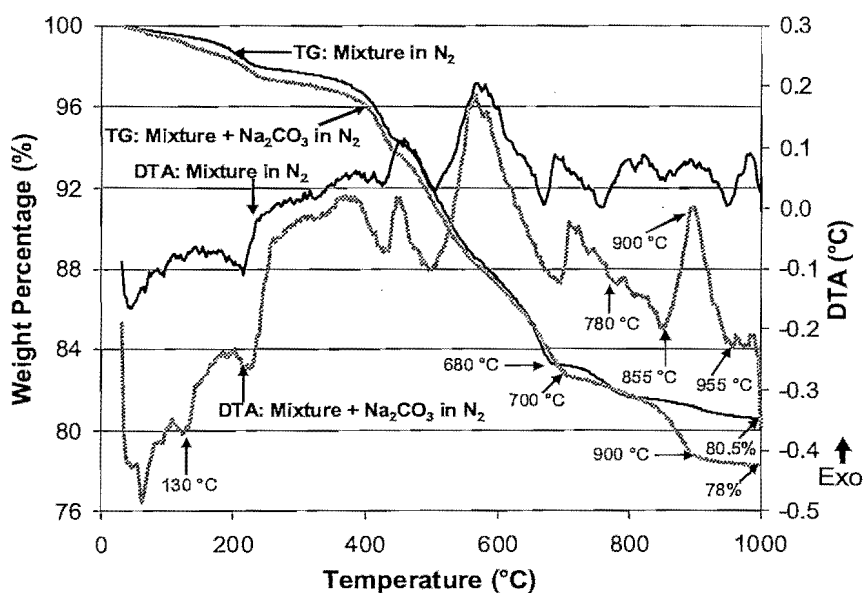


Figure 5.8 TG/DTA results of the mineral mixture with Na_2CO_3 as additive heated in N_2

Figure 5.8 presents the TG/DTA results of the mineral mixture with Na_2CO_3 as additive heated in N_2 . Weight loss patterns and DTA curves of the sample

containing additive and the neat mineral mixture sample were comparable up to a temperature of approximately 650 °C. From 650 °C to 800 °C slight rate difference occurred between the two samples. The sample containing Na_2CO_3 had a weight loss of approximately 2.5% from 800 °C to 900 °C. The weight loss is associated with an endothermic peak in the DTA curve at 855 °C. The temperature of the endothermic peak, which is absent from the neat mineral mixture sample, also corresponds to the melting temperature of Na_2CO_3 (851 °C). The DTA curve of the sample with additives shows an exothermic peak not associated with weight loss from 855 °C to 955 °C. This may represent the incorporation of sodium into aluminosilicate phases. The crystallization of glass-ceramics from sodium- and calcium-doped coal ashes has been reported to be exothermic [Leroy et al., 2001].

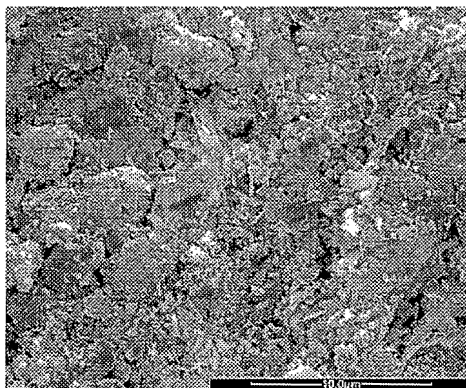


Figure 5.9 SEM image of mineral mixture pellets with Na_2CO_3 as additive sintered in air at 500 °C

The addition of Na_2CO_3 to desulfurization systems, like NaCl , enhances the sulfation of limestone to form anhydrite, and both follow the same mechanisms (increasing the ionic mobility of both the reactant and product) [Chen et al., Hu et al., 2007]. Figure 5.9 represents a SEM image from pellets containing Na_2CO_3 as additive sintered at 500 °C in air. Addition of NaCl to limestone systems resulted in the formation of larger grain sizes [Hu et al., 2007]. To the left side of the image larger grains or clumps are visible that may be due to the sulfation enhancement effect of Na_2CO_3 . EDS analysis of the grains indicated that the largest weight fractions, apart from oxygen, were contributed by Ca (12.6%) and S (9.3%) (elemental wt%). Sodium (1.0%) was also detected, and the concentrations of Al, Si, Mg and C ranged from 4% to 6.5%.

Compressive strength results in Figure 5.6 indicated that the compressive strength increased substantially from sintering temperatures of 500 °C to 800 °C. The increase in compressive strength is most probably due to the enhanced sulfation of limestone. Unfortunately, quantitative XRD results were not obtained for the samples to confirm this conclusion, as only qualitative XRD analyses were performed on the pellets. Chen and co-workers [2009] reported that the influence of Na₂CO₃ increases with an increase in temperature, as demonstrated in Figure 5.6. The slight increase in the weight of the mineral mixture containing Na₂CO₃, compared to the neat mineral mixture in the TG/DTA curve from 430 °C to 650 °C, could also represent the formation of small amounts of Na₂SO₄. As stated previously, the formation of sodium sulphate inhibits the formation of sodium silicates below 1030 °C [Erickson et al., 1991]. Sodium sulfate can form from the reaction of Na₂CO₃ with SO₂ and O₂, as presented in Equation 5.5. Lan and co-workers [2008] stated that Na₂SO₄ is more stable than Na₂CO₃, and therefore the Na₂CO₃ will undergo sulfation. However, the results obtained in this study are too limited to confirm the extent of Na₂SO₄ formation. The existence of Na₂SO₄ in the pellets was not confirmed with XRD, because only major phases were identified.

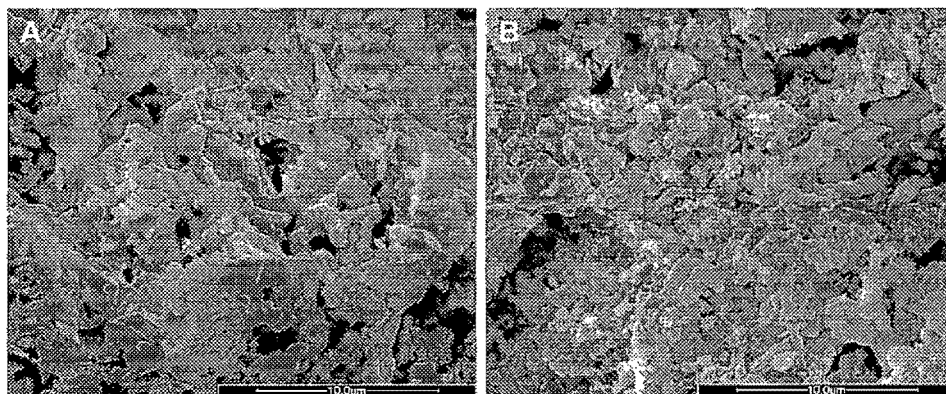
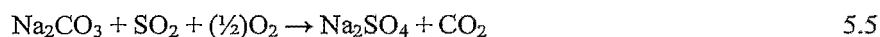


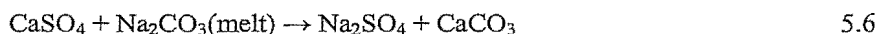
Figure 5.10 SEM images of mineral mixture pellets with Na₂CO₃ sintered at 800 °C (image A) and mineral mixture pellets (without additive) sintered at 900 °C (image B) in air

Figure 5.10 presents images of mineral mixture pellets containing Na₂CO₃ as additive sintered in air at 800 °C (image A), and mineral mixture pellets (without additive) sintered at 900 °C (image B). Comparison of image A with image B clearly

indicates the increased sintering and solid network formed due to the addition of Na_2CO_3 . EDS analysis of the sintered areas in image A indicated the presence of Na (1.0%), S (11.5%), Ca (8.0%) and O (50.3%), together with C, Al, Si and Mg concentrations of 4% to 7% (elemental wt%). These elements suggest that the enhanced sintering was most probably due to the formation of Na_2SO_4 and CaSO_4 . Na_2CO_3 may also have been present.

Similar to the results obtained for the addition of NaCl, the compressive strength results in Figure 5.6 indicated that the compressive strength of the pellets containing Na_2CO_3 as additive decreased considerably from a sintering temperature of 800 °C to 900 °C. The results were comparable to these of the neat mineral mixture at sintering temperatures of 900 °C and 1000 °C. The sharp decrease from 800 °C to 900 °C could also be explained by the decomposition of Na_2SO_4 or Na_2CO_3 to Na_2O and SO_3 or CO_2 . Na_2O is incorporated into sodium aluminosilicates. The incorporation of sodium into aluminosilicates would render the sodium unavailable to participate in sulfation reactions. The weight loss results in Figure 5.7 do not indicate a significant difference in the weight loss of the sample containing Na_2CO_3 and the neat mineral mixture. However, the weight percentage of the mixture with additive before heat treatment (100%) includes the 4% from the additive. The weight loss due to the decomposition of Na_2CO_3 , and subsequent release of CO_2 , could have resembled the decomposition of some of the other minerals in the mixture. Theoretically, the complete decomposition of 4% (by weight) Na_2CO_3 to Na_2O and CO_2 should contribute 1.7% of the weight loss of the mineral mixture.

Wang and co-workers [2007c] reported that two double salts can form between CaSO_4 and Na_2CO_3 at temperatures above the melting temperature of Na_2CO_3 (851 °C), i.e. $\text{Na}_6(\text{CO}_3)_2\text{SO}_4$ and $\text{Na}_4\text{CO}_3\text{SO}_4$. They suggested that the formation of the double salts was most likely due to the interaction given in Equation 5.6. The CaCO_3 formed in the reaction will decompose to lime and CO_2 .



SEM/EDS analysis of the pellets sintered at 1000 °C detected 2 to 3% carbon in the pellets, which could be due to the occurrence of the double salts, or purely the presence of simple carbonates. The formation of the double salts would also result in reduced weight loss due to limited decomposition of Na_2SO_4 , Na_2CO_3 and CaSO_4 .

The authors stated that, in general, the formation of similar double salts result in the formation of a porous structure. Local melting and the solution of sulfates would also inhibit the formation of a solid product [Wang et al., 2007c]. Therefore, the formation of double salts could also in part be responsible for the decrease in the compressive strength in air from a sintering temperature of 800 °C to 900 °C. Further analysis is required to verify the occurrence of the double salts in the heat-treated mineral mixture.

However, similar compressive strength trends were observed for the addition of NaCl and Na₂CO₃ at sintering temperatures of 800 °C to 1000 °C, and in both atmospheres for both additives for sintering temperatures from 700 °C to 1000 °C (excluding the increase due to enhanced sulfation in air). Therefore, the immobilisation of sodium, and the characteristics of the sodium aluminosilicate species, was most probably primarily responsible for the decrease in compressive strengths from 800 °C to 900 °C. The results suggest that the sodium aluminosilicates were more friable than the aluminosilicates that formed in the neat mineral mixture pellets.

The enhanced sintering at lower temperatures due to the additive could also have caused a considerable increase in the porosity at lower temperatures compared to the neat mineral mixture. An increase in porosity compared to the pellets prepared from the neat mineral mixture could decrease the compressive strength. As stated earlier, an increase in porosity would result in better crack propagation through the heterogeneous pellets.

Na₂CO₃ persisted in the N₂ atmosphere and could not form Na₂SO₄ due to the lack of SO₂. Results are too limited to suggest the formation of Na₂S. Based on the compressive strength results in N₂, it appears that the influence from Na₂CO₃ at lower sintering temperatures were not only due to enhanced sulfation. At a sintering temperature of 500 °C the addition of Na₂CO₃ increased the compressive strength of the pellets sintered in N₂ by approximately 50%. It is possible that Na₂CO₃ was incorporated into aluminosilicates to an extent at these lower temperatures, or the addition resulted in a reduction of the porosity due the formation of possible eutectics. At the lower sintering temperatures (500 °C to 800 °C) in N₂ the pellets were therefore more resistant to an applied force than the neat mineral mixture due to the addition of Na₂CO₃.

The endothermic peak in the DTA curve (Figure 5.8) at 855 °C corresponds to the melting of Na_2CO_3 . The exothermic peak from 855 °C to 955 °C represents the incorporation of Na_2O into aluminosilicate phases. Theoretically, the incorporation of Na_2O into aluminosilicates, and release of CO_2 , only accounts for 1.7% of the additional weight loss (compared to the neat mineral mixture) in the sample with additive. However, the weight loss in the samples was determined as 2.5% more than the neat mineral mixture. The additional weight loss may be due to the repeatability of the method, or the addition of Na_2CO_3 increased the volatility of some of the other species in the mixture. The results suggest that the sodium aluminosilicates may be more friable than the aluminosilicates that formed in the neat mineral mixture pellets at sintering temperatures of 900 °C and 1000 °C. The decomposition of Na_2CO_3 will also increase the porosity in the pellets and may have contributed to the decrease in compressive strength at these sintering temperatures.

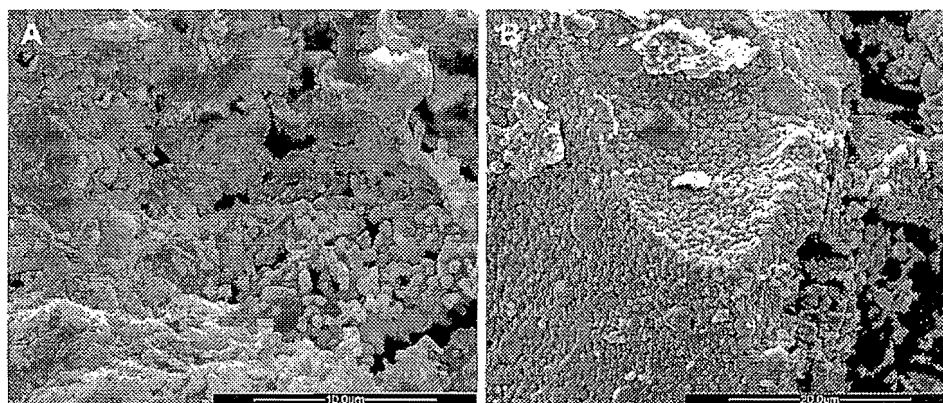


Figure 5.11 SEM images of iron-containing species in mineral mixture pellets with Na_2CO_3 sintered in air at 1000 °C

Figure 5.11 presents SEM images of iron-containing species in mineral mixture pellets with Na_2CO_3 sintered in air at 1000 °C. In both images the formation of pores due to sintering processes and decomposition of species are evident. EDS analysis of the sintered drops in image A indicated the presence of Fe (39.9%), O (41.0%) and Mg (10.8%) (elemental wt%). The weight ratios of the elements imply that the drops are of mixed composition. The presence of Mg suggests that some magnesioferrite may have formed, but some of the Mg should also be in other forms, e.g. MgO. The Fe and O could occur as a mixture of FeO and Fe_2O_3 or Fe_3O_4 , but the majority is probably FeO, based on the molten particles (drops).

The melted drops in image B consisted almost exclusively of Fe and O. The low melting point probably indicates the occurrence of FeO. FeO has a melting point of 1370 °C, but a eutectic of FeS and FeO melts at 920 °C to 940 °C [Laursen and Frandsen, 1998; Marinov et al., 1992]. Further oxidation of the FeS-FeO eutectic yields an FeO-melt (see Section 2.3.2.1) [Bool et al., 1995; Jensen and Austin, 1977; McLennan et al., 2000a, 2000b]. In the absence of sufficient oxygen (perhaps in the centre of the pellets), oxidation of FeO to magnetite and hematite will not occur. Cooling at an adequate rate will inhibit crystallisation. However, it appears as if some crystalline species occurred too. Further oxidation of FeO results in the formation of hematite (Fe_2O_3) or magnetite (Fe_3O_4). XRD analysis identified the occurrence of hematite as iron species in the sample.

5.1.3 *Conclusions and Comparisons of Sodium Additives*

Both NaCl and Na_2CO_3 as additives increase the compressive strength of the mineral mixture at lower sintering temperatures. Na_2CO_3 had the largest influence. The increase is mostly due to the enhancement of limestone sulfation to CaSO_4 . Enhanced sulfation causes coalescence and irregular shaped anhydrite crystals [Hu et al., 2007]. The enhanced sintering ensured the formation of a more extensive solid sintered network which gave more resistance to the applied force, and thus increased the compressive strength. The maximum influence from the addition of NaCl was at a sintering temperature of 500 °C, and the maximum from the addition of Na_2CO_3 at 800 °C (see Figures 5.1 and 5.6). Sulfation increased with sintering temperature in the case of Na_2CO_3 , but the loss of chlorine as HCl and/or NaCl reduced the effect from NaCl with an increase in temperature. No chlorine was detected in pellets sintered at 800 °C in air. The results of both additives were similar to the neat mineral mixture at sintering temperatures of 900 °C and 1000 °C in air, due to the dissociation of the additives or Na_2SO_4 , and incorporation of Na_2O into friable aluminosilicate phases.

NaCl as additive did not increase the compressive strength in N_2 . At sintering temperatures of 700 °C to 1000 °C the addition of NaCl in pellets sintered in N_2 lowered the compressive strength. The decrease can be ascribed to an increase in porosity due to the volatilisation of NaCl and/or HCl, and incorporation of Na_2O into friable aluminosilicate phases.

Na_2CO_3 as additive in pellets sintered in N_2 increased the compressive strength at sintering temperatures of 500 °C to 800 °C. The increase indicated that the

effect from Na_2CO_3 was not only due to enhanced sulfation in air, but most probably also due to the incorporation of sodium into the aluminosilicate matrix. However, the species formed at sintering temperatures of 900°C and 1000 °C appeared to be more friable than the species formed in the neat mineral mixture pellets. Na_2CO_3 may also have formed double salts with CaSO_4 at temperatures above 850 °C. The decomposition of Na_2CO_3 at temperatures higher than 800 °C also caused an increase in porosity. These factors probably all contributed to the reduction in compressive strength at these sintering temperatures.

5.2 Coal

Table 5.1 Results from proximate, ultimate and ash analyses of the Highveld coal

Proximate Analysis (air dried, wt%)		Ash analysis (wt%)	
Inherent Moisture	3.6	SiO_2	46.9
Volatile Matter	21.5	Al_2O_3	31.7
Ash	29.2	Fe_2O_3	2.2
Fixed Carbon	45.7	P_2O_5	0.9
	100	TiO_2	1.8
Ultimate Analysis (daf, wt%)		CaO	6.8
Carbon	78.6	MgO	2.4
Hydrogen	4.8	K_2O	1.2
Nitrogen	2.0	Na_2O	0.5
Sulfur	1.2	SO_3	4.7
Oxygen	13.4		
	100		

A South African Highveld coal blend was used as coal additive. The results from the proximate and ultimate analyses are presented in Table 5.1.

Figure 5.12 presents the compressive strength results of the mineral mixture with coal as additive sintered in air. The addition of coal lowered the compressive strengths of the pellets sintered in air by approximately 20% at all the sintering temperatures.

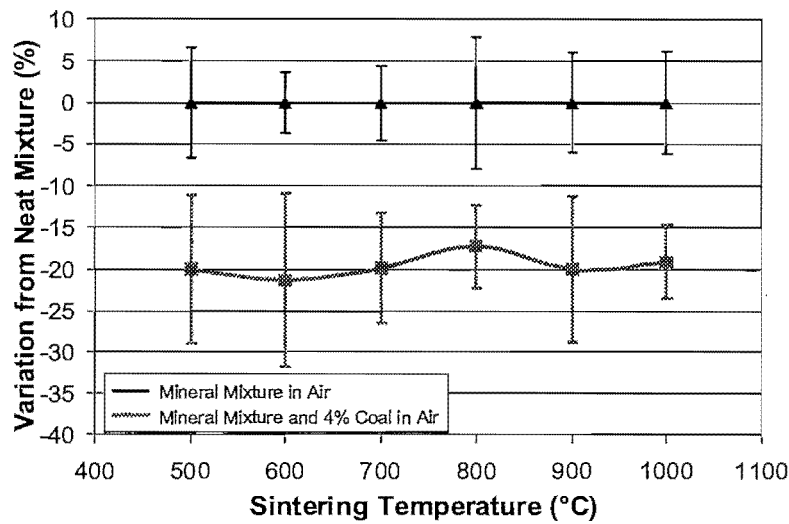


Figure 5.12 Compressive strength results of coal as additive sintered in air

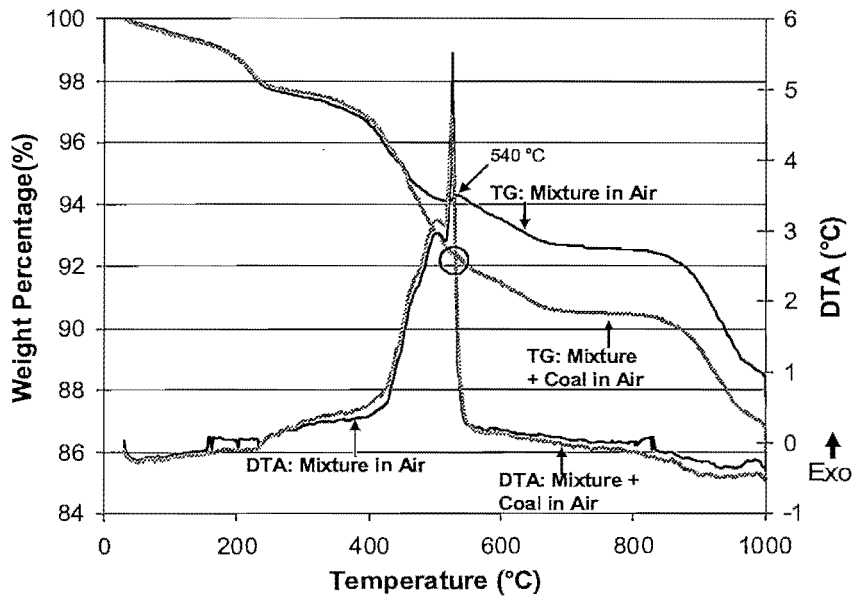


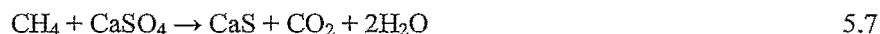
Figure 5.13 TG/DTA results of coal as additive heated in air

Figure 5.13 presents the TG/DTA results of the mineral mixture with coal as additive heated in air. The weight loss patterns of the mineral mixture with additive and the neat mineral mixture were comparable up to 450 °C. Weight loss in the sample with additive was 2% more than the neat mineral mixture from 450 °C to 540 °C. The additional weight loss was most probably due to the devolatilisation and

combustion of the coal. The proximate analysis (Table 5.1) showed that the volatile matter content of the coal was 21.5% (air dried basis, wt%). TG analysis of the coal in a N₂ atmosphere indicated that volatilization occurred between 400 °C and 770 °C (results not shown).

At 540 °C the neat mineral mixture gained weight ascribed to the decomposition and oxidation of pyrite (see Section 4.2.3). However, in the mixture with additive the weight loss due to the devolatilisation and combustion of coal occurring simultaneously with the oxidation of pyrite resulted in a net weight loss, instead of a gain as seen in the neat mineral mixture. The DTA curve of the mixture with additive was comparable to the DTA curve of the mineral mixture. Therefore, decomposition and oxidation of pyrite was not delayed or did not occur at a slower rate due to the addition of coal to the mixture. The coal used as additive had an ash content of 29.2%.

Anthony [2008] suggested that the reaction of methane with CaSO₄ can be used in chemical looping gasification systems. The reaction is given in Equation 5.7.



The reaction of pyrolysis products with CaSO₄ could potentially weaken the sintered matrix by breaking down the CaSO₄ responsible for strength formation. Analysis of the gas produced during pyrolysis of the coal blend indicated that the gas contained approximately 10% methane (J.R. Bunt, Personal Communication).

Coal is combusted in the oxidizing atmosphere. The combustion of coal will increase the porosity of the pellets, and subsequently result in a weakening of the structure, and decrease in the compressive strength. Based on the available data, the increase in porosity is the most likely explanation for the decrease in the compressive strength.

Figure 5.14 presents the compressive strength results of pellets sintered in N₂. In N₂, the addition of coal only significantly lowered the compressive strength of pellets at sintering temperatures of 700 °C (lowered by 27%), and 800 °C (lowered by 18%). At the other sintering temperatures in N₂ the results were comparable to the neat mineral mixture pellets.

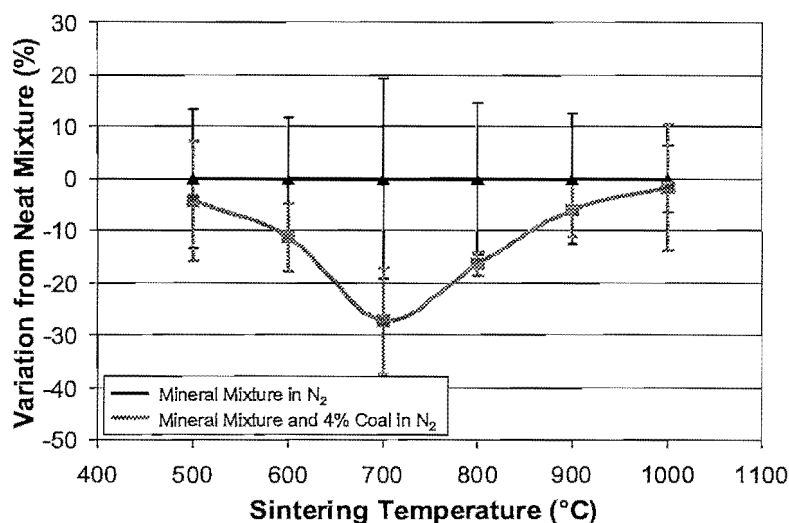


Figure 5.14 Compressive strength results of coal as additive sintered in N₂

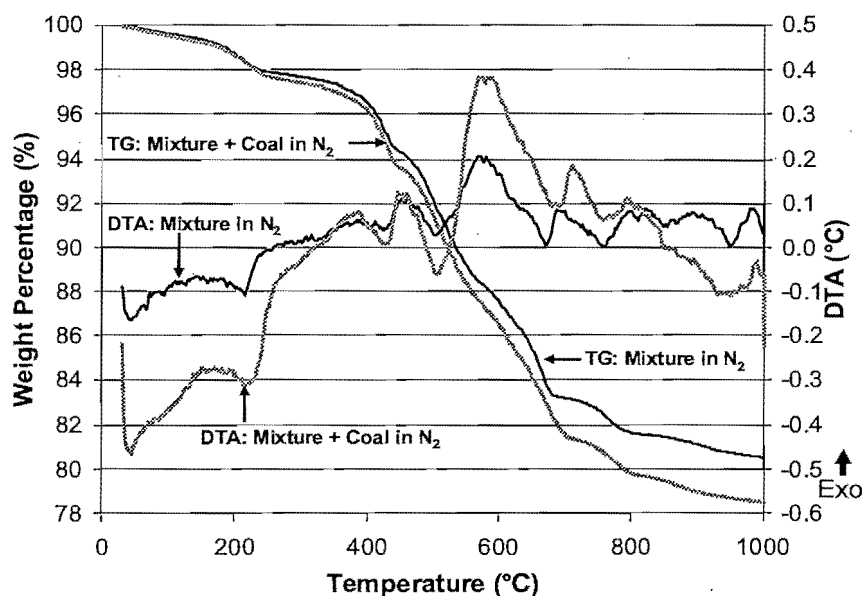


Figure 5.15 TG/DTA results of coal as additive heated in air

Figure 5.15 presents the TG/DTA results of the mineral mixture with coal as additive heated in N₂. As with the results in air, the weight loss patterns were similar from 30 °C to 450 °C. The weight loss in the sample with coal was slightly more (~2%) than for the mineral mixture sample. This difference can be ascribed to the devolatilisation of coal. Pyrolysis of coal occurs in the inert atmosphere, but not

combustion. From 450 °C to 540 °C the sample with coal had a weight loss of less than 1%, compared to 2% in air. The rate of weight loss of the sample with additive was comparable to the neat mineral mixture from 500 °C to 680 °C. Weight loss in the sample with additive was approximately 2% more than the neat mineral mixture from 680 °C to 1000 °C.

Weight loss of the sample with additive in N₂ also started to deviate from the neat mineral mixture from 450 °C, due to the pyrolysis of coal. The strength reduction at 700 °C corresponds with an increase in the weight loss observed in the TG/DTA curve. The CO₂ released from the decomposition of minerals may result in limited CO₂ gasification of the coal, which would result in the additional weight loss, and an increased porosity.

The interactions of coal with minerals in the pellets in air and N₂ are probably more complex than can be deduced from the experiments chosen for this study. However, the combustion of coal would definitely have increased the porosity in the pellets, and therefore the addition of coal reduced the strength of the pellets at all the sintering temperatures in air.

5.3 Effect of Simultaneous Addition of Sodium Species and Coal

Sodium species significantly increased the compressive strengths of pellets sintered in air, but coal lowered the compressive strengths. Coal and sodium additives were added to the mineral mixture simultaneously to determine how the co-addition would affect the compressive strengths of pellets. The co-addition may also reveal more of the effect of coal on the mineral mixture. Compressive strength experiments were conducted at sintering temperatures of 500 °C, 800 °C and 1000 °C in air. The compressive strength results and SEM analysis are presented below. Both the coal and sodium species were added as 4% by weight.

5.3.1 *Simultaneous Addition of NaCl and Coal*

Figure 5.16 presents the compressive strength results of mineral mixture pellets sintered at 500 °C, 800 °C and 1000 °C, with the separate addition of NaCl and coal, and the co-addition of NaCl and coal as additives. At sintering temperatures of 500 °C and 800 °C, the influence of the co-addition of species appears to be

approximately the sum of the results obtained for the separate addition of the additives. However, at a sintering temperature of 1000 °C, the co-addition of the additives did not yield a result equal to the sum of the individual additives.

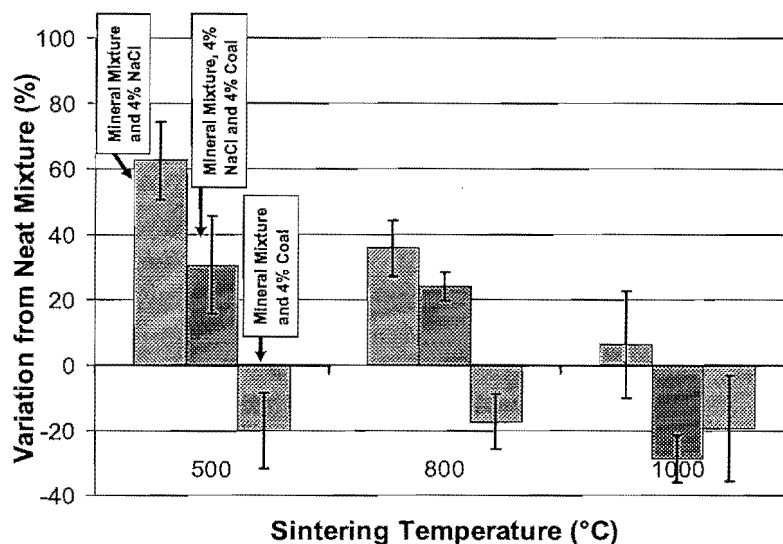


Figure 5.16 Compressive strength results of the combined addition of NaCl and coal as additives, compared to separate additions of NaCl and coal

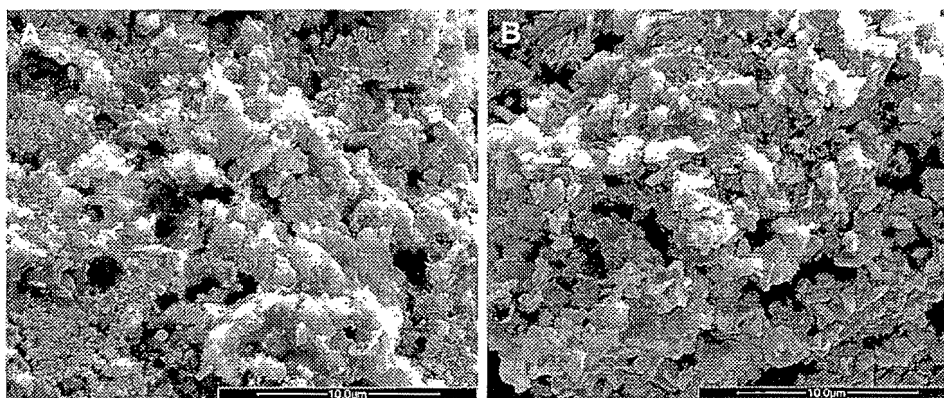


Figure 5.17 SEM images of mineral mixture pellets sintered in air at 800 °C. A) NaCl as additive; B) NaCl and coal as additives

Figure 5.17 presents SEM images of mineral mixture pellets sintered in air at 800 °C. Image A presents mineral mixture pellets with NaCl as additive, and pellets in image B contained both NaCl and coal. Comparison of images A and B suggests that the coal affected the formation of the sintered CaSO_4 matrix. Hu and co-workers

[2007] stated that the enhanced sulfation of limestone due to NaCl caused the formation of deformed anhydrite crystals that coalesced. No clearly defined crystals are visible in image A. However, many well developed, discrete crystals are visible in image B. The identity of the crystals in image B is not known, but SEM/EDS analysis indicated that some of the elements detected in areas in image B were O (41.5%), Ca (11.1%), Fe (13.3%), S (5.7%), Si (11.8%), Al (7.6%), Na (0.9%) and Cl (1.0%). The addition of coal may have inhibited the enhanced sulfation of limestone from the addition of NaCl, and not only affected the compressive strength through the formation of pores.

It is unclear whether the addition of coal inhibited the sulfation reaction, or only caused the formation of more structured crystals that did not coalesce. Both interactions can explain the reduction in compressive strength from the co-addition compared to the addition of NaCl at sintering temperatures of 500 °C and 800 °C, where CaSO_4 plays an important role in strength formation. Further investigation is necessary to confirm this result. If the discrete crystals were FeS_2 or FeS , the addition of coal may have delayed or prevented the oxidation of pyrite, but the TG/DTA results in Figure 5.13 for the addition of coal do not suggest that such an interaction occurred. However, the results obtained at sintering temperatures of 500 °C and 800 °C may simply be the increased compressive strength due to enhanced sulfation from NaCl, “minus” the decreased compressive strength due to increased porosity from the combustion of the coal.

SEM/EDS analysis of the areas in image B (Figure 5.17) indicated that chlorine was still present at 800 °C, but no chlorine was detected in the sample with only NaCl as additive. The addition of coal with NaCl may have affected the volatilization of NaCl and the formation of Na_2SO_4 . The combined influence of the additives at 1000 °C was most likely due to an increase in porosity and changes in the characteristics of the aluminosilicate phases.

5.3.2 Simultaneous Addition of Na_2CO_3 and Coal

Figure 5.18 presents the compressive strength results of mineral mixture pellets sintered at 500 °C, 800 °C and 1000 °C, with the separate addition of Na_2CO_3 and coal, and the co-addition of Na_2CO_3 and coal as additives. Similar to the co-addition of NaCl and coal, the results of the co-addition of Na_2CO_3 and coal appear to be approximately the sum of the results obtained for the separate addition of the

additives at sintering temperatures of 500 °C and 800 °C. At a sintering temperature of 1000 °C, the co-addition of the additives did not yield a result equal to the sum of the individual additives.

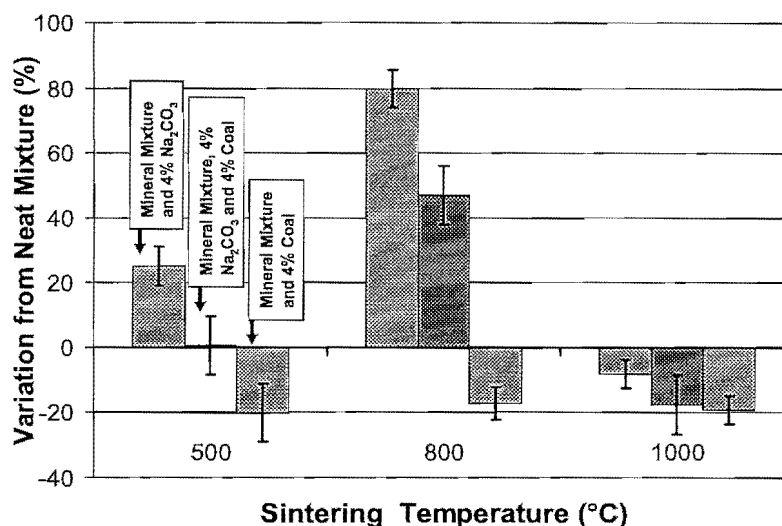


Figure 5.18 Compressive strength results of the combined addition of Na₂CO₃ and coal as additives, compared to separate additions of Na₂CO₃ and coal

Figure 5.19 presents SEM images of mineral mixture pellets sintered in air at 800 °C. Image A presents mineral mixture pellets with Na₂CO₃ as additive, and pellets in image B contained both Na₂CO₃ and coal. Comparison of images A and B suggests that the coal also affected the formation of the sintered CaSO₄ matrix, as with the simultaneous addition of NaCl and coal. The particles in image A are extensively sintered, as explained by enhanced sulfation from the addition of Na₂CO₃. However, in image B, extensive sintering is not evident. SEM/EDS analysis indicated that the circular grain consisted mainly of Fe and O. The flaky area consisted of O (53.5%), C (4.6%), Ca (5.9%), S (14.8%), Mg (8.9), Al (4.2%), Si (5.0%), Fe (1.8%) and Na (0.5%). The high concentration of sulfur, and lack of iron, suggest the formation of sulfates.

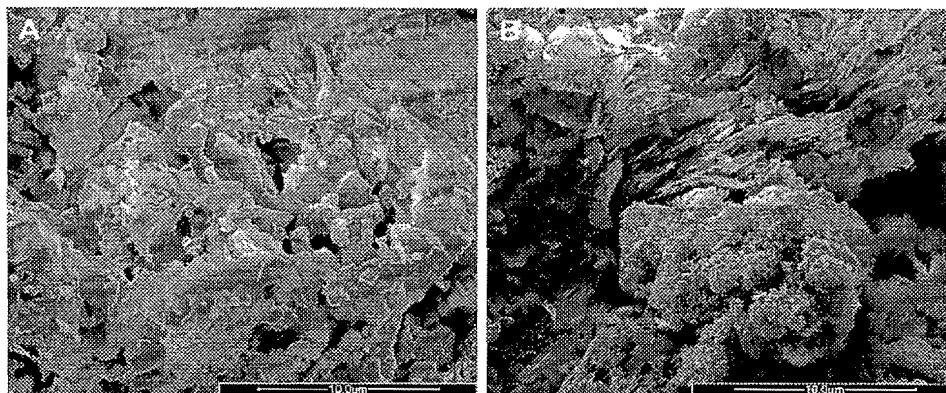


Figure 5.19 SEM images of mineral mixture pellets sintered in air at 800 °C. A) Na_2CO_3 as additive; B) Na_2CO_3 and coal as additives

The results suggest that the same interactions observed for the co-addition of NaCl and coal occurred for the co-addition of Na_2CO_3 and coal. The same explanation will therefore also be valid for the co-addition of Na_2CO_3 and coal. However, the results obtained at sintering temperatures of 500 °C and 800 °C may again simply be the increased compressive strength due to enhanced sulfation from Na_2CO_3 addition, “minus” the decreased compressive strength due to increased porosity from combustion of the coal. A more extensive investigation is required to confirm whether the addition of coal affects sulfation of limestone.

Kosminski and co-workers [2006b] suggested that Na_2CO_3 can react with carbon to form elemental sodium and carbon monoxide. Elemental sodium has a boiling point of 881 °C and will react with water and oxygen in the pellets [Lee, 1996]. However, not enough data are available to determine whether the Na_2CO_3 and coal reacted with each other. The combined influence of the additives at 1000 °C was most likely due to an increase in porosity and changes in the characteristics of the aluminosilicate phases.

5.4 Influence of NaCl on Ash Fusion Temperatures of the Mineral Mixture

Figure 5.20 presents the ash fusion temperatures obtained for the addition of NaCl to the mineral mixture and ashed at different temperatures. The addition of 4% NaCl reduced the ash fusion temperatures by 30 °C to 70 °C for both ashing temperatures.

NaCl is well known for the formation of agglomerates during fluidized-bed gasification. The initial deformation temperatures of the mixture with additive were 1070 °C and 1080 °C. Initial melting most probably occurred at temperatures much lower than indicated by the deformation temperatures. Initial melting most likely occurred at temperatures below 1000 °C, which is in the operation range of fluidized-bed reactors. Low melting point species include sodium aluminosilicates, FeO, and eutectics.

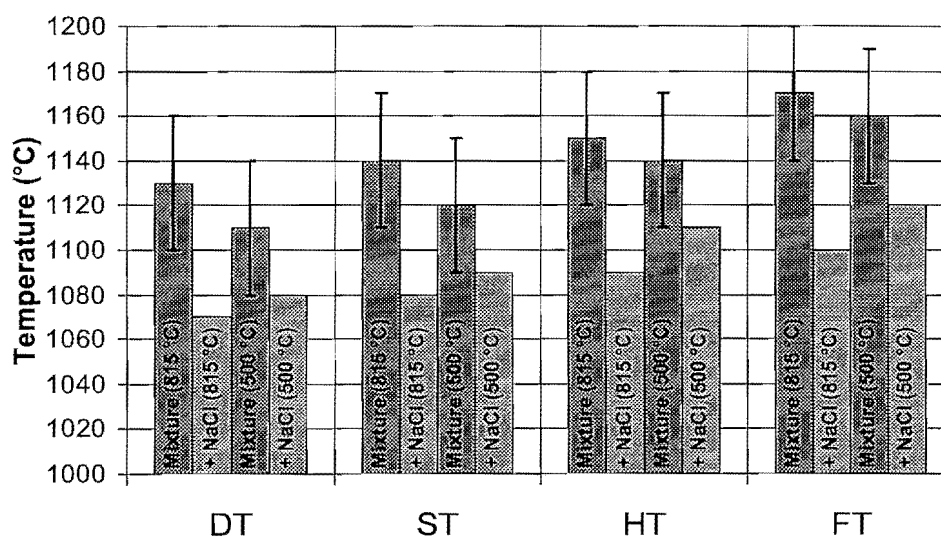


Figure 5.20 Reducing ash fusion temperatures for NaCl as additive to the mineral mixture. Ashing temperatures are given in parentheses

Chapter 6

Results and Discussion

Arsenic, Chromium, Cobalt, Copper and Germanium

6.1 Arsenic Trioxide

Arsenic as trace element in coal, its speciation, and reactions during combustion and gasification, has been extensively investigated using both analytical methods and modelling. Arsenic in coal has predominantly an inorganic association with pyrite, with arsenic substituting sulfur [Finkelman, 1994; Galbreath et al., 2000; Gürdal, 2007; Hower et al., 2008; Sterling and Helble, 2003]. Arsenic occurs in two oxidation states, namely As^{3+} and As^{5+} [Goodarzi, 2002]. Common inorganic arsenic-containing compounds associated with coal and ash include: arsenical pyrite (FeAsS_2), arsenopyrite (FeAsS), complex arsenates (AsO_4^{3-}), AsS , As_2S_3 , arsenic in acid-soluble oxides, and in association with sulfides of copper, zinc and lead [Bool and Helble, 1995; Bunt and Waanders, 2008; Huggins et al., 1993, Liu et al., 2007c]. Arsenic is also found dispersed through macerals and is bound via carboxyl groups or other hydrated oxygen functional groups [Galbreath and Zygarlicke, 2004]. Ting and Manahan [1979] determined that organically bound arsenic was non-volatile during pyrolysis.

Arsenic-containing pyrite and macerals decompose during combustion and release gaseous As^0 [Galbreath et al., 2000]. As^0 is readily oxidized to gaseous arsenic oxides such as AsO , As_2O_3 and As_2O_5 [Galbreath et al., 2000; Galbreath and Zygarlicke, 2004]. Arsenic oxides volatilize at low temperatures [Folgueras et al., 2007]. As_2O_3 is a dominant arsenic species in the gas formed during combustion [Bool and Helble, 1995; Shah et al., 2007; Sterling and Helble, 2003]. Therefore, solid As_2O_3 was chosen as arsenic-containing additive.

As described in Section 3.1.2, arsenic trioxide was not included in the oxidizing and inert atmosphere experiments, due to the lack of proper ventilation and the potential release of toxic gasses. The influence of As_2O_3 on the compressive strength of the pellets was therefore not investigated. However, research has indicated that As_2O_3 can interact with mineral matter in coal or ash, as summarized in the next

paragraph. It could therefore potentially have an influence on sintering and agglomeration.

Arsenic species can interact with ash during combustion to form solid arsenates, or it can dissolve into silicate glasses [Folgueras et al., 2007; Galbreath et al., 2000; Huffman et al., 1994]. Possible arsenates that can form include $\text{Ca}_3(\text{AsO}_4)_2$, $\text{Fe}(\text{AsO}_4)$ and $\text{Mg}_3(\text{AsO}_4)_2$ [Folgueras et al., 2007]. Lime is known to capture gaseous arsenic species and retain it in solid phases [Folgueras et al., 2007; Jadhav and Fan, 2001]. Jadhav and Fan [2001] determined that tricalcium orthoarsenate ($\text{Ca}_3(\text{AsO}_4)_2$) occurs below 600 °C, and dicalcium pyroarsenate ($\text{Ca}_2\text{As}_2\text{O}_7$) is found in the range of 700 °C to 900 °C. $\text{Ca}_3(\text{AsO}_4)_2$ occurs again above 950 °C. However, equilibrium calculations performed by Linak and Wendt [1994] did not predict the formation of calcium arsenate in the presence of sulfur.

The incorporation of calcium in calcium arsenates may reduce the amount of anhydrite formed in the mineral mixture pellets, and can therefore also reduce the extent of sintering. The retention of arsenic in calcium-containing species may also affect the stability of the CaSO_4 network responsible for strength development in the pellets, by reducing particle growth. The formation of arsenates can incorporate defects in the anhydrite particles and so limit grain development. Arsenates also dissolve into aluminosilicate glasses [Huffman et al., 1994; Kim and Kazonich, 2004]. Arsenic has been detected in iron-rich glass phases [Kim and Kazonich, 2004]. Huffman and co-workers [1994] suggested that arsenates may be incorporated into aluminosilicate glasses as network formers from the reaction of arsenical pyrite with clays and quartz. The inclusion of network formers will increase the stability in the pellets and possibly increase the compressive strength. The incorporation of arsenates in aluminosilicates may also affect the characteristics of the phases; rendering them more or less friable than the aluminosilicate phases in the neat mineral mixture pellets. However, experiments with arsenic species as additives are necessary to confirm whether arsenic compounds influence the compressive strength of pellets prepared from the mineral mixture.

The reducing-atmosphere ash fusion temperature results of As_2O_3 as additive are presented in Figure 6.1. The addition of arsenic trioxide did not affect the ash fusion temperatures of the mineral mixture ashed at 500 °C or 815 °C. Bunt and Waanders [2008] determined with equilibrium calculations that gaseous arsenic species form at temperatures higher than 220 °C in reducing conditions. The

calculations also predicted that all the arsenic in the coal will occur as gaseous AsH_3 at temperatures above 725°C . AsH_3 and AsS are major gaseous arsenic species under reducing conditions [Bunt and Waanders, 2008; Helble et al., 1996]. During ashing of the mineral mixture, volatilization of arsenic species most likely dominated the arsenic transformations in the reducing atmosphere. However, if arsenic was captured by constituents in the mineral mixture during ashing, the formation of arsenic-containing compounds did not significantly influence the ash fusion temperatures.

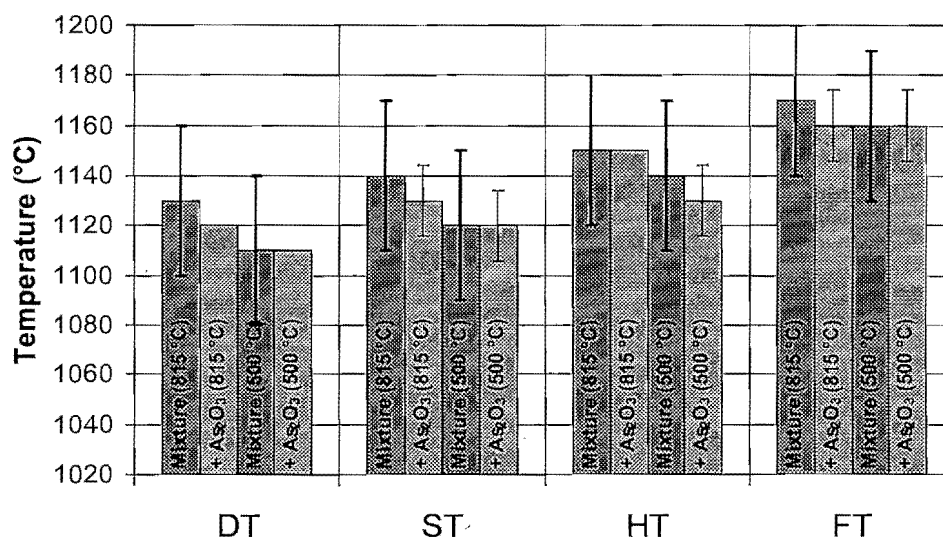


Figure 6.1 Reducing-atmosphere ash fusion temperatures for As_2O_3 as additive. Ashing temperatures are given in parentheses

6.2 Chromium Compounds

Chromium in coal occurs mostly in the trivalent state (Cr^{3+}), but small amounts of Cr^{6+} species are found in some coals [Huggins et al., 2009; Shah et al., 2008; Wagner and Hlatswayo, 2005]. Hexavalent species more commonly form during coal utilization [Wagner and Hlatswayo, 2005]. Chromium in coal is mostly associated with sulfates, clays (especially illite), silicates, oxides and pyrite [Bool and Helble, 1995; Huggins and Huffman, 2004; Galbreath et al., 2000; Galbreath and Zygarlicke, 2004]. Coals with high chromium may contain chromite (FeCrO_4) [Finkelman, 1994]. Chromium in coal is also associated with macerals, especially in bituminous coals [Finkelman, 1994; Galbreath and Zygarlicke, 2004; Huggins et al.,

2009; Wagner and Hlatshwayo, 2005]. Possible organically bound chromium species include chromium oxyhydroxide (CrOOH) and $\text{Cr}(\text{OH})_3$ [Galbreath et al., 2000; Huffman et al., 1994]. Trivalent chromium is not toxic, but hexavalent chromium is carcinogenic [IARC, 1997; Goodarzi, 2002; Narukawa et al., 2007; Wagner and Hlatshwayo, 2005].

The chromium-containing compounds that were selected as additives are $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ (trivalent) (from here on noted as $\text{Cr}_2(\text{SO}_4)_3$) and CrO_3 (hexavalent). Linak and Wendt [1994] determined with equilibrium calculations that $\text{Cr}_2(\text{SO}_4)_3$, CrO_3 and $\text{CrO}_2(\text{OH})_2$ are possible stable species occurring in notable quantities during coal combustion. Chromium is often found associated with sulfates [Bool and Helble, 1995]. CrO_3 was only included in the ash fusion temperature tests for reasons previously stated (see Section 3.1.2).

6.2.1 Chromium(III) Sulfate

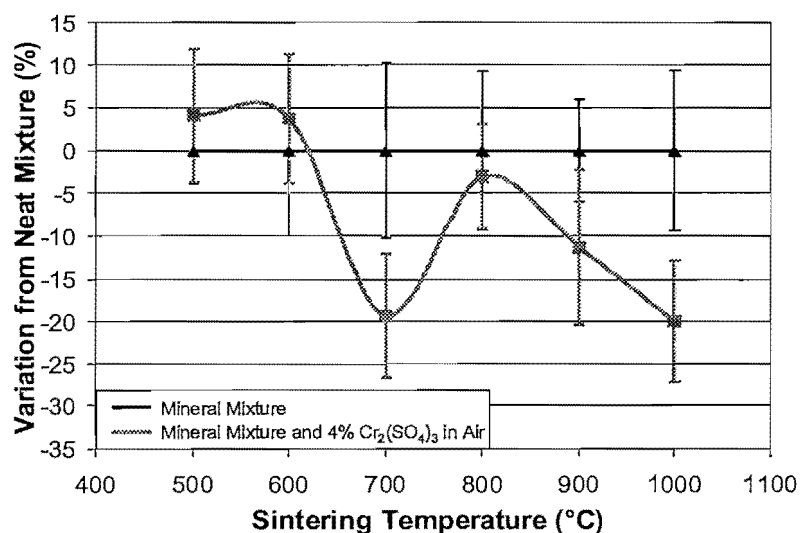


Figure 6.2 Compressive strength results of chromium(III) sulfate as additive sintered in air

Figure 6.2 presents the compressive strength results of $\text{Cr}_2(\text{SO}_4)_3$ as additive sintered in air. The addition of $\text{Cr}_2(\text{SO}_4)_3$ significantly decreased the compressive strength of the mineral mixture at sintering temperatures of 700 °C and 1000 °C. In both cases the compressive strengths were lowered by approximately 20%. The

compressive strengths were comparable to the neat mineral mixture at the other sintering temperatures.

Figure 6.3 presents the compressive strength results of $\text{Cr}_2(\text{SO}_4)_3$ as additive sintered in N_2 . Based on the confidence limits, the addition of $\text{Cr}_2(\text{SO}_4)_3$ did not significantly affect the compressive strength of the mineral mixture pellets at any of the sintering temperatures.

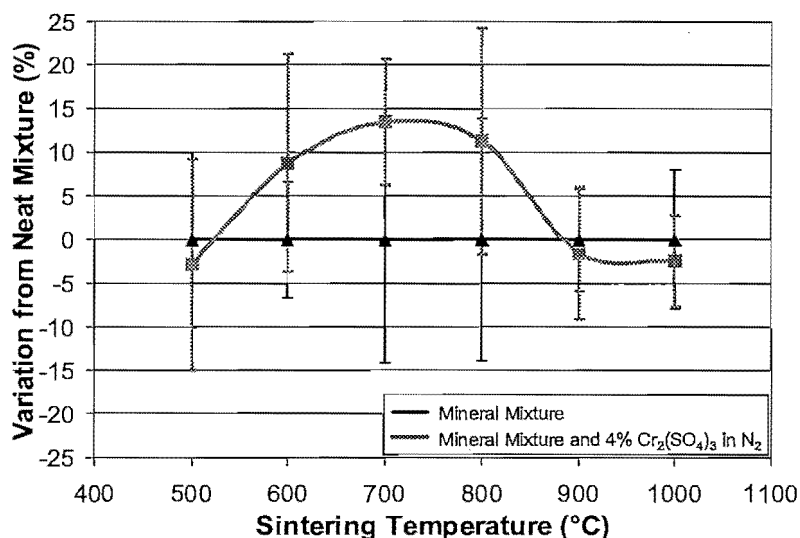


Figure 6.3 Compressive strength results of chromium(III) sulfate as additive sintered in N_2

The TG/DTA results of $\text{Cr}_2(\text{SO}_4)_3$ as additive heated in air are presented in Figure 6.4. The total weight loss in the sample with additive was 2% more than the weight loss of the neat mineral mixture sample over the temperature range. The difference in weight loss between the two samples was less than 1% from 400 °C to 900 °C. The additive was added as chromium(III) sulfate hydrate ($\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$). The initial difference in weight loss was therefore most likely due to dehydration of the chromium species. The exact amount of water associated with each molecule is unknown. The weight loss difference increased to 2% from 900 °C to 1000 °C due to the decomposition in the sulfate. $\text{Cr}_2(\text{SO}_4)_3$ decomposes to Cr_2O_3 and SO_3 between 575 °C and 675 °C, with complete decomposition reported at 700 °C [Atkinson et al., 2004]. However, the decomposition is impeded in the mineral mixture due to the presence of SO_2 from the decomposition and oxidation of pyrite. Decomposition is

only apparent at temperatures higher than 900 °C. Calculations based on the weight loss obtained in the TG analysis in air indicate that decomposition of the sulfate was not completed at 1000 °C.

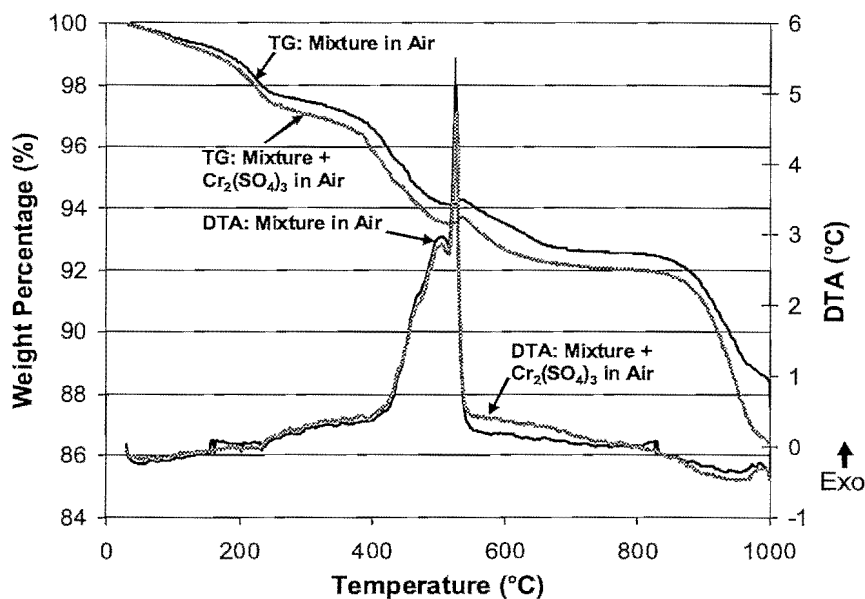


Figure 6.4 TG/DTA results of chromium(III) sulfate as additive heated in air

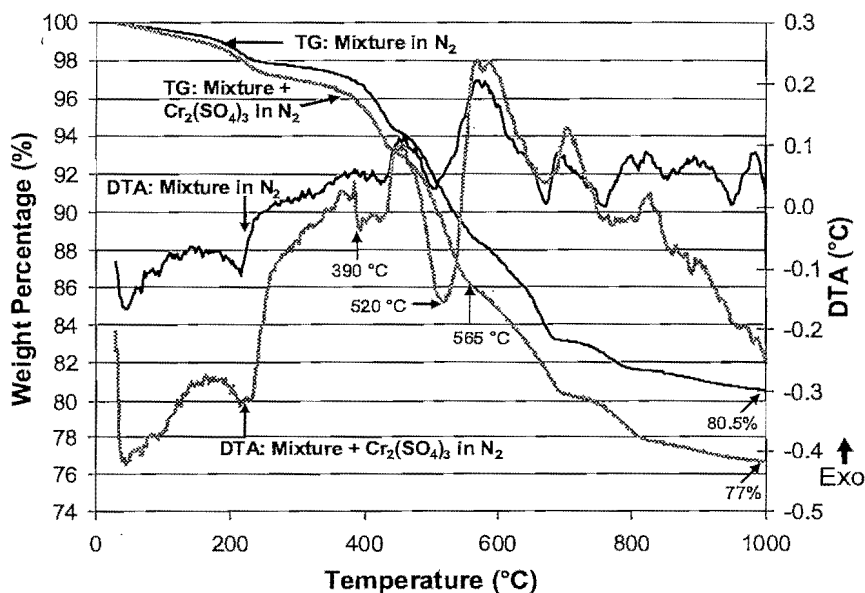


Figure 6.5 TG/DTA results of chromium(III) sulfate as additive heated in N₂

Figure 6.5 presents the TG/DTA results of $\text{Cr}_2(\text{SO}_4)_3$ as additive heated in N_2 . The difference in weight loss between the two samples increased continuously from 30 °C to 800 °C. The initial difference in the weight loss patterns from 30 °C to 400 °C was most likely due to dehydration of the additive. From the weight loss pattern of the sample with additive heated in air and N_2 , it seems that the additive contained less than 25% water (based on a weight loss of approximately 1% up to 400 °C in the mineral mixture, and a 4% addition of the additive. Thus, less than one quarter of the additive). Weight loss in the sample with additive was 3.5% more than the weight loss of the neat mineral mixture sample at 1000 °C in N_2 . The increase in weight loss from approximately 565 °C is comparable to the temperature range of decomposition determined by Atkinson and co-workers [2004]. According to the weight loss results obtained in the TG experiment, complete decomposition of $\text{Cr}_2(\text{SO}_4)_3$ was obtained at 800 °C, together with the release of some volatile chromium species.

The addition of $\text{Cr}_2(\text{SO}_4)_3$ to the mineral mixture lowered the compressive strength of the mineral mixture at sintering temperatures of 700 °C and 1000 °C. The reason for the decrease in compressive strength at a sintering temperature of 700 °C is unclear. The experiment was repeated three times, and in each experiment the compressive strength of the mineral mixture was reduced by 18% to 22%. Viewing the surface of a pellet under an optical microscope indicated that the decomposition and dehydration of the chromium sulfate particles resulted in cracking in the areas of the green additive particles. The formation of the cracks and pores at a sintering temperature of 700 °C can explain the decrease in the compressive strength value, and maybe also the slight decrease of the compressive strength at the higher sintering temperatures. However, if the formation of cracks and pores were solely responsible for the decrease in the compressive strength at a sintering temperature of 700 °C, it is assumed that larger reductions in the compressive strength values should also be evident at higher sintering temperatures. Conversely, the same effect on the compressive strength values at sintering temperatures of 800 °C and 900 °C will be observed if the additive increased the strengths of the pellets, combined with an increase in porosity that simultaneously reduced the stability of the pellets. Thus, the two effects may have cancelled each other, creating the appearance that the additive had no effect at those sintering temperatures.

The literature on chromium transformation in coal ash is limited. However, it has been established that chromium in fly ash can be in the form of CrO_2 ; spinels, e.g. chromite (FeCr_2O_4), MgCr_2O_4 , and CaCr_2O_4 ; or incorporated into aluminosilicate slag phases [Díaz-Somoano et al., 2006; Folgueras et al., 2007; Huffman et al., 1994]. FeCr_2O_4 is stable to temperatures much higher than the 1000 °C used in the compressive strength experiments [Bunt and Waanders, 2009b].

Backscattered electron SEM/EDS analysis indicated that chromium was associated with iron particles in the pellets sintered at 700 °C. A limited amount of chromium may have been incorporated into FeCr_2O_4 . The possible incorporation of Cr (from Cr_2O_3 or direct reaction of $\text{Cr}_2(\text{SO}_4)_3$) into FeCr_2O_4 could have influenced the characteristics of the pellets and also the compressive strength, as no significant weight loss was observed for the sample with additive up to 900 °C, apart from dehydration.

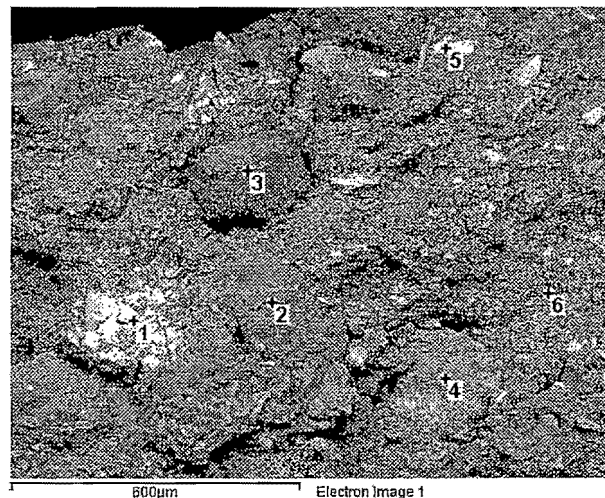


Figure 6.6 Backscattered electron image of a mineral mixture pellet with $\text{Cr}_2(\text{SO}_4)_3$ as additive sintered at 1000 °C in air

Figure 6.6 is a backscattered electron image of a mineral mixture pellet with $\text{Cr}_2(\text{SO}_4)_3$ sintered in air at 1000 °C. Chromium was enriched in all areas, except at point number 5. EDS analysis indicated that the particle at number 5 was iron-rich, but the weight ratio of Fe to O (1.4) was not helpful in identifying the iron species involved. Area 1 consisted mostly of Fe and O. Chromium (1.5%, elemental wt%) was also detected and most probably indicates the formation of some FeCr_2O_4 . The

EDS results are too limited to determine the extent of chromite formation. The particles indicated by numbers 2 and 3 were most likely SiO_2 particles with an aluminosilicate layer. The chromium concentrations detected in these areas were 0.3–0.6%. Particle number 4 was also predominantly Fe and O with a possible aluminosilicate layer. A chromium concentration of 1% (elemental wt%) was detected at this position on the sample. The chromium was most likely a combination of FeCr_2O_4 and chromium incorporated into the aluminosilicate layer. The area indicated by point number 6 consisted of approximately 4% to 13% (elemental wt%) Mg, Al, Si, S, and Fe (apart from 47% oxygen), and represents the aluminosilicate/anhydrite matrix. A chromium concentration of 1.3% (elemental wt%) was detected in this area. The EDS results of the pellets with additive sintered at 1000 °C verify that chromium was incorporated into aluminosilicates and possibly also chromite and MgCr_2O_4 in the mineral mixture pellets. The incorporation of chromium in aluminosilicate phases was not observed for pellets sintered at 700 °C.

The incorporation of chromium into aluminosilicates can be responsible for the decrease in the compressive strength results of the mineral mixture pellets sintered at 1000 °C in air. The addition of chromium may have influenced the characteristics of the phases by increasing the friability, compared to the neat mineral mixture pellets. The decomposition of $\text{Cr}_2(\text{SO}_4)_3$ also increased the porosity in the pellets, thereby increasing the potential for crack propagation and lowering the resistance to an applied force. XRD analysis was unable to identify crystalline chromium-containing phases. The majority of the chromium species was most likely amorphous, especially in the aluminosilicate phases, or present in low concentrations.

More volatilization occurred in the sample with additive heated in N_2 , compared to the neat mineral mixture (see Figure 6.5). The weight loss in the sample with additive was 3.5% more than the neat mineral mixture sample. Complete decomposition of $\text{Cr}_2(\text{SO}_4)_3$ to Cr_2O_3 and SO_3 should result in a weight difference of less than 3%. The large weight loss of the sample with additive heated in N_2 (see Figure 6.5) suggest that volatile chromium species formed in the inert atmosphere. Bool and Helble [1995] stated that the initial form of chromium is important to determine its speciation during coal utilization. Galbreath and co-workers [2000] and Galbreath and Zygarrlicke [2004] suggested that the chromium associated with macerals in coal is released as a mixture of gaseous species during combustion, i.e. CrO_2 , $\text{CrO}(\text{OH})$, $\text{CrO}_2(\text{OH})$, $\text{CrO}(\text{OH})_2$ and $\text{CrO}_2(\text{OH})_2$. Other researchers have also

noted the volatilization of chromium species during combustion [Bool and Helble, 1995; Helble, 1994; Miller et al., 2002]. It is unclear which volatile chromium species formed in the N_2 atmosphere during heating of the mineral mixture with additive. Chromium in coal is reported to be largely non-volatile [Linak and Wendt, 1994; Thompson and Argent, 2002].

Addition of the chromium additive did not significantly influence the compressive strength of the mineral mixture pellets sintered in N_2 (see Figure 6.3), even though significant volatilization occurred. The reason for this is unclear. However, similar to the suggestion for the pellets sintered in air, opposing effects may have created the appearance that the additive had no effect on the pellets sintered in N_2 . The difference in the compressive strength trends of the pellets with additive sintered in air and N_2 suggest that the additive reacted differently with the aluminosilicates in the two atmospheres. CrS or Cr_2S_3 are possible products formed in N_2 instead of Cr_2O_3 . Further investigation into the characteristics of the additive and its interactions with the mineral mixture in the inert atmosphere is necessary to confirm the compressive strength trends.

6.2.2 Reducing-Atmosphere Ash Fusion Temperature Test

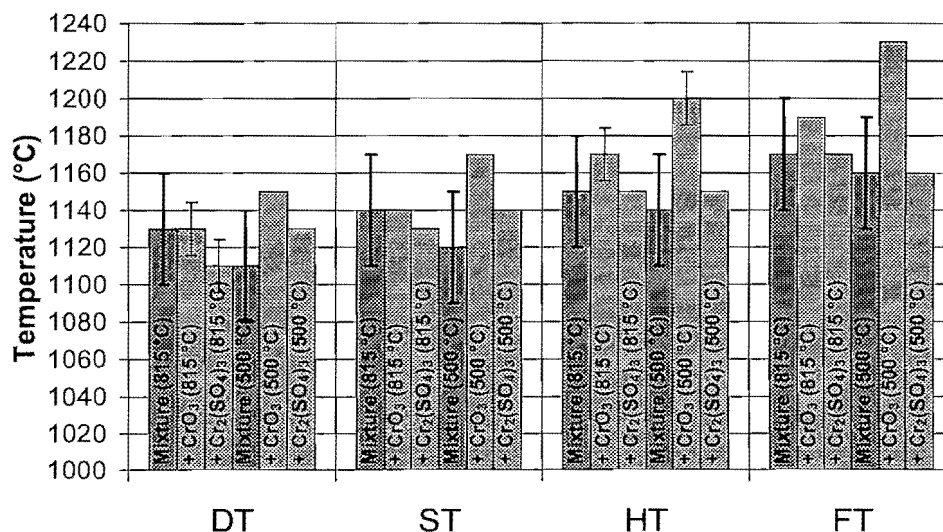


Figure 6.7 Reducing-atmosphere ash fusion temperatures for Cr species as additives. Ashing temperatures are given in parentheses

Figure 6.7 presents the reducing-atmosphere ash fusion temperature results of $\text{Cr}_2(\text{SO}_4)_3$ and CrO_3 as additives. $\text{Cr}_2(\text{SO}_4)_3$ did not have a significant influence on the ash fusion temperatures at either of the ashing temperatures. However, CrO_3 as additive increased the AFTs of the mineral mixture ashed at 500 °C. The addition of CrO_3 increased the AFTs by 40–70 °C. CrO_3 is a strong oxidizing agent, which decomposes to Cr_2O_3 and O_2 at temperatures higher than 100 °C [Atkins et al., 2004; Lee, 1996]. It appears that the additive caused oxidation of some of the components in the mineral mixture, instead of reduction as intended. The locally oxidizing environment due to the additive may have caused the formation of species with higher melting points than would have formed in the neat mineral mixture in a reducing atmosphere. For example, it has been reported that the iron aluminosilicates formed from the reaction of included pyrite with silicates and aluminosilicates partially melt at significantly higher temperatures under oxidizing conditions, compared to reducing conditions [Bool et al., 1995; McLennan et al., 2000b; Ram et al., 1995].

6.3 Cobalt Sulfate

Cobalt in coal is incorporated into pyrite and other sulfides, and also associated with the organic matrix of coal [Finkelman, 1994; Galbreath et al., 2000; Gürdal, 2007; Laban and Atkin, 1999]. Cobalt was found in some Australian coals as part of linnaeite ($(\text{Co},\text{Ni})_3\text{S}_4$) and linnaeite group minerals [Finkelman, 1994]. Folgueras and co-workers [2007] determined that cobalt in coal forms CoSO_4 during combustion at temperatures lower than 800 °C. Díaz-Somoano and co-workers [2006] also reported that CoSO_4 is the only condensed phase formed at lower temperatures, but depending on the SO_2 concentration, the formation of CoO is also possible. Cobalt sulfate was therefore chosen as additive representing cobalt as trace element. The compound obtained for addition was cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$).

Figure 6.8 presents the compressive strength results of mineral mixture pellets with CoSO_4 as additive, sintered in air. Based on the confidence limits, the addition of CoSO_4 did not influence the compressive strength results significantly, but it may have caused the reducing trend over the total temperature range. It was therefore not selected for further investigation.

Even though the addition of CoSO_4 did not affect the compressive strength of the mineral mixture, Co species can interact with ash constituents during combustion. Investigations have detected cobalt retained in ashes, most likely due to incorporation into ferrite spinels [Díaz-Somoano et al. 2006, Folgueras et al., 2007]. Possible solid species from interaction with ash constituents include CoFe_2O_4 and CoAl_2O_4 . Ferrite spinel is an important host for cobalt [Galbreath et al., 2000; Folgueras et al., 2007]. Díaz-Somoano and co-workers [2006] performed equilibrium calculations for coal co-combusted with biowaste. They predicted that CoFe_2O_4 is the most stable species at temperatures higher than 500 °C when considering cobalt-iron interactions; and CoAl_2O_4 is the most stable species at temperatures higher than 600 °C for cobalt-aluminium interactions.

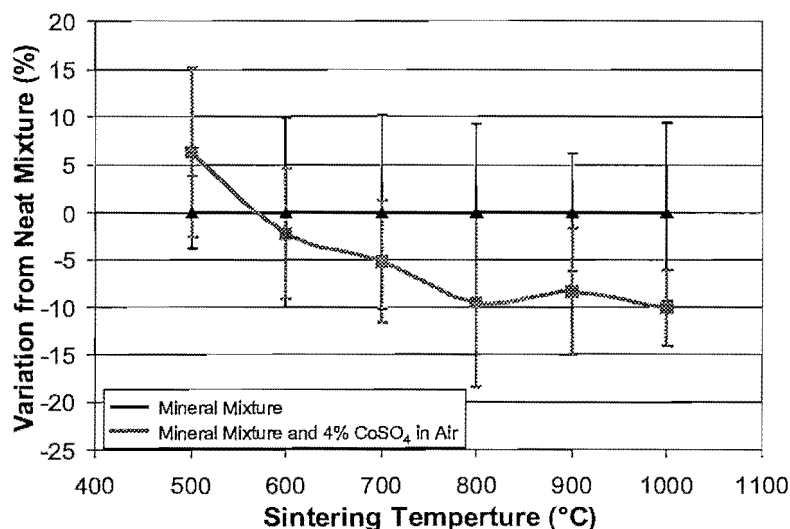


Figure 6.8 Compressive strength results of CoSO_4 as additive sintered in air

Figure 6.9 presents the reducing-atmosphere ash fusion temperatures of CoSO_4 as additive. The addition of CoSO_4 to the mineral mixture did not have an effect on the ash fusion temperatures at either ashing temperature. Bunt and Waanders [2009b] determined through equilibrium calculations that CoS_2 in coal is stable below 225 °C under reducing conditions, and Co_9S_8 is stable between 225 °C and 725 °C. At higher temperatures, the existence of solid elemental cobalt and a small amount of gaseous cobalt is predicted [Bunt and Waanders, 2009b].

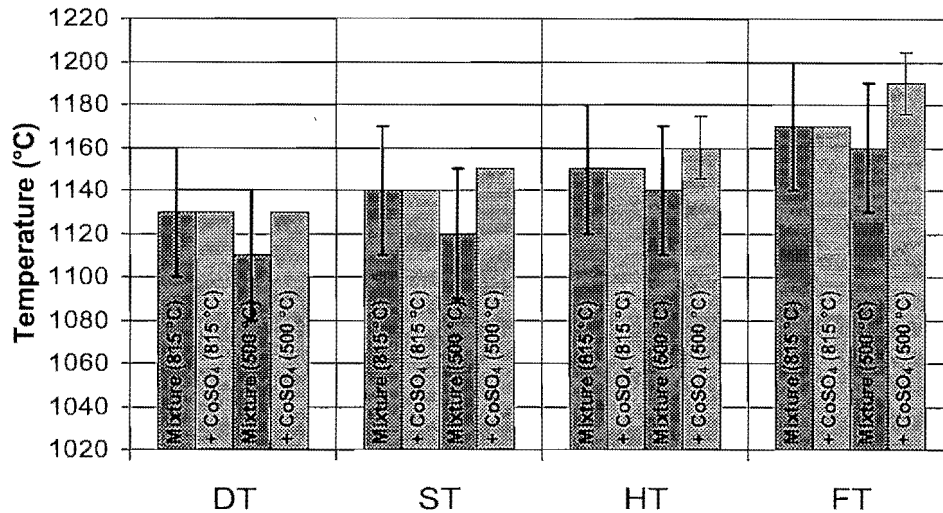


Figure 6.9 Reducing-atmosphere ash fusion temperatures for CoSO₄ as additive. Ashing temperatures are given in parentheses

6.4 Copper Compounds

Copper is mostly associated with pyrite and the organic matrix in coal [Galbreath et al., 2000; Gürdal, 2007]. The most common association of copper in coal is chalcopyrite (CuFeS₂) [Bunt and Waanders, 2009a; Goodarzi, 2002; Laban and Atkin, 1999]. Copper can also substitute into clays or be associated with carbonates [Goodarzi, 2002; Laban and Atkin, 1999]. Copper is either a semi-volatile or non-volatile element in coal, depending on the reaction conditions [Bunt and Waanders, 2009a; Galbreath et al., 2000]. The additives selected to represent copper as trace element are CuS (covellite) and Cu₂S (chalcocite).

6.4.1 Experiments in an Oxidizing Atmosphere

Figure 6.10 presents the compressive strength results of Cu₂S as additive sintered in air. The addition of Cu₂S decreased the compressive strength of the mineral mixture by approximately 19% at sintering temperatures of 700 °C and 900 °C, and by approximately 45% at a sintering temperature of 1000 °C. Figure 6.11 presents the compressive strength results of CuS as additive sintered in air. The addition of CuS increased the compressive strength of the mineral mixture sintered at 500 °C by approximately 17%, but lowered the compressive strength of the mineral mixture at a

sintering temperature of 1000 °C by approximately 39%. The trends are similar over the temperature range for both additives, but the compressive strength values were 10% to 15% higher for the addition of CuS than for the addition of Cu₂S, compared to the neat mineral mixture pellets.

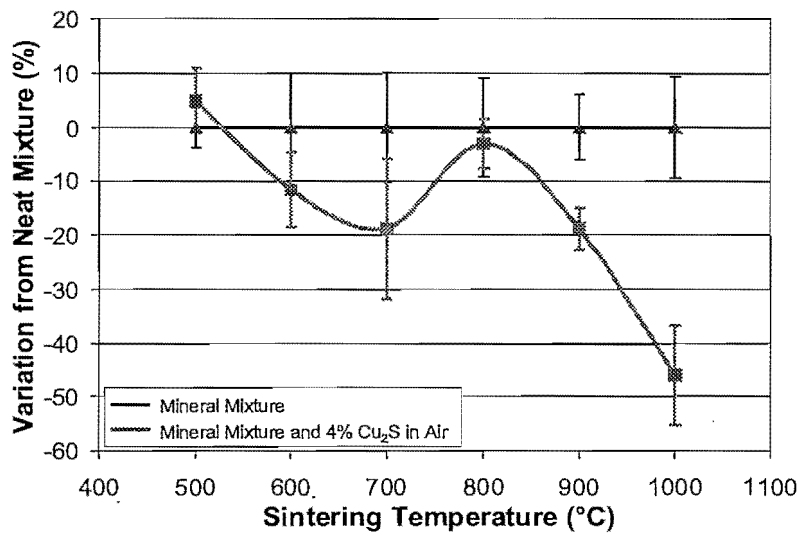


Figure 6.10 Compressive strength results of Cu₂S as additive sintered in air

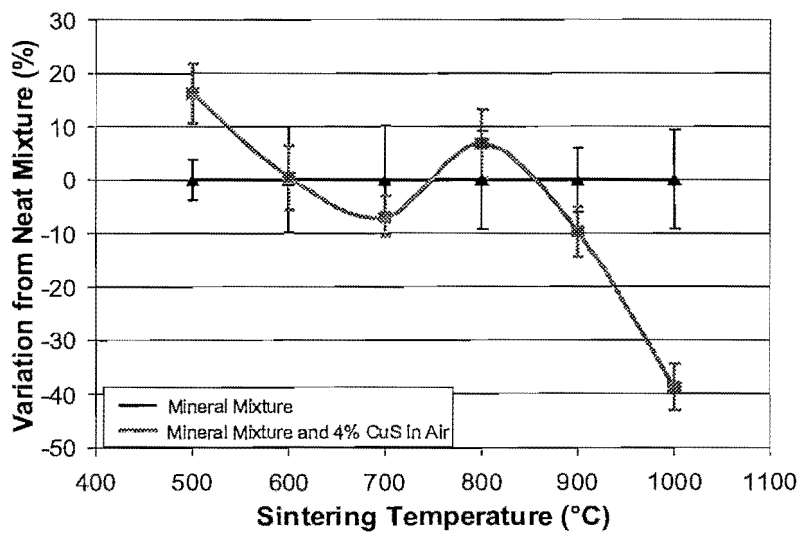


Figure 6.11 Compressive strength results of CuS as additive sintered in air

The transformations involved in the oxidation of CuS are complex. The thermal oxidation of CuS (covellite) has been studied extensively [Dunn and Muzenda, 2001; Prasad and Pandey, 1998]. Many reactions have been suggested, but the temperature ranges in which they occur can overlap. In general, the transformations during the oxidation of CuS are summarized by reaction scheme 6.1 [Prasad and Pandey, 1998]:



It is assumed that the transformations of Cu₂S will proceed in the same order, from the second transformation in reaction scheme 6.1 onwards. This explains the similar weight loss patterns for the addition of both copper compounds (see Figures 6.12 and 6.13), and also the similar trends in the compressive strength values. The source of Cu₂S used as additive contained a slight excess of S, and is therefore a nonstoichiometric substance (Aldrich, 2007). This may be the reason why the weight loss percentages are so similar for both compounds. Due to the simultaneous occurring of reactions, it is difficult to confidently assign changes in weight percentages to specific transformations. Major transformations will therefore be assigned based on either weight gains or losses, and information presented in literature.

Figures 6.12 and 6.13 present the TG/DTA results for the addition of Cu₂S and CuS heated in air. Both additives had similar weight loss patterns. The weights of the samples with additives remained constant from approximately 290 °C to 440 °C, while the weight of the neat mineral sample decreased. The weight of the additives therefore had to increase in order to keep the weight of the sample more or less constant. Based on the weight loss patterns of the samples with additives (Figures 6.12 and 6.13), CuSO₄ formation occurred from 270 °C to 450 °C from direct oxidation of Cu₂S, or via oxidative sulfation of CuS (via Cu₂S and Cu₂O formation). The excess sulfur included in the additive most probably also contributed to the formation of CuSO₄ in the samples with Cu₂S. The exothermic peak at 335 °C in the DTA curve of CuS (Figure 6.13) represents the transformation of CuS to Cu₁₁S₈ [Dunn and Muzenda, 2001]. The complete formation of CuSO₄ from the reaction of 4% Cu₂S with SO₂ and O₂ represents a weight gain of approximately 4%; and the complete formation of CuSO₄ from CuS represents a weight gain of approximately 3%.

However, the weight gain observed for both Cu_2S and CuS as additives from 270 °C to 440 °C was only 2%. Therefore, the samples probably contained some unreacted Cu_2S , CuS or Cu_2O , due to insufficient amounts of SO_2 (SO_2 may have been removed due to the constant gas flow in the TG instrument). It is difficult to achieve complete sulfation to CuSO_4 without an additional sulfur source, since CuSO_4 tends to decompose [Prasad and Pandey, 1998]. The formation of an oxide layer will also inhibit further sulfation or oxidation [Dunn, 1997; Dunn and Muzenda, 2001].

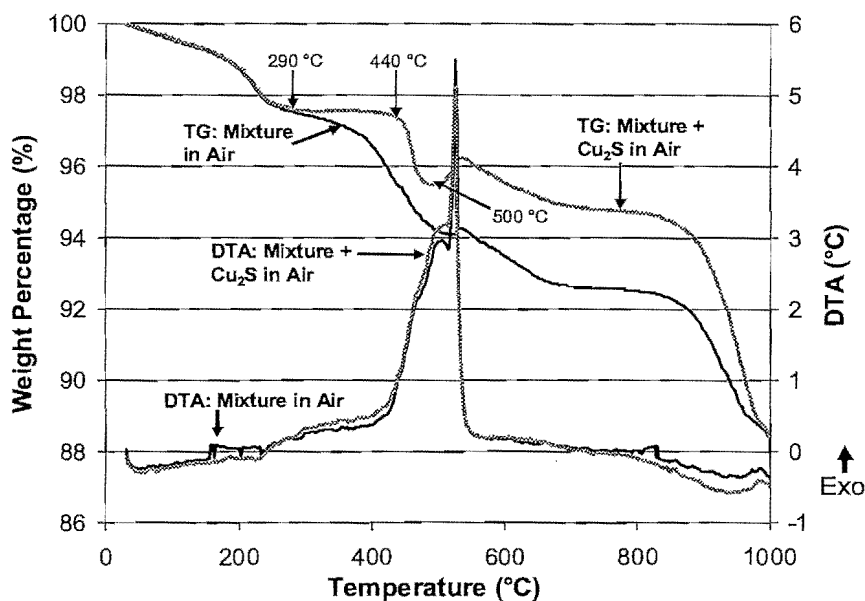


Figure 6.12 TG/DTA results of Cu_2S as additive heated in air

Copper sulfate production supposedly continues until 460 °C, after which decomposition to CuO occurs [Prasad and Pandey, 1998]. The decomposition of CuSO_4 explains the weight loss of approximately 2% from 440 °C to 500 °C observed in both samples with additives. Dunn and Muzenda [2001] reported that solid state reactions occur between Cu_2S and CuSO_4 in the range of 474 – 585 °C. The solid state reactions are responsible for the formation of a melt phase. The melt phase disrupts the outer oxide/sulfate layer and allows further oxidation and sulfation to occur. Further oxidation of CuS or Cu_2S may also have contributed to the 2% weight loss in the samples from 440 °C to 500 °C. The weight gain observed in the samples from 500 °C to 560 °C was due to sulfation of the additives. Additional SO_2 was available

in this temperature range from the decomposition of pyrite. CuO and CuSO_4 react to form $\text{CuO}\cdot\text{CuSO}_4$. CuO and $\text{CuO}\cdot\text{CuSO}_4$ have been identified in melt phases or films at temperatures higher than 460°C [Dunn, 1997; Dunn and Muzenda, 2001; Prasad and Pandey, 1998].

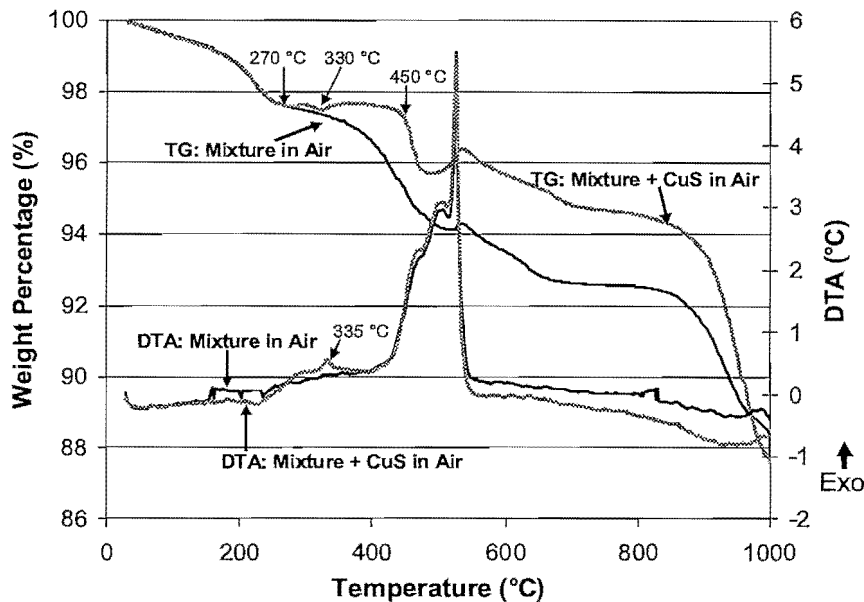


Figure 6.13 TG/DTA results of CuS as additive heated in air

The weight of the samples with additive was 2% more than the weight of the neat mineral mixture sample in the range of 540°C to 800°C . The oxidation and sulfation of 4% Cu_2S to $\text{CuO}\cdot\text{CuSO}_4$ represent a weight gain of 2 %. Weight loss occurred from 800°C to 1000°C , attributed to the decomposition of CuSO_4 in $\text{CuO}\cdot\text{CuSO}_4$ to CuO . At 1000°C the weights of the sample with Cu_2S and the neat mineral mixture were comparable. Complete oxidation of 4% Cu_2S to CuO accounts for a zero net weight gain or loss compared to the neat mineral mixture. However, the weight of the sample with CuS was slightly less ($<1\%$) than the weight of the neat mineral mixture at 1000°C . Theoretically, the complete oxidation of 4% CuS to CuO accounts for an additional weight loss of approximately 0.7%, compared to the neat mineral mixture.

As presented in Figures 6.10 and 6.11, the compressive strength trends for both additives were similar over the temperature range, but the compressive strength

values obtained for Cu_2S as additive were slightly lower than for CuS . The difference may be attributed to the difference in molar concentrations. The addition of CuS increased the compressive strength of the mineral mixture sintered at $500\text{ }^\circ\text{C}$. Most of the major interactions occurred below $500\text{ }^\circ\text{C}$. The addition of 4% CuS equates to 4.2×10^{-4} moles CuS per pellet, but the addition of 4% Cu_2S to only 2.5×10^{-4} moles of Cu_2S (if the excess sulfur is ignored). The transition of CuS to Cu_2S and the release of sulfur could have affected the compressive strength at a sintering temperature of $500\text{ }^\circ\text{C}$ in the sample with CuS . The sulfur may have contributed to the sulfation of limestone to anhydrite and increased sintering. Conversely, the Cu_2S additive had a slight excess of sulfur, but the same effect was not observed (the amount of sulfur in excess is unknown). The interactions responsible for the increase in the compressive strength are unknown as XRD, TG/DTA and SEM/EDS analyses were unable to shed more light on the matter.

CuO can interact with ash constituents to produce spinels (CuFe_2O_4 and CuAl_2O_4) [Díaz-Somoano et al., 2006; Folgueras et al., 2007]. The reaction of CuO with Fe_2O_3 to form CuFe_2O_4 occurs at $820\text{ }^\circ\text{C}$ to $840\text{ }^\circ\text{C}$ [Dunn, 1997]. CuO can also dissolve in silicate melts. CuO is commonly added to glasses to give colour [Kido et al., 2006; La Delfa et al., 2008]. After oxidation, the Cu_2S additive supplied a higher concentration of CuO than the CuS additive. CuS (4.2×10^{-4} moles) produced 4.2×10^{-4} moles of CuO after oxidation, but the oxidation of Cu_2S (2.5×10^{-4} moles) produced 5.0×10^{-4} moles of CuO . Therefore, the effect of CuO from Cu_2S was probably larger on the mineral mixture than the effect of CuO from CuS , due to a larger concentration, or the reactivity of Cu_2S was higher than the reactivity of CuS . However, the same trend was observed in the compressive strength results of the pellets sintered in N_2 (results presented after the oxidation results), but CuO was not formed in N_2 . The reactivity of the different additives therefore had a more important role than the concentration differences. Perhaps the excess sulfur in Cu_2S increased the reactivity of the additive.

The addition of Cu_2S lowered the compressive strength of the mineral mixture by 19% at a sintering temperature of $900\text{ }^\circ\text{C}$, and by 47% at a sintering temperature of $1000\text{ }^\circ\text{C}$ in air. The addition of CuS lowered the compressive strength by 39% at a sintering temperature of $1000\text{ }^\circ\text{C}$. The decrease in the compressive strength values can be due to an increase in porosity from the decomposition of $\text{CuO}\cdot\text{CuSO}_4$. The incorporation of CuO into aluminosilicate phases most probably

also changed the characteristics of the phases and affected the friability. The reaction of CuO with Fe and Al species would result in a lower concentration of iron aluminosilicates. The formation of discrete CuFe_2O_4 and CuAl_2O_4 particles will also incorporate instability into the pellets through non-uniform densification and additional breaks in the aluminosilicate/anhydrite matrix.

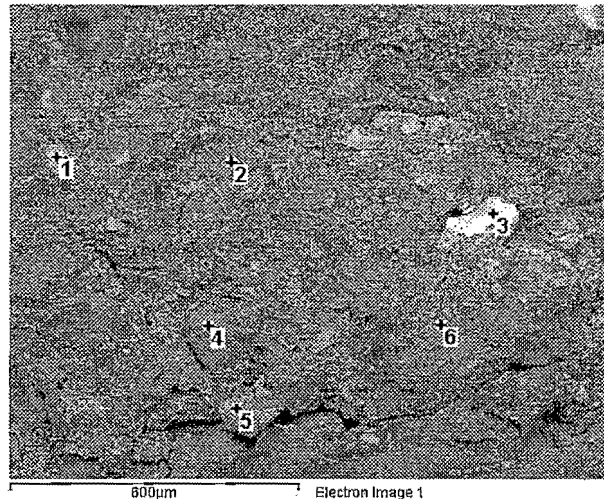


Figure 6.14 Backscattered electron image of a mineral mixture pellet with Cu_2S as additive sintered in air at 1000 °C

Figure 6.14 presents a backscattered electron image of a mineral mixture pellet with Cu_2S as additive sintered in air at 1000 °C. EDS analysis determined that the content of particle number 3 consisted mostly of Cu and O. The theoretical Cu to O weight ratio of CuO is approximately 4. EDS analysis indicated the weight ratio of Cu to O in the particle to be approximately 3.2. A weight ratio of 3 for Cu to O is achieved through the formation of a compound such as Cu_3O_4 . Folgueras and co-workers [2007] mentioned Cu_3O_4 in a list of copper oxides, but whether the compound can form is unclear. It is not listed as a common oxide of copper [Lee, 1996], and none of the papers investigating oxidation of copper sulfides mentioned its formation. The most probable copper oxide would be CuO (Cu to O ratio of 4). A mixture of CuO and Cu_2O may also be possible (Cu to O ratio of 2.6 for a 50% mixture, by weight). CuO decomposes to Cu_2O at temperatures higher than 1000 °C [Dunn and Muzenda, 2001]. The ash constituents may have lowered the decomposition temperature.

Particle 5 in Figure 6.14 probably consisted of CuFe_2O_4 . The Fe to Cu weight ratio in CuFe_2O_4 is 1.8, similar to the Fe to Cu ratio calculated for the particle in the image. CuFe_2O_4 formation from the reaction of CuO and Fe_2O_3 occurs between 820 °C and 840 °C [Dunn, 1997]. Copper was also detected in areas/particles 2, 4 and 6. These represent SiO_2 particles with a possible aluminosilicate layer, or the aluminosilicate/anhydrite matrix.

Backscattered electron SEM analyses of pellets sintered in air at 1000 °C with CuS and Cu_2S as additives suggest that some of the additive particles may have reacted differently, even though the same products were predicted for both additives. Figure 6.15 presents a backscattered electron image of a mineral mixture pellet with CuS as additive sintered in air at 1000 °C. Melt phases were observed in area 2. EDS analysis confirmed the presence of high amounts of Cu.

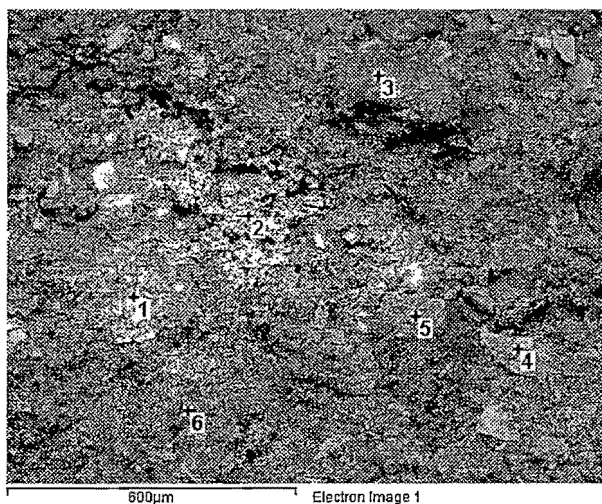


Figure 6.15 Backscattered electron image of a mineral mixture pellet with CuS as additive sintered in air at 1000 °C

The image presented by Figure 6.16 is a higher magnification of area 2 in Figure 6.15. Melting and sintering is clearly visible in Figure 6.16. EDS analysis indicated the occurrence of Cu and O. The weight ratio of Cu to O (2.8) suggests a mixture of CuO and Cu_2O , or the formation of Cu_3O_4 , as noted earlier. The melt phase was most probably originally from $\text{CuO}\cdot\text{CuSO}_4$. Further oxidation of the melt phase resulted in the formation of CuO , but the appearance of the molten particles was retained. Both $\text{CuO}\cdot\text{CuSO}_4$ and solid-state interactions of Cu_2S with CuSO_4 have been

indicated to form a melt, but references to the different interactions were found in separate papers [Dunn, 1997; Prasad and Pandey, 1998]. It is therefore unclear whether both contribute to melt formation, whether the solid state interactions produce $\text{CuO}\cdot\text{CuSO}_4$ as a molten product, or whether the initial melt is oxidized to solid $\text{CuO}\cdot\text{CuSO}_4$. Area 2 in Figure 6.16 represents the aluminosilicate/anhydrite matrix.

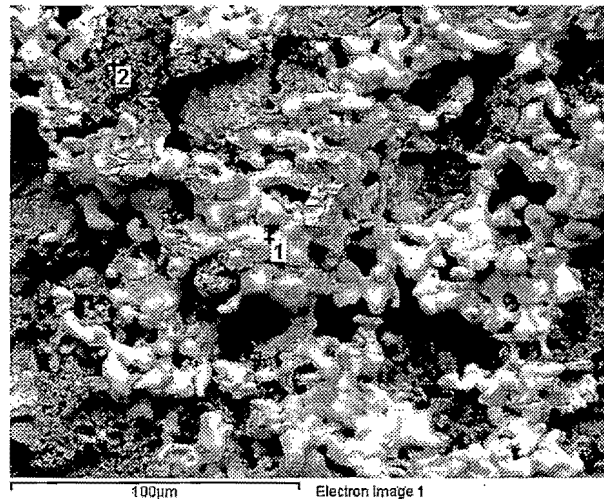


Figure 6.16 Backscattered electron image of copper-containing melt phases in a mineral mixture pellet with CuS as additive sintered in air at 1000 °C

6.4.2 Experiments in an Inert Atmosphere

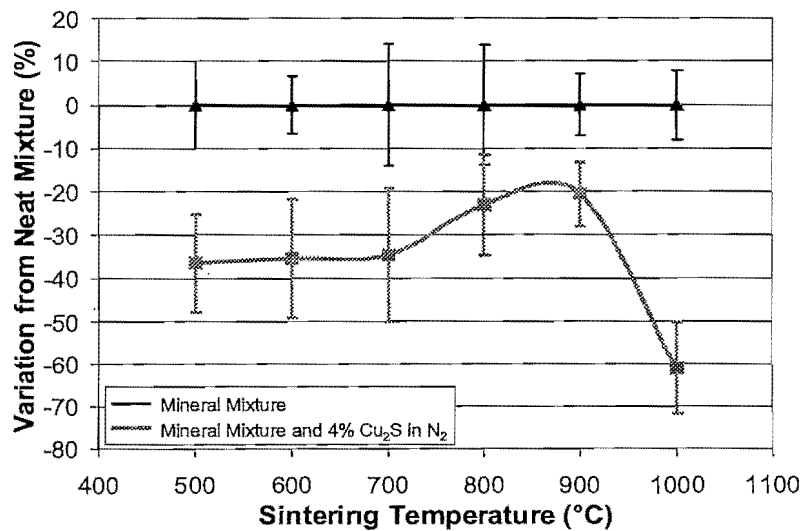


Figure 6.17 Compressive strength results of Cu_2S as additive sintered in N_2

Figures 6.17 and 6.18 present the compressive strength results of Cu_2S and CuS as additives sintered in N_2 , respectively. The addition of Cu_2S lowered the compressive strength of the mineral mixture by 20–60% at all the sintering temperatures. The addition of CuS followed the same trend, but the compressive strength values were 15–25% higher than for the addition of Cu_2S , compared to the neat mineral mixture pellets. CuS lowered the compressive strength of the mineral mixture by 45% in N_2 at a sintering temperature of 1000 °C.

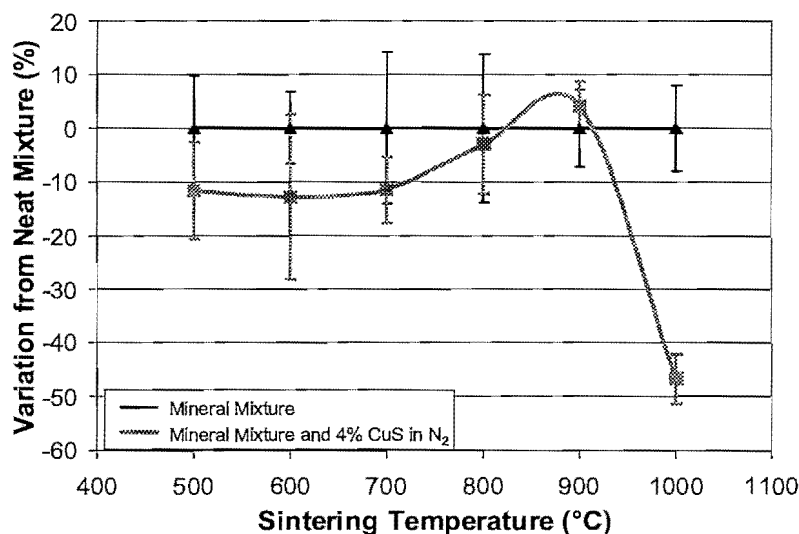


Figure 6.18 Compressive strength results of CuS as additive sintered in N_2

Figures 6.19 and 6.20 present the TG/DTA results of Cu_2S and CuS as additives heated in N_2 . In both samples containing additives the weight loss was similar to the neat mineral mixture up to 780 °C. The exothermic peak at 400 °C in the DTA curve of CuS heated in N_2 represents the transformation of CuS to $\text{Cu}_{1.8}\text{S}$ (digenite) (see Figure 6.13) [Dunn, 1997]. Slight weight changes are also associated with the exothermic peak, representing weight fluctuations due to the possible release of sulfur during the transformation. Based on the weight loss patterns, the additives remained unchanged from 440 °C to 780 °C in the mineral mixture in N_2 . Insignificant weight loss (<0.5%) was observed in both samples from 780 °C to 1000 °C. However, small amounts of weight loss may be due to the formation of Cu^0 from the redox reaction of Cu^+ (from Cu_2S) with Fe^{2+} , during which sulfur is liberated [Holzheid and Lodders, 2001]. Cu_2S also transforms to Cu^0 in the absence of iron [Dunn and

Muzenda, 2001]. The weight loss could also be due to the vaporization of excess sulfur, either the excess sulfur in the Cu_2S additive, or the transformation of CuS to Cu_2S that is associated with the liberation of sulfur.

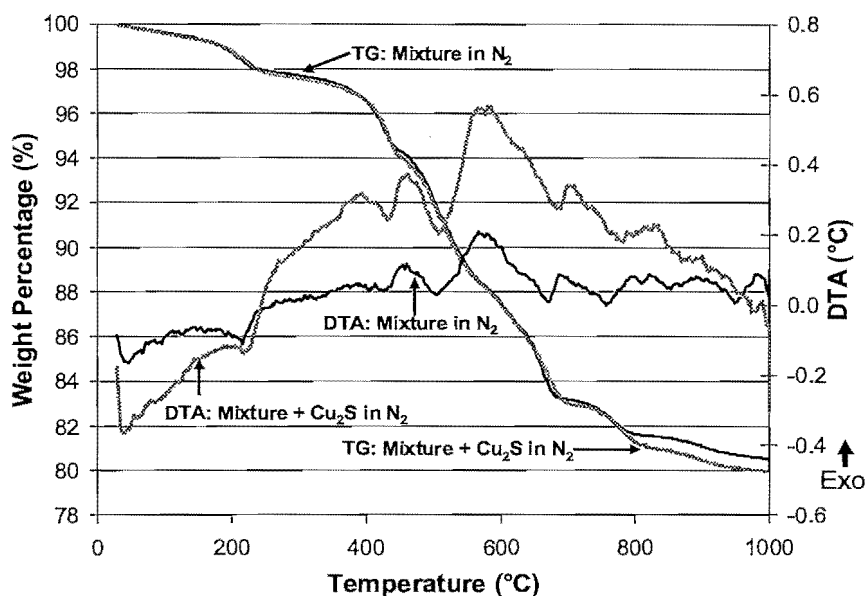


Figure 6.19 TG/DTA results of Cu_2S as additive heated in N_2

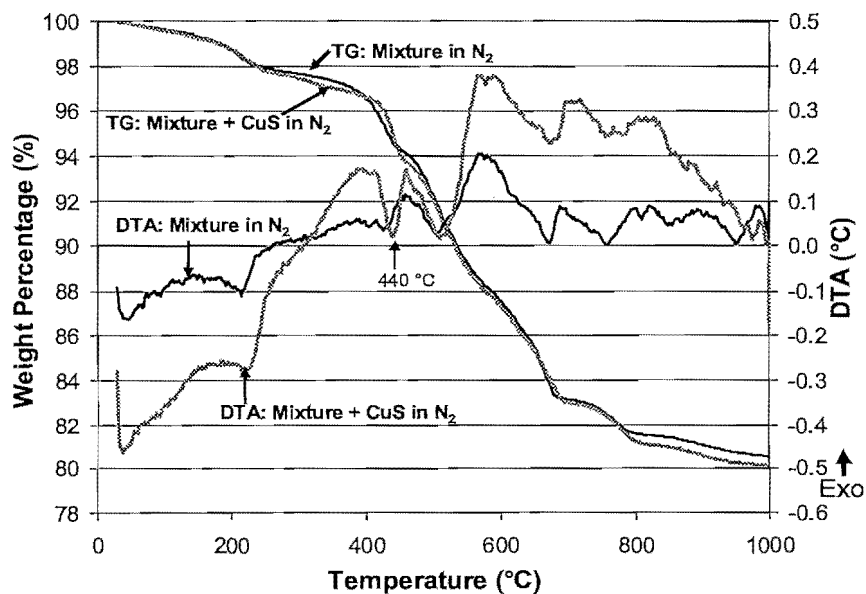


Figure 6.20 TG/DTA results of CuS as additive heated in N_2

Similar to the compressive strength results in air, the addition of Cu_2S resulted in a larger influence on the compressive strength values than the addition of CuS . An explanation for this difference may be different reactivities, but further investigation is necessary to substantiate the reason for the larger influence from Cu_2S . As described earlier, the compressive strength results in N_2 indicate that the higher molar concentration of one additive does not explain the different results. TG/DTA results confirm that an increase in porosity due to volatilization was not the reason for the decrease in the compressive strength values at the lower sintering temperatures. The fact that the compressive strength values were affected at low sintering temperatures in N_2 indicates that the influence on the compressive strengths was as a result of interactions with the aluminosilicate matrix.

The results obtained in both air and N_2 suggest that the Cu^+ species is more reactive than the Cu^{2+} species. Cu^+ is more unstable than Cu^{2+} [Lee, 1996]. Whether this is only characteristic of the additives obtained, or whether this is due to the difference in oxidation state can not be confirmed by the experimental methods applied, and warrants further investigation.

6.4.3 Reducing-Atmosphere Ash Fusion Temperature Test

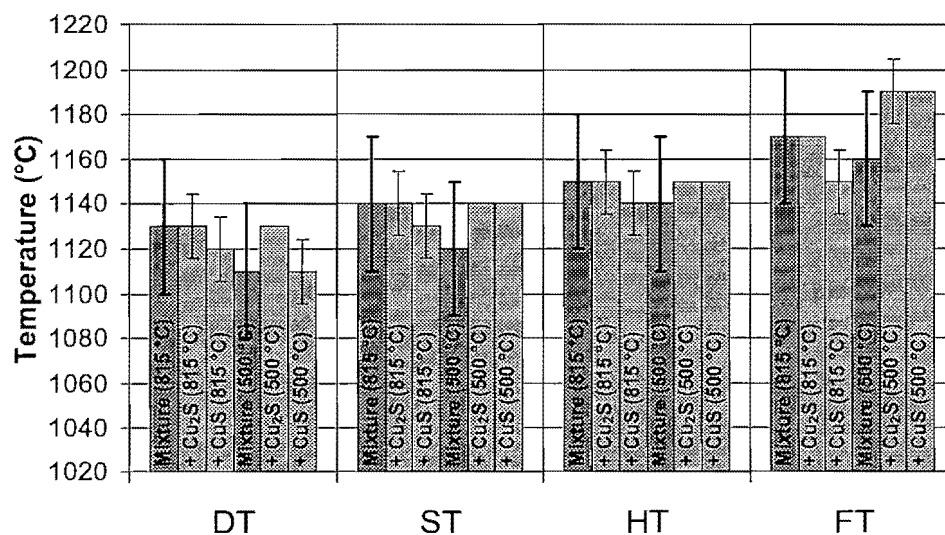


Figure 6.21 Reducing-atmosphere ash fusion temperatures for the addition of copper species as additives. Ashing temperatures are given in parentheses

Figure 6.21 presents the reducing-atmosphere ash fusion temperatures of copper species as additives. Both additives had no significant effect on the ash fusion temperatures of the mineral mixture ashed at 500 °C or 815 °C. The copper species were probably reduced to Cu^0 , or the sulfides could have persisted. Pure elemental copper has a melting point of 1083 °C [Holzheid and Lodders, 2001; Lee, 1996]. Elemental copper can dissolve into aluminosilicates. Bunt and Waanders [2009a] reported that the volatilization of copper increases with temperature in the reduction zone of a gasifier. They reported 10% volatilization at 1025 °C, and 75% percent at 1125 °C (CO_2 gasification). They found complete volatilization of gaseous Cu at a temperature of 1316 °C. Therefore, the volatilization of copper from the mineral mixture, and lack of retention in the ashes, may have resulted in the lack of influence on the ash fusion temperatures.

6.5 Germanium

Germanium is in the same group as silicon and carbon on the periodic table. Literature on the reactions and speciation of germanium species in coal ash are limited, as it is not a well studied trace element, or commonly reported. Most studies on germanium are involved with surface science and glass formation, since it has uses in the electronics and optical industries [Arroyo et al., 2009; Sastre et al., 2005].

Germanium is largely associated with sphalerite [Font et al., 2005a; Höll, 2007]. Germanium production is mostly from the processing of sphalerite, and germanium is also recovered from coal ash in parts of the world [Arroyo et al., 2009; Font et al., 2005a, 2005b; Höll et al., 2007]. Some coal deposits contain large amounts of germanium, mostly associated with sphalerite and wurtzite [Arroyo et al., 2009; Höll et al., 2007]. Huggins and co-workers [2009] determined that germanium in bituminous coal has a strong organic association. Höll and co-workers [2007] stated that the reported maximum concentration for germanium in coal is 0.4 wt%, and the maximum reported value for germanium in coal ash is 9 wt%. Germanium species found in coal ash include GeO_2 , GeS , GeS_2 and germanates [Arroyo et al., 2009; Font, 2005b]. GeO_2 and GeS were selected to represent germanium as trace element. The GeO_2 obtained as additive was amorphous, and had a melting point higher than 400 °C (Aldrich, 2007).

6.5.1 Germanium (II) sulfide

Figure 6.22 presents the compressive strength results of GeS as additive sintered in air. The addition of GeS did not significantly influence the compressive strength of the mineral mixture at any of the sintering temperatures. Therefore, GeS as additive was not included in further experiments, except in ash fusion temperature experiments (see Section 6.5.3). It is difficult to specify why GeS did not influence the compressive strength values without further investigations. However, GeS has a melting point of 530 °C, but sublimation already starts at 430 °C [Weast, 1977]. The oxidizing atmosphere may have influenced the sublimation temperature. Therefore, most of the GeS was probably volatilized from the pellets at all the sintering temperatures, especially with each experiment held at the desired temperature for 2.5 hours. GeS may have been oxidized to GeO or GeO₂. GeO has a sublimation temperature of 710 °C [Weast, 1977]. If GeO or GeO₂ formed, it is unclear why it did not influence the mineral mixture, as they are network formers in aluminosilicate phases [Martinez et al., 2003].

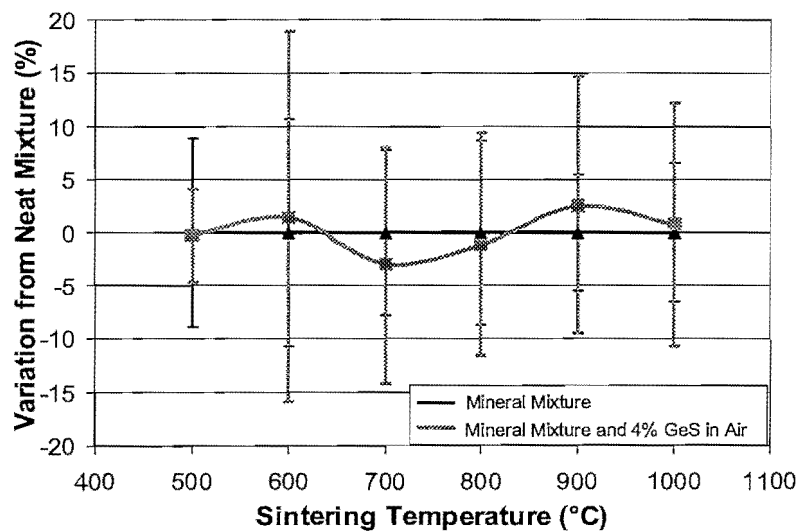


Figure 6.22 Compressive strength results of GeS as additive sintered in air

6.5.2 Germanium (IV) oxide

Figure 6.23 presents the compressive strength results of GeO₂ as additive sintered in air and N₂. The addition of GeO₂ to the mineral mixture sintered in air increased the compressive strength by approximately 30% at sintering temperatures of

600 °C to 800 °C. At the other sintering temperatures the results were comparable to the neat mineral mixture. At a sintering temperature of 500 °C the addition of GeO₂ to the mineral mixture sintered in N₂ increased the compressive strength by approximately 110%. The compressive strength value at a sintering temperature of 500 °C in N₂ (13.3 N/mm²) was comparable to the value obtained for the neat mineral mixture pellets sintered in air at 500 °C (14.0 N/mm²). At sintering temperatures of 600 °C to 800 °C the addition of GeO₂ increased the compressive strength in N₂ by 40–50%. At the other sintering temperatures the results were comparable to the neat mineral mixture.

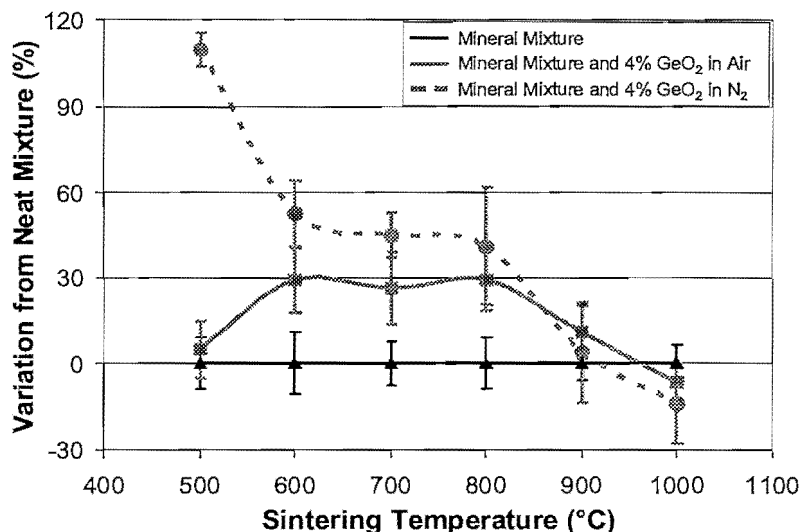


Figure 6.23 Compressive strength results of GeO₂ as additive in air and N₂

Figure 6.24 presents the TG/DTA results of GeO₂ as additive heated in air. The weight loss results were comparable to the neat mineral mixture over the entire temperature range. Therefore, the additive persisted in air, with no volatilization occurring. The exothermic peak associated with the transformation of FeS₂ to hematite was significantly less exothermic in the mixture with additive.

Based on similar trends in the compressive strength results obtained in both atmospheres, it can be deduced that GeO₂ had an influence on the aluminosilicate phases. Ge⁴⁺ is isomorphous to Si⁴⁺, and substitutes for the silicon in minerals and aluminosilicate phases [Höll et al., 2007; Martinez et al., 2003]. GeO₂ is a network former [Martinez et al., 2003]. It is reported that the structure of SiO₂-GeO₂ glasses

consists of interconnected SiO_4 and GeO_4 tetrahedra in a continuous three-dimensional network. Michel and co-workers [1996] studied the germanium mullite structure (gels, glasses and ceramics) and determined that the lower melting point of GeO_2 (compared to SiO_2) resulted in obtaining stable states at lower temperatures, compared to silicon-containing homologues.

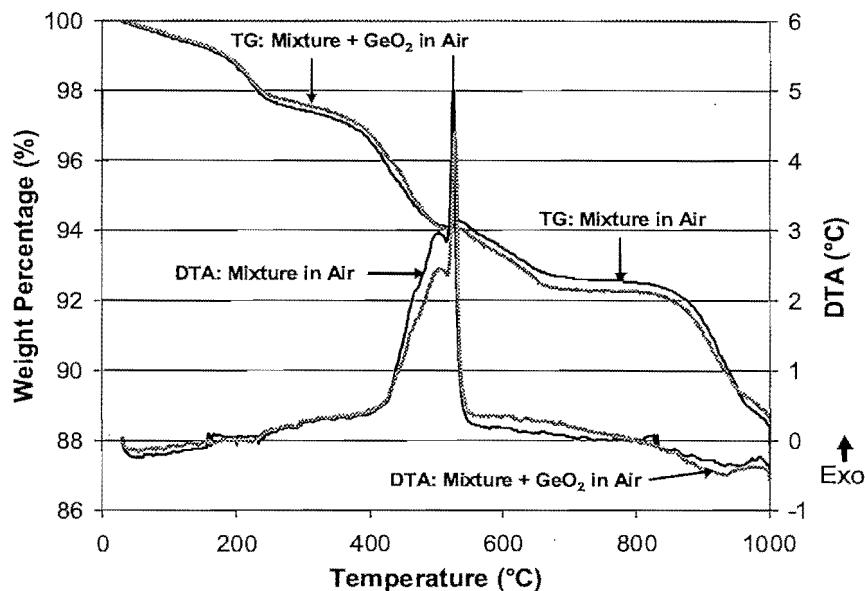


Figure 6.24 TG/DTA results of GeO_2 as additive heated in air

Therefore, the addition of GeO_2 to the mineral mixture pellets sintered in air resulted in a more continuous and dense aluminosilicate/anhydrite matrix at lower temperatures. The more extensive sintering and agglomeration due to the addition of GeO_2 added stability to the pellets and resulted in an increase in the compressive strength values.

Figure 6.25 presents backscattered electron images of mineral mixture pellets with GeO_2 as additive, sintered in air at 600 °C (image A), and 800 °C (image B), respectively. Germanium was enriched in all the areas indicated on image A and B. EDS analysis determined that particle 1 in image A contained 35.2% Fe and 10.8% Ge (elemental wt%). The Fe to Ge weight ratio for the particle is therefore 3.3. Insignificant amounts of Al and Si were detected in the analysis. Therefore, the particle was not an iron-rich particle covered by a Ge-containing aluminosilicate layer.

The weight ratio of Fe to Ge suggests a solid solution of Fe_2O_3 and GeO_2 ($2\text{Fe}_2\text{O}_3 \cdot \text{GeO}_2$) or FeO and GeO_4 ($4\text{FeO} \cdot \text{GeO}_4$). A compound with the formula of Fe_4GeO_8 (or $\text{Fe}_2\text{Ge}_{0.5}\text{O}_4$) would satisfy the Fe to Ge ratio. No reference was found as to whether such a solution could form in the mineral mixture. The reduction in the exothermic peak in the TG/DTA results (Figure 6.24) may be due to the interaction of iron and germanium species, but further investigations or modelling is necessary to investigate the extent and possibility of interactions between germanium and iron oxides. Area 2 in image A represents the aluminosilicate/anhydrite matrix.

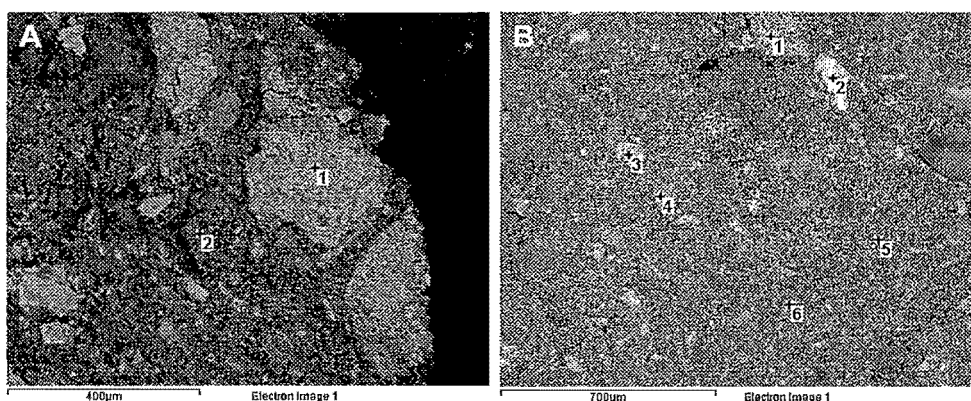


Figure 6.25 Backscattered electron images of mineral mixture pellets with GeO_2 as additive sintered in air at 600 °C (image A) and 800 °C (image B)

EDS analysis of the pellet in image B indicated that the elements were quite homogeneously distributed through all areas, except in particle 1. Particle 1 in image B was iron rich (40.2%, elemental wt%), but the same enrichment of Ge as in particle 1 in image 1 was not observed.

EDS analysis of a mineral mixture pellet with GeO_2 as additive sintered in air at 900 °C and 1000 °C, and results from TG/DTA experiments, indicated that volatilization of the additive was not responsible for the decrease in the compressive strength values at sintering temperatures of 900 °C and 1000 °C, compared to sintering at 800 °C. The same trend was observed in the pellets sintered in N_2 . The reason for the decrease is unknown, but was probably due to changes in the characteristics of the Ge-aluminosilicates.

It is expected that the addition of GeO_2 should also have an influence on the compressive strength in air at 500 °C, but the formation of anhydrite may have

dominated at that sintering temperature. The influence on the compressive strength from the addition of GeO_2 sintered in N_2 is the largest from all the additives, including the sodium species. The influence on the mineral mixture from the addition of GeO_2 , sintered in N_2 at 500 °C (increase of 110%), is larger than the influence from Na_2CO_3 addition sintered in air at 800 °C (increase of 80%).

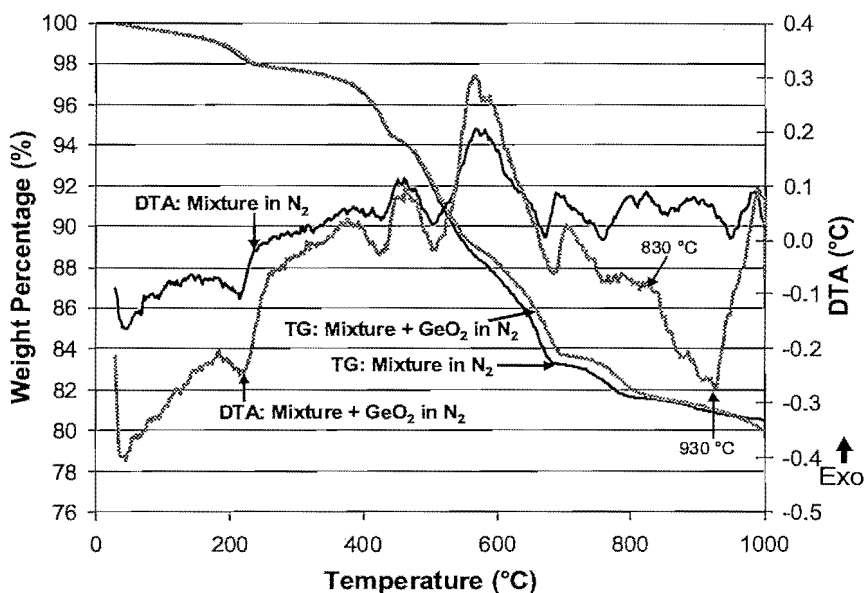


Figure 6.26 TG/DTA results of GeO_2 as additive heated in N_2

Figure 6.26 presents the TG/DTA results of GeO_2 as additive heated in N_2 . Based on the reproducibility of the method, the weight loss patterns were similar over the total temperature range. A large endothermic transformation also occurred from 830 °C to 1000 °C, with the peak at 930 °C.

Figure 6.27 is a photograph of the heat shield removed from the tube furnace after pellets were sintered at 1000 °C in N_2 . Figure 6.28 represents a backscattered electron image of the orange crystals deposited on the heat shield. EDS analysis of the orange deposit (position 2 in Figure 2.8) indicated that the crystals consisted mainly of Ge and S, with a Ge to S weight ratio of 1.0. The ratio suggests that the orange crystals were GeS_2 (Ge to S ratio of 1.1). Particle 1 in Figure 6.28 consisted of a mixture of elements. The composition included 32.7% Ge, 44.5% S, Cl, O, Mg, Sr, and 8.6% Rh, hence the light colour of the particle (elements with higher atomic

numbers appear lighter in colour than elements with lower atomic numbers on a backscattered image). The origin of the Rh is unknown. It may have been part of the heat shield or ceramic tube. XRF analysis of the minerals (see Table 4.1) did not include analysis for Rh.

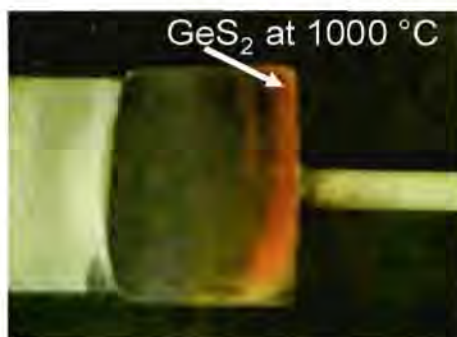


Figure 6.27 Heat shield removed from tube furnace after a sintering experiment at 1000 °C in N₂. Pellets with GeO₂ as additive were included in the experiment

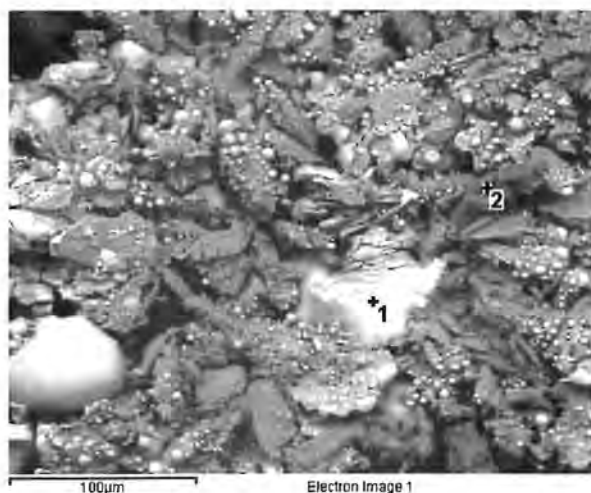


Figure 6.28 Backscattered electron image of the orange crystal (Figure 6.27) collected after sintering pellets in N₂ at 1000 °C, including pellets with GeO₂ as additive

The deposit of GeS₂ indicates that volatilization occurred from the pellets sintered in N₂, even though it could not be confirmed by the TG/DTA experiment. The discrepancy is most probably due to the difference in the reaction times of the two experiments. In the compressive strength test the pellets were held at 1000 °C for 2.5

hours, allowing enough time for the GeS_2 to form and volatilize. The TG/DTA experiment was terminated as soon as the temperature reached 1000 °C. GeS_2 has a melting point of 800 °C, but sublimation occurs at temperatures higher than 600 °C [Weast, 1977]. GeS_2 is a good glass former, similar to GeO_2 [Kim et al., 2005; Sutherland et al., 2004]. The volatilization of GeS_2 probably contributed to the decrease in the influence on the compressive strength values from sintering temperatures of 800 °C to 1000 °C in N_2 . Transformation of GeO_2 to GeS_2 with subsequent volatilization would reduce the stability of the aluminosilicate network and increase the porosity.

6.5.3 *Reducing-Atmosphere Ash Fusion Temperature Test*

Figure 6.29 presents the ash fusion temperature results of GeS and GeO_2 as additives. The addition of GeO_2 did not have an effect on the ash fusion temperatures of the mineral mixture ashed at 500 °C or 815 °C. The addition of GeS also did not have a significant influence on the ash fusion temperatures of the mixture ashed at 815 °C. However, the inclusion of GeS in the mineral mixture ashed at 500 °C lowered the ash fusion temperatures significantly. The ash fusion temperatures (AFTs) were lowered by 30–40 °C.

GeS has a melting point of 530 °C, but sublimation can start at 430 °C [Weast, 1977]. Ashing at 500 °C may have allowed the GeS to remain in the mineral mixture. However, 815 °C is much higher than the melting or sublimation temperature of GeS. Ashing the mineral mixture at 815 °C most probably caused the volatilization of some of the GeS from the mineral mixture and it could therefore not influence the ash fusion temperatures. GeS in the mixture ashed at 500 °C were likely to react with the minerals in the mixture. Germanium sulfides are known glass formers [Kim et al., 2005; Málek and Shánělová, 1999; Sutherland et al., 2004].

Font and co-workers [2005a, 2005b] and Arroyo and co-workers [2009] studied the extraction of germanium from gasification fly ash. Font and co-workers [2005a, 2005b] determined that GeS_2 , GeS and hexagonal GeO_2 are formed during gasification, and that germanium is distributed more into the sulfide phases. They also determined that Ge–O phases are most probably germanates in the fly ash, or GeO_4 tetrahedra substitutes for SiO_4 tetrahedra in silicates, aluminosilicates and glass phases.

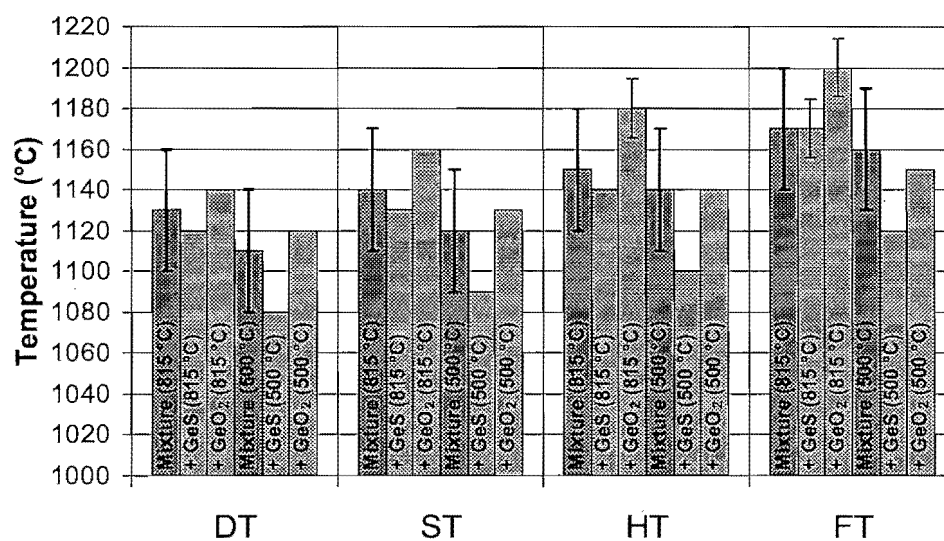


Figure 6.29 Reducing-atmosphere ash fusion temperatures of germanium species as additives. Ashing temperatures are given in parentheses

Chapter 7

Results and Discussion

Lead, Manganese and Mercury

7.1 Lead

The most common lead species in coal are PbS (galena) and PbSe, with PbS being the main species [Bunt and Waanders, 2008; Finkelman, 1994; Shah et al., 2009; Wagner and Hlatshwayo, 2005]. Pyrite is the dominant host for Pb [Finkelman, 1994; Galbreath et al., 2000]. Lead can also be associated with carbonates, silicates, aluminosilicates and other sulfides [Clarke, 1993; Laban and Atkin, 1999; Wagner and Hlatshwayo, 2005]. PbCO_3 is the most toxic form of lead when inhaled or ingested [Shah et al., 2009]. Lead in coal can also be organically associated with the macerals [Galbreath et al., 2000]. The compounds selected as additives to represent lead as trace element are PbS, basic PbCO_3 , PbSO_4 and PbMoO_4 . PbMoO_4 (wulfenite) occurs in lead veins together with other lead ores [Eissa et al., 1996].

7.1.1 Lead Carbonate

Figure 7.1 presents the compressive strength results of PbCO_3 as additive sintered in air. The addition of PbCO_3 to the mineral mixture did not significantly influence the compressive strength values based on the confidence limits. At a sintering temperature of 700 °C the addition of PbCO_3 may have lowered the compressive strength values by approximately 14%. However, due to the overlap of confidence limits the additive did not comply with both selection criteria (see Section 3.2.5). It was therefore not included in further experiments, except in the ash fusion temperature tests (results in Section 7.1.6). The influence on the compressive strengths increased from a sintering temperature of 700 °C to 800 °C, followed by a decrease to sintering temperatures of 900 °C and 1000 °C. PbCO_3 decomposes at temperatures higher than 400 °C to PbO and CO_2 [Weast, 1977].

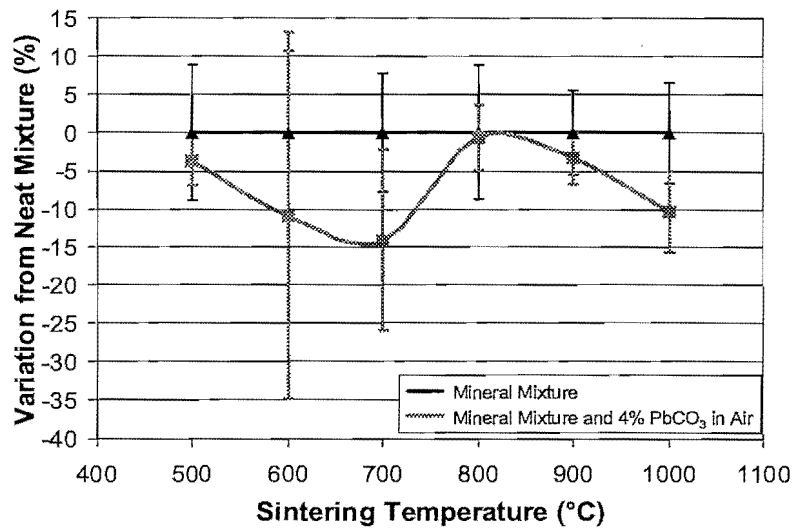


Figure 7.1 Compressive strength results of PbCO₃ as additive sintered in air

7.1.2 Lead Sulfate

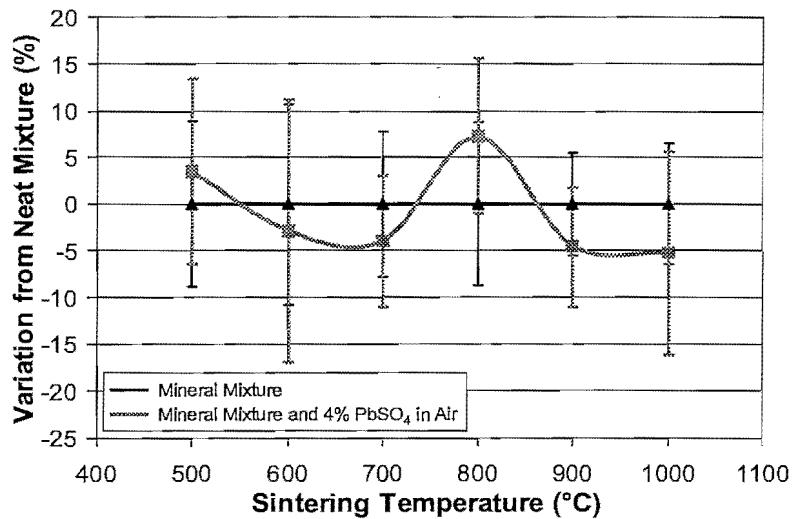


Figure 7.2 Compressive strength results of PbSO₄ as additive sintered in air

Figure 7.2 presents the compressive strength results of PbSO₄ as additive sintered in air. Based on the values and confidence limits, the addition of PbSO₄ to the mineral mixture did not significantly influence the compressive strength values. It was therefore not included in further experiments, except in the ash fusion temperature

tests (results in Section 7.1.6). However, as with the addition of PbCO_3 , the influence on the compressive strengths due to the addition of PbSO_4 increased from a sintering temperature of 700 °C to 800 °C, followed by a decrease to 900 °C.

PbSO_4 has a melting point of 1170 °C [Weast, 1977]. PbSO_4 is a product from PbS oxidation and forms at temperatures lower than 900 °C [Folgueras et al., 2007; Shah et al., 2009]. Folgueras and co-workers [2007] stated that lead from coal will be predominantly in the form of PbSO_4 at temperatures below 900 °C. The presence of sulfur compounds, such as pyrite, favours the formation of condensed PbSO_4 [Díaz-Somoano et al., 2006]. PbSO_4 has been found condensed on the surface of fly ash particles [Shah et al., 2009; Swaine, 1994].

7.1.3 Lead Sulfide

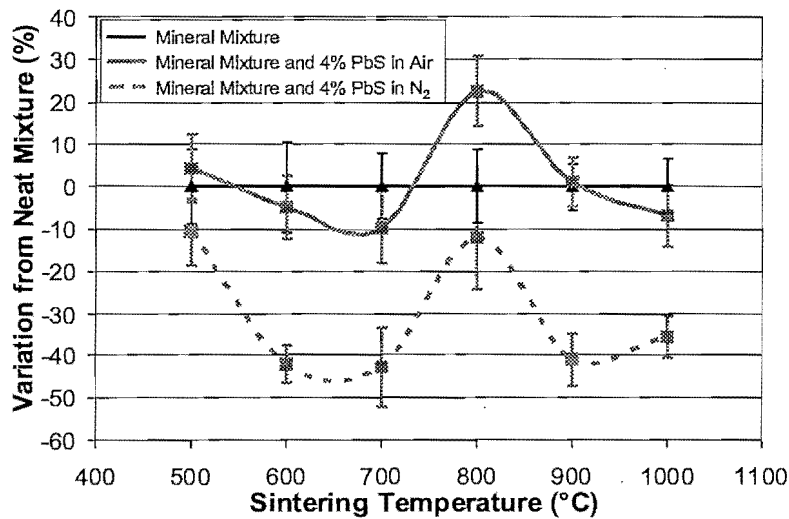


Figure 7.3 Compressive strength results of PbS as additive sintered in air and N₂

Figure 7.3 presents the compressive strength results of PbS as additive sintered in air and N₂. The addition of PbS to the mineral mixture significantly increased the compressive strength results at a sintering temperature of 800 °C in air (22%). At the other sintering temperatures the results were comparable to the neat mineral mixture. As with the addition of PbCO_3 and PbSO_4 , the influence on the compressive strengths increased from a sintering temperature of 700 °C to 800 °C, followed by a decrease to 900 °C.

The addition of PbS to the mineral mixture sintered in N₂ significantly reduced the compressive strength values at sintering temperatures of 600 °C, 700 °C, 900 °C and 1000 °C. The compressive strength values were decreased by 35–45%. At sintering temperatures of 500 °C and 800 °C the results were comparable to that of the neat mineral mixture. However, the influence on the compressive strength values also increased from a sintering temperature of 700 °C to 800 °C, followed by a decreased influence at a sintering temperature of 900 °C, thereby indicating that the trend is independent of the atmosphere and possibly also of the lead species. The fact that the trend is the same in both atmospheres is an indication that the influence is on the aluminosilicate matrix.

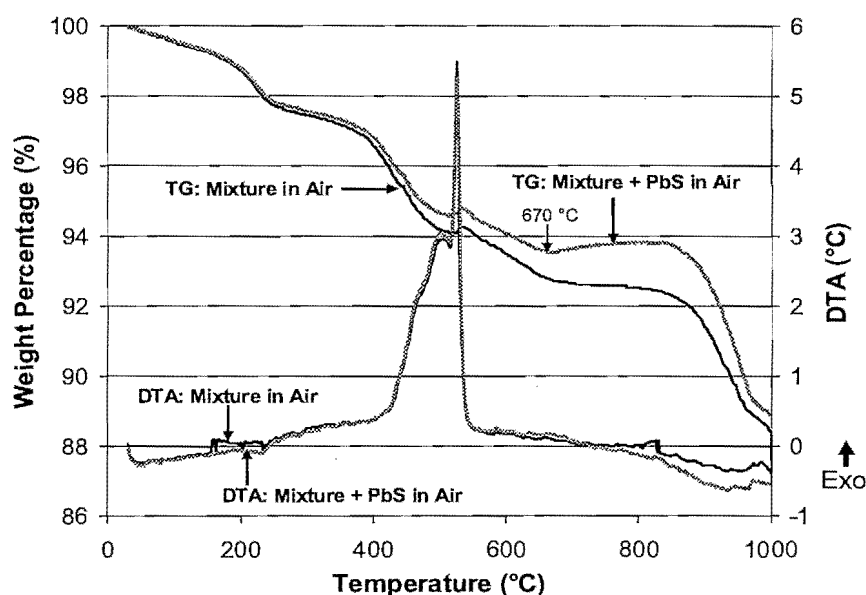


Figure 7.4 TG/DTA results of PbS as additive heated in air

The TG/DTA results of PbS as additive heated in air are presented in Figure 7.4. The weight loss patterns for the sample with additive and the neat mixture were similar to approximately 400 °C. At temperatures above 400 °C the weight loss in the neat mineral mixture was greater than the sample with additive. The sample with additive gained weight continuously from 400 °C to 850 °C, compared to the neat mineral mixture. The weight percentage of the sample with additive was 1.5% larger than the neat mineral mixture at 850 °C. Both samples showed considerable weight

loss from 850 °C to 1000 °C. At 1000 °C the weight loss in the sample with additive was slightly less than for the neat mineral mixture.

The increase in weight in the sample with additive from 400 °C to 850 °C indicates that sulfation occurred. PbSO_4 is a product from PbS oxidation and forms at temperatures lower than 900 °C [Folgueras et al., 2007; Shah et al., 2009]. Folgueras and co-workers [2007] stated that lead from coal will predominantly be in the form of PbSO_4 at temperatures below 900 °C. The presence of sulfur compounds, such as pyrite, favours the formation of condensed PbSO_4 [Díaz-Somoano et al., 2006]. PbS reportedly decomposes to Pb^0 and PbO during combustion [Galbreath et al., 2000]. However, the formation of Pb^0 from PbS generally requires the participation of the carbon in coal, or self-reduction of PbS with PbO [Lee, 1996; Wang and Tomita, 2003]. Carbon was not present in the mineral mixture, except as carbonates. The transformation of PbS to PbO and/or Pb^0 would result in a weight loss compared to the neat mineral mixture, and not a weight gain as observed in the TG/DTA results. The transformation of 4% PbS to PbSO_4 would theoretically result in a weight gain of 1.1% in the mineral mixture.

The increase in the compressive strength values at a sintering temperature of 800 °C was due to the incorporation of PbO into the aluminosilicate matrix. The weight loss pattern determined with TG/DTA indicated that PbSO_4 formed. However, the TG/DTA sample was heated at a constant rate from 30 °C to 1000 °C. In the compressive strength experiments the pellets were kept at the sintering temperature for 2.5 hours. Either the PbSO_4 decomposed to PbO and SO_3 during the reaction time, or other interactions with the mineral mixture constituents allowed the incorporation of PbO into the aluminosilicate matrix. The addition of PbSO_4 to the mineral mixture (Figure 7.2) had a similar influence on the compressive strength of the mineral mixture, except at a sintering temperature of 800 °C. It is unclear why the addition of PbSO_4 to the mineral mixture did not yield similar results at a sintering temperature of 800 °C. At a sintering temperature of 800 °C the addition of PbSO_4 increased the compressive strength of the mineral mixture by only 7%. The addition of PbS sintered at 800 °C increased the compressive strength of the mineral mixture by 22%. The difference could partially be due to differences in the molar concentrations. The addition of 4% PbS to the mineral mixture is equal to 1.7×10^{-4} moles of PbSO_4 and will produce 1.7×10^{-4} moles of PbO in each pellet. However, the addition of 4% PbSO_4 is equal to 1.3×10^{-4} moles of PbSO_4 , and will produce 1.3×10^{-4} moles of

PbO upon decomposition. However, the addition of PbS resulted in a three times higher influence on the compressive strength value than the addition of PbSO₄, which is not proportional to the 0.25% increase in the concentration of PbS.

Folgueras and co-workers [2007] and Álvarez-Rodríguez and co-workers [2007] stated that PbO can react with silicates to form species such as PbSiO₃ (fusion point 764 °C), and Pb₂SiO₄ (fusion point of 743 °C). Since the fusion points of these compounds are below 800 °C, it is possible that they formed in the pellets sintered at 800 °C. Other species may include PbO·Al₂O₃ and PbO·Al₂O₃·2SiO₂ [Folgueras et al., 2007; Lachas et al., 2003]. PbO is a network former or modifier [La Delfa et al., 2008; Milanova et al., 2009]. The addition of PbO to the aluminosilicate/anhydrite matrix in the pellets probably caused extensive sintering, and so increased the compressive strength in the pellets. The addition of PbO to the matrix could also have affected the friability of the aluminosilicate phases and rendered the pellets less fragile. Reed and co-workers [2001] stated that Pb-silicates, formed from the reaction of lead with silica, in general tend to agglomerate.

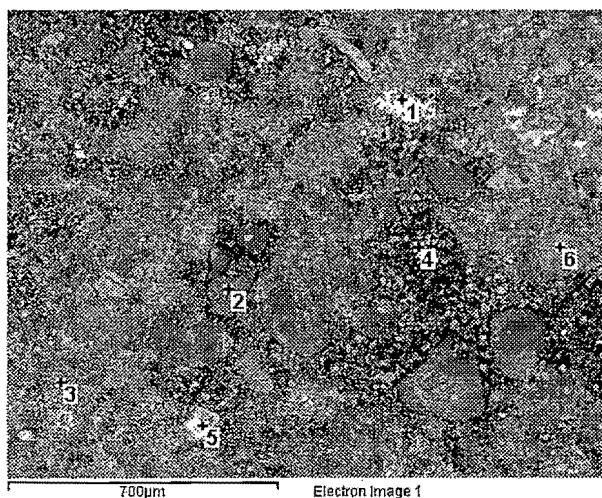


Figure 7.5 Backscattered electron image of mineral mixture pellets with PbS as additive sintered at 800 °C in air

Figure 7.5 presents a backscattered electron image of a mineral mixture pellet with PbS as additive sintered at 800 °C in air. Lead was enriched in all areas, especially area 1. In areas 1, 3, 4, and particle 5, relatively high concentrations of iron was also detected. Lead may thus be incorporated into iron-aluminosilicates. Area 1

contained 14.7% Fe and 26.3% Pb (elemental wt%), including elements representative of the aluminosilicate/anhydrite matrix. The Pb to Fe weight ratio of 1.8 calculated for area 1 is comparable with the Pb to Fe weight ratio of a solid solution of $\text{PbO-Fe}_2\text{O}_3$ (ratio of 1.9). Particle 5 contained 31.4% Fe and 9.8% Pb. EDS analysis indicated Pb concentrations of 5% to 6% in areas 3 and 4. Based on the respective Si and Ti concentrations, particle 2 was most probably a SiO_2 particle with an aluminosilicate layer, and particle 6 was a TiO_2 particle.

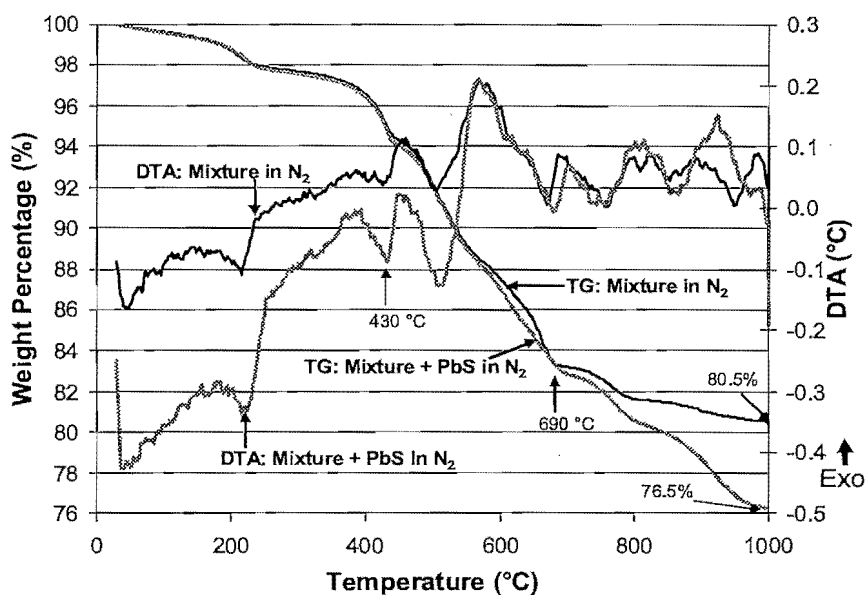


Figure 7.6 TG/DTA results of PbS as additive heated in N_2

The TG/DTA results of PbS as additive heated in N_2 are presented in Figure 7.6. The weight loss patterns of the sample with additive and the neat mineral mixture were comparable to 700 °C. At temperatures higher than 700 °C the weight loss of the sample with additive was considerably more than the neat mineral mixture. At 1000 °C the weight loss in the sample with additive was 4% more than the neat mineral mixture, indicating that all of the trace compound volatilized as PbS.

Figure 7.7 is a photograph of the heat shield removed from the tube furnace after pellets were sintered at 1000 °C in N_2 . Figure 7.8 represents a backscattered electron image of the dark grey deposit on the heat shield. EDS analysis of the deposit indicated that the crystals consisted mainly of Pb and S, with a Pb to S weight ratio of

6.2. The ratio is comparable to the Pb to S weight ratio in PbS (6.5). Galena has a cubic structure, as clearly visible in Figure 7.8 [Klein, 2002].

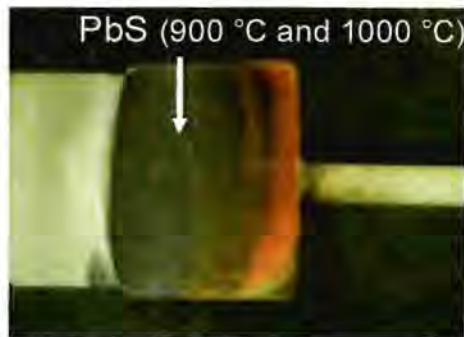


Figure 7.7 Heat shield removed from the tube furnace after a sintering experiment at 1000 °C in N₂. Pellets with PbS as additive were included in the experiment

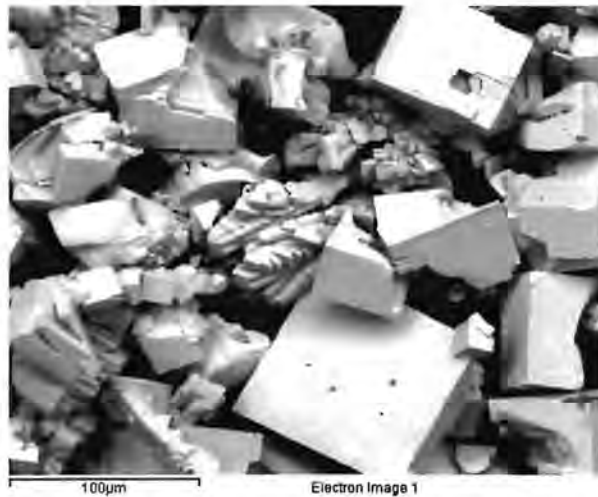


Figure 7.8 Backscattered electron image of the dark grey deposit (Figure 7.7) collected after sintering pellets in N₂ at 1000 °C, including pellets with PbS as additive

The addition of PbS to the mineral mixture sintered in N₂ reduced the compressive strength of the mineral mixture at sintering temperatures of 600 °C, 700 °C, 900 °C and 1000 °C (see Figure 7.3). The reduction of the compressive strength values was most likely due to an increase in porosity from the volatilization of PbS. However, the addition of PbS to the mineral mixture sintered at 800 °C in N₂ did not significantly affect the compressive strength value of the mineral mixture. This

is most likely due to the existence of opposing effects. The addition of PbS probably reduced the compressive strength due to an increase in porosity, as seen at sintering temperatures of 700 °C and 900 °C, and simultaneously also increased the sintering and strength formation. The insignificant influence on the sintering temperature appears to be the net result of the two opposing effects. In both atmospheres the influence from the addition of PbS increased by approximately 30% from a sintering temperature of 700 °C to 800 °C (see Figure 7.3).

Similar to the compressive strength values obtained for the addition of PbSO_4 , PbCO_3 and PbS to the mineral mixture sintered in air at 800 °C, the influence from the addition of PbS sintered at 800 °C in N_2 increased compared to the influence observed at 700 °C and 900 °C. The compressive strength graphs therefore have a “peak” at a sintering temperature of 800 °C. The fact that it is observed in both atmospheres is an indication that the lead species influence the aluminosilicate phases. The influence appears to be independent of the anion or the atmosphere.

7.1.4 Lead Molybdate

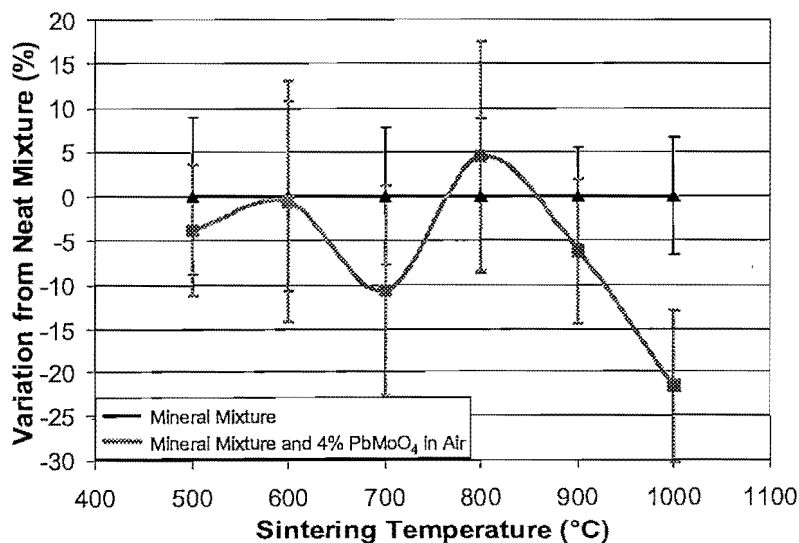


Figure 7.9 Compressive strength results of PbMoO_4 as additive sintered in air

The compressive strength results of PbMoO_4 as additive sintered in air are presented in Figure 7.9. The addition of PbMoO_4 to the mineral mixture lowered the compressive strength value at a sintering temperature of 1000 °C by approximately

22%. The compressive strength results at the other sintering temperatures were comparable to the neat mineral mixture. Similarly to the addition of the other lead species, the addition of PbMoO_4 also increased the compressive strength values from a sintering temperature of 700 °C to 800 °C, followed by a decrease to 900 °C.

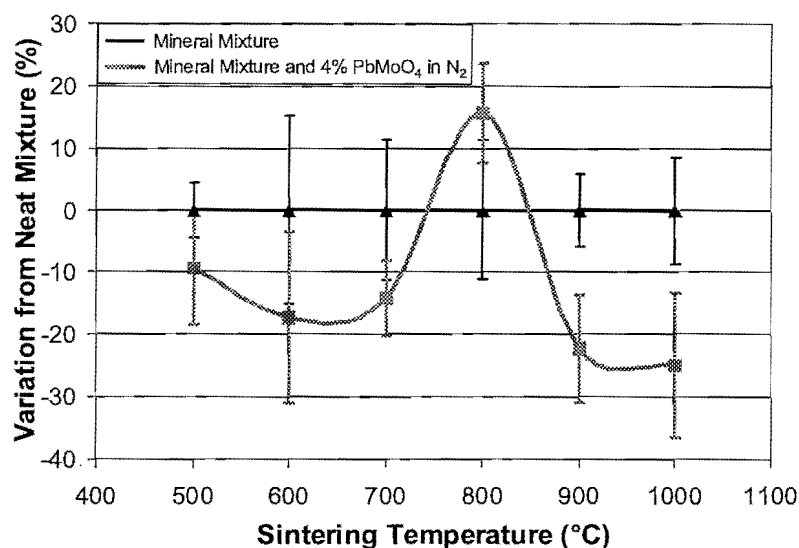


Figure 7.10 Compressive strength results of PbMoO_4 as additive sintered in N_2

The compressive strength results of PbMoO_4 as additive sintered in N_2 are presented in Figure 7.10. The addition of PbMoO_4 decreased the compressive strength of the mineral mixture by approximately 22% and 25% at sintering temperatures of 900 °C and 1000 °C, respectively. The addition of PbMoO_4 to the mineral mixture sintered in N_2 also increased the compressive strength from sintering temperatures of 700 °C to 800 °C, followed by a decrease to 900 °C. The addition of PbMoO_4 therefore also caused a “peak” at a sintering temperature of 800 °C in both atmospheres.

The TG/DTA results of PbMoO_4 as additive heated in air are presented by Figure 7.11. The weight loss patterns of the sample with additive and the neat mineral mixture were similar over the total temperature range. It appears that PbMoO_4 was stable over the temperature range with no observed decomposition. PbMoO_4 has a melting temperature in the range of 1060 – 1070 °C. Eissa and co-workers [1996] referenced a report stating that PbMoO_4 melts without decomposition in air.

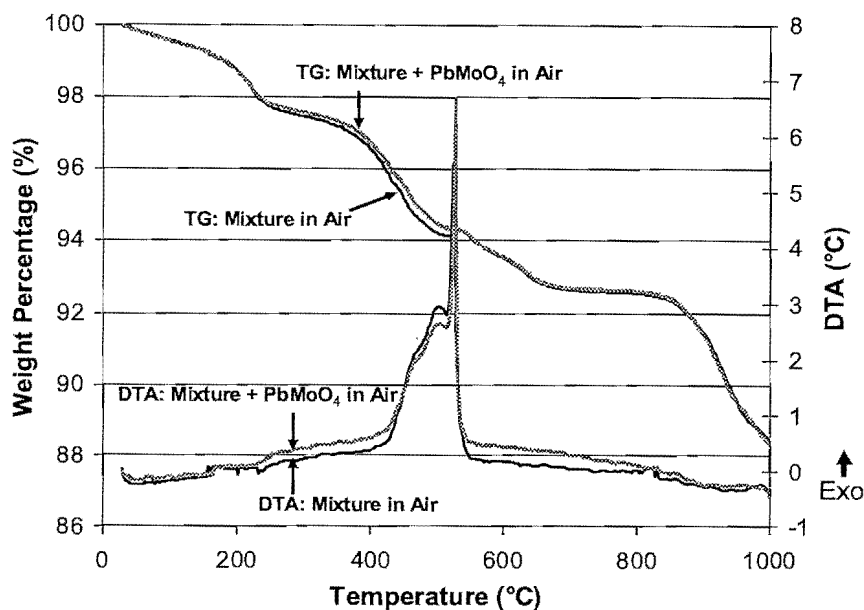


Figure 7.11 TG/DTA results of PbMoO_4 as additive heated in air

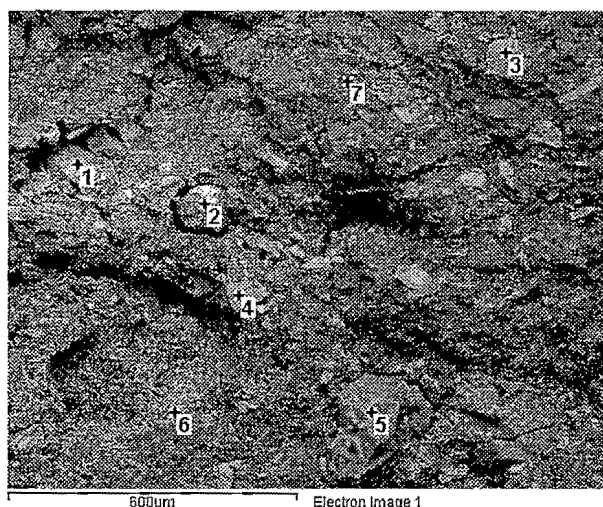


Figure 7.12 Backscattered electron image of a mineral mixture pellet with PbMoO_4 as additive sintered in air at 1000 °C

Figure 7.12 is a backscattered electron image of a mineral mixture pellets with PbMoO_4 as additive sintered in air at 1000 °C. Particles 1 to 4 were iron oxides and no Pb was detected associated with those particles. Lead was enriched in areas 5, 6, and 7. However, no molybdenum was detected in any of the areas of analysis or the bulk analysis. $K\alpha$ is equal to 2.3 for S, and $L\alpha$ is 2.29 for Mo. Both elements absorb

electrons of the same energy, resulting in an overlap in the EDS analysis. At low amounts of Mo, the instrument is unable to discriminate between Mo and S, and any signal from Mo might be included in the S [Tiedt, 2009]. The Mo content in the sample may therefore have been included in the S content. However, the reported S concentrations in the analysed areas were low (<4%). It is therefore unclear from the SEM/EDS analysis whether the Mo was still present in the pellets, but TG/DTA results suggest that it was. The weight percentage of Mo in PbMoO_4 is 26%.

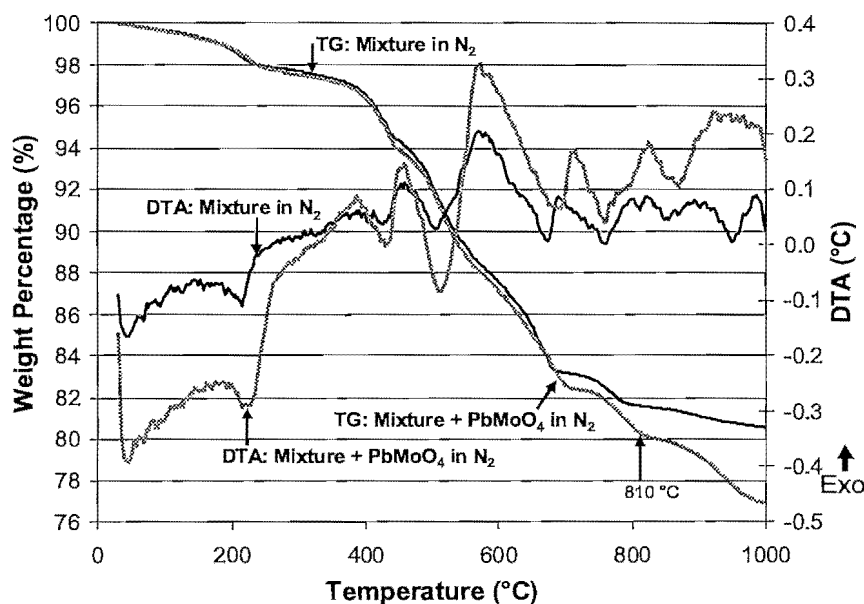


Figure 7.13 TG/DTA results of PbMoO_4 as additive heated in N_2

Figure 7.13 presents the TG/DTA results of PbMoO_4 as additive heated in N_2 . It appears as if the atmosphere had an influence on the thermal stability of the PbMoO_4 additive. The weight loss patterns of the sample with additive and the neat mineral mixture were similar from 30 °C to 700 °C. From 700 °C to 1000 °C the weight loss in the mixture with additive was larger than the weight loss in the neat mineral mixture. At 1000 °C the weight loss in the sample with additive was approximately 4% more than the neat mineral mixture.

The additive decomposed in the inert atmosphere to PbO and MoO_3 . The PbO was probably transformed to PbS . As determined for the addition of PbS in N_2 , PbS volatilized at temperatures higher than 700 °C, similar to the weight loss results

observed in Figure 7.13. MoO_3 has a melting point of 795°C [Lee, 1996]. Eissa and co-workers [1996] stated that the volatility of MoO_3 created difficulties in obtaining heat curves at temperatures higher than 800°C , suggesting that significant volatilization of MoO_3 occurred at temperatures higher than 800°C . According to Tietz and Wilson [1965], MoO_3 begins to sublime above 500°C , with significant volatilization above 600°C . Anand Rao and co-workers [2001] stated that volatilisation of MoO_3 starts at 620°C at atmospheric pressure. Therefore, the 4% weight loss observed in Figure 7.13 was due to the decomposition of PbMoO_4 , followed by transformation of PbO to PbS , and volatilization of PbS and MoO_3 at temperatures higher than 700°C .

Very limited information is available in literature on the reactions and transformations of PbMoO_4 , except for studies regarding single crystal growth of PbMoO_4 , and its electronic, laser and optical applications [Desai, 2006; Eissa et al., 1996; Spassky et al., 2004]. By comparing the results obtained for PbS , PbMoO_4 and MoS_2 (see Section 8.1.1) it was determined that the decreased compressive strength value for the addition of PbMoO_4 at a sintering temperature of 1000°C was due to the influence from the molybdate anion. A detailed discussion is included in Section 8.1.2.

7.1.5 *Compressive Strength Trends*

The same trend was observed in the compressive strength results at sintering temperatures of 700°C to 900°C , with an increase in the influence observed at a sintering temperature of 800°C . PbO has been indicated as a network former or modifier, with a possible increase in the compressive strength values from its incorporation into aluminosilicates [La Delfa et al., 2008; Milanova et al., 2009]. However, the effect appears to be due to the addition of Pb^{2+} . The results obtained in this study suggest that the effect is independent of the anion or the atmosphere, but the anion may influence the extent of the interactions. The results indicate that the addition of PbCO_3 , PbSO_4 and PbMoO_4 increased the influence on the compressive strength values from a sintering temperature of 700°C to 800°C by 15% in air. The addition of PbS sintered in air, as well as the addition of PbS and PbMoO_4 in N_2 , increased the influence by 30%. The influence obtained for the addition of lead compounds seems to be greater in N_2 than in air, with the exception of PbS sintered in air.

7.1.6 Reducing-Atmosphere Ash Fusion Temperature Test

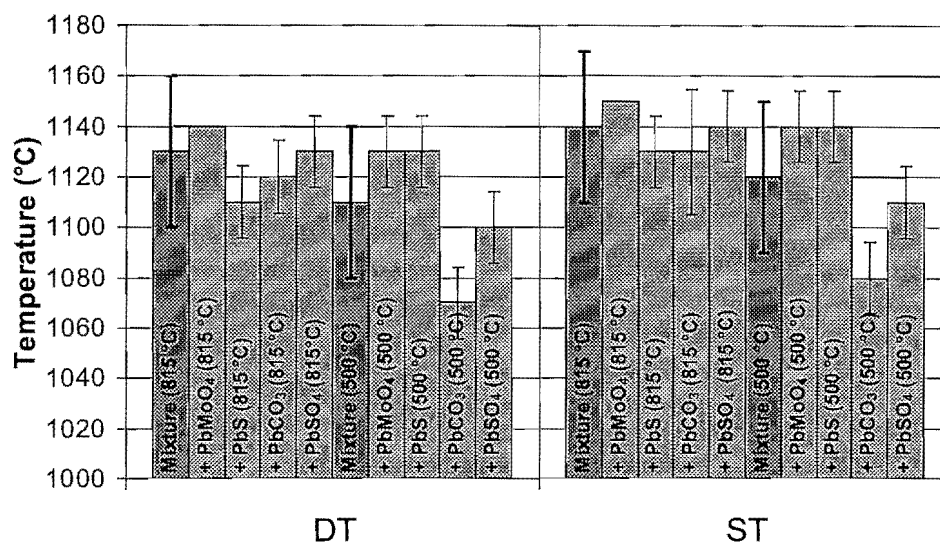


Figure 7.14 Reducing-atmosphere deformation and softening temperatures of lead species as additives. Ashing temperatures are given in parentheses

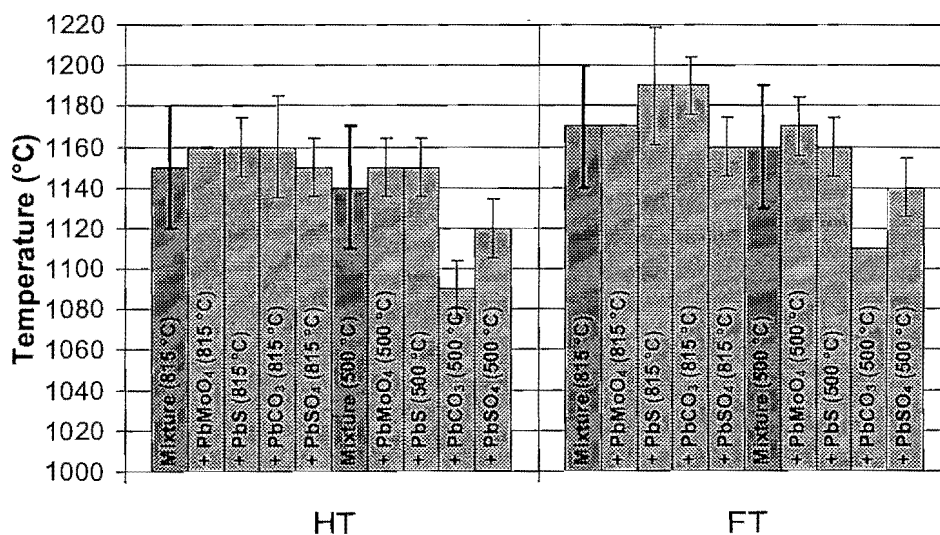


Figure 7.15 Reducing-atmosphere hemispherical and flow temperatures of lead species as additives. Ashing temperatures are given in parentheses

Figures 7.14 and 7.15 present the ash fusion temperatures of lead species as additives. The deformation and softening temperatures are presented in Figure 7.14 and the hemispherical and flow temperatures in Figure 7.15. All the species, except PbCO_3 , had no significant influence on the ash fusion temperatures. Its addition lowered the ash fusion temperatures of the mixture ashed at 500 °C by 40–50 °C. This is comparable to the influence of NaCl addition ashed at 815 °C, and greater than the influence of NaCl addition ashed at 500 °C (see Figure 5.20). The addition of PbCO_3 had no significant influence at an ashing temperature of 815 °C.

In the reducing conditions of the ash fusion temperature tests, the lead species were most likely reduced to gaseous compounds, such as PbS or Pb^0 [Bunt and Waanders, 2008]. Bunt and Waanders [2008] determined that the reduction of PbS produced trace amounts of PbO . The reduction of PbSO_4 , PbS and PbMoO_4 therefore probably primarily produced Pb^0 and/or PbS at both ashing temperatures. However, PbCO_3 decomposes at temperatures higher than 400 °C to PbO and CO_2 [Weast, 1977]. Ashing at 500 °C most likely favoured the incorporation of PbO into aluminosilicates, which crystallizes upon cooling. However, ashing to 815 °C probably resulted in further reduction of PbO to Pb^0 without retention of PbO in aluminosilicates. The ash fusion temperature results suggest that the incorporation of lead species into aluminosilicates reduced the ash fusion temperatures of the mineral mixture, comparable to the reduction observed for NaCl addition.

7.2 Manganese

Manganese in coal is predominantly associated with carbonates, by substituting Fe in siderite and ankerite, and Ca in calcite [Finkelman, 1994; Folgueras et al., 2007; Laban and Atkin, 1999]. Organic associations of manganese are mostly limited to low-rank coals [Swaine, 1986; Wagner and Hlatshwayo, 2005]. Some manganese may also be found in sphalerite [Swaine, 1986]. The compounds selected to represent manganese are MnCO_3 , MnO , Mn_2O_3 and MnO_2 .

7.2.1 Manganese (II) Oxide

Figure 7.16 presents the compressive strength results of MnO as additive sintered in air. Based on the results and the confidence limits, the addition of MnO to the mineral mixture did not significantly influence the compressive strength values. It

was therefore not included in further experiments, except for in ash fusion temperature tests (results in Section 7.2.5). MnO can be incorporated into spinels and silicates at temperatures higher than 700 °C, e.g. Fe_2MnO_4 , Al_2MnO_4 , and MnSiO_3 [Folgueras et al., 2007]. However, the possible incorporation of MnO into spinels and silicates did not significantly affect the compressive strength values at any of the sintering temperatures. MnO was most likely transformed to Mn_3O_4 at a sintering temperature of 1000 °C [Lee, 1996].

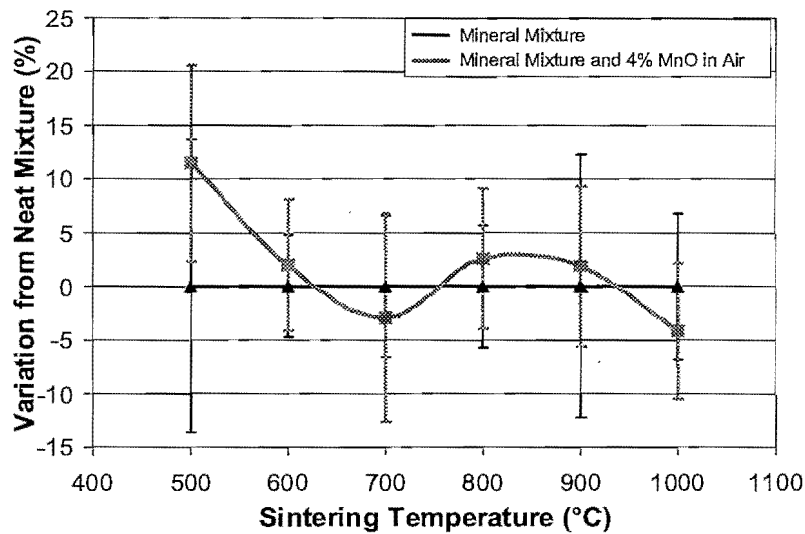


Figure 7.16 Compressive strength results of MnO as additive sintered in air

7.2.2 Manganese (IV) Oxide

Figure 7.17 presents the compressive strength results of MnO_2 as additive sintered in air. Based on the results and the confidence limits, the addition of MnO_2 to the mineral mixture did not significantly influence the compressive strength values. It was therefore not included in further experiments, except in the ash fusion temperature tests (results in Section 7.2.5). MnO_2 decomposes to Mn_3O_4 at 530 °C [Lee, 1996].

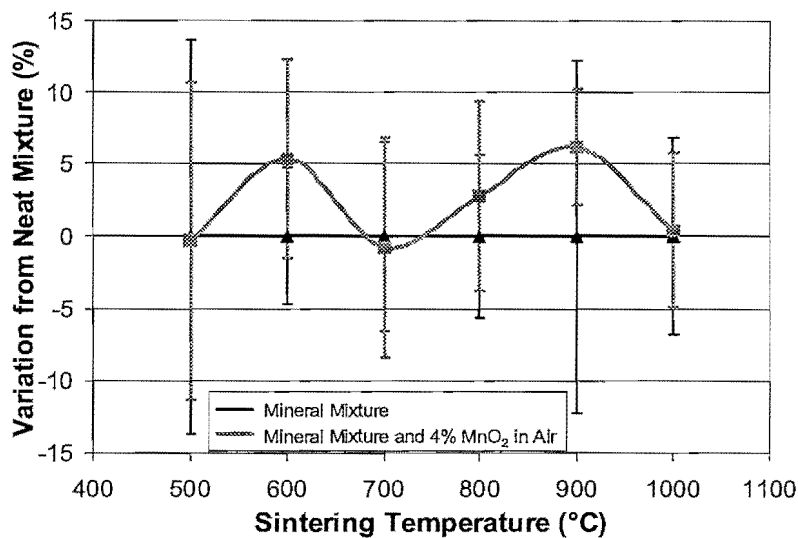


Figure 7.17 Compressive strength results of MnO₂ as additive sintered in air

7.2.3 Manganese (III) Oxide

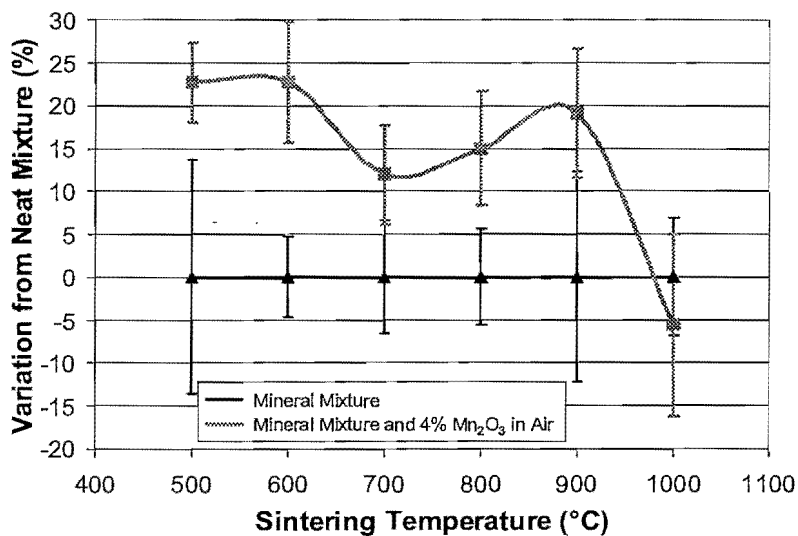


Figure 7.18 Compressive strength results of Mn₂O₃ as additive sintered in air

The compressive strength results of Mn₂O₃ as additive sintered in air are presented in Figure 7.18. The addition of Mn₂O₃ significantly increased the compressive strength results of the mineral mixture at sintering temperatures of

500 °C, 600 °C, 800 °C and 900 °C. At sintering temperatures of 700 °C and 1000 °C the results were comparable to the neat mineral mixture.

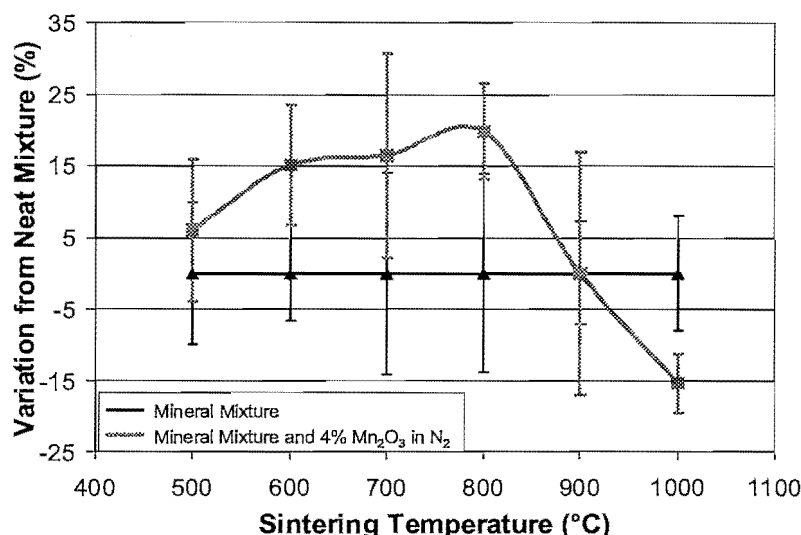


Figure 7.19 Compressive strength results of Mn₂O₃ as additive sintered in N₂

Figure 7.19 presents the compressive strength results of Mn₂O₃ as additive sintered in N₂. The addition of Mn₂O₃ to the mineral mixture significantly decreased the compressive strength by approximately 15% at a sintering temperature of 1000 °C. The addition of Mn₂O₃ increased the compressive strengths of the mineral mixture at sintering temperatures of 600 °C to 800 °C by 15–20%. The confidence limits overlap at 700 °C and slightly at 800 °C. Due to the precision of the method it is not possible to confirm whether the increases are significant.

The TG/DTA results of Mn₂O₃ as additive heated in air are presented in Figure 7.20. Based on the reproducibility of the method, the weight loss patterns of the sample with additive and the neat mineral mixture was similar over the total temperature range. XRD analysis detected Mn₂O₃ in the samples sintered at 500 °C, 600 °C, 800 °C and 900 °C. Mn₂O₃ was transformed to Mn₃O₄ at a sintering temperature of 1000 °C [Lee, 1996].

Figure 7.21 represents the TG/DTA results of Mn₂O₃ as additive heated in N₂. The weight loss patterns of the sample with additive and the neat mineral mixture was similar up to 680 °C. The weight loss difference between the two samples was 1%

at 700 °C, and at 1000 °C the weight loss in the sample with additive was approximately 1.5% more than in the neat mineral mixture.

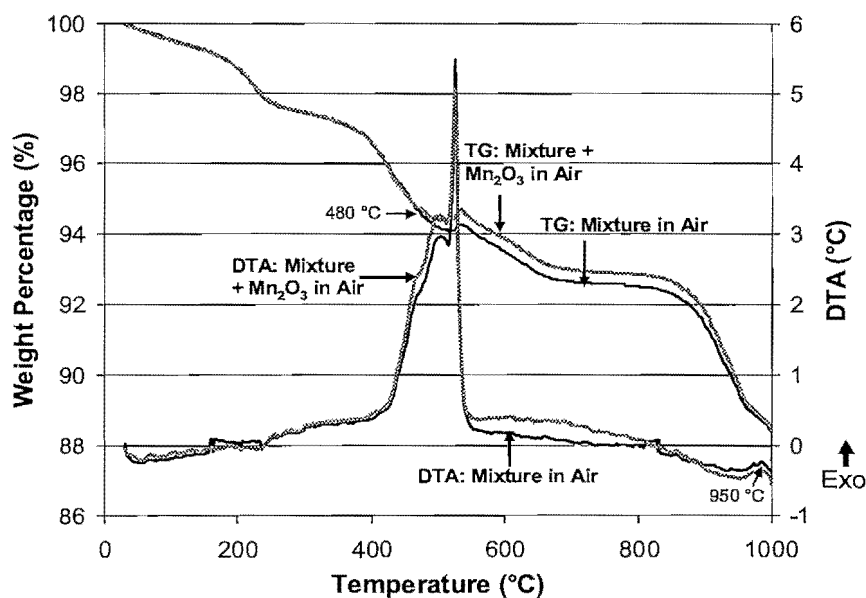


Figure 7.20 TG/DTA results of Mn_2O_3 as additive heated in air

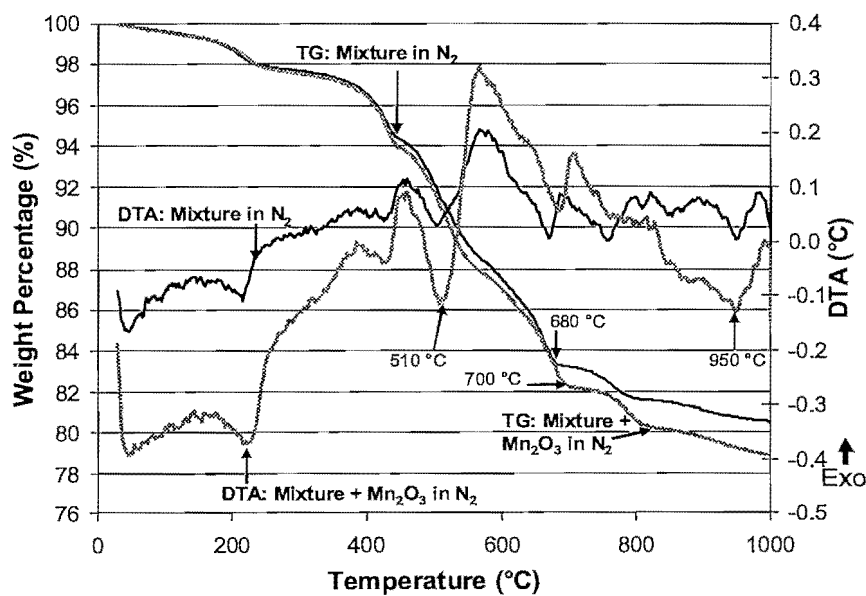


Figure 7.21 TG/DTA results of Mn_2O_3 as additive heated in N_2

The weight loss of the sample with additive at 1000 °C suggests that the Mn_2O_3 decomposed to elemental Mn in the inert atmosphere. However, reaction with sulfur yields MnS , but the weight loss pattern does not support the formation of manganese sulfide [Lee, 1996; Yan et al., 2001a]. Theoretically, the transformation of 4% Mn_2O_3 to Mn constitutes a weight loss of 1.2% in the mineral mixture. The volatilization of manganese compounds is unlikely, as manganese is regarded as a highly non-volatile element in coal at temperatures less than 1100 °C [Clarke, 1993; Wagner and Hlatshwayo, 2005; Yan et al., 2001a]. However, some volatilization of elemental manganese has been reported, and could be included in the weight loss observed in the TG/DTA results [Bunt and Waanders, 2009b; Helble, 1994]. Manganese melts at 1244°C [Lee, 1996].

Figure 7.22 presents a backscattered electron image of a mineral mixture pellet with Mn_2O_3 sintered in air at 600 °C. EDS analysis indicated that manganese was associated to the aluminosilicate /anhydrite matrix (area 6), and also with particles high in titanium (particle 5). In particle 5, a small amount of MnTiO_3 may have formed on the surface of a TiO_2 particle.

Manganese oxide could have acted as a nucleation catalyst, and enhanced the development of the aluminosilicate/anhydrite matrix and also the strength of the pellets. The same compressive strength trend is not observed in both atmospheres. The results suggest that the addition of Mn_2O_3 contributed to enhanced sulfation of limestone at sintering temperatures of 500 °C to 900 °C. The increased compressive strength values for the addition of Mn_2O_3 in N_2 indicates that Mn_2O_3 probably also influenced the strength or the development of the aluminosilicate phases, and not just the sulfation of limestone. The enhanced effect is not visible at a sintering temperature of 1000 °C, but Mn_2O_3 is expected to have transformed to Mn_3O_4 at that temperature. It appears that Mn_2O_3 enhanced the sintering in the pellets, but not Mn_3O_4 . EDS analysis suggested that manganese ferrite (manganese iron oxides) did not form, as no manganese was detected in association with high amounts of iron. Manganese iron oxide spinels ($(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$) form in air at temperatures higher than 950 °C from the reaction of Mn_3O_4 with Fe_3O_4 [Guillemet-Fritsch et al., 2005]. The decreasing influence on the compressive strength in the pellets with additive sintered at 1000 °C in N_2 was probably due to the increased porosity from the decomposition of the additive, and subsequent volatilization of the decomposition products.

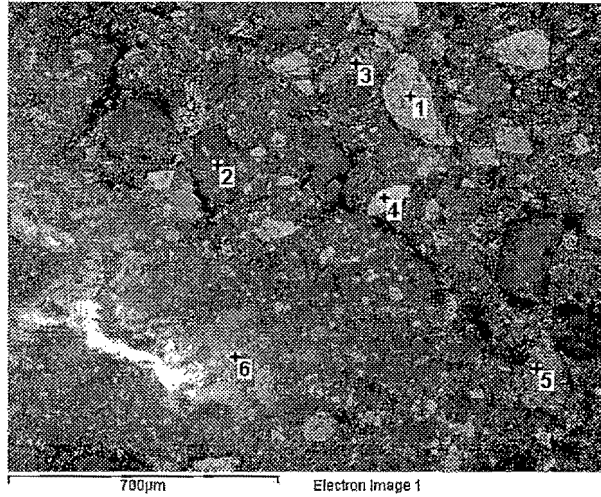


Figure 7.22 Backscattered electron image of a mineral mixture pellet with Mn_2O_3 as additive sintered at 600 °C in air

7.2.4 Manganese Carbonate

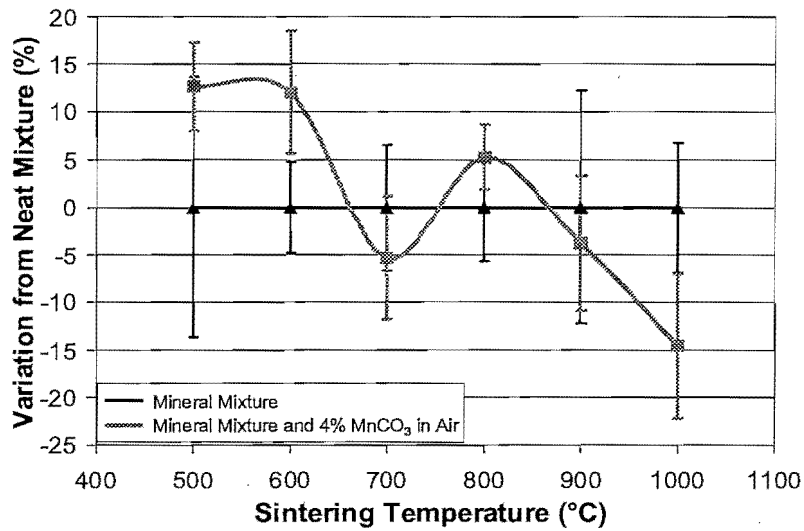


Figure 7.23 Compressive strength results of MnCO_3 as additive sintered in air

Figure 7.23 presents the compressive strength results of MnCO_3 as additive sintered in air. The addition of MnCO_3 decreased the compressive strength results of the mineral mixture at a sintering temperature of 1000 °C. At the other sintering

temperature the results were comparable to the neat mineral mixture, based on the applied selection criteria.

Figure 7.24 presents the compressive strength results of MnCO_3 as additive sintered in N_2 . The addition of MnCO_3 to the mineral mixture decreased the compressive strength at a sintering temperature of 600 °C by approximately 17%, and 29% at 1000 °C. The addition of MnCO_3 increased the compressive strengths of the mineral mixture at a sintering temperature of 800 °C by 17%, but the confidence limits overlap, and therefore it is not possible to confirm whether the increase is significant.

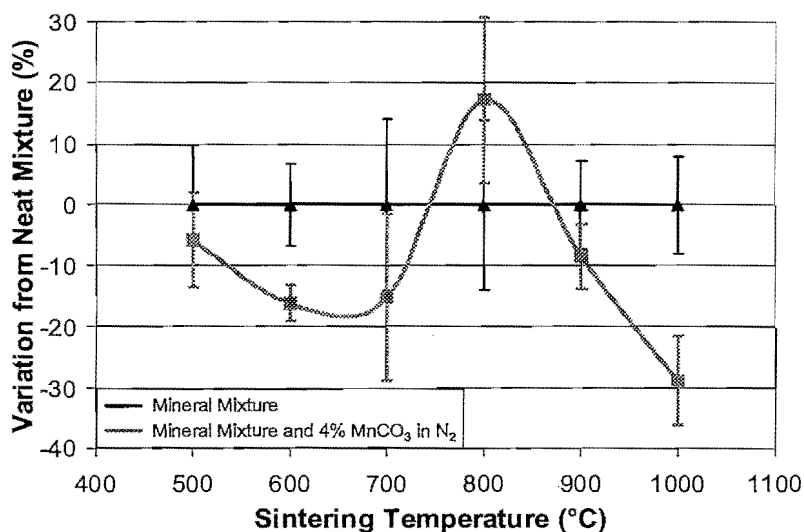


Figure 7.24 Compressive strength results of MnCO_3 as additive sintered in N_2

The TG/DTA results of MnCO_3 as additive heated in air are presented in Figure 7.25. The weight loss patterns of the sample with additive and the neat mineral mixture were similar from 30 °C to approximately 900 °C. At 1000 °C the weight loss in the sample with additive was 1.5% more than the neat mineral mixture. MnCO_3 reportedly decomposes to MnO_2 from 300 °C. At temperatures higher than 440 °C the MnO_2 is transformed to Mn_2O_3 , followed by a transformation to Mn_3O_4 at temperatures higher than 900 °C [Shaheen and Selim, 1998]. However, the same series of transformations was not observed in the weight loss pattern of the sample with additive. It appears that the additive only decomposed at temperatures higher than 900 °C. The constituents in the mineral mixture may have delayed the

decomposition of MnCO_3 , or a combination of sulfation and decomposition could have masked the MnCO_3 transformations so that they are not discernable on the TG curve. The difference in weight loss observed at 1000 °C is consistent with the weight loss associated with the transformation of MnCO_3 to Mn_3O_4 . XRD analysis confirmed the present of Mn_3O_4 in the pellets sintered at 1000 °C. Small amounts of Mn_2O_3 may also have been present.

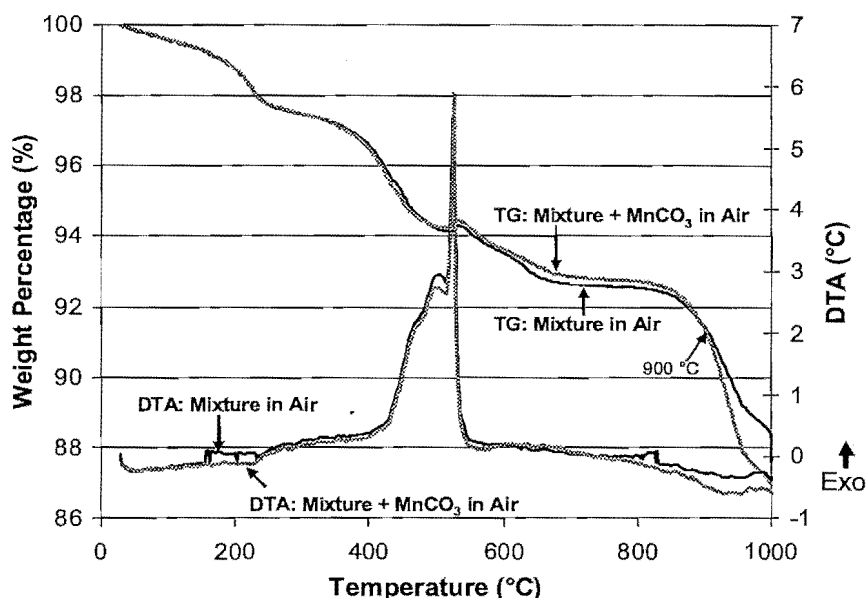


Figure 7.25 TG/DTA results of MnCO_3 as additive heated in air

EDS analysis of a pellet with MnCO_3 sintered at 600 °C indicated that the manganese was associated with the aluminosilicate/anhydrite matrix. No manganese was detected in association with high amounts of Ti or Fe.

The TG/DTA results of MnCO_3 as additive heated in N_2 are presented in Figure 7.26. The weight loss patterns of the sample with additive and the neat mineral mixture were comparable from 30 °C to 220 °C. At temperatures above 220 °C the weight loss in the sample with additive was more than the neat mineral mixture. The weight loss in the sample with additive was 2% more than the neat mineral mixture from approximately 400 °C to 780 °C. At 1000 °C the weight loss in the sample with additive was 2.5% more than the neat mineral mixture.

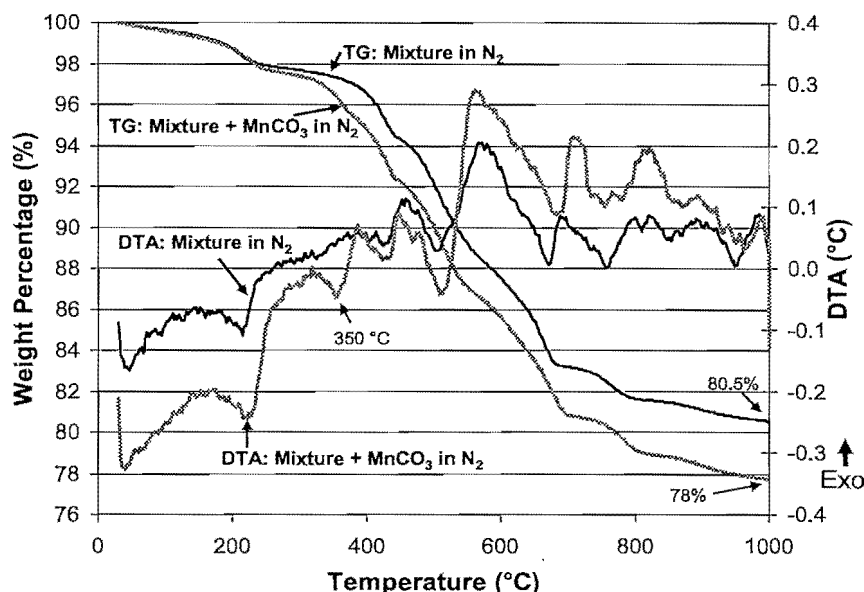


Figure 7.26 TG/DTA results of MnCO_3 as additive heated in N_2

Theoretically, the transformation of 4% MnCO_3 to Mn constitutes a weight loss of 2.1% in the mineral mixture. The volatilization of manganese compounds is unlikely, as manganese is regarded as a highly non-volatile element in coal at temperatures less than 1100 °C [Clarke, 1993; Wagner and Hlatshwayo, 2005; Yan et al., 2001a]. However, the weight loss results suggest that some volatilization of elemental manganese may have occurred [Bunt and Waanders, 2009b].

The decrease in the compressive strength observed for the pellets with MnCO_3 sintered in air at 1000 °C was most likely due to an increase in porosity from the decomposition of MnCO_3 . The increased trend at lower sintering temperatures (500 °C and 600 °C) in air may be attributed to the association of manganese species with the aluminosilicate/anhydrite matrix. However, the effect was not as large as was observed for the addition of Mn_2O_3 .

The decreased compressive strength values for the addition of MnCO_3 in N_2 was also probably due to an increased porosity from the decomposition of MnCO_3 to Mn. However, the influence from the additive increased by approximately 30% from a sintering temperature of 700 °C to 800 °C, followed by a decrease of approximately 25% to a sintering temperature of 900 °C. The reason for this “peak” at a sintering temperature of 800 °C is unclear.

7.2.5 Reducing-Atmosphere Ash Fusion Temperature Test

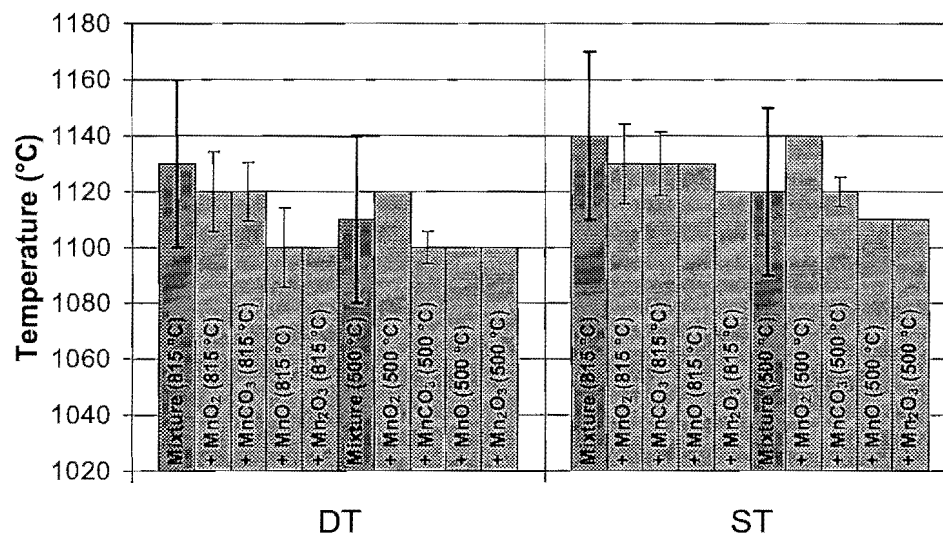


Figure 7.27 Reducing-atmosphere deformation and softening temperatures of manganese species as additives. Ashing temperatures are given in parentheses

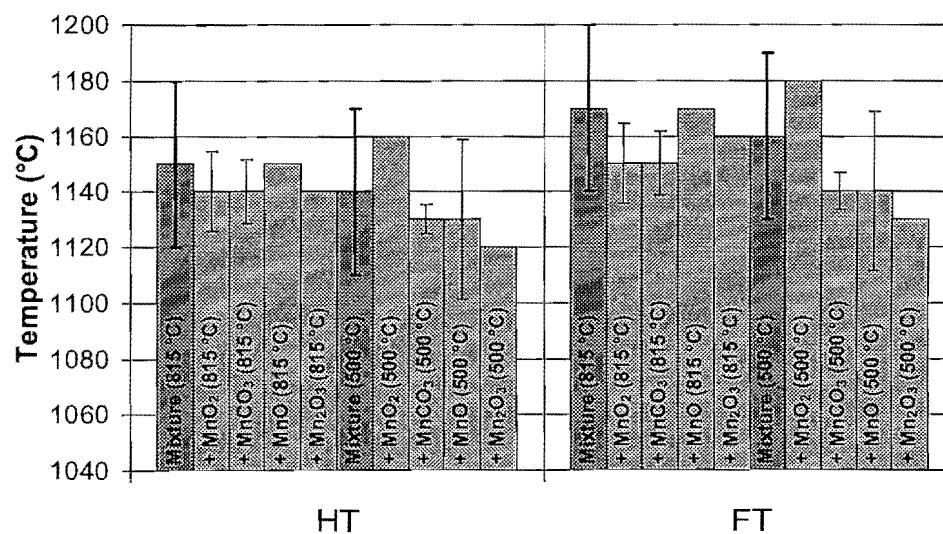


Figure 7.28 Reducing-atmosphere hemispherical and flow temperatures of manganese species as additives. Ashing temperatures are given in parentheses

Figures 7.27 and 7.28 present the ash fusion temperatures of manganese species as additives. The deformation and softening temperatures are presented in Figure 7.27, and the hemispherical and flow temperatures in Figure 7.28. None of the species had a significant influence on the ash fusion temperatures at either of the ashing temperatures. Bunt and Waanders [2009b] reported that solid manganese-containing aluminosilicates are predicted to form in gasification ash, with $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ melting at 925 °C to form a slag [Bunt and Waanders, 2009b]. Manganese species are easily incorporated into slag phases [Klein et al., 1975; Thompson and Argent, 2002]. However, it does not appear as if the incorporation of manganese into solid and slag phases affected the ash fusion temperatures of the mixture.

7.3 Mercury

Mercury in coal is mostly associated with pyrite and sulfides, such as HgS (cinnabar) [Bool and Helble, 1995; Gürdal, 2007; Hower et al., 2008]. Other associations include calcite, chlorite and sphalerite [Finkelman, 1994; Hower et al., 2008]. Mercury can also be included in macerals [Bool and Helble, 1995; Galbreath et al., 2000; Hower et al., 2008]. HgS was chosen to represent mercury as trace element.

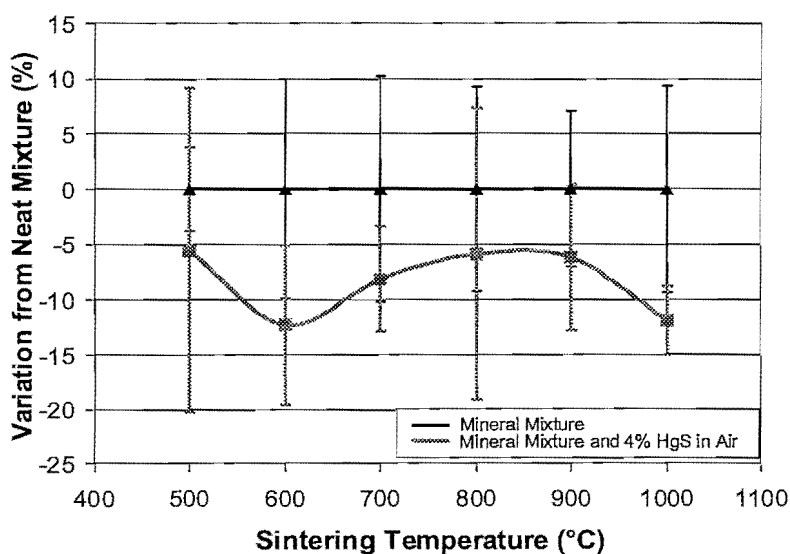


Figure 7.29 Compressive strength results of HgS as additive sintered in air

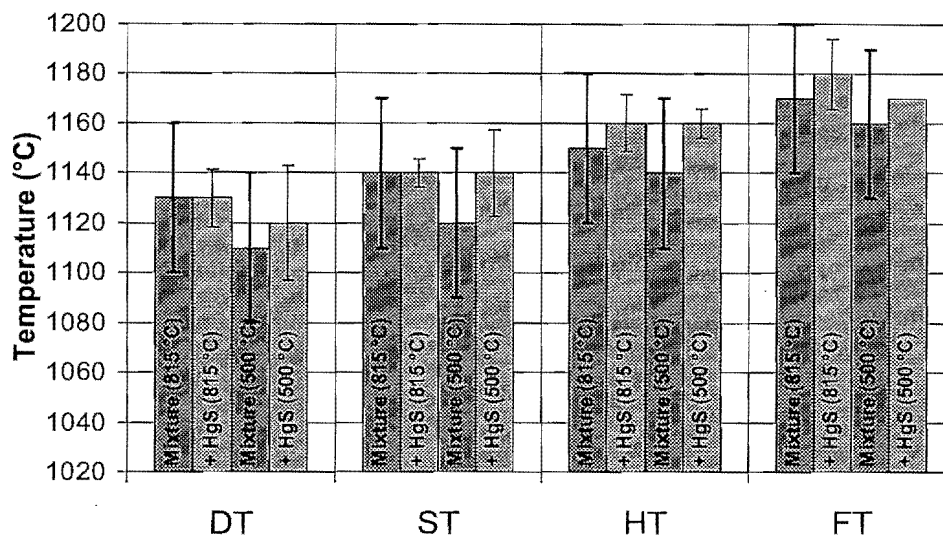


Figure 7.30 Reducing-atmosphere ash fusion temperatures of HgS as additive. Ashing temperatures are given in parentheses

Figure 7.29 presents the compressive strength results of HgS as additive sintered in air. Based on the results and confidence limits, the addition of HgS to the mineral mixture did not significantly influence the compressive strength values. However, it appears that the addition of HgS had a decreasing trend on the compressive strengths over the temperature range compared to the baseline, i.e. the values are lower than the baseline at all the sintering temperatures. The slight decreases in the compressive strength values are most probably due to an increase in porosity from the volatilization of HgS. Mercury volatilizes as Hg or HgO between 500 °C and 600 °C [Bool and Helble, 1995; Helble et al., 1996; Sekine et al., 2008]. Folgueras and co-workers [2007] predicted that mercury would be completely volatilized at 800 °C.

Figure 7.30 presents the ash fusion temperatures of HgS as additive. The addition of HgS did not significantly influence the ash fusion temperatures of the mineral mixture at both the ashing temperatures. Similar to oxidizing conditions, mercury volatilizes at low temperatures as Hg⁰ in reducing conditions [Helble et al., 1996]. Mercury was therefore removed from the mixture at both ashing temperatures, and was not present anymore to influence the ash fusion temperatures.

Chapter 8

Results and Discussion

Molybdenum, Nickel, Strontium, Vanadium and Zinc

8.1 Molybdenum

Molybdenum is associated with organic species and sulfide minerals in coal [Gürdal, 2007; Wagner and Hlatshwayo, 2006]. MoS_2 was selected to represent molybdenum as trace element, and PbMoO_4 has molybdenum as part of the molybdate anion. Molybdenum is in the same group as chromium on the periodic table.

8.1.1 Molybdenum Sulfide

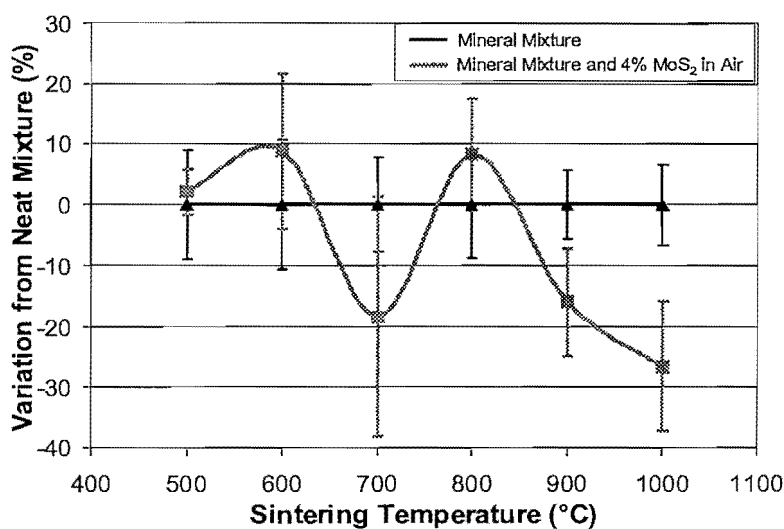


Figure 8.1 Compressive strength results of MoS_2 as additive sintered in air

Figure 8.1 presents the compressive strength results of MoS_2 as additive sintered in air. The addition of MoS_2 to the mineral mixture significantly decreased the compressive strength results at sintering temperatures of 900 °C (16%) and 1000 °C (27%). The addition of MoS_2 may also have lowered the compressive strength value at a sintering temperature of 700 °C by approximately 18%, but the

confidence limits overlap. Therefore, it is not possible to confirm whether the decrease is significant. At the other sintering temperatures the results were comparable to that of the neat mineral mixture.

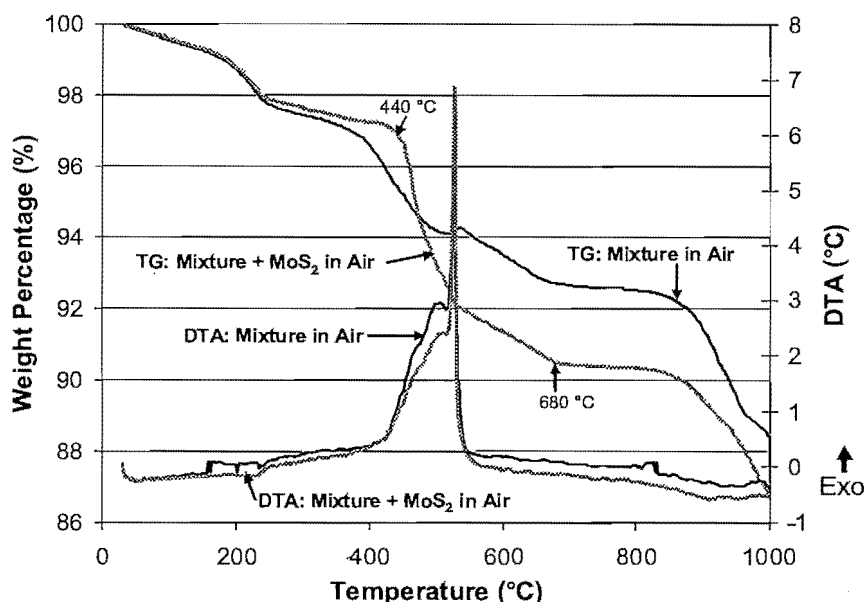


Figure 8.2 TG/DTA results of MoS_2 as additive heated in air

Figure 8.2 presents the TG/DTA results of MoS_2 as additive heated in air. The weight loss patterns of the sample with additive and the neat mineral mixture were similar from 30 °C to 220 °C. From 220 °C to 440 °C the weight loss in the sample with additive occurred at a slower rate than for the neat mineral mixture. MoS_2 roasted in air is oxidized to MoO_2 , followed by oxidation to MoO_3 at temperatures below 500 °C [Anand Rao et al., 2001; Kholmogorov and Kononova, 2005]. However the weight gain in the sample with additive, compared to the neat mineral mixture, suggests that the sulfate was formed. The weight gain of 2% at 440 °C indicates that MoS_2 was not completely transformed to molybdenum sulfate, but rather a mixture of MoS_2 and/or MoO_2 and $\text{Mo}(\text{SO}_4)_2$ were present. It appears as if the oxidation of MoS_2 to MoO_2 occurs via the formation of a $\text{Mo}(\text{SO}_4)_2$ intermediate. Based on the results, the weight percentage of $\text{Mo}(\text{SO}_4)_2$ was larger than the weight percentage of MoO_2 at 440 °C.

The weight of the sample with additive decreased at a considerable rate from 440 °C to 540 °C. At 540 °C the weight of the sample with additive was 2% less than the neat mineral mixture. Theoretically, the oxidation of 4% MoS₂ to MoO₂ represents a weight loss of approximately 1%, and oxidation to MoO₃, a weight loss of less than 0.5% in the mineral mixture. However, the additional weight loss in the sample with additive was 2% in the temperature interval, compared to the neat mineral mixture sample. The TG/DTA results in Figure 8.2 suggest that volatilization of molybdenum species occurred in the temperature interval of 440 °C to 540 °C. According to Tietz and Wilson [1965], MoO₃ begins to sublime above 500 °C, with significant volatilization above 600 °C. However, Anand Rao and co-workers [2001] stated that volatilisation of MoO₃ starts at 620 °C at atmospheric pressure. Eissa and co-workers [1996] reported that the volatilization of MoO₃ occurred at temperatures higher than 800 °C, and the maximum weight loss of MoO₃ at 700 °C was 0.93%. Based on the wide range of different volatilization temperatures reported for MoO₃, it can be concluded that the volatilization of MoO₃ is affected by different reaction conditions.

The rate of weight loss in the two samples was similar from 540 °C to 800 °C, indicating that no additional molybdenum species volatilized. MoO₃ has a melting point of 795 °C [Lee, 1996]. At 1000 °C the weight difference between the two samples was approximately 1.5%, with the rate of weight loss slower in the sample with additive than in the neat mineral mixture sample. As determined in Chapter 4 (see Section 4.2.3), the weight loss in the neat mineral mixture sample at temperatures higher than 820 °C was mostly due to the decomposition of CaSO₄ to CaO and SO₃. The slower rate of weight loss in the sample with additive suggests that less CaSO₄ was available to decompose, and that additional molybdenum species did not volatilize. Molybdenum in coal is regarded as a semi-volatile element [Bunt and Waanders, 2009a; Ratafia-Brown, 1994].

The retention of molybdenum in calcium and iron molybdate species explains the lack of volatilization of molybdenum species at temperatures higher than 540 °C, and the reduced formation of CaSO₄. No reference was found pertaining to the temperature where molybdenum species react with calcium and iron species, but French and co-workers [2001] detected CaMoO₄ and Fe₃MoO₈ phases in slag prepared from coal ash. Kholmogorov and Kononova [2005] also reported the formation of CaMoO₄ from “oxidative leaching of molybdenum in basic media”, and Anand Rao and co-workers [2001] recovered molybdenum from MoS₂-containing

ores by alkali leaching after roasting at low temperatures. MoO_3 is strongly acidic [Lee, 1996]. Reaction with CaCO_3 at temperatures below 540°C could be responsible for the formation of CaMoO_4 . The same interaction is also possible with FeCO_3 . Water was present in the relevant temperature range from the dehydration of kaolinite. The oxidation of MoS_2 in the presence of water results in the formation of molybdic acid and sulphuric acid [Kholmogorov and Kononova, 2005]. The formation of CaMoO_4 will reduce the amount of CaCO_3 available for CaSO_4 formation, and cause the reduced weight loss in the TG/DTA results from 800°C to 1000°C .

The lack of volatilization of any remaining MoO_3 (not retained at the lower temperatures) at temperatures higher than 800°C , could be facilitated by reaction with CaO as CaSO_4 decomposes [O'Neill and Eggins, 2002]. Gibbs and co-workers [2008] also noted that MoO_3 polymerizes at low temperatures to form Mo_3O_9 and Mo_4O_{12} , which only become unstable and volatilize at high temperatures.

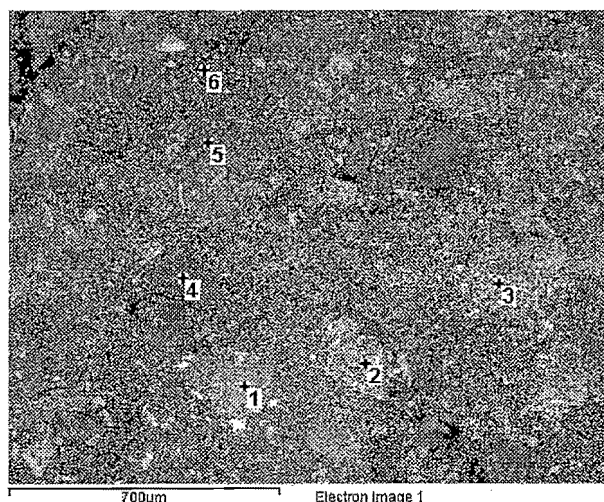


Figure 8.3 Backscattered electron image of mineral mixture pellets with MoS_2 sintered in air at 700°C

MoO_2 and MoO_3 reportedly dissolve in silicate melt phases [O'Neill and Eggins, 2002]. Ratafia-Brown [1994] detected molybdenum in glass phases in fly ash particles. Figure 8.3 represents a backscattered electron image of a mineral mixture pellet with MoS_2 as additive heated in air at 700°C . Molybdenum was enriched in all the analyzed areas. Areas 2 and 3 contained high amounts of iron, and may represent the formation of iron molybdates on the surface of iron-rich particles. Areas 5 and 6

represent the aluminosilicate/anhydrite matrix. Bulk EDS analysis of the pellets sintered in air at 1000 °C detected a total Mo concentration of approximately 2% (elemental wt%), confirming the lack of volatilization of Mo species. XRD did not identify any crystalline molybdenum-containing species in the pellets sintered at 700 °C, 900 °C or 1000 °C. The concentrations may have been too low, or the Mo species were incorporated into amorphous aluminosilicate phases.

MoO₃ is known as a non-conventional network former [Milanova et al., 2009]. The incorporation of molybdenum into silicates can influence the phases and also the characteristics of the phases in the pellets. As an example, the addition of a molybdate to silica rock to facilitate tridimite formation was patented in 1930 [Searle, 1940]. The decrease in the compressive strength values of the mineral mixture at sintering temperatures of 900 °C and 1000 °C was most likely due to the incorporation of molybdenum in aluminosilicate phases. The effect may be due to the network-forming properties of isolated MoO₄ tetrahedra that influence the characteristics of the aluminosilicate/anhydrite matrix [Milanova et al., 2009]. No notable additional volatilization occurred at these sintering temperatures to increase the porosity and cause the decrease in the compressive strength values.

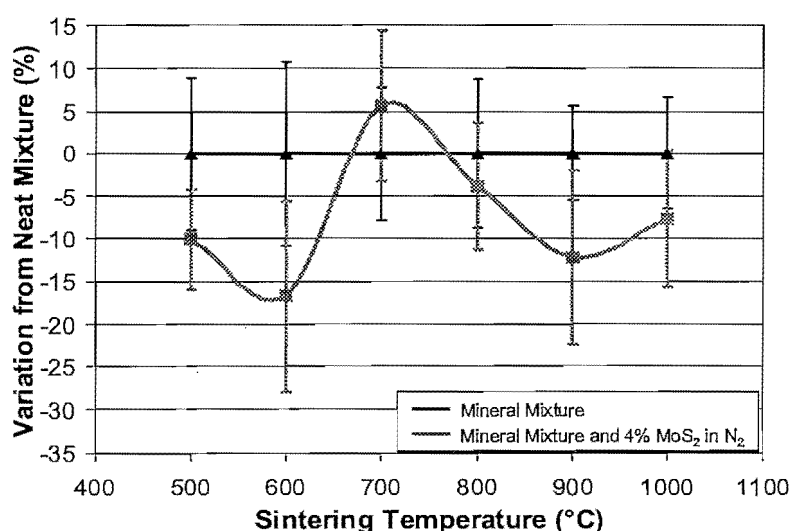


Figure 8.4 Compressive strength results of MoS₂ as additive sintered in N₂

The compressive strength results of MoS₂ as additive sintered in N₂ are presented in Figure 8.4. The addition of MoS₂ may have reduced the compressive

strength of the mineral mixture by 17% at a sintering temperature of 600 °C, but the confidence limits overlap. The decrease is therefore deemed as insignificant. At the other sintering temperatures the results were comparable to the neat mineral mixture.

Figure 8.5 presents the TG/DTA results of MoS₂ as additive heated in N₂. Weight loss in the sample with additive and the neat mineral mixture was similar over the total temperature range, when considering the reproducibility of the method. The weight loss results of the sample with additive heated in N₂ suggest that MoS₂ did not volatilize in the inert atmosphere. Vasilyeva and Nikolaev [2008] determined that solid MoS₂ begins to decompose at 1580 °C in helium (1 bar) at high heating rates. The inactivity of the additive is responsible for the lack of influence on the compressive strength values of the mineral mixture (Figure 8.4).

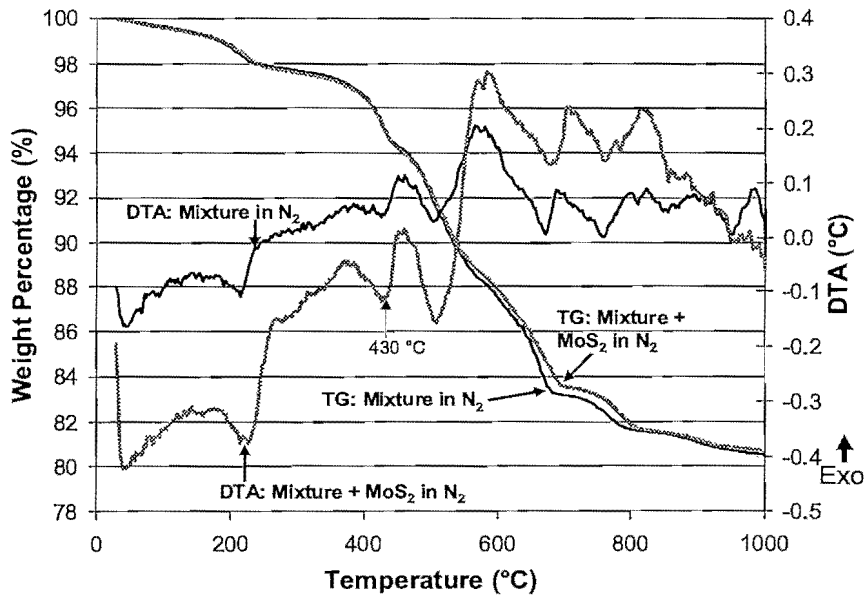


Figure 8.5 TG/DTA results of MoS₂ as additive heated in N₂

8.1.2 Lead Molybdate

Lead molybdate as additive was discussed in detail in Chapter 7, Section 7.1.4. It is included here again, since molybdenum is part of the anion in the compound. The additive will only be discussed in comparison to MoS₂ as additive.

Figure 8.6 presents the compressive strength results of PbMoO₄ as additive sintered in air. The same results were presented as Figure 7.9. It appears that the

influence on the compressive strength results from the addition of PbMoO_4 and MoS_2 followed the same trend in the pellets sintered in air. The same increase in the influence on the compressive strength values from a sintering temperature of 700 °C to 800 °C is observed, followed by a decrease to a sintering temperature of 900 °C. In section 7.1 it was determined that the trend is due to the addition of lead, irrespective of the anion. However, it appears as if the molybdenum anion also had an influence on the trend for the addition of PbMoO_4 .

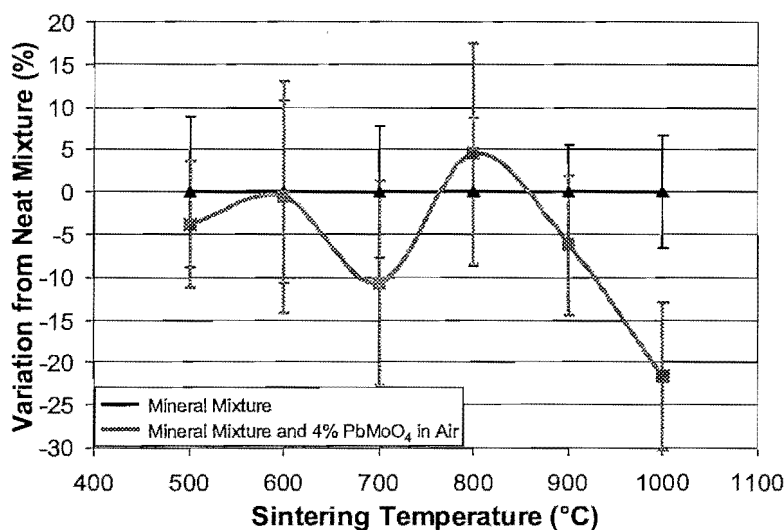


Figure 8.6 Compressive strength results of PbMoO_4 as additive sintered in air

The weight loss results for the addition of PbMoO_4 (Figure 7.11) suggested that no volatilization of the additive occurred. However, EDS analysis was unable to detect Mo in the pellets with PbMoO_4 sintered at 1000 °C. The reasons are discussed in Section 7.1.4. The molybdate anion had the same effect on the compressive strength values for the addition of MoS_2 and PbMoO_4 at a sintering temperature of 1000 °C. It seems that the molybdate anion is responsible for the decrease in the compressive strength. The compressive strength results for the addition of PbS (Figure 7.3), where PbO is incorporated into the aluminosilicate phases, did not result in a decreased compressive strength at 1000 °C. Therefore, comparison with the results obtained for MoS_2 and PbS confirm that the decreased compressive strength value at a sintering temperature of 1000 °C observed for the addition of PbMoO_4 to the mineral mixture was due to the molybdate anion. The effect may be due to the network-forming

properties of isolated MoO_4 tetrahedra that affected the characteristics of the aluminosilicate/anhydrite matrix [Milanova et al., 2009].

8.1.3 Reducing-Atmosphere Ash Fusion Temperature Test

Figure 8.7 presents the ash fusion temperature results of molybdenum species as additives. Based on the confidence limits, neither the addition of MoS_2 nor the addition of PbMoO_4 significantly affected the ash fusion temperatures of the mineral mixture at either ashing temperature. Limited information is available on the characteristics of MoS_2 and PbMoO_4 in the reducing atmosphere to indicate which interactions may occur in proximity to the mineral mixture constituents. Work by Bunt and Waanders [2009a] suggests that Mo is completely volatilized at 1025 °C under reducing conditions.

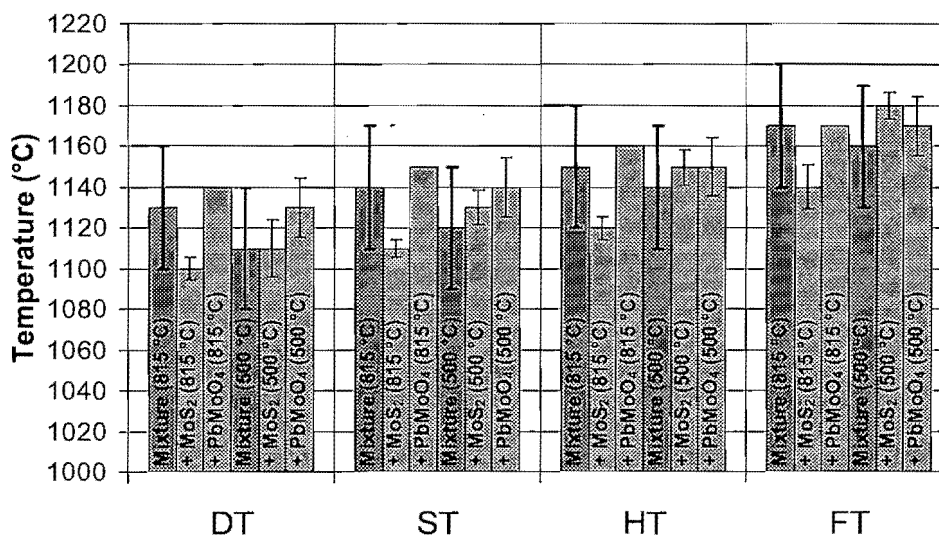


Figure 8.7 Reducing-atmosphere ash fusion temperatures of molybdenum species as additives. Ashing temperatures are given in parentheses

8.2 Nickel

Nickel in coal has many different associations. Nickel is found in pyrite, sulfide minerals, clay minerals, macerals, and small portions may also be associated with carbonates [Folgueras et al., 2007; Galbreath et al., 2000; Shah et al., 2009]. Nickel-containing species include: nickeline (NiAs), millerite (NiS), linnaeite

((Co,Ni)₃S₄), ullmannite (NiSbS), and ferrite spinels [Finkelman, 1994; Font et al., 2005b; Galbreath and Zygarlicke, 2004]. The compounds selected to represent nickel as trace element are Ni₃S₂ and NiCO₃. Partial oxidation of millerite produces Ni₃S₂ (heaslewoodite) [Weast, 1977; Dunn, 1997; Tölke et al., 2007]. The carbonate was obtained as nickel carbonate, basic hydrate (NiCO₃·2Ni(OH)₂·H₂O). The compound will be referred to as NiCO₃ in the discussion where applicable.

8.2.1 Experiments in an Oxidizing Atmosphere

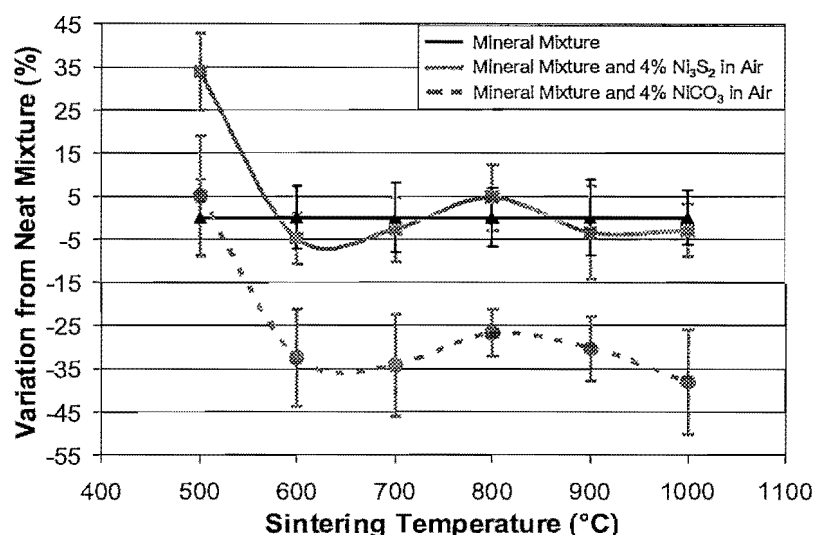


Figure 8.8 Compressive strength results of NiCO₃ and Ni₃S₂ as additives sintered in air

Figure 8.8 presents the compressive strength results of NiCO₃ and Ni₃S₂ as additives sintered in air. The addition of NiCO₃ significantly reduced the compressive strength results of the mineral mixture at sintering temperatures of 600 °C to 1000 °C. The compressive strength results were decreased by 27% to 38%. The results were comparable to the neat mineral mixture at a sintering temperature of 500 °C. However, the addition of Ni₃S₂ increased the compressive strength results by 35% at a sintering temperature of 500 °C, but at the other sintering temperatures the results were comparable to the neat mineral mixture. The influence from Ni₃S₂ and NiCO₃ followed the same trend, but the results from the addition of Ni₂S₃ produced

compressive strength values 30% larger than the results from NiCO_3 , when compared to the neat mineral mixture values.

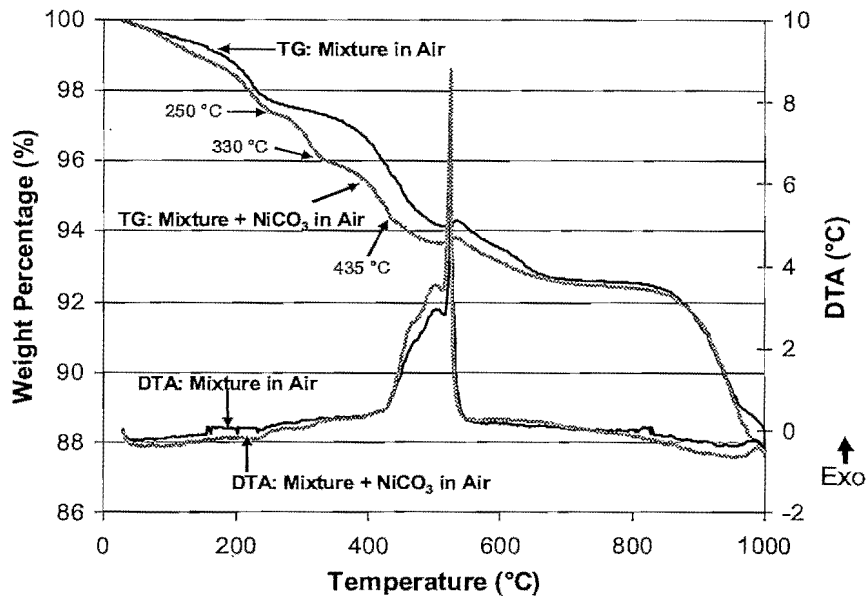


Figure 8.9 TG/DTA results of NiCO_3 as additive heated in air

Figure 8.9 presents the TG/DTA results of NiCO_3 as additive heated in air. The weight loss in the sample with additive was more than the weight loss of the neat mineral mixture sample from 30 °C to 650 °C. The additional weight loss in the sample with additive occurred from 30 °C to 250 °C, and from 250 °C to 330 °C. The additive was obtained as $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$. The additional weight loss from 30 °C to 250 °C in the sample with additive corresponds to the dehydration of the compound to $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2$. Calculations indicate that further dehydration occurred from 250 °C to 330 °C to yield NiO . The weight percentage difference between the two samples at 330 °C was less than 1.5%. The transformation of 4% $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$ to NiO would result in a weight loss of 1.2% in the mineral mixture.

The weight loss in the sample with additive was at a slower rate than the neat mineral mixture from 440 °C to 650 °C, indicating weight gain compared to the neat mineral mixture. The weight gain was due to sulfation and oxidation of NiO to NiSO_4 [Shah et al., 2009]. However, calculations indicate the formation of a mixture of NiO

and NiSO_4 , and not complete transformation to NiSO_4 . Folgueras and co-workers [2007] determined with equilibrium calculations that NiO and NiSO_4 would be dominant at temperatures below 800°C in co-combustion of coal and biomass. Considerable amounts of NiSO_4 have been detected in combustion fly ash [Shah et al., 2009].

The weight loss of the two samples was similar from 650°C to 950°C (Figure 8.9). Different sources list different decomposition temperatures for NiSO_4 . These include 700°C [Anand Rao et al., 2001] and 850°C [Weast, 1977], but the partial pressure of SO_2 affects the decomposition point [Anand Rao et al., 2001]. The weight loss patterns suggest that the sulfate was stable up to 850°C . At temperatures higher than 850°C the sulfate decomposed to NiO , as represented by the broad endothermic peak in the DTA curve of the sample with additive, and the difference in weight loss for the two samples. XRD analysis confirmed the occurrence of NiO in the pellets sintered at 600°C to 1000°C in air. Theoretically, the complete decomposition of $4\% \text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$ to NiO constitutes a total weight loss of approximately 1.2% in the mineral mixture.

The TG/DTA results of Ni_3S_2 as additive heated in air are presented in Figure 8.10. Unlike the addition of NiCO_3 , the weight loss results of the sample with additive and the neat mineral mixture were similar from 30°C to 450°C . The sample with additive increased in weight from 450°C to 700°C , compared to the neat mineral sample. The weight gain from 540°C to 700°C in the sample with additive was associated with a broad exothermic peak in the DTA curve. At 700°C the weight percentage of the sample with additive was approximately 2% more than the neat mineral mixture. The weight gain was due to the oxidation of Ni_3S_2 to produce NiSO_4 [Shah et al., 2009]. Calculations indicate that, similar to NiCO_3 , NiO and NiSO_4 were formed, instead of complete transformation to NiSO_4 . Shah and co-workers [2009] reported that Ni_3S_2 , originating from NiS in coal, can be converted to NiSO_4 and NiO under combustion conditions. Dunn [1997] also indicated that the oxidation of NiS at 535°C yielded a mixture of products, i.e. NiS , NiO and NiSO_4 . XRD analysis confirmed the presence of NiO in the pellets with additive sintered at 500°C in air.

The weight remained approximately constant in the sample with additive from 700°C to 850°C , after which decomposition of the sulfate to NiO occurred (Figure 8.10). At 1000°C the total weight losses in the two samples were similar.

Theoretically, the complete oxidation of 4% Ni_3S_2 to NiO constitutes a total weight loss in the mineral mixture of less than 0.3%.

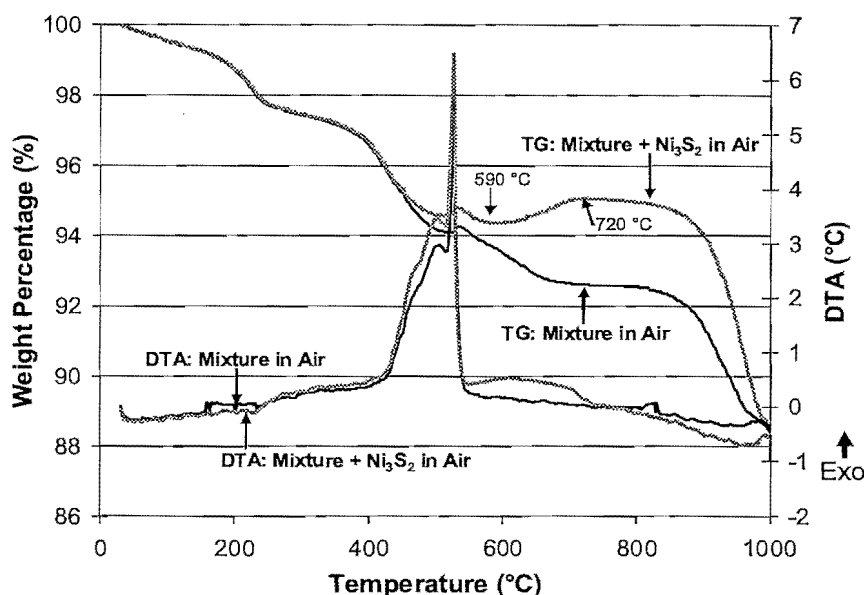


Figure 8.10 TG/DTA results of Ni_3S_2 as additive heated in air

Pellets sintered in air with nickel compounds as additives were subjected to backscattered electron EDS analysis. Pellets with Ni_3S_2 sintered at 500 °C, and pellets with NiCO_3 sintered at 600 °C and 1000 °C, were analyzed. In all the pellets the largest enrichment of Ni was detected in areas representing the aluminosilicate/anhydrite matrix (elemental wt%). Some Ni was detected in areas with high amounts of Fe, but due to the high concentration of Fe, EDS analysis was unable to confirm whether NiFe_2O_4 formed. However, the EDS results suggest the formation of NiFe_2O_4 on the surface of Fe_2O_3 particles. Ni compounds associated with the aluminosilicate network may include NiAl_2O_4 at the higher sintering temperatures [Shih et al., 2006]. Díaz-Somoano and co-workers [2006] and Folgueras and co-workers [2007] predicted that formation of NiFe_2O_4 and NiAl_2O_4 at temperatures higher than 600 °C. The results available can only suggest the formation of spinels, but are unable to confirm whether these compounds were formed, or at which temperatures the formation was most likely.

The TG/DTA and XRD results for the addition of both nickel compounds indicate that the same species were present in the pellets at the same sintering temperatures. However, the compressive strength values obtained for the addition of the carbonate were approximately 30% lower than for the addition of the sulfide, compared to the neat mineral mixture pellets (Figure 8.8). The only clear difference between the two additives is the volatilization of H_2O and CO_2 released from the carbonate species at low temperatures. Based on the results obtained for the addition of Ni_3S_2 at a sintering temperature of 500 °C, it can be deduced that the addition of Ni_3S_2 , and probably also the nickel carbonate, affected the sintering of the mineral mixture. The decreased values for the addition of NiCO_3 , compared to the addition of Ni_3S_2 at all the sintering temperatures were most likely due to the increase of porosity from the volatilization of H_2O and CO_2 during the decomposition of the carbonate.

It is unlikely that the difference in molar concentrations resulted in the different values for the two additives, since the addition of the carbonate resulted in a lower molar concentration of NiO in the mineral mixture than the addition of Ni_3S_2 . Therefore, the addition of NiO and/or NiSO_4 to the mixture increased the sintering in the pellets, compared to the neat mineral mixture pellets, but only at a sintering temperature of 500 °C. It is unclear why sintering was only affected at a temperature of 500 °C, but it is assumed that sintering due to anhydrite formation dominated the total influence on the compressive strength values of the pellets at higher sintering temperatures. Perhaps the retention of nickel in spinels at temperatures of 600 °C and higher reduced the effect of NiO on the aluminosilicate phases. Ratafia-Brown [1994] detected Ni associated with iron oxides in combustion fly ash, and not with glass or mullite. It is not possible to deduce whether the increased effect was due to enhanced sulfation of limestone, or solely due to changes in the aluminosilicate phases, as the same nickel species did not form in the inert atmosphere (see Section 8.2.2). NiO dissolves into aluminosilicate glass melt phases [O'Neill and Eggins, 2002; Tölke et al., 2007].

8.2.2 *Experiments in an Inert Atmosphere*

Figure 8.11 presents the compressive strength results of NiCO_3 as additive sintered in N_2 . The addition of NiCO_3 significantly reduced the compressive strength results of the mineral mixture at sintering temperatures of 600 °C, 700 °C, 900 °C and 1000 °C in N_2 . The compressive strength results were decreased by 18% to 25%. At

sintering temperatures of 500 °C and 800 °C the results were comparable to the neat mineral mixture.

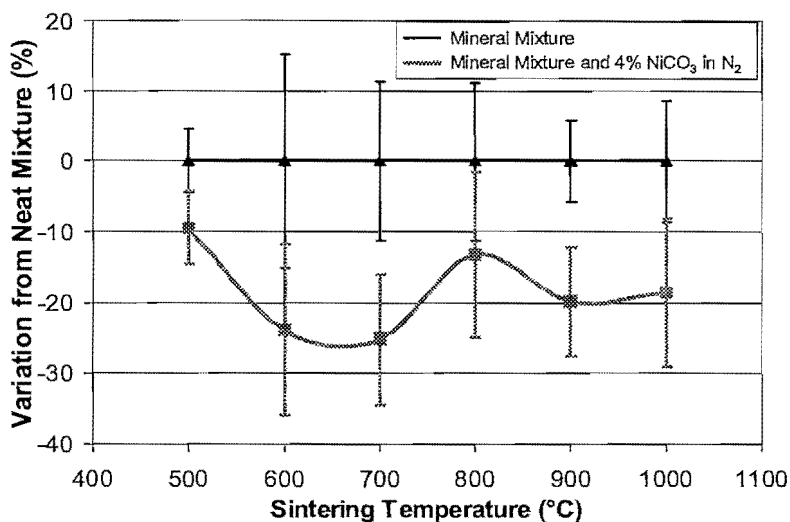


Figure 8.11 Compressive strength results of NiCO₃ as additive sintered in N₂

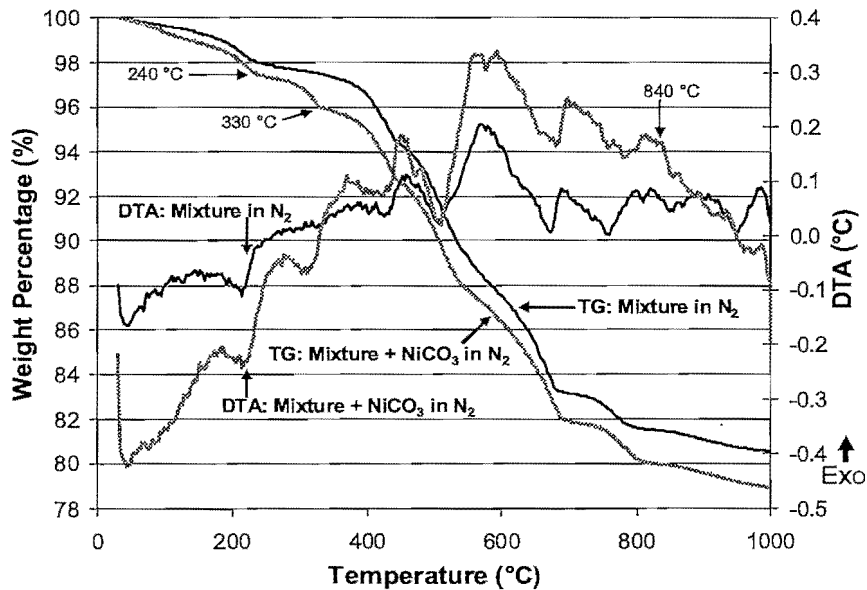


Figure 8.12 TG/DTA results of NiCO₃ as additive heated in N₂

Figure 8.12 presents the TG/DTA results of NiCO₃ as additive heated in N₂. The weight loss in the sample with additive was more than the weight loss in the neat

mineral mixture sample. Similar to the results in air, the additional weight loss from 30 °C to 250 °C in the sample with additive represents dehydration of $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$ to $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2$. The weight loss from 250 °C to 330 °C represents the dehydration and decomposition of $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2$ to NiO. The weight loss from 250 °C to 330 °C is associated with an endothermic peak in the DTA curve from 300 °C to 330 °C. The weight difference between the two samples was approximately constant (~1.5 %) from 330 °C to 1000 °C. From the weight loss results it is not possible to determine whether the NiO remained as is up to 1000 °C (theoretical weight loss of 1.2% in the mineral mixture), or formed Ni_3S_2 (weight loss of 1%). It is unlikely that the NiO was transformed to NiS. The theoretical weight loss value for the formation of this compound is 0.6%.

Similar to the results obtained in air, the decreases in the compressive strength values were most likely due to the increase in the porosity from the volatilization associated with the decomposition of the additive. The increase at a sintering temperature of 500 °C, compared to a sintering temperature of 600 °C, could be due to the influence of NiO on the aluminosilicate matrix, as seen for the results in air.

The compressive strength results of Ni_3S_2 as additive sintered in N_2 are presented in Figure 8.13. Compared to the neat mineral mixture, the addition of Ni_3S_2 did not significantly influence the compressive strength values in N_2 .

The TG/DTA results of Ni_3S_2 as additive heated in N_2 are presented in Figure 8.14. The weight loss patterns of the sample with additive and the neat mineral mixture were similar over the total temperature range, when considering the repeatability of the method. This is an indication that the sulfide persisted in the inert atmosphere at the temperatures of interest. However, the slight weight difference from 550 °C to 800 °C may include the formation of NiS from Ni_3S_2 , but due to the small theoretical weight gain associated with this transformation (0.5%), the TG/DTA results are inconclusive. Ni_3S_2 has a melting point of 790 °C, and NiS has a melting point of 797 °C [Weast, 1977]. The endothermic peak at 805 °C in the DTA curve of the sample with additive may represent melting of the additive. The temperature is closer to the melting point of NiS than the melting point of Ni_3S_2 . However, Tölke and co-workers [2007] determined that NiS easily loses sulfur to form Ni_3S_2 when heated in the absence of oxygen.

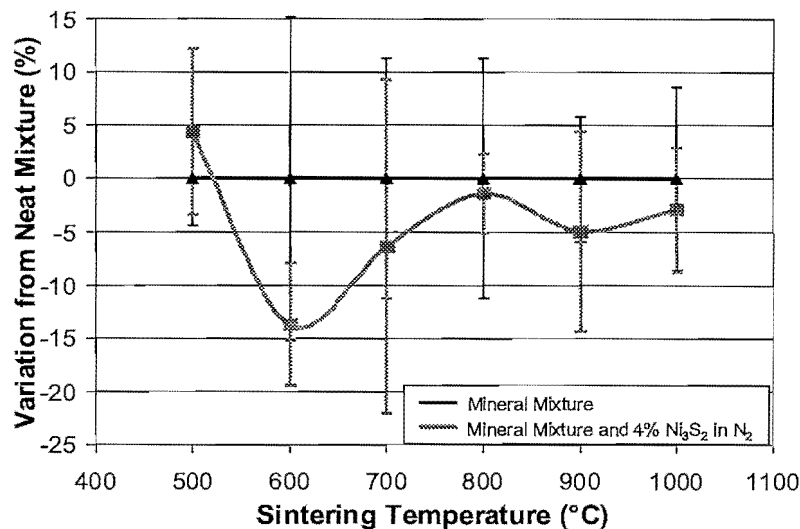


Figure 8.13 Compressive strength results of Ni_3S_2 as additive sintered in N_2

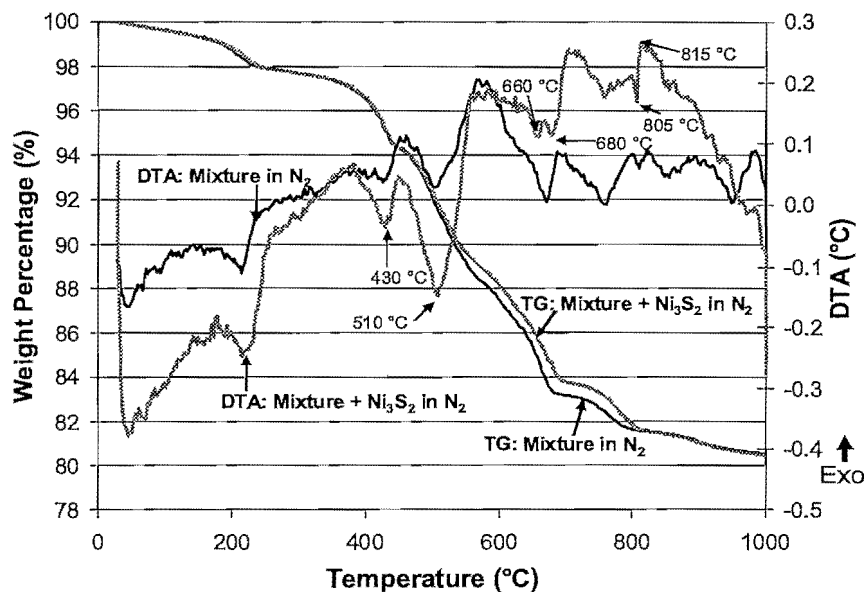


Figure 8.14 TG/DTA results of Ni_3S_2 as additive heated in N_2

8.2.3 Reducing-Atmosphere Ash Fusion Temperature Test

Figure 8.15 presents the ash fusion temperature results of nickel species as additives. Neither the addition of Ni_3S_2 nor NiCO_3 affected the ash fusion temperatures of the mineral mixture at either of the ashing temperatures. In the reducing atmosphere of the ash fusion temperature tests, the nickel is most probably

reduced to Ni^0 . Bunt and Waanders [2009a] predicted that solid Ni^0 would form from the reduction of Ni_3S_2 at temperatures higher than 770 °C under reducing conditions. It appears that, unlike PbO from the decomposition of PbCO_3 , NiO from the initial decomposition of NiCO_3 did not affect the ash fusion temperatures. Ni has a melting temperature of 1453 °C, and NiO has a melting temperature of 1955 °C [Weast, 1977; Holzheid et al., 1997].

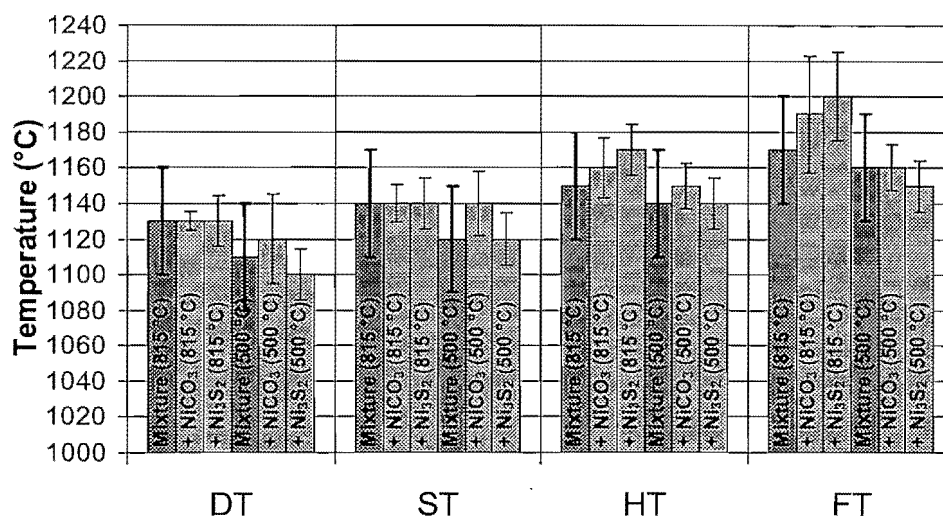


Figure 8.15 Reducing-atmosphere ash fusion temperatures of nickel species as additives. Ashing temperatures are given in parentheses

8.3 Strontium

Strontium in coal is associated with sulphates, carbonates, clays, aluminium phosphates, and also the organic matrix [Laban and Atkin, 1999]. Strontium is an alkaline earth element and is in group 2 on the periodic table, together with Mg, Ca and Ba. Common strontium-containing minerals include celestite (SrSO_4) and strontianite (SrCO_3). The compounds selected to represent strontium as trace element are SrSO_4 and SrCO_3 .

8.3.1 Strontium Sulfate

Figure 8.16 presents the compressive strength results of SrSO_4 as additive sintered in air. The addition of SrSO_4 to the mineral mixture did not significantly

influence the compressive strength values. It was therefore not included in further experiments, except in the ash fusion temperature tests (results in Section 8.3.3). Pure SrSO_4 decomposes at 1374 °C [Lee, 1996].

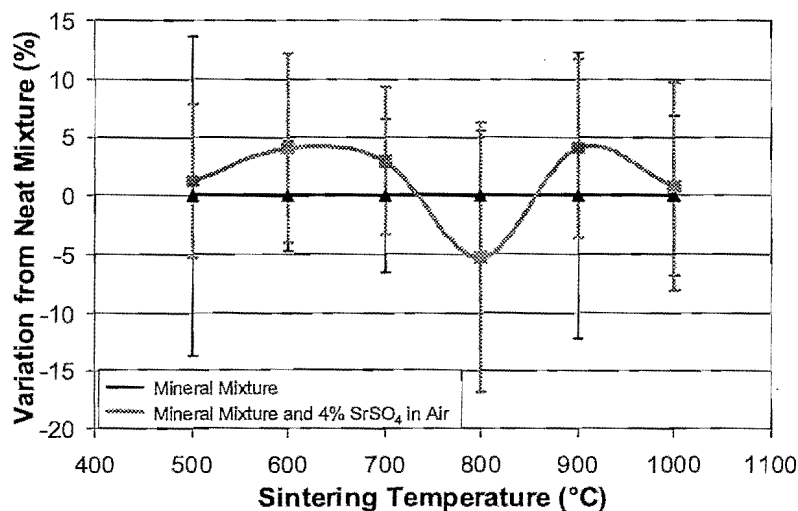


Figure 8.16 Compressive strength results of SrSO_4 as additive sintered in air

8.3.2 Strontium Carbonate

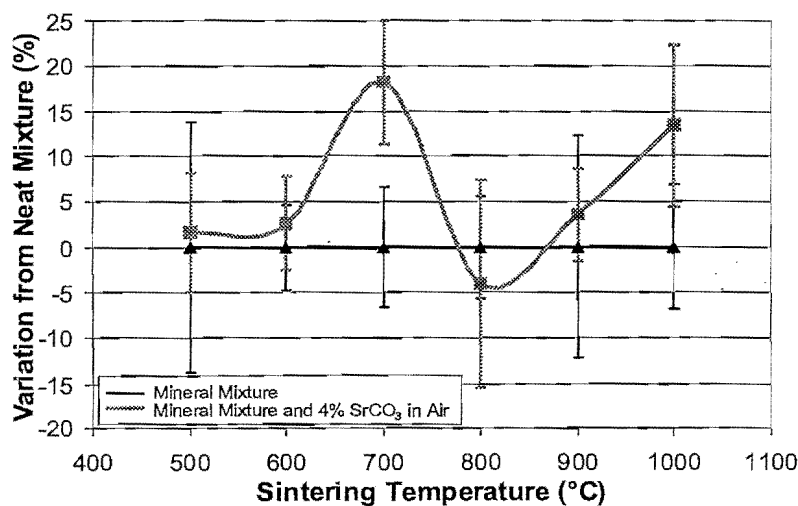


Figure 8.17 Compressive strength results of SrCO_3 as additive sintered in air

Figure 8.17 presents the compressive strength results of SrCO_3 as additive sintered in air. The addition of SrCO_3 to the mineral mixture increased the compressive strength of the mixture by 18% at a sintering temperature of 700 °C. At the other sintering temperatures the results were comparable to the neat mineral mixture, based on the values and confidence limits. However, it is the only additive that showed a considerable increase in the compressive strength at a sintering temperature of 1000 °C, even though the confidence limits overlap slightly.

Figure 8.18 presents the compressive strength results of SrCO_3 as additive sintered in N_2 . The addition of SrCO_3 to the mineral mixture did not significantly influence the compressive strength values in N_2 .

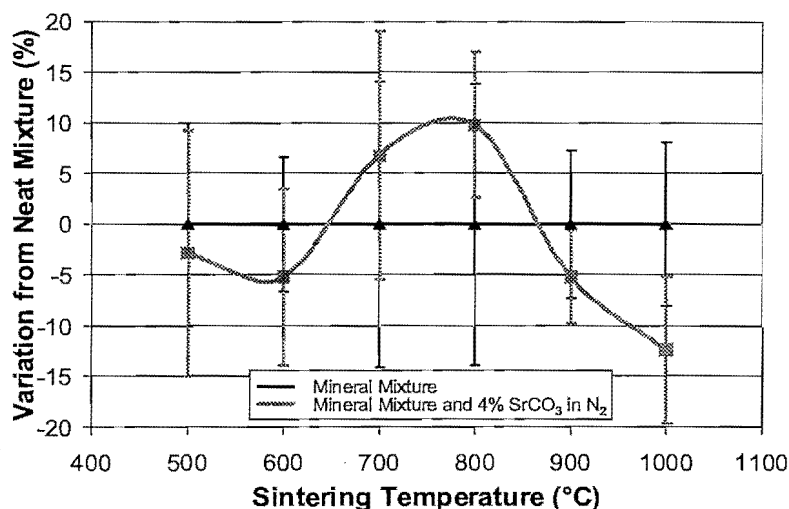


Figure 8.18 Compressive strength results of SrCO_3 as additive sintered in N_2

The TG/DTA results of SrCO_3 as additive heated in air are presented by Figure 8.19. The weight loss patterns for the sample with additive and the neat mineral mixture were similar from 30 °C to 650 °C. The decomposition temperature of pure SrCO_3 is 1290 °C [Lee, 1996]. Torres and co-workers [2007] stated that the decomposition of SrCO_3 occurs above 900 °C. It is clear from the weight loss results that the constituents in the mineral mixture affected the decomposition temperature of the carbonate. The TG/DTA results indicate that decomposition of SrCO_3 in the mineral mixture started at 650 °C. From 650 °C to 850 °C the weight of the neat mineral mixture remained constant, but the weight loss continued in the sample with

additive. At 850 °C the difference in weight percentage between the two samples was approximately 1%. Theoretically, the complete decomposition of 4% SrCO_3 to SrO corresponds to an additional weight loss in the mineral mixture of 1.2%.

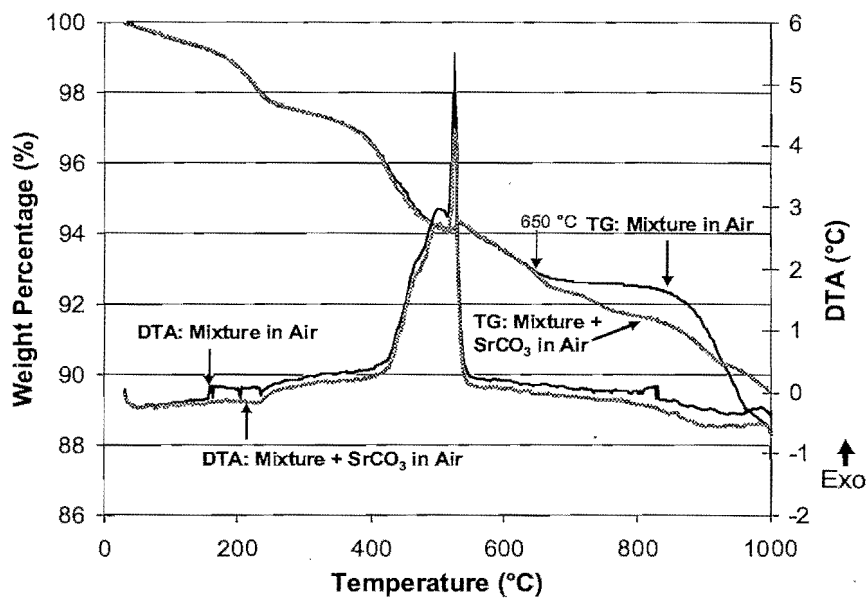


Figure 8.19 TG/DTA results of SrCO_3 as additive heated in air

The weight percentages of both samples were the same at 930 °C, but at 1000 °C, the weight loss in the sample with additive was approximately 1% less than in the neat mineral sample. The conversion of 4% SrCO_3 to SrSO_4 represents a weight gain of approximately 1%, compared to the neat mineral mixture. Therefore, the TG/DTA results indicate that decomposition of SrCO_3 started at 650 °C, followed by sulfation of the resultant oxide to SrSO_4 . SO_3 was available at temperatures higher than 830 °C from the decomposition of CaSO_4 (see Section 4.2.3).

Figure 8.20 is a backscattered electron image of a mineral mixture pellet with SrCO_3 as additive sintered in air. The highest concentrations of Sr were detected in particle 2 (0.7%) and area 5 (1.6%) (elemental wt%). Particle 2 consisted mostly of Ti and O, indicating the occurrence of TiO_2 . Approximately 1% to 2% of Al, Si, S, Ca and Fe, respectively, were also detected at this point of analysis. The Sr associated with the particle could be an indication of the formation of SrTiO_3 on the surface of the particle from the decomposition of SrCO_3 to SrO [Berbenni et al., 2001]. Area 5

represents the aluminosilicate/anhydrite matrix. SrO can be incorporated into aluminosilicate phases, similar to other group 2 metal oxides (CaO, MgO, BaO). Ratafia-Brown [1994] detected strontium associated with glass and mullite in combustion fly ash. The association was not due to surface enrichment.

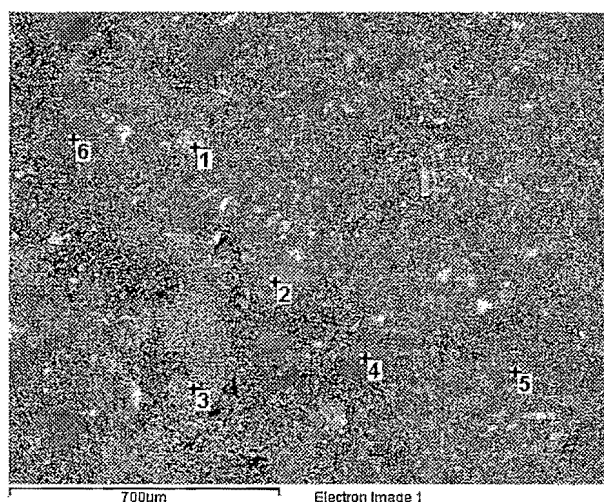


Figure 8.20 Backscattered electron image of a mineral mixture pellet with SrCO_3 as additive sintered in air at 700 °C

Torres and co-workers [2007] stated that SrO is a cement-forming compound, and its addition to cement (<20 wt%) increases the compressive strength. Therefore, the addition of SrCO_3 to the mineral mixture and decomposition to SrO at temperatures from 650 °C to 700 °C, was most probably responsible for the increase in the compressive strength at a sintering temperature of 700 °C. The same result is expected at sintering temperatures of 800 °C and 900 °C, but the decomposition of the carbonate would have increased the porosity in the pellets. The increased porosity combined with increased sintering would therefore have reduced the observed influence on the compressive strength of the pellets at these sintering temperatures. The increase in the observed compressive strength from a sintering temperature of 800 °C to 1000 °C, would be due to reduced porosity from the formation of SrSO_4 , combined with the increased sintering as a result of the remaining SrO.

Figure 8.21 presents the TG/DTA results of SrCO_3 as additive heated in N_2 . The weight loss patterns for the sample with additive and the neat mineral mixture were similar from 30 °C to 680 °C. At 700 °C, the weight loss difference in the

sample with additive was more than 1%, compared to the neat mineral sample. This difference was most probably due to the formation of SrS from SrCO₃. The reduction of 4% SrCO₃ to SrS is theoretically responsible for an additional weight loss in the mineral mixture of 0.8%. The weight loss results indicate that an additional weight loss of approximately 3% was obtained at 1000 °C, compared to that of the neat mineral mixture. The additional weight loss was therefore due to the volatilization of gaseous Sr compounds. The decreasing trend in the compressive strength values at sintering temperatures of 800 °C to 1000 °C, from the addition of SrCO₃ sintered in N₂, was most likely due to the increase in porosity from the volatilization of Sr species.

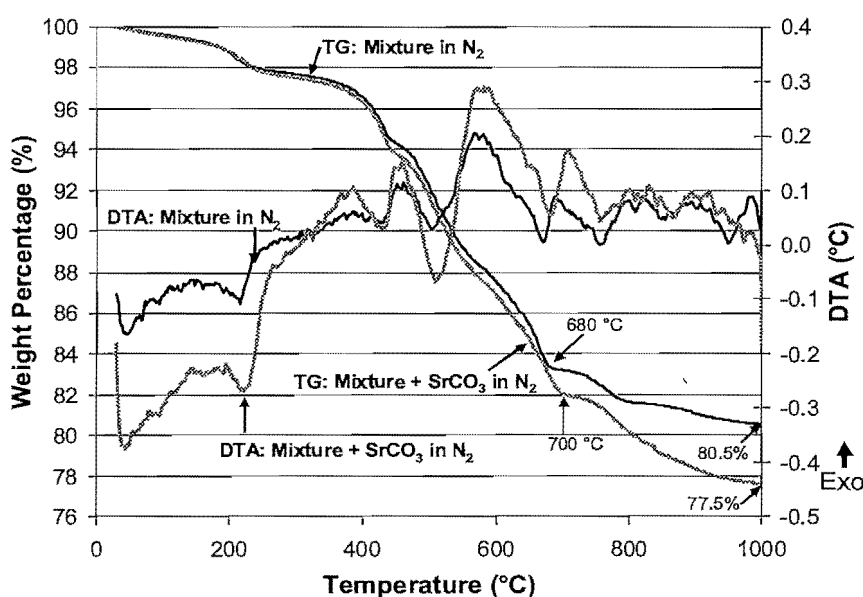


Figure 8.21 TG/DTA results of SrCO₃ as additive heated in N₂

8.3.3 Reducing-Atmosphere Ash Fusion Temperature Test

The reducing-atmosphere ash fusion temperatures obtained for strontium species as additives are presented by Figure 8.22. The addition of SrCO₃ to the mineral mixture, ashed at 815 °C, reduced the deformation, spherical and flow temperatures by 50 °C. At an ashing temperature of 500 °C the addition of SrCO₃ did not influence the ash fusion temperatures. The addition of SrSO₄ did not influence the ash fusion temperatures ashed at either of the ashing temperatures.

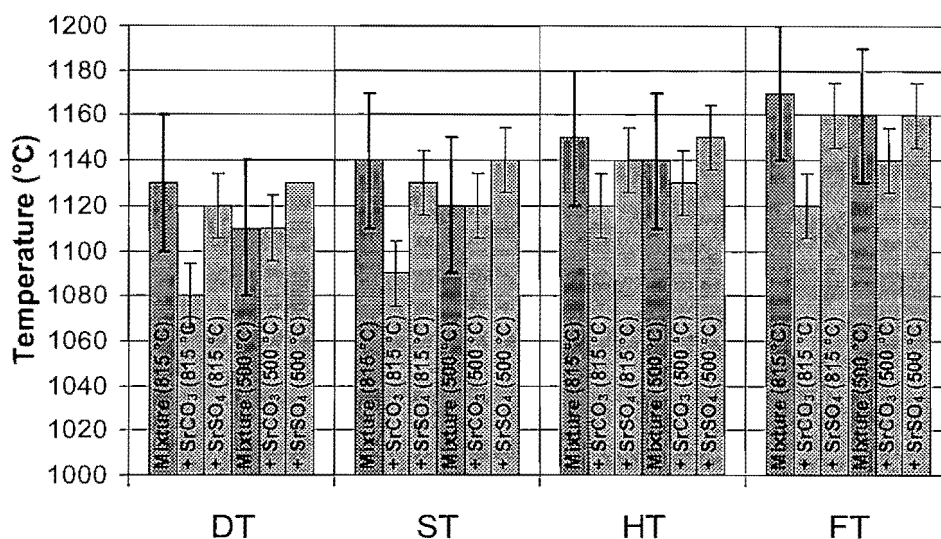


Figure 8.22 Reducing-atmosphere ash fusion temperatures of strontium species as additives. Ashing temperatures are given in parentheses

The decrease in the ash fusion temperatures from the addition of SrCO_3 ashed at 815 °C was most probably due to the initial decomposition of SrCO_3 to SrO . The SrO therefore reacted with the aluminosilicates during the ashing procedure and was allowed to crystallize upon cooling. The addition of SrCO_3 ashed at 500 °C had no effect on the ash fusion temperatures, since the ashing temperature was most probably not high enough to facilitate the decomposition of SrCO_3 . Decomposition of the SrCO_3 in the sample ashed at 500 °C would have occurred during the ash fusion temperature test, but the fast heating rate possibly did not allow enough time for the SrO to be incorporated into aluminosilicate phases before further reduction. Therefore, it can be deduced that SrSO_4 did not have an influence on the ash fusion temperatures due to a lack of decomposition at either of the ashing temperatures.

Torres and co-workers [2007] stated that SrSO_4 transforms to SrS and/or SrCO_3 in the presence of H_2 or in a CO-CO_2 atmosphere at temperatures higher than 780 °C. The transformation and products are dependent on the temperature and gas composition. SrS is formed in the temperature range of 850 °C to 910 °C in a gas composition of 10% CO and 90% CO_2 . SrCO_3 is the product in the same gas composition in the temperature range of 1010 °C to 1130 °C. It may be possible to manipulate the gas environment of the reducing ash fusion temperature test to allow SrSO_4 to influence the ash fusion temperatures of the mineral mixture.

8.4 Vanadium

Vanadium in coal is mainly associated with macerals, clays and feldspars [Folgueras et al., 2007; Galbreath et al., 2000; Huggins and Huffman, 2004; Huggins et al., 2009]. Huggins and co-workers [2009] stated that vanadium and chromium have similar modes of occurrence in coal. Vanadium can occur in coal as having three different oxidation states, i.e. V^{3+} , V^{4+} , V^{5+} , with V^{4+} and V^{5+} most common in oxidizing conditions [Folgueras et al., 2007]. Vanadium readily reacts with oxygen to form oxides, or is present as oxides in macerals and clays [Huggins et al., 2009]. The most stable oxides in oxidizing conditions are VO_2 and V_2O_5 ; and V_2O_3 is most stable under reducing conditions [Bunt and Waanders, 2010; Folgueras et al., 2007; Font et al., 2005b; Lee and Wu, 2002]. V_2O_3 and V_2O_5 were selected to represent vanadium as trace element.

As described in Section 3.1.2, vanadium compounds were not included in oxidizing and inert experiments, due to the lack of proper ventilation and the potential release of toxic gasses. The influence of vanadium compounds on the compressive strength of the pellets was therefore not investigated. However, research has indicated that vanadium compounds can interact with mineral matter in coal or ash, and can potentially have an influence on sintering and agglomeration.

Vanadium pentoxide has a melting point of 673 °C [Iribarne et al., 2003]. Conn [1995] suggested that vanadium in petroleum coke fluidized-bed combustion interacted with ash and sorbent constituents to form molten phases at temperatures lower than 900 °C. However, later work indicated otherwise [Iribarne et al., 2003].

Equilibrium calculations predicted that vanadium occurs as oxides and sulphates at temperatures lower than 600 °C [Díaz-Somoano et al., 2006]. Interactions with calcium species at higher temperatures result in the formation of calcium vanadates, i.e. $CaO \cdot V_2O_5$, $2CaO \cdot V_2O_5$ and $3CaO \cdot V_2O_5$ [Díaz-Somoano et al., 2006; Folgueras et al., 2007; Lee and Wu, 2002]. Interactions with MgO are also possible to yield magnesium vanadates [Lee and Wu, 2002]. The interactions with ash constituents are most probably the reason for the relative non-volatility of vanadium during combustion [Folgueras et al., 2007]. The vanadium associated with macerals tends to be more volatile than the vanadium associated with clays and feldspars [Folgueras et al., 2007; Galbreath et al., 2000].

Reactions of vanadium with CaO can affect the sintering in the mineral pellets by reducing the amount of CaSO₄ formed, and also the stability of the anhydrite network by reducing particle growth. Ratafia-Brown [1994] detected vanadium associated with glass phases, mullite and iron-oxides in fly ash. The association of vanadium species with the aluminosilicate matrix in the pellets can affect the characteristics of the phases, and influence the compressive strength values of the pellets. Experiments with vanadium species as additives are necessary to confirm whether vanadium compounds influence the compressive strength of pellets prepared from the mineral mixture.

Figure 8.23 presents the ash fusion temperatures of vanadium species as additives. Based on the confidence limits, the addition of vanadium species did not significantly affect the ash fusion temperatures of the mineral mixture at either of the ashing temperatures.

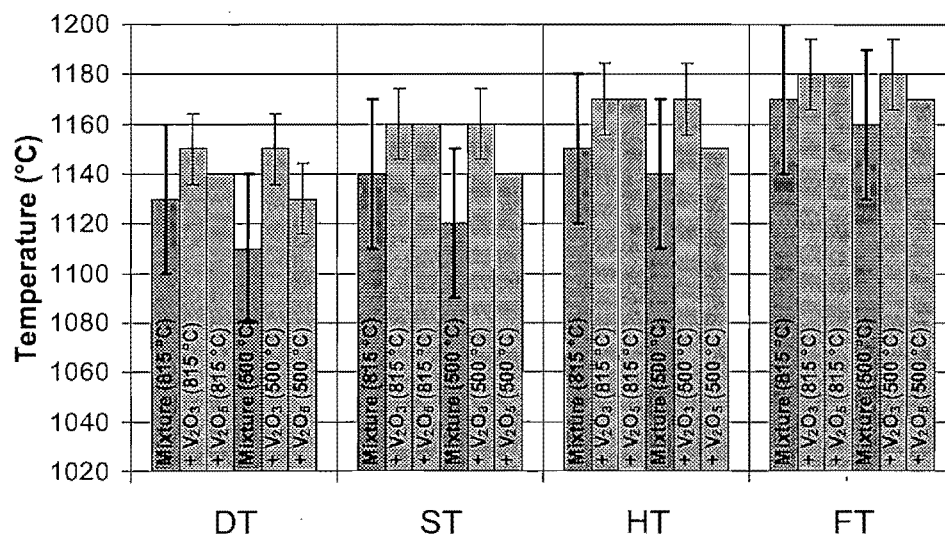


Figure 8.23 Reducing-atmosphere ash fusion temperatures of vanadium species as additives. Ashing temperatures are given in parentheses

In the reducing condition of the ash fusion temperature experiments, V₂O₅ was reduced to V₂O₃ [Bunt and Waanders, 2010; Lee, 1996]. Bunt and Waanders [2010] predicted with equilibrium calculations that the reduction to V₂O₃ will occur at temperatures higher than 325 °C, and the trioxide will remain stable up to 1225 °C. At higher temperatures volatile VO₂ is formed [Bunt and Waanders, 2010]. V₂O₃ has a

melting point of 1970 °C [Weast, 1977]. After ashing of the mineral mixture, vanadium had the same speciation in the samples ashed at different temperatures.

Under reducing conditions the vanadium species can also interact with ash constituents [Font et al., 2005b]. Gibbs and co-workers [2008] determined that the volatilities of vanadium under mildly reducing conditions and oxidizing conditions are similar. However, any possible interactions with the mineral constituents did not significantly influence the ash fusion temperatures.

8.5 Zinc

Zinc in coal is mainly associated with pyrite and sphalerite (ZnS) [Bool and Helble, 1995; Font et al., 2005b; Galbreath et al., 2000; Laban and Atkin, 1999]. Some organic association may also occur, as well as small amounts in carbonates and silicates [Bool and Helble, 1995; Galbreath et al., 2000; Laban and Atkin, 1999]. The compound selected to represent zinc is ZnS.

8.5.1 Experiments in Oxidizing and Inert Atmospheres

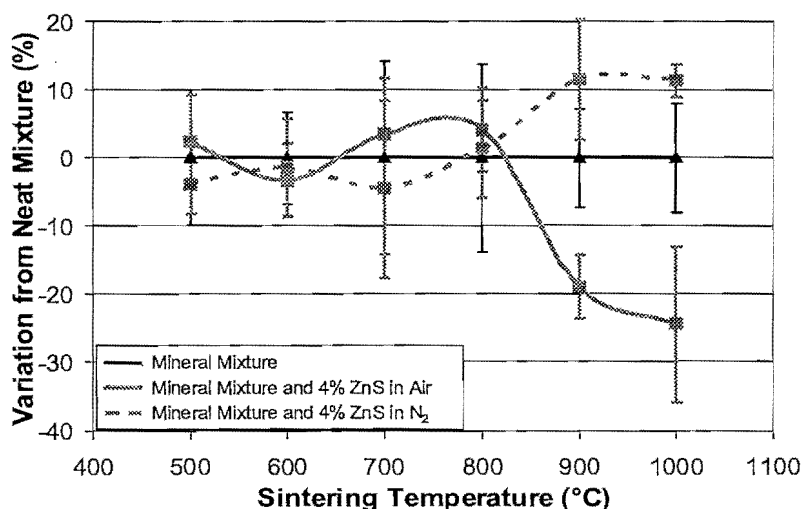


Figure 8.24 Compressive strength results of ZnS as additive sintered in air and N₂

Figure 8.24 presents the compressive strength results of ZnS as additive sintered in air and N₂. The addition of ZnS to the mineral mixture significantly

reduced the compressive strength values at sintering temperatures of 900 °C (20%) and 1000 °C (25%). At the other sintering temperatures the results were comparable to the neat mineral mixture. The influence from the addition of ZnS decreased significantly from a sintering temperature of 800 °C to 900 °C. The addition of ZnS to the mineral mixture sintered in N₂ did not significantly influence the compressive strength values, except perhaps at a sintering temperature of 1000 °C. At a sintering temperature of 1000 °C the confidence limits do not overlap, but the value is less than 14% as specified in the selection criteria (see Section 3.2.5).

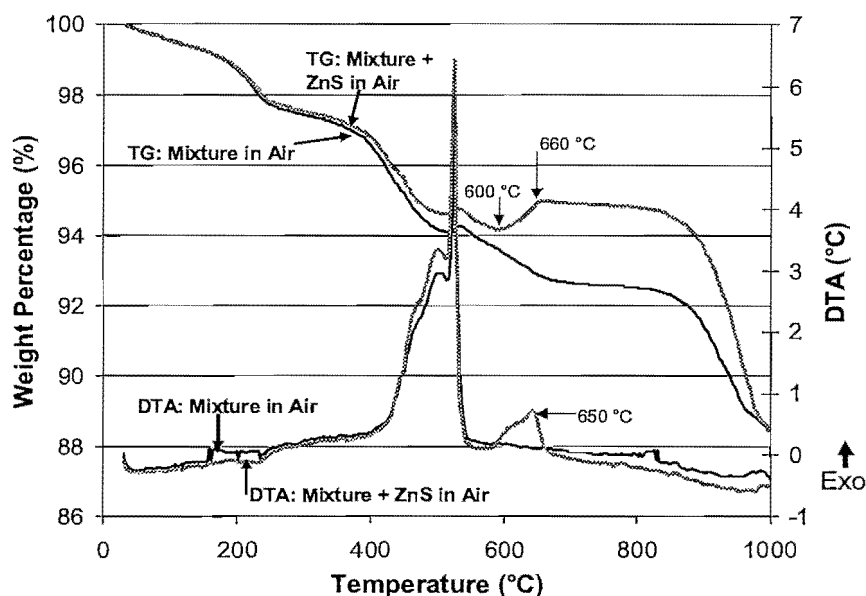


Figure 8.25 TG/DTA results of ZnS as additive heated in air

The TG/DTA results of ZnS as additive heated in air are presented in Figure 8.25. The addition of ZnS to the mineral mixture yielded similar TG/DTA results to the addition of Ni₃S₂ (see Figure 8.10). The weight loss patterns of the sample with additive and the neat mineral mixture were similar from 30 °C to 400 °C. The weight loss in the sample with additive occurred at a slower rate from 400 °C to 600 °C. Contrary to the continuous weight loss observed in the neat mineral mixture at temperature higher than 540 °C, the sample with additive increased in weight from 600 °C to 660 °C. The weight gain from 600 °C to 660 °C in the sample with additive was associated with an exothermic peak in the DTA curve. The weight gain represents

the formation of ZnSO_4 [Akcil and Ciftci, 2003]. The increase in weight occurred over a smaller temperature interval than the weight gain observed for the addition of Ni_3S_2 . The TG/DTA results indicate that the oxidation of ZnS started at approximately 400°C . At 660°C the weight difference between the two samples was approximately 2.3%. Calculations indicate that the complete oxidation of 4% ZnS to ZnSO_4 constitutes a weight gain of 2.6% in the mineral mixture. A combination of ZnO and ZnSO_4 was also possible [Akcil and Ciftci, 2003], but the weight percentage suggests that ZnSO_4 was the major product. The weight remained approximately constant from 660°C to 850°C . At 1000°C the total weight loss in the two samples was the same. Theoretically, the transformation of 4% ZnS to ZnO constitutes a total weight loss of approximately 0.7% in the mineral mixture. It is not possible to deduce from the weight loss percentages whether the decomposition of ZnSO_4 to ZnO was completed at a temperature of 1000°C .

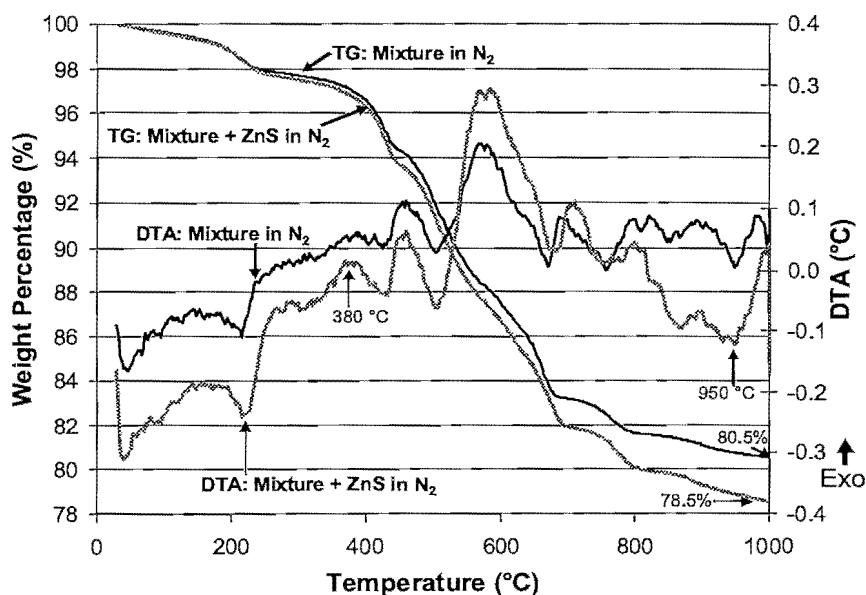


Figure 8.26 TG/DTA results of ZnS as additive heated in N_2

Figure 8.26 presents the TG/DTA results of ZnS as additive heated in N_2 . The results were similar to the weight loss observed for the addition of SrCO_3 in N_2 . At 700°C the weight loss in the sample with additive was approximately 1% more than the neat mineral sample. The weight difference increased from 700°C to 1000°C . At

1000 °C the weight loss in the sample with additive was 2% more than the neat mineral mixture. The weight difference of 2% at 1000 °C suggests that some of the zinc volatilized. Sekine and co-workers [2008] stated that ZnS can be volatilized under N₂ from 800 °C to 1000 °C. The volatilization is associated with a broad endothermic peak in the DTA curve of the sample with additive from 800 °C to 1000 °C.

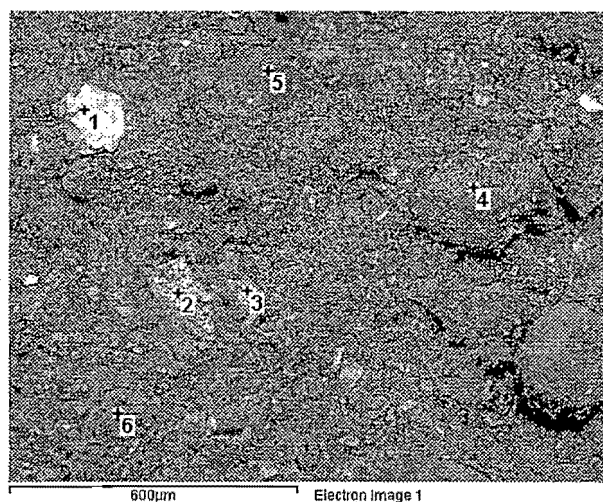


Figure 8.27 Backscattered electron image of a mineral mixture pellets with ZnS as additive sintered in air at 1000 °C

Figure 8.27 is a backscattered electron image of a mineral mixture pellet with ZnS as additive sintered in air at 1000 °C. Zn was enriched at all the analyzed areas. The Zn to O weight ratio of approximately 4 calculated for particle 2 identified the particle as ZnO. Particles 1 and 3 consisted mostly of Fe and O. Zn concentrations of 1.8% and 3.0% (elemental wt%) were detected in particles 1 and 3, respectively. The association of Zn with the iron-rich particles suggests the formation of ZnFe₂O₄ on the surface of the particles [Shoji et al., 2002]. EDS analysis identified particles 4 and 5 as SiO₂ particles covered with an aluminosilicate layer. Area 6 represented the aluminosilicate/anhydrite matrix and contained that highest concentration of Zn (5.5%) of all the analyzed spots, excluding the ZnO particle. Ratafia-Brown [1994] detected Zn associated with glass phases and iron oxides in combustion fly ash.

Qualitative XRD analysis detected ZnO in the pellets sintered in air at 900 °C and 1000 °C. ZnO can react with aluminosilicates at suitable temperatures to form

compounds such as zinc orthosilicate (ZnSiO_3), Zn_2SiO_4 , ZnAl_2O_4 , $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ and zinc-aluminosilicates [El-Shennawi et al., 2001; Salman et al., 2008; Tkalec et al., 2005]. The addition of ZnO to the mineral mixture sintered in air reduced the compressive strength of pellets sintered at 900 °C and 1000 °C (Figure 8.24). This indicates that the inclusion of ZnO into aluminosilicate phases increased the friability of the aluminosilicate matrix, and as a result decreased the compressive strength of the pellets.

The compressive strength results for the addition of ZnS to the pellets sintered in N_2 suggest that ZnS affected the sintering in the pellets at 900 °C and 1000 °C. Considerable volatilization occurred at these temperatures, but the increase in porosity associated with the volatilization did not result in a decrease in the compressive strength values.

8.5.2 Reducing-Atmosphere Ash Fusion Temperature Test

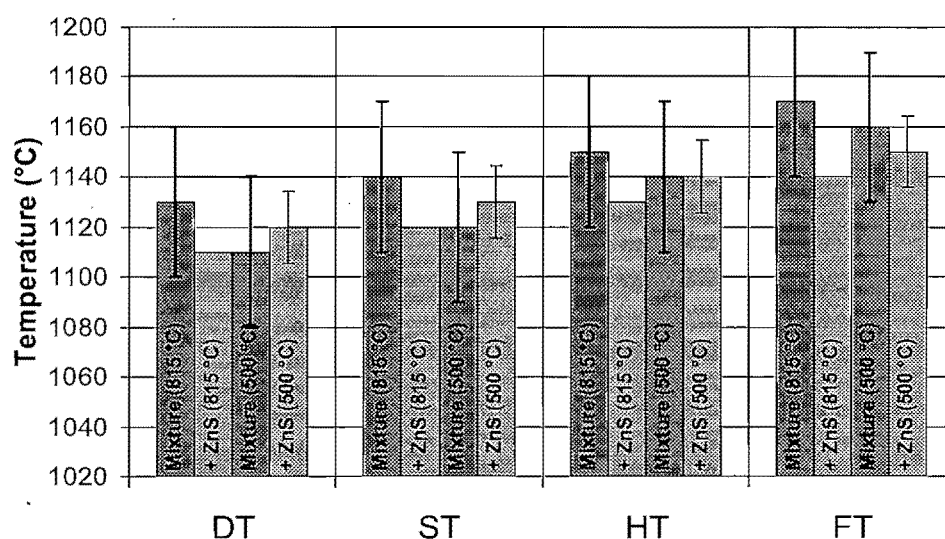


Figure 8.28 Reducing-atmosphere ash fusion temperatures of ZnS as additive. Ashing temperatures are given in parentheses

Figure 8.28 presents the ash fusion temperature results of ZnS as additive. The addition of ZnS did not affect the ash fusion temperatures of the mineral mixture at either of the ashing temperatures.

ZnS is reduced to gaseous elemental Zn under reducing conditions [Wang and Tomita, 2003]. Thermodynamic calculations predicted the volatilization of zinc at temperatures lower than 730 °C [Yan et al., 2001a]. Bunt and Waanders [2009a] predicted that volatilization of Zn starts at 725 °C from the reduction of ZnS, with all the Zn in the gaseous form at temperatures higher than 825 °C. Therefore, the lack of influence from the addition of ZnS on the ash fusion temperatures is consistent with the volatilization of Zn at low temperatures without retention in the ash.

This concludes the discussions relating to the influence of the trace element compounds on the mineral mixture. Conclusions and trends are summarized in the next chapter, as well as recommendations for future studies.

Chapter 9

Conclusions, Trends and Recommendations

9.1 Summary of Results

The results obtained in the study are summarized in tables for simplification. Tables 9.1 and 9.2 contain the results obtained in experiments performed in oxidizing and inert atmospheres, and Table 9.3 the ash fusion temperature test results. The results will be discussed in the conclusions included in Section 9.2.

Table 9.1 Summary of results obtained in an oxidizing atmosphere

Oxidizing Atmosphere (Air)	Additives			
Additive not included in oxidizing experiments	As ₂ O ₃ , V ₂ O ₃ , V ₂ O ₅ , CrO ₃			
No influence on compressive strength of mineral mixture	CoSO ₄ , PbSO ₄ , PbCO ₃ , MnO, MnO ₂ , HgS, SrSO ₄			
Increased CS values at 500 °C	NaCl, Na ₂ CO ₃ , Mn ₂ O ₃ , Ni ₃ S ₂			
Increased CS values at 600 °C	NaCl, Na ₂ CO ₃ , GeO ₂ , Mn ₂ O ₃			
Increased CS values at 700 °C	Na ₂ CO ₃ , GeO ₂ , SrCO ₃			
Increased CS values at 800 °C	NaCl, Na ₂ CO ₃ , GeO ₂ , Mn ₂ O ₃ , PbS			
Increased CS values at 900 °C	Mn ₂ O ₃			
Increased CS values at 1000 °C	—			
Decreased CS values at 500 °C	Coal			
Decreased CS values at 600 °C	Coal, NiCO ₃			
Decreased CS values at 700 °C	Coal, NiCO ₃ , Cr ₂ (SO ₄) ₃			
Decreased CS values at 800 °C	Coal, NiCO ₃			
Decreased CS values at 900 °C	Coal, NiCO ₃ , Cu ₂ S, MoS ₂ , ZnS			
Decreased CS values at 1000 °C	Coal, NiCO ₃ , Cu ₂ S, CuS, Cr ₂ (SO ₄) ₃ , MoS ₂ , PbMoO ₄ , MnCO ₃ , ZnS			
Confirmed melt phases	Detected in pellets with CuS as additive			
Significant volatilization (temperature range)	NaCl	(>780 °C)	Cr ₂ (SO ₄) ₃	(>400 °C)
	MnCO ₃	(>900 °C)	MoS ₂	(440 – 530 °C)
	SrCO ₃	(650 – 850 °C)	Coal	(>450 °C)
	NiCO ₃	(100 – 400 °C)		
Additives that form the sulfate during heating (temperature range of formation, onset of decomposition)	Cu ₂ S	(290 – 540 °C, 850 °C)	MoS ₂	(220 – 440 °C, 440 °C)
	CuS	(290 – 540 °C, 850 °C)	Ni ₃ S ₂	(450 – 720 °C, 850 °C)
	PbS	(400 – 850 °C, 850 °C)	NiCO ₃	(450 – 650 °C, 850 °C)
	ZnS	(450 – 660 °C, 850 °C)	SrCO ₃	(~850 – 1000 °C, >1000 °C)
No significant volatilization*	GeO ₂ , PbMoO ₄ , Cu ₂ S, CuS, PbS, Mn ₂ O ₃ , Ni ₃ S ₂ , ZnS			
CS – compressive strength	*except decomposition of the sulfate, where applicable			

Table 9.2 Summary of results obtained in an inert atmosphere

Inert Atmosphere (N ₂)	Additives			
Additives not included in inert experiments	As ₂ O ₃ , V ₂ O ₃ , V ₂ O ₅ , CrO ₃ , CoSO ₄ , PbSO ₄ , PbCO ₃ , MnO, MnO ₂ , HgS, SrSO ₄			
No influence on compressive strength of mineral mixture	Cr ₂ (SO ₄) ₃ , MoS ₂ , Ni ₃ S ₂ , SrCO ₃ , ZnS			
Increased CS values at 500 °C	Na ₂ CO ₃ , GeO ₂			
Increased CS values at 600 °C	Na ₂ CO ₃ , GeO ₂ , Mn ₂ O ₃			
Increased CS values at 700 °C	Na ₂ CO ₃ , GeO ₂			
Increased CS values at 800 °C	Na ₂ CO ₃ , GeO ₂ , Mn ₂ O ₃			
Increased CS values at 900 °C	—			
Increased CS values at 1000 °C	—			
Decreased CS values at 500 °C	Cu ₂ S			
Decreased CS values at 600 °C	Cu ₂ S, PbS, MnCO ₃			
Decreased CS values at 700 °C	NaCl, Cu ₂ S, PbS, NiCO ₃			
Decreased CS values at 800 °C	—			
Decreased CS values at 900 °C	NaCl, Na ₂ CO ₃ , Cu ₂ S, PbS, PbMoO ₄ , NiCO ₃			
Decreased CS values at 1000 °C	NaCl, Na ₂ CO ₃ , Cu ₂ S, CuS, PbS, PbMoO ₄ , Mn ₂ O ₃ , MnCO ₃ , NiCO ₃			
Significant volatilization (temperature range)	NaCl	(>720 °C)	Na ₂ CO ₃	(>800 °C)
	Cr ₂ (SO ₄) ₃	(>200 °C)	Coal	(>600 °C)
	SrCO ₃	(>700 °C)	GeO ₂	(CS exp at 1000 °C)
	MnCO ₃	(>350 °C)	PbS	(>700 °C)
	Mn ₂ O ₃	(>700 °C)	PbMoO ₄	(>700 °C)
	NiCO ₃	(>100 °C)	ZnS	(>700 °C)
Relatively non-volatile over total temperature range	Cu ₂ S and CuS (<1% weight loss in mineral mixture at 1000 °C) GeO ₂ (according to TG/DTA results), MoS ₂ , Ni ₃ S ₂			

CS – compressive strength

Table 9.3 Summary of results obtained in the ash fusion temperature test

Reducing Atmosphere	Additives
Increased AFTs of mineral mixture ashed at 500 °C	CrO ₃
Increased AFTs of mineral mixture ashed at 815 °C	—
Decreased AFTs of mineral mixture ashed at 500 °C	NaCl, GeS, PbCO ₃
Decreased AFTs of mineral mixture ashed at 815 °C	NaCl, SrCO ₃
No influence on AFTs at either ashing temperature	All the remaining additives (those not already mentioned in this table)

AFTs – ash fusion temperatures

9.2 Conclusions

This study is very data rich. Only the conclusions relevant to the hypothesis and some general trends are included in this chapter. See the main body of text under the sections for each trace element for conclusions on the mineral transformations and speciation of the additives. The hypothesis as stated in Section 1.2 is the following:

‘Trace element species interact with associated minerals in coal during ash formation. Solid-state interactions may contribute or inhibit sintering and agglomeration processes in oxidizing and inert environments. Differences in trace element speciation (oxidation numbers and anions) will have different effects on these processes’.

9.2.1 Oxidizing and Inert Experiments

Conclusion 1: Trace elements affect sintering and/or agglomeration in the mineral mixture at temperatures from 500 °C to 1000 °C in air and N₂

Based on the principle of the compressive strength test, an increase in the compressive strength values confirm that the additive increased sintering in the mineral mixture. Therefore:

- The additives that increased sintering in the mineral mixture in air at one or more of the sintering temperatures are NaCl, Na₂CO₃, GeO₂, Mn₂O₃, Ni₃S₂, SrCO₃ and PbS.
- The additives that increased sintering in the mineral mixture in N₂ at one or more of the sintering temperatures are Na₂CO₃, GeO₂ and Mn₂O₃.

It is not possible to directly link a reduction in the compressive strength values with a decrease in sintering or an increase in the friability of aluminosilicate phases. An increase in volatilization increases the porosity in the pellets, which subsequently decreases compressive strength values, compared to the mineral mixture pellets without additives. A decrease in sintering and/or an increase in the friability of the aluminosilicate phases can therefore only be confirmed if the addition reduced the

compressive strength values, but was not associated with considerable volatilization at the temperatures of interest. Therefore:

- The additives that decreased sintering or increased the friability of aluminosilicate phases in the mineral mixture in air at one or more of the sintering temperatures are MoS_2 and PbMoO_4 .
- The additives that decreased sintering or increased the friability of aluminosilicate phases in the mineral mixture in N_2 at one or more of the sintering temperatures are Cu_2S , CuS , PbS (only at 600 °C) and NaCl (only at 700 °C). Melt phases were confirmed for the addition of CuS .

Conclusion 2: Trace elements affect sintering or agglomeration in the mineral mixture by influencing the formation of anhydrite and/or the aluminosilicate network

Experiments with the mineral mixture without additives indicated that strength formation in the pellets is mainly due to the formation and sintering of anhydrite (CaSO_4). Anhydrite formation does not occur in the inert atmosphere due to a lack of SO_2 as reagent from the decomposition and oxidation of pyrite. Therefore, strength formation in the pellets sintered in N_2 can only be due to the characteristics of the aluminosilicate phases. If the additive remained in the same form in both atmospheres, and the same effect is observed on the compressive strength values obtained in both atmospheres, then the additive influenced the characteristics and/or sintering of the aluminosilicate network. If the same trend is not observed in both atmospheres, the additive most probably influenced the anhydrite formation in air. If the same species did not remain in both atmospheres, the results are unable to indicate which mechanism was followed. Therefore:

- Additives that increased sintering in the mineral mixture in air at one or more of the sintering temperatures based on increased sulfation of limestone are NaCl , Na_2CO_3 , and possibly also Mn_2O_3 at lower temperatures.
- Additives that increased sintering in the mineral mixture in air at one or more of the sintering temperatures by affecting the aluminosilicate phases are Na_2CO_3 , GeO_2 and Mn_2O_3 .

Conclusion 3: Different oxidation numbers of the cation associated with the same anion have different effects on sintering of the mineral mixture

Three oxides were selected with different oxidation numbers for the metal to investigate manganese as trace element, i.e. MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}) and MnO_2 (Mn^{4+}). The addition of manganese compounds was discussed in Section 7.2. The only oxide that influenced sintering of the mineral mixture in air was Mn_2O_3 . The other two oxides did not influence sintering in air, and was therefore not included in the inert experiments. The molar concentrations of Mn associated with each oxide in decreasing order (calculated based on 4% additive per pellet) are MnO (5.6×10^{-4} moles) > Mn_2O_3 (5.1×10^{-4} moles) > MnO_2 (4.6×10^{-4} moles). Therefore, the effect on the sintering observed for Mn_2O_3 was not associated with an increased Mn concentration compared to the other oxides, but was due to the different oxidation number of the additive.

Conclusion 4: Different anions associated with the same cation have different effects on sintering of the mineral mixture

All the lead compounds investigated contained lead as Pb^{2+} , but the anions were varied, i.e. PbS, PbSO_4 , PbCO_3 . PbMoO_4 is largely excluded from this discussion as it contains a trace element in the anion (see Conclusion 5). The addition of lead compounds was discussed in Section 7.1. PbS was the only additive of the three that significantly influenced sintering of the mineral mixture in air. The other two additives did not influence the sintering in air, and was therefore excluded from inert experiments. However, a similar trend was observed for all of the lead-containing additives from a sintering temperature of 700 °C to 900 °C, including PbMoO_4 . The influence on the compressive strength values increased from a sintering temperature of 700 °C to 800 °C, followed by a decrease to 900 °C, compared to the neat mineral mixture baseline. The same trend was observed in air and N_2 . It can therefore be concluded that the Pb^{2+} ion was responsible for the observed trend and the Pb^{2+} ion influenced the aluminosilicate phases.

When evaluating the averages (i.e. disregarding the confidence limits), the addition of PbS resulted in a 30% increase in the influence at a sintering temperature of 700 °C to 800 °C. The addition of PbCO_3 and PbSO_4 resulted in increases at the

same sintering temperatures of 15% and 12%, respectively. Calculations of the molar concentrations associated with 4% of each additive per pellet yield Pb^{2+} concentrations of 1.7×10^{-4} moles in PbS, 1.5×10^{-4} moles in PbCO_3 , and 1.3×10^{-4} moles in PbSO_4 . The order of decreasing molar concentrations is repeated in the decreasing order of influence on the trend, i.e. $\text{PbS} > \text{PbCO}_3 > \text{PbSO}_4$. However, the influence from the addition of PbS is twice as large as the influence from PbCO_3 (30% vs 15%), but the Pb^{2+} concentration in PbS is not twice as large as the concentration in PbCO_3 . Likewise, the decrease in the Pb^{2+} mole concentrations is approximately 0.2×10^{-4} moles from PbS to PbCO_3 , and also from PbCO_3 to PbSO_4 . However, the influence on the compressive strength values did not decrease from PbS to PbCO_3 , and PbCO_3 to PbSO_4 in a fixed ratio.

It can therefore be concluded that the anions associated with the same cation can have an influence on the ability of the cation to affect sintering of the mineral mixture. The results suggest that the environment created by the anion affects the reactivity of the cation.

Conclusion 5: Both the cation and the anion can have an influence on sintering and/or agglomeration of the mineral mixture

The conclusion stated above becomes apparent when comparing the results obtained for PbS, PbMoO_4 and MoS_2 . The results obtained for the addition of PbS, PbMoO_4 and MoS_2 were discussed in Sections 7.1 and 8.1. PbMoO_4 and PbS share the same cation, and Mo is incorporated into PbMoO_4 as a molybdate ion. The TG/DTA results for the addition of MoS_2 heated in air indicated that Mo was retained in the mineral mixture as molybdate species. MoS_2 and PbMoO_4 are the only two confirmed additives that decreased the sintering of the mineral mixture or affected the friability of the aluminosilicate phases in air (see Conclusion 1). Comparison of the compressive strength results indicates that the same trend was observed for PbMoO_4 and PbS in air and N_2 at sintering temperatures of 700 °C to 900 °C, and the same trend was observed for PbMoO_4 and MoS_2 at sintering temperatures of 800 °C to 1000 °C in air. Therefore, for the addition of PbMoO_4 , both the cation and the anion influenced sintering and/or agglomeration of the mineral mixture.

Conclusion 6: Interactions with the mineral mixture affect volatilization and decomposition of the additives

- Pure SrCO_3 has a decomposition temperature of 1290 °C. However, interactions with the mineral constituents in the mixture reduced the decomposition temperature to 650 °C. The lowered decomposition temperature allowed the incorporation of SrO into aluminosilicate phases, which increased sintering and/or agglomeration of the mineral pellets at a sintering temperature of 700 °C (see Section 8.3.2).
- MoS_2 is oxidized to MoO_3 , which has an initial volatilization temperature in the range of 500 °C and 800 °C. However, the results obtained for MoS_2 as additive indicated that interactions with mineral constituents in the mixture incorporated MoO_3 into molybdate species (see Section 8.1.1). The formation of the molybdate species prevented volatilization of Mo at temperatures lower than 1000 °C (the volatilization temperatures of the molybdate species were not determined).

Therefore, the results obtained in the study prove that trace element species can interact with associated minerals in coal during ash formation to contribute to or inhibit sintering and/or agglomeration in the ash; and also that the influence is dependent on the oxidation number of the cation, and the anion associated with the species.

9.2.2 Reducing-Atmosphere Ash Fusion Temperature Test

Conclusion 7: Trace element additives can form low melting point species and decrease the ash fusion temperatures of the mineral mixture under reducing conditions

The ash fusion temperatures obtained for the mineral mixture with additives indicated that the addition of 4% NaCl, GeS, PbCO_3 and SrCO_3 lowered some or all of the ash fusion temperatures of the mixture at one or both of the ashing temperatures.

Conclusion 8: Trace element additives can increase the ash fusion temperatures of the mineral mixture under reducing conditions

The ash fusion temperatures obtained for the mineral mixture with additives indicated that the addition of 4% CrO_3 increased all the ash fusion temperatures of the mixture ashed at 500 °C.

Conclusion 9: The initial ashing temperature affects the ash fusion temperatures of the mixture with additives

- The addition of GeS and PbCO_3 decreased the ash fusion temperatures of the mixture ashed at 500 °C, but not at 815 °C.
- The addition of SrCO_3 decreased the ash fusion temperatures of the mixture ashed at 815 °C, but not at 500 °C.
- The addition of CrO_3 increased the ash fusion temperatures of the mixture ashed at 500 °C, but not at 815 °C.

Therefore, the results prove that a selection of trace element compounds form low melting point species or raise the melting temperatures of species in coal ash during ash formation under reducing conditions. Trace element compounds can thus inhibit or contribute to agglomeration during ash formation. The effect of the trace element species is dependent on the initial ashing temperature.

9.2 General Trends and Theories

- The results indicate that all of the sulfides subjected to TG/DTA analysis transform to the sulfate when heated in air. In some instances oxidation is not complete, but rather a mixture of the metal sulfate and metal oxide is obtained in approximately a 1:1 ratio.
- The addition of sulfates to the mineral mixture has little or no effect on sintering and/or agglomeration of the mineral mixture. However, if the sulfate is formed during heating of the mixture with the additive, the sulfate can have an influence on sintering and/or agglomeration. The difference is

attributed to the reactivity of the additive based on the initial anion (see Conclusion 4). $\text{Cr}_2(\text{SO}_4)_3$ decreased the compressive strength values at some of the sintering temperatures, but the influence on sintering can not be confirmed due to considerable volatilization.

- Species of Group 14 elements (Si, Ge, Pb) tend to increase sintering and/or agglomeration in the mineral mixture, as they are confirmed network formers of modifiers. However, the effect is temperature and atmosphere dependent. PbS and GeO_2 enhanced sintering of the mineral mixture in air, but only GeO_2 enhanced sintering in N_2 . PbCO_3 and GeS had an insignificant influence in both atmospheres. However, PbCO_3 and GeS lowered the ash fusion temperatures of the mineral mixture under reducing conditions, but the influence of GeO_2 and PbS were insignificant. PbCO_3 and GeS only affected the ash fusion temperatures at an initial ashing temperature of 500 °C, but not at 815 °C. PbS only increased sintering in the mineral mixture at a sintering temperature of 800 °C, compared to the range of 500 °C to 800 °C for the addition of GeO_2 .
- GeO_2 has the largest influence of all the additives on sintering of the mineral mixture in N_2 . The effect from the addition of GeO_2 at a sintering temperature of 500 °C is more than twice as large as the influence from Na_2CO_3 , which is the additive with the second largest influence in N_2 .
- The reduction in the ash fusion temperatures due to the addition of PbCO_3 (ashed at 500 °C) was comparable to the reduction observed for the addition of NaCl (ashed at 815 °C). The addition of PbCO_3 to the mineral mixture ashed at 500 °C reduced the ash fusion temperatures more than the addition of NaCl ashed at 500 °C. NaCl is known to form low melting point species and affect agglomeration in fluidized-bed gasification.
- The influence from metal carbonates on the reducing-atmosphere ash fusion temperatures is dependent on a) whether the ashing temperature is higher than the decomposition temperature of the carbonate; b) whether the ashing temperature is lower than the temperature at which the resultant oxide is

further reduced; and c) whether the oxide incorporated into aluminosilicate phases result in low-melting point eutectics or phases. SrCO_3 only reduced the AFTs in the mixture ashed at 815 °C. The decomposition temperature of the carbonate in air and N_2 was in the range of 650 °C to 700 °C. PbCO_3 only decreased the AFTs in the mineral mixture ash at 500 °C. PbCO_3 decomposes at temperatures higher than 400 °C to PbO and CO_2 . The addition of NiCO_3 did not influence the ash fusion temperatures of the mixture at either of the ashing temperatures. The NiCO_3 additive decomposed to NiO at 250 °C to 330 °C in both air and N_2 .

9.3 Recommendations for Future Studies

This study addresses to some extent the lack of information available in literature detailing the influence of different trace species on sintering and agglomeration in coal ash in the temperature range associated with fluidized-bed combustion. Based on the results and trends observed, some aspects may be investigated in more depth. Suggested areas of investigation include the following:

- Experiments to determine the lowest concentrations at which the additives still affect sintering and agglomeration.
- In situ high-temperature XRD and QEMSCAN studies of the sintering in the mineral mixture to track changes of the species, especially anhydrite, over the temperature range, and also to map minor phases such as spinels for the experiments with additives.
- Complete compressive strength tests and TG/DTA experiments for all the additives over the temperature range sintered under reducing conditions.
- Ash fusion temperature experiments for the addition of the inorganic compounds to the mineral mixture in an oxidizing atmosphere to confirm whether low-melting point species form.
- Compressive strength experiments with arsenic and vanadium compounds to determine whether they have an influence on sintering of the mineral mixture in an oxidizing environment.

- Investigate the effect of coal addition on the ash fusion temperatures of the mineral mixture in reducing and oxidizing atmospheres.
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