



The influence of various potassium compound additions on the plasticity of a high-swelling South African coal under pyrolyzing conditions

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ABSTRACT

The influence of the anion attached to a potassium cation on the decrease of plastic properties of a high swelling vitrinite-rich medium rank B South African coal was investigated by adding potassium hydroxide (KOH), potassium carbonate (K_2CO_3), potassium acetate (KCH_3CO_2) and potassium chloride (KCl) to a partially demineralized coal sample. 5 and 10 weight percentages (determined as the amount of potassium in the potassium salt) were added to the demineralized coal and FSI, TMA and dilatometry of the blends measured. Thermogravimetric analyses of the added compounds indicated that all of the potassium salts evaporate to some extent at different temperatures. It was found that the addition of KCl does not decrease the swelling or plastic properties of the coal. However, with the addition of the oxygen – containing potassium compounds to the demineralized coal, a decrease in the swelling was observed; with the addition of KCH_3CO_2 showing the largest influence, followed by KOH and K_2CO_3 . Dilatation results indicated that not all of the plastic properties of the coal were eliminated in the case of addition of KCH_3CO_2 (as was for K_2CO_3), although K_2CO_3 is also the decomposition product of KCH_3CO_2 . K_2CO_3 starts to form from KCH_3CO_2 at temperatures higher than the softening temperature of the coal. The main influence on the plastic properties of the added compounds thus seems to be crucial in the temperature range from 380 to 480 °C. The large decrease in the FSI value for the KCH_3CO_2 loaded demineralized coal sample seems to be due to a physical effect of forming a large amount of acetone vapour at the softening point of the coal, which ruptures the fluid coal pores, leading to a decrease in the FSI value. K_2CO_3 decreases the plastic behaviour of the vitrinite-rich medium rank B coal to a larger extent than KCH_3CO_2 .

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1. Introduction

Upon heat treatment, moisture and volatiles are released from coal to produce a porous solid called coke or char. Caking coals are bituminous coals that also fuse and re-solidify during heating [1,2]. During thermal processing caking coals undergo softening, fusing, swelling and re-solidification within specific temperature ranges [3]. Swelling causes char and coke with varying physical and chemical structures to be formed. The physical and chemical structures of the char or coke influence the coal conversion processes and the nature and amounts of products (gaseous and solid) that are formed [3]. Swelling of coal during the pyrolysis stage of

thermal processing is also associated with operational problems as it may result in excessive internal reactor pressure, which may lead to unsafe operating conditions [4]. During the fluid stage of thermal plastic behaviour of the swelling coal, agglomeration may occur, which renders the coal unsuitable for use in fixed-bed and fluidised-bed gasifiers. Agglomerated coal reduces the permeability of gases through the coal bed and causes channel formation [5].

Swelling of coal during the heating process occurs due to physical changes occurring, which results from chemical and physical reactions within the coal [6–8]. As described by Gale et al. [9], when coal is heated and starts to melt, volatiles are released and trapped within pores in the coal structure. As the temperature increases during the heating process, the volatiles in the pores expand, thereby also increasing the pore volumes and thus volume of the fluid coal. Swelling of coal is thus a result of the formation of high pressure areas occurring within the coal system, which cause swelling of coal with plasticity properties followed by the release of

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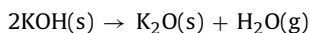
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the volatiles [10]. The amount of volatiles released from the pores in coal during the heating process will depend on how fluid the coal is during the process [11]. The fluidity of coal may be influenced by the conditions of the heating procedure and mineral matter in coal [11].

Inorganic matter within coal has a catalytic effect on coal thermal processing, influencing the nature and amounts of volatiles being formed during the chemical decomposition reactions, and thus also the swelling behaviour [6,7]. The degree to which the inorganic matter influences the coal behaviour during the heating processes depends on various characteristics of which the nature of the anion, attached to the catalyst's cation (in the case of an ionic compound), seems to be important. Alkali and alkali earth metal salts, (more specifically the oxides, hydroxides and carbonates) are shown to be catalytically more active with regards to coal thermal processing and have been found to also decrease the caking and swelling properties of certain non-South African coals [12,13].

A number of different potassium and calcium compounds have been investigated for their influence on coal properties and their ability to act as catalyst during heat treatments [6,10,12]. Of these compounds the potassium containing compounds were shown to give the best reactivity-enhancing results. To investigate the influence of the anion of the added potassium compound on the swelling behaviour of a vitrinite-rich South African coal, it was decided to add potassium hydroxide (KOH), potassium chloride (KCl), potassium carbonate (K_2CO_3) and potassium acetate (KCH_3CO_2) to a partially demineralised coal. Thermal decomposition of these potassium compounds also results in varying amounts of gaseous products at different temperatures being formed by the decomposing potassium salt.

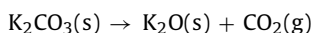
Potassium salts react differently when subjected to heat. When potassium hydroxide (KOH) is heated in an inert atmosphere, decomposition takes place and potassium oxide and water is formed during the following decomposition step [14]:



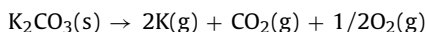
Literature indicates that KOH starts to decompose at a temperature of 380–406 °C, giving off 0.5 mol water vapour per mol potassium at this temperature [14]. KOH is also highly hygroscopic, forming KOH·H₂O, and is sometimes used as a dehumidifier. KOH·H₂O decomposes to KOH only at temperatures higher than 150 °C.

Similar to the thermal behaviour of NaCl, heat treatment of KCl in an inert atmosphere will cause the compound to evaporate at 1 atm at around 900 °C [15].

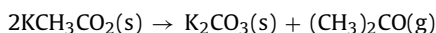
The thermal decomposition of potassium carbonate (K_2CO_3) will yield potassium oxide and 0.5 mol carbon dioxide per mol potassium around 900 °C, just below its melting point of 905 °C [16]. Literature also reports that potassium carbonate starts to evaporate just below its melting point [17].



Afzal et al. [16] reported that they found potassium carbonate to decompose to potassium metal in an inert atmosphere at 900 °C, with the potassium metal then evaporating:



Thermal decomposition of potassium acetate (KCH_3CO_2) occurs in two steps, where the first step results in the formation of solid potassium carbonate and 0.5 mol gaseous acetone per mol potassium at 400 °C [16]. The second step is similar to the mentioned thermal decomposition of K_2CO_3 .



Bexley et al. [6] found that the addition of alkali metal carbonates (Li_2CO_3 , $NaHCO_3$, Na_2CO_3 , $KHCO_3$, K_2CO_3 , $CaCO_3$, $SrCO_3$, Rb_2CO_3 and Cs_2CO_3) to a Manvers Wath vitrinite rich (78%) high swelling coal reduces the dilatation volume (thus swelling) until only contraction is observed. Bexley et al. [6] proposed that potassium carbonate reacts chemically with coal to change the plastic properties of the coal. The interaction may increase methylene cross-linking reactions and/or catalyse coal dehydrogenation, with a resulting reduction in plasticity [18]. Bexley et al. [6] postulated that potassium or sodium salts (carbonates, bicarbonates, and oxides) may also react with the coal's phenolic or carboxylate groups.

2. Material and methods

2.1. Sample preparation

A high swelling vitrinite-rich coal (medium rank-B) from the Tshikondeni mine (located in the Limpopo province) in South Africa was obtained. The coal was crushed to less than 75 μm and vacuum sealed. The sealed bags were stored at low temperatures, until the samples were needed, to prevent oxidation of the coal. An Elite thermal system TSH 12/75/610-2416CG + 2116 O/T furnace was used to prepare the coal char samples. The nitrogen flow through the tube was 100 ml/min. Sample masses of 30 g were subjected to a heating rate of 10 °C/min from ambient temperature up to a maximum of 900 °C. Once 900 °C was reached, the samples were cooled to room temperature under nitrogen.

2.2. Demineralization

The crushed coal was partially demineralized using a HCl/HF/HCl acid leaching technique as described elsewhere [19]. The demineralized coal was dried under vacuum at 60 °C and stored in a desiccator, under nitrogen until needed.

2.3. Potassium compound dopants

Pure (>99%) potassium hydroxide (KOH), potassium carbonate (K_2CO_3) and potassium acetate (KCH_3CO_2) obtained from Merck and potassium chloride (KCl) from Rochelle Chemicals, were crushed and dried under vacuum at 60 °C, to ensure that no absorbed water was present. A ball mill was used during the dry mixing of the dried alkali compounds and demineralized coal. Coal-alkali blends were prepared to contain 10 wt% of potassium (calculated as the metallic percentage in the blends) for the thermo-mechanical analysis and dilatometry, and 5 wt% potassium in the blends subjected to free swelling index analyses. To compare the influence of the different potassium compounds, the added weight percentage potassium was thus kept constant (and not the added weight percentage of the potassium salt). Each blended sample was prepared just before the sample was subjected to the experimental technique.

2.4. Ultimate and proximate analysis

The composition of the raw coal, demineralized coal and also the raw coal char, demineralized coal char and coal-alkali blended char samples were determined by the ASTM standard methods listed in Table 1. The demineralized coal-alkali blends were prepared with 10 K-wt% addition of the potassium compounds.

2.5. XRF analysis

XRF analyses were performed according to the ASTM D4326 standard method [25]. Analyses were done on the raw and demineralized coal and also on the raw coal char, demineralized coal

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