

QUANTITATIVE XRD ANALYSIS OF DIFFERENT COAL SAMPLES TO UNDERSTAND THEIR ASHING PROCESS DURING THE INITIAL STAGES OF COMBUSTION.

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ABSTRACT

Coals in general have very complex chemistry and depending on the intended usage, further challenges are experienced. Such challenges vary from the methods mining and cleaning that should be employed to yield the best quality coal for the specified usage and the final products which are produced from coal use. It is therefore very important to understand the chemistry of raw coal and the ashing properties of such coals and the information from this work can also assist in highlighting the environmental and health aspects that are linked to processing and usage of coal. This work focused on a qualitative studies using XRD to analyze five different coal samples and the chemistry change during the ashing process which takes place during the coal combustion process. An ashing process was conducted on the five samples at 350⁰C, 500⁰C, 750⁰C and 1000⁰C and their results where compared to the composition of the raw coal. The results from this work showed that there are a total of up to 40 major phase-mineral compositions found in the samples analyzed, of which some of them are one phase-mineral composition that appears as different phases/forms in the coal ash.

Key words: ash composition, XRD analysis, combustion, phase-mineral

1. INTRODUCTION

Coal in South Africa is used dominantly in electricity generation followed by the metallurgical industry and a smaller percentage in synthetic fuel. For these different intended usages of coal there are requirements from the user that coal producers should know and ensure that their beneficiation processes are able to effectively produce coals that meets those specifications. Before designing a coal processing and beneficiation method or the proper utilization it is very important to determine the

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different minerals contained in the coal body and their effects on the utilization processes. In so doing, coal producers should also be mindful of environmental pollutions that are associated with the production and usage of coal due to its mineral composition. Such environmental pollutions include the solid and effluents wastes generated in the beneficiation process, the waste produced in coal usage such as the fly ash, bottom ash and the off gases that are released (Winburn et al. 2000). All this requires a good understanding of the formation, mineral compositions and properties of coal associated with both beneficiation and utilization process. Previous research have been done on the compositions and properties of solid combustion waste from various coal fired power stations around the world (Vassilev et al. 2005), and emphasis was made on the importance of knowledge relating to the origin, utilization, environmental, technological problems and chemical and phase-mineral compositions associated with coal.

There are different analytical methods used to determine the minerals which can be used to determine the mineral composition of coal and there have been numerous authors who have studied these. Of these methods, powder X-ray diffraction (XRD) has been the most utilised (van Alphen 2007)(Winburn et al. 2000)(Saikia, Boruah, and Gogoi 2007)(Mahadevan 1940) (Ritz and Klika 2010). Scanning electron microscopy with XRF combination (SEM-XRF) is another method used widely (Ritz and Klika 2010)for determination of elemental individual minerals. There are also other sophisticated methods like Computer-controlled SEM (CC_SEM)as stated in (van Alphen 2007) (Ritz and Klika 2010)and automatic image analysis SEM (AIA_SEM) (Ritz and Klika 2010) and simple methods based on the recalculation of chemical analysis to normative minerals.

There are various limitations that are linked to the methods listed above, and such include XRD which has low detection limit for minerals with low ash content (Ritz and Klika 2010). Quantitative XRD analysis appears to be better suited for characterising complex materials (Winburn et al. 2000) like coal and coal ash which has many phase compositions.

Analysis of the waste products from coal combustions are just as important to understand as they are similarly complex in composition depending on the coal. The ash is formed from Inorganic matter in coal which includes (Ritz and Klika 2010) (Vassilev et al. 2005)(Zhang, Han, and Xu 2003) compounds dissolved in pore solutions in coal, chemical elements bonded to organic parts, and crystalline or amorphous form of minerals. Determination of qualitative and quantitative determination of organic minerals is impacted greatly by crystalline minerals (Ritz and Klika 2010).

Inorganic elements in coal is comprised of three group; major elements group (more than 1000 ppm concentration), minor elements group (between 100 and 1000 ppm concentration) and trace elements group (less than 100ppm concentration) (Zhang, Han, and Xu 2003). Of the latter elements groups; elements like Al, Si, Fe, Ca, Mg, Na, K, Cl and S are the typical major elements, elements such as Ba, P and Ti are the most common minor elements found in coal,(Zhang, Han, and Xu 2003) and there is a wide range of trace elements in coal and ash waste. The major elements are highly responsible for slag formation and environmental pollutions associated with coal combustion. Minor and trace elements do not have proven impact on the environment.

The current paper is aiming at ashing the coal sample at different temperatures to assess the improvement that can be made in the detection limit of the studied samples. Objectives of this work is to characterise and understand phase-mineral and chemical compositions of the different South African coal, and to predict potential possible environmental concerns related to ash formed from this coals.

2. EXPERIMENTAL

2.1 Sample preparations

Five different coal samples from around South Africa where used for this study. The samples where ground to powder form. The samples where split using a rotary splitter and packaged, and samples of approximately 1g were taken for the different test performed. Proximate analysis was conducted to obtain the moisture content, volatile matter, ash composition and calorific value.

2.2 Combustion process

A temperature controlled furnace was used to ash the samples at the different temperatures. The furnace was preheated to the stabilised required temperature. A crucible containing the samples was placed in the furnace for 90 minutes. The samples were left to cool down in ambient temperature overnight. The samples were analysed using XRD in the in-house laboratory.

3. RESULTS AND DISCUSSIONS

Organic and inorganic matter in coal can be identified easily because of the colour difference even from a naked eye. This is shown by Figure 1 depleting difference in reflection and dullness in colour, at the same time indicating complexity in composition of a single coal particle.



Figure 1: Coal Samples with mineral matter and different maceral compositions.

3.1 Characterisation of coal samples

Proximate analysis was conducted on the initial coal samples for percentage moisture, volatile matter (VM), ash composition and calorific value (CV). This were conducted five times on the same conditions and the average results are tabulated below.

Table 1: Proximate analysis results for the 5 samples considered.

Sample	%Moisture	% Vol Matter	% Ash	Fixed carbon	CV
1	6.15	22.32	20.70	50.82	23.63
2	2.86	17.15	38.75	41.24	18.23
3	7.35	22.39	24.60	45.66	20.91
4	4.29	23.04	31.29	41.37	20.30
5	7.35	22.12	24.36	46.17	20.59

From the proximate analysis all of the sample had displayed similar results except for sample 2 with less than 3% moisture content while the reset are between 4% and 8%, they also have between 22%-23% volatile matter while sample 2 has only 17% volatile matter. In terms of percentage ash, sample two is still the odd one out at above 38% while the rest are between 20-31%. The same behaviour is displayed on CV and the only composite of coal that displayed a different behaviour even though still the lowest fixed carbon was closer to sample 4.

3.2 Evaluations of minerals in the samples by XRD

XRD analysis yielded 40 inclusive phase-minerals were observed in the samples. During the combustion process the first stage is characterised by decompositions of coal organic components followed by the release when ignited as per the combustion process. This work was conducted to understand the volatilization or release of major elements at different temperature and their modes of occurrence, concentration, physical changes and chemical reactions that takes place during the

combustion process. This was assessed by the amount of phase minerals detected on the raw coal as compared to what is detected on various ash compositions analysed by XRF.

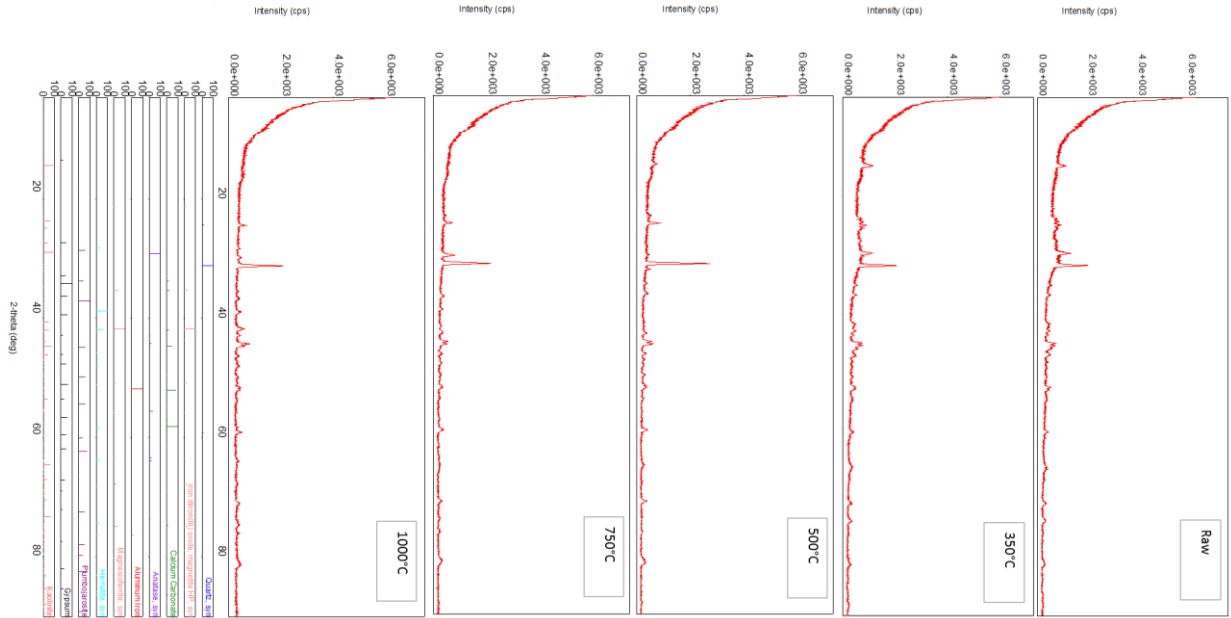


Figure 2: Chemical profiles as analysed using XRD indicating phase mineral peaks at different temperatures for sample 1

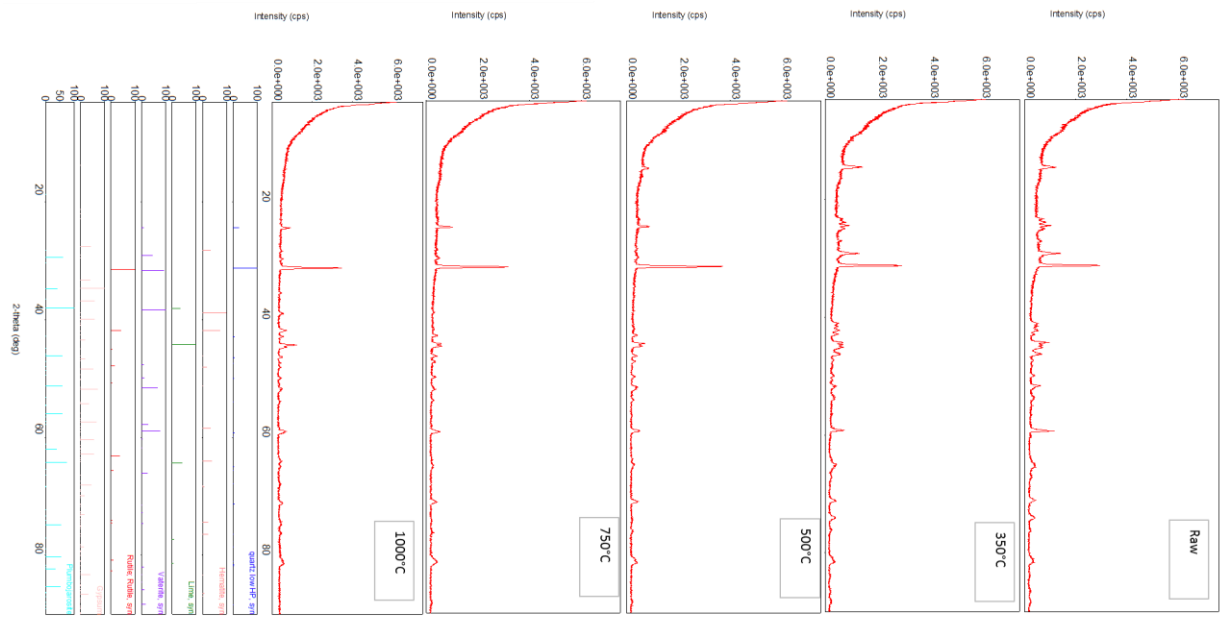


Figure 3: Chemical profiles as analysed using XRD indicating phase mineral peaks at different temperatures for sample 2

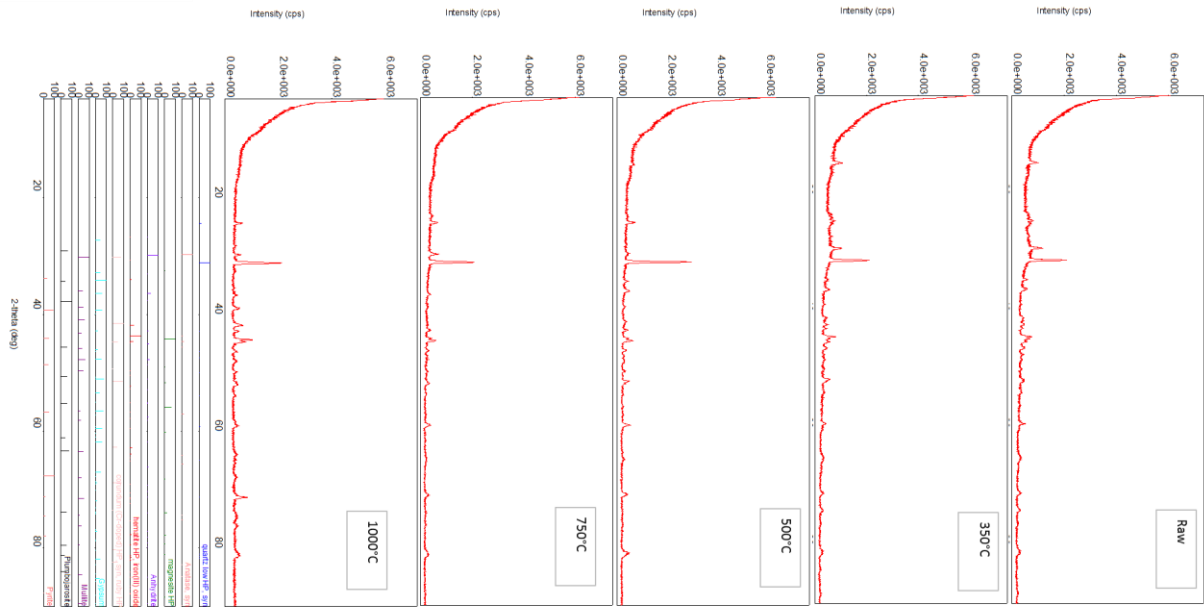


Figure 4: Chemical profiles as analysed using XRD indicating phase mineral peaks at different temperatures for sample 3.

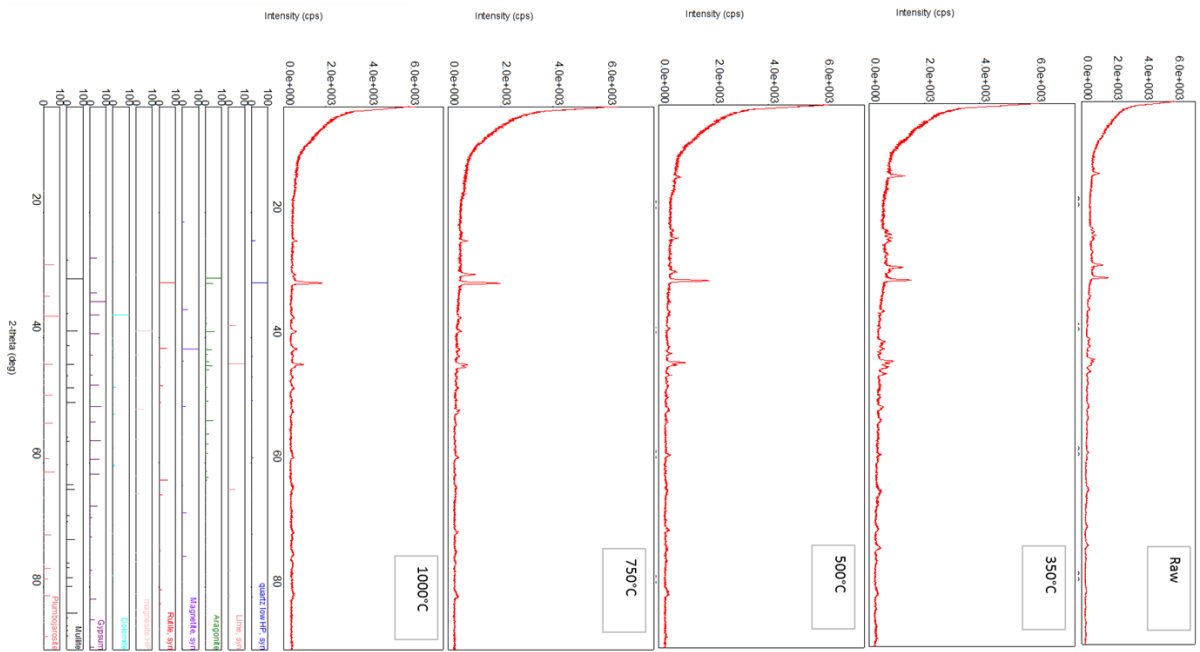


Figure 5: Chemical profiles as analysed using XRD indicating phase mineral peaks at different temperatures for sample 4

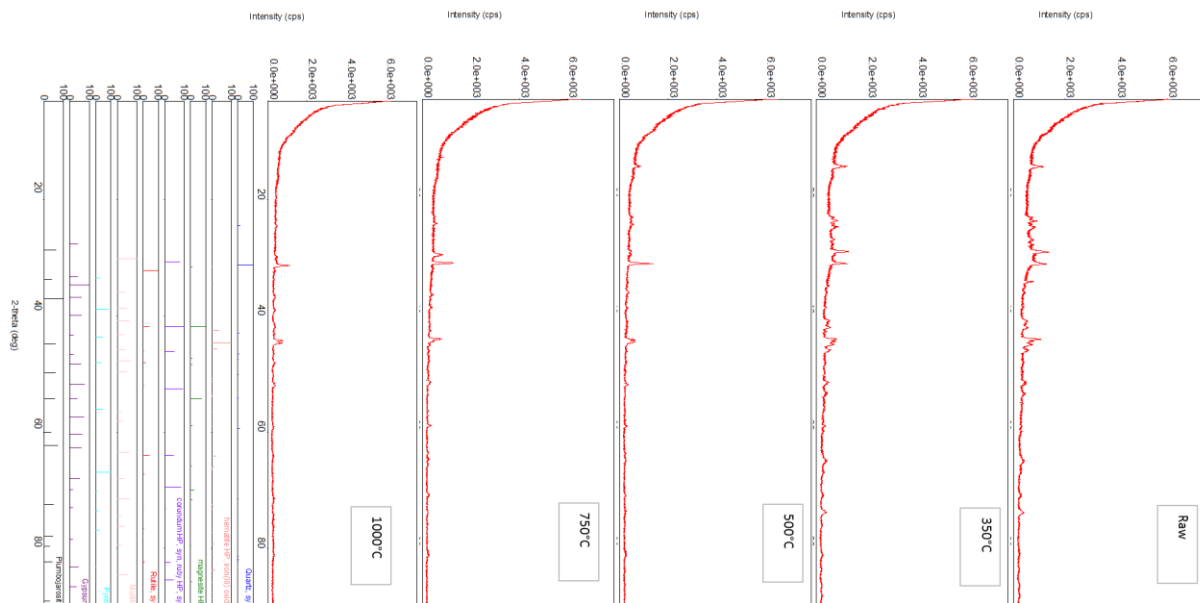


Figure 6: Chemical profiles as analysed using XRD indicating phase mineral peaks at different temperatures for sample 5

From the results it can be seen that aluminium appears as part of two phase minerals (Aluminium Iron and Kaolinite. From the two phase minerals there are no traces of Aluminium Iron detected on raw coal and those combusted at lower temperatures from (350-750°C), the only observation of this mineral is at 1000°C. When compared to Kaolinite, smaller content where detected at lower temperatures and a higher amount at 1000°C.

Silicon was observed in four phase minerals where Calcium Silicon oxide was observed in higher temperatures and Monticellite, HP at lower temperature but the other occurrence being Kaolinite and Quartz are observed on all temperatures. Calcium Silicon oxide is formed from reactions of coal compositions and this reaction of formation from Lime and Quartz according to the following reaction (Wang et al. 2016);



The relationship of Monticellite and Calcium Silicon oxide is illustrated by the equilibrium phase diagram where they exist together but one decreases in weight% as the other increases. This explains the results were either one is found at lower temperatures and the other at high temperature respectively.

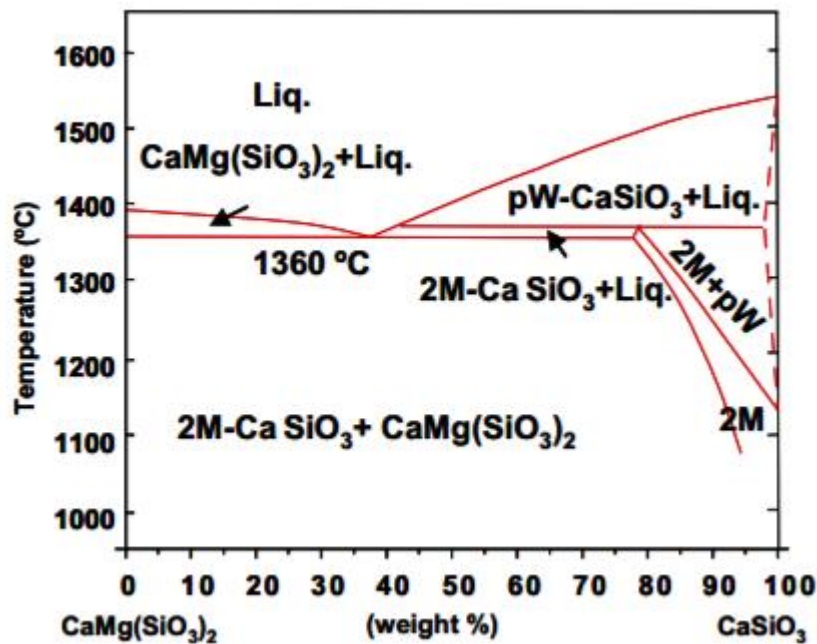


Figure 7: Phase equilibrium diagram of the join W–D of the ternary system SiO₂–CaO–MgO (Diba et al. 2014)

From the phase equilibrium above, it is evident that most of the SiO₂-CaO-MgO phase minerals exists together and this is proven by the obtained results. Their compositions even at the low ash temperatures investigated in this work is always vice-versa for example where compositions of Monticellite is higher there is lower composition in %weight of Calcium Silicon Oxide . This behaviour is noted by the results were either one will be observed at any temperature.

4. SUMMARY

From the proximate analysis, sample 2 is the least desirable as it has higher ash content, low volatiles and lower CV as compared to the other samples.

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