HIGH TEMPERATURE BEHAVIOR OF PCI COAL ASHES AS FUNCTION OF CHEMICAL AND MINERALOGICAL COMPOSITION – EXPERIMENTAL AND COMPUTATIONAL ANALYSIS[1]

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Abstract

The selection practice of coals for PCI is generally restricted to the evaluation of the carbonaceous matter. However, the loss of permeability in the lower region of the blast furnace, for high rates of PCI, can usually be related to the ashes of the coal combustion process. This work is intended to evaluate the behavior of the coal ashes in high temperatures relating it to their chemical and mineralogical compositions. The coal ashes were subjected to the following analysis: chemical (XRF), mineralogical (XRD), fusibility (heating microscopy) and viscosity (rotational viscometer). The software *FactSage* was also used to help understanding of the coal ashes behavior. The samples showed distinct chemical and mineralogical compositions. This, consequently, reflected in the fusibility and viscosity behavior of the coal ashes. Phases and their proportions were determined with the help of computational thermodynamics and related to the experimental work.

Key words: PCI; Coal ashes; Computational thermodynamics.

COMPORTAMENTO DE CINZAS DE CARVÕES PARA PCI EM ALTAS TEMPERATURAS EM FUNÇÃO DA COMPOSIÇÃO QUÍMICA E MINERALÓGICA – ANÁLISE COMPUTACIONAL E EXPERIMENTAL

Resumo

A seleção de carvões para PCI usualmente consiste na avaliação da matéria carbonosa. No entanto, o decréscimo de permeabilidade na região inferior do alto-forno, para elevadas taxas de PCI, pode estar relacionado às cinzas remanescentes da combustão do carvão. O objetivo deste trabalho foi avaliar o comportamento das cinzas de carvão em altas temperaturas, relacionando-o com a composição química e mineralógica. As seguintes análises foram realizadas: química (FRX), mineralógica (DRX), fusibilidade (microscópio de aquecimento) e viscosidade (viscosímetro rotacional). O aplicativo *FactSage* também foi utilizado para avaliar o comportamento das cinzas de carvão. Verificou-se que as amostras têm diferentes composições químicas e mineralógicas, o que se reflete na fusibilidade e na viscosidade das cinzas. As fases pertinentes e suas proporções foram determinadas através da termodinâmica computacional, e relacionadas com os experimentos realizados.

Palavras-chave: PCI; Cinzas de carvão; Termodinâmica computacional.

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1 INTRODUCTION

The Pulverized Coal Injection (PCI) technique, consolidated worldwide, stands out as an attractive technology for a cleaner production of iron by the blast furnace route. The injection of pulverized coal through blast furnace tuyeres promotes the formation of reducing gases, allowing for the partial replacement of coke.[1] The coke in turn is the raw material of greater cost in the production of pig iron and is the primary source for environmental damage caused by the steel industry.[2] There is, therefore, a general objective of achieving high rates in PCI, in order to reduce both the pig iron production cost as well as the environmental impact caused by the coking plants.[3]

Meanwhile, some operational difficulties slow down the implementation of high rates of PCI in the blast furnace. One of these problems is the loss of permeability in reactor bottom, which causes operational instabilities and productivity losses.[4] Some experts[5,6] point out the possibility for this phenomenon to be related to the inorganic matter (ashes) remaining of the coal combustion. It is believed that the loss of permeability results in part from the influence of the PCI ashes on the bed of coke (deadman) before they are incorporated into the process slag.[5]

At the same time as studies and practice of selection of coal employed in PCI concentrate their investigation efforts on the carbonaceous matter, the evaluation of inorganic matter is generally limited to few aspects: ash, alkalis, sulfur and phosphorus content.[7] It is believed, however, that in order to optimize the BF coal injection rates a detailed knowledge of *both* organic as well as inorganic matter is required.[6]

Ashes remaining from coal combustion are a complex mixture of crystalline and amorphous phases without a melting point set. The composition of the inorganic fraction coal is characterized by a combination of a wide variety of oxides, including SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, K_2O and Na_2O. The grouping of these oxides is related to some mineral phases, such as quartz, clays, feldspars, calcium silicates, hematite and anhydrite, which are usually found in the coal ashes.[8] However, when inorganic coal matter melts, it consists primarily of a silicate liquid, forming a chaotic mixture of anions and cations.[9] Ash fusibility and viscosity are the properties normally used to evaluate the behavior of the coal inorganic matter at high temperatures.[10]

Coals already assessed in a previous study were analyzed in this work.[11] Regarding the carbonaceous matter, they showed combustibility behavior (via thermobalance and DTF (drop tube furnace) suitable for injection. Though they did not demonstrate equivalent performance in blast furnaces.

Recalling the factors described so far, the purpose of this study is to evaluate the behavior of ashes (from coals for PCI) at high temperatures, linking it with ash mineralogy and chemical composition. The advancement of the knowledge in this area aims to improve the screening of coals for injection into blast furnaces in order to provide high injection rates without the resulting operational instability.

2 METHODOLOGY

2.1 Raw Materials

In this study, ashes of four different types of coal for PCI (ash content <10%) were analyzed. Data on them can be seen in a previous work.[12]

2.2 Experiments and Analyses

In order to generate the ashes, samples were submitted to a combustion process in air at the temperature of 850ºC for two hours in muffle type oven.

Ashes obtained under these conditions were characterized by the following techniques:

- X-ray fluorescence, XRF (determines qualitatively and quantitatively the major elements contained in samples); and
- X-ray diffraction, XRD (identifies the crystalline phases over 5% in the material – that figure may vary, however, depending on the crystallinity stage).

The fluidity behavior was evaluated by the following tests:

- Fusibility test: determines critical temperatures that occur at specific deformation stages (softening, hemisphere and flow temperature) during the heating of probes produced with coal ashes. These tests were performed with a heating microscope according to DIN 51730, with cylindrical test probes (h = 3mm, ext. diam. = 3mm) in an oxidant atmosphere (air);[13]
- Viscosity test: measures the viscosity of the fluid as a function of the temperature. This test was conducted on a high temperature rotational viscometer (coupled to a data acquisition system) under an atmosphere of CO_2.

2.3 Computational Analysis

The FactSage 5.5 thermodynamic software package as well as FACT group databases[14,15] were used in the present work to determine equilibrium states for the coal-ash systems.

The FToxid solution database (FToxid53Soln.sda) contains oxide solutions evaluated/optimized by the FACT group. The most important phase in this database for the present work is the liquid slag (FToxid-SLAG), which includes the following constituents: Al, As, B, Ca, Co, Cr, Cu, Fe, Ge, K, Mg, Mn, Na, Ni, Pb, Si, Sn, Ti, Zn, Zr and also dilute S, SO_4, PO_4, H_2O/OH, CO_3, F, Cl, I.

Another database used, which can be coupled with the previous, is the FToxid compound database (FToxid53Base.cdb). It contains all stoichiometric solid and liquid oxide compounds evaluated and optimized by the FACT group to be thermodynamically consistent with the FToxid solution database.

A third database is the FACT53 (FS53Base.cdb) general compound database, which includes data for over 4500 compounds (pure substances). It contains data for those compounds which have been evaluated and optimized to be thermodynamically consistent with the FACT FToxid and other solution databases.

The equilibrium state of the system was determined as a function of the temperature. Temperature range was defined to vary accordingly to the experiments and lies between 1200 and 1600 ºC.

3 RESULTS AND DISCUSSION

3.1 Ash Characterization

The several techniques of analysis used to characterize the ashes allowed to detail the properties concerning the inorganic matter remaining from the combustion of coals under study.

3.1.1 XRF- Chemical analisys

Table 1 presents the ashes chemical compositions obtained by the X-ray fluorescence technique (XRF); element content is given as oxides.

Table 1: Ashes chemical compositions as per XRF-technique

Components	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_4	I.L.*
Sample 1	70,70	18,47	5,87	0,86	0,92	0,33	1,41	0,61	0,26	0,84	0,65
Sample 2	59,13	20,97	7,66	2,70	2,68	0,44	1,81	0,82	0,10	3,46	1,30
Sample 3	42,00	34,20	8,30	1,10	4,00	0,72	2,00	1,84	1,90	1,98	1,77
Sample 4	42,62	34,51	4,87	1,48	6,71	0,55	0,37	2,03	0,09	3,93	1,85

** I.L.=Ignition loss at 1000^{o}C*

Silicon and aluminum appear as major elements to all ash samples. It is worth mentioning, however, that variation in oxide proportion is relevant; Sample 1 is the richest in silicon while Samples 3 and 4 are richer in aluminum.

In a secondary position are the elements iron and calcium; their proportion vary in a significant way in the ashes under study. The content of iron is higher in Sample 3 (8.30%) while the amount of calcium is higher in Sample 4 (6.71%).

Other elements are present in irrelevant quantities. Nevertheless, the existence of different mineral phases can be explained by the dissimilar proportion of those elements in ashes. The Mg content – much higher in Sample 2 –, or P in Sample 3 and S in Sample 4, are examples of differences with regard to minority elements contained in ashes.

3.1.2 XRD - Mineralogical analysis

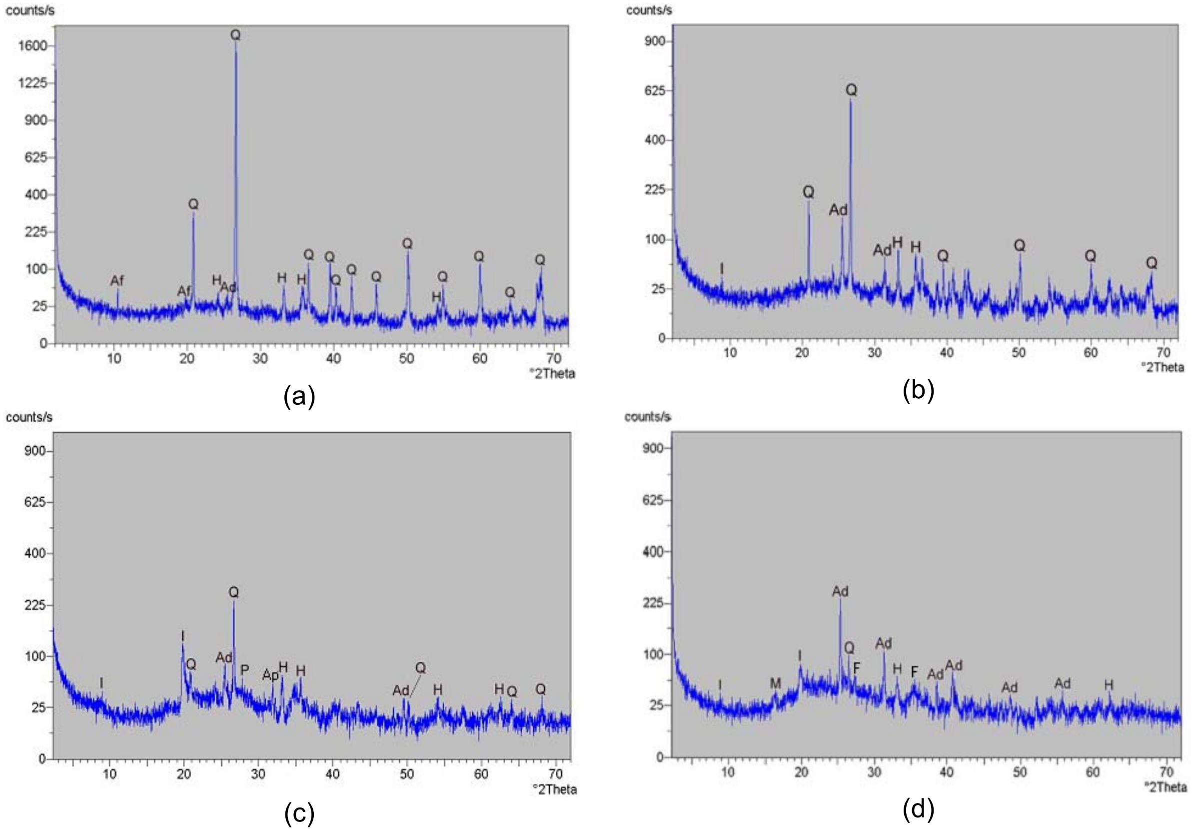
Since ash can be seeing as a kind of 'concentrate' made up of the inorganic matter present in coal, it opens the possibility to identify the minerals present in coal bellow the XRD-threshold concentration (the carbon matter acts as a 'solvent'). This, however, is not a simple task because the combustion process (performed at 850ºC) produces a number of changes (phase changes, breakdowns and reactions) that alters the original coal mineralogy.

In diffractogram of Sample 1 (Figure 1a) the following minerals were identified: quartz, hematite, anhydrite and amphibole. In Figure 1b, referring to Sample 2, phases which are similar to Sample 1 (quartz, hematite and anhydrite) were detected, with the distinction that, instead of amphibole phase, illite was found. In Sample 3 (Figure 1c) alongside with phases which are common to Sample 2 two new phases were identified: plagioclase and apatite. Sample 4 exhibits quartz, anhydrite, hematite and illite and, as Figure 1d shows, plus mullite and potassium feldspar.

In a general way the phases illite, apatite, albite, potassium feldspar, mullite and amphibole exist in lower quantities than the phases quartz, anhydrite and hematite, according to the elementary proportions of the oxides K_2O, P_2O_5, Na_2O e MgO. These proportions are determined by XRF and XRD (intensity of peaks).

Regarding quartz it is possible to get a semi-qualitative analysis according to the intensity of the main peak of this mineral at difratograms and by XRF results. From these data the quartz amount decreases in the sequence: sample 1 > sample 2 > sample 3 > sample 4.

Amount of anhydrite probably is proportional to calcium and sulfur quantities, which are showed by XRF analysis. Thus Sample 1 and Sample 4 are the ones with lower and higher anhydrite content, respectively.



(a) (b)

(c) (d)

Figure 1.X-Ray diffractograms of ashes from Samples 1 (a), 2 (b), 3 (c) e 4 (d).
Key for minerals: Q= quartz - SiO_2; H= hematite - Fe_2O_3; Ad= anhydrite - $Ca(SO_4)$; P= plagioclase (albite) $NaAlSi_3O_8$; M= mullite - $Al_6Si_2O_{13}$; F= Potassium feldspar - $KAlSi_3O_8$; Af= amphibole - $Ca_2Mg_4Al_{0,75}Fe^{3+}_{0,25}(Si_7AlO_{22})(OH)_2$; I= illite - $K_{0,5}(Al,Fe,Mg)_3(Si,Al)_4O_{10}(OH)_2$; Ap= apatite - $Ca_5F(PO_4)_3$

The mineral kaolinite, which is found in all kinds of *in natura* coal, suffers dehydration and turns into metakaolinite (amorphous) after combustion; in this way its identification by XRD is prevented.[8] The mineral phases which contain aluminum such as illite, albite, potassium feldspar, mullite and amphibolite are present in low quantities. Then it can be suggested that, according to aluminum content of ashes, the amount of metakaolinite decreases following the sequence: Sample 4> Sample 3> Sample 2> Sample 1.

3.2 Assessment of Fluidity Behavior of Ashes

From fusibility and viscosity tests, which were conducted for the four coals, it was possible to assess the behavior of the inorganic matter of these coals when they were exposed to high temperatures.

3.2.1 Fusibility test

Fusibility test permit to assess the softening and fusion behaviors of the coal ashes which are also related with the fluidity characteristics of the samples. Figure 2 show fusibility test results for samples 1, 2, 3 and 4.

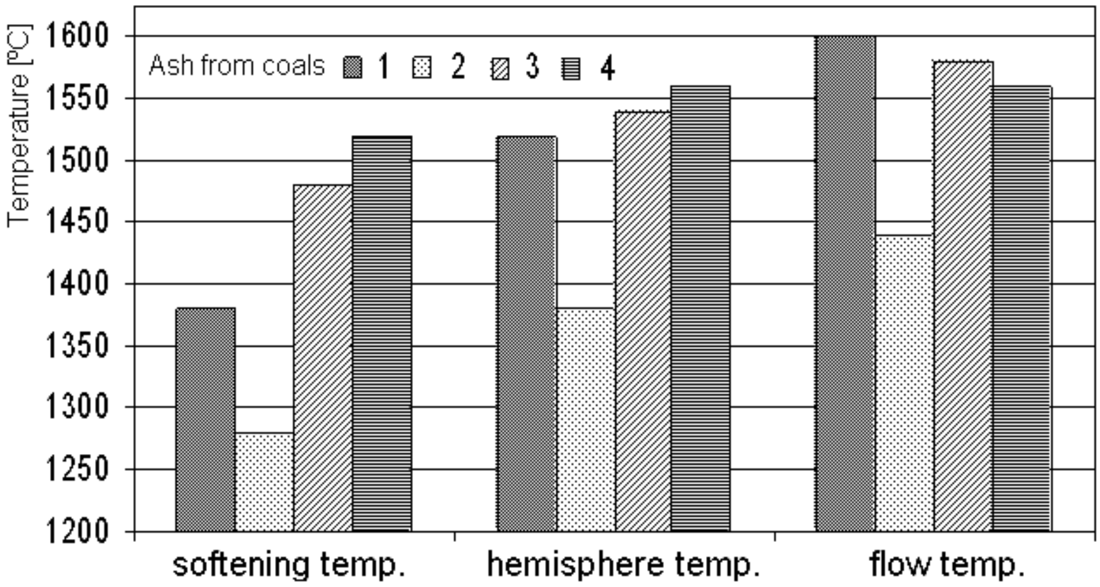


Figure 2. Fusibility test results

According Figure 2 different behaviors can be seen. Besides temperature differences in each fusibility stages, there are distinct ranges between softening temperature (T_s) and flow temperature (T_f). These ranges are also relevant data for this study.

Sample 2 was the one which got the lower fusibility temperature at all stages. Around 1280°C sample 2 has already been softened and around 1440°C it has reached the flow temperature. The resulting range $T_f - T_s$ is 160ºC.

Regarding sample 1, an intermediate behavior with respect to softening and hemisphere temperature (T_s = 1380°C e T_h = 1520°C) can be verified. However, this sample has got the higher flow temperature (T_f = 1600°C), which causes a long range from softening to flow temperatures ($T_f - T_s$ = 220°C).

The samples 3 and 4 have showed a similar behavior, that is, they have got high softening (1480 e 1520°C, respectively) and hemisphere (1540 e 1560°C respectively) temperatures. However, the flow temperatures of these were lower than sample 1. The ranges $T_f - T_s$ of samples 3 and 4 are 100°C e 40°C, respectively. These ranges are shorter than the ones of samples 1 and 2.

In the following the points of greatest interest in this study (softening and flow temperatures) are discussed in terms of chemical and mineralogical composition.

- **Softening point**

Regarding softening point, deformations of samples come from transformations of minerals and phases, solid-solid reactions, softening and local fusion of some minerals.[8]

Usually the softening temperature is related to the illite fusion (1000 – 1300ºC) and to the initial softening of quartz (~1300ºC), when these phases are present in the mineralogical composition of ashes. The lower softening temperature of sample 2 is probably related to the presence of the phases quartz and illite. However sample 1, which has got more quartz, showed higher softening temperature then sample 2. To explain this behavior it can be suggested the presence of mineral amphibolite instead of illite caused an important influence. In the case of samples 3 and 4, the low content of quartz and the high content of aluminum indicate the importance of the refractory phase metakaolinite, which has got an elevated fusion temperature. Thus there is an explanation for the higher softening temperature, although the presence of illite.

- **Flow point**

The flow temperature is usually related to the solution of the high melting point phases (refractory ones) such as metakaolinite and quartz.[8]

Sample 1 has exhibited the highest flow temperature and the highest range $T_f - T_s$ among the samples. These facts can be explained by the high content of quartz and low levels of fluxing as indicated by XRF and XRD. Regarding sample 2, the balanced quantities of quartz and metakaolinite, associated with the fluxing illite, hematite and anhydrite probably have contributed to diminish the flow temperature of these ashes.

With respect to samples 3 and 4, low levels of quartz and action of products from decomposition of anhydrite (Ca and S) explain the flow temperature lower than sample 1 even with the presence of metakaolinite at a significant amount.

Furthermore, the highest amount of calcium and sulfur and the lowest amount of quartz contained in sample 4 probably have contributed to a range $T_f - T_s$ lower than sample 3.

3.2.2 Viscosity test

The viscosity tests have allowed observations on the fluidity behavior of ashes at high temperatures. The viscosity is intrinsically related to the nature of chemical bonds of fluid.

Figure 3 shows experimental values of viscosity (Poise) in function of temperature (°C) for the four samples. The maximum temperature which was used in the viscosity tests was approximately 1650 ºC.

In a general way, increasing temperature decreases viscosity of the samples. However, it can be noted at Figure 3 that the variation of viscosity in function of temperature is different for each sample. The temperature at which the sample becomes fluid also varies for each sample.

Making a link between viscosity test and fusibility test is a way to confirm and to complement the obtained results of each technique. However, it is important to note that the different conditions of each technique do not give a precise relation between them but the trends.

During viscosity tests sample 2 has reached the flow point around 1400ºC, that is, at lower temperatures than samples 1, 3 and 4. It can be verified sample 2 presents lower viscosity values than the other samples for all the range of temperatures; at 1600 ºC the measured viscosity reaches 10 P. This result is in line with the lowest fusibility temperatures of sample 2.

According to Figure 3 Sample 1 begins to flow around 1480ºC, which is a temperature higher than the initial flow temperature of sample 2 and lower than the flow temperatures of samples 3 and 4. However, sample 1 has got high viscosity values even in temperatures close to 1600ºC. The long range between softening temperature and flow temperature of sample 1 at fusibility test is coherent with this viscosity behavior.

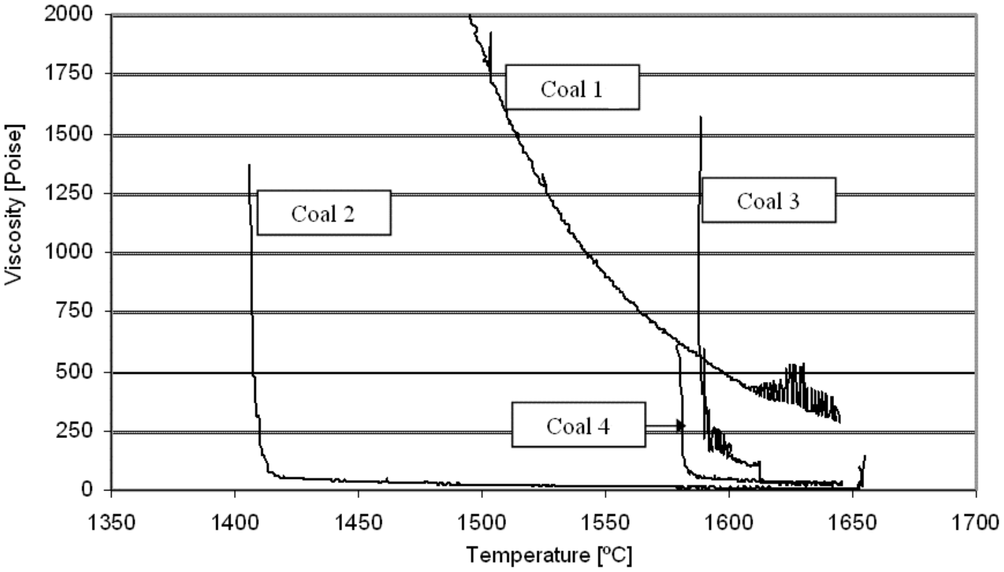


Figure 3. Viscosity (measured values) of coal ashes as function of temperature

Samples 3 and 4 have reached the flow point at 1580ºC and 1590ºC, respectively. However, when they become fluid the ashes have showed a steep drop of viscosity according to a small increase at temperature. At 1600°C the viscosity values for samples 3 and 4 are 145P and 43P, respectively. From 1615ºC there are no great differences with respect to viscosity of these samples – the values remain around 30 P. The high softening and hemisphere temperatures and the short range T_f - T_s of these samples (fusibility test) are coherent with these results.

The following is an analysis of viscosity according to chemical composition, since in the liquid state there are no mineral phases but a disorderly association of elements.

- **Viscosity x chemical composition**

High silica content and low levels of fluxing such as calcium and sulfur probably are the factors of greatest influence in the verified behavior of Sample 1. According to literature[9] the chemical bonds of silica network are very cohesive even at high temperatures. Thus, the flow of material is more difficult.

With respect to samples 3 and 4 is likely that high content of aluminum is the main cause of high flow temperatures. On the other hand, the low silicon content and the stronger presence of calcium and sulfur probably cooperate for the slight decrease in viscosity of these samples after they become fluid.

The verified differences between sample 3 and sample 4 up to 1615ºC is likely to be assigned to the highest level of calcium (network modifier) and lower level of phosphorus (network builder) of sample 4.

The ratio SiO_2/Al_2O_3 of sample 2 is an intermediate value when a comparison is made among samples 1, 3 and 4. Then, the lower silicon content of sample 2 in relation to sample 1 causes lower fluid viscosity, whereas the lower content of aluminum of sample 2 in relation to samples 3 and 4 causes lower flow temperature. Furthermore, other elements such as magnesium, calcium and sulfur probably act as fluxes (network modifiers) in sample 2.

3.3 Computational Analysis

From the results of equilibrium determinations two types of analyses were made. First, a simple classification of each phase as solid or liquid phase was made and the phase mass was summed up accordingly in order to give the total amount of both types. Results were plotted as a function of the temperature. Second, the mass of every single stable phase was depicted, again, as a function of temperature.

As can be seen in Figure 4, regarding to the first analysis type, computational thermodynamic results uncover two different kinds of behavior. The first one is depicted by samples 1 and 2, and the second by samples 3 e 4.

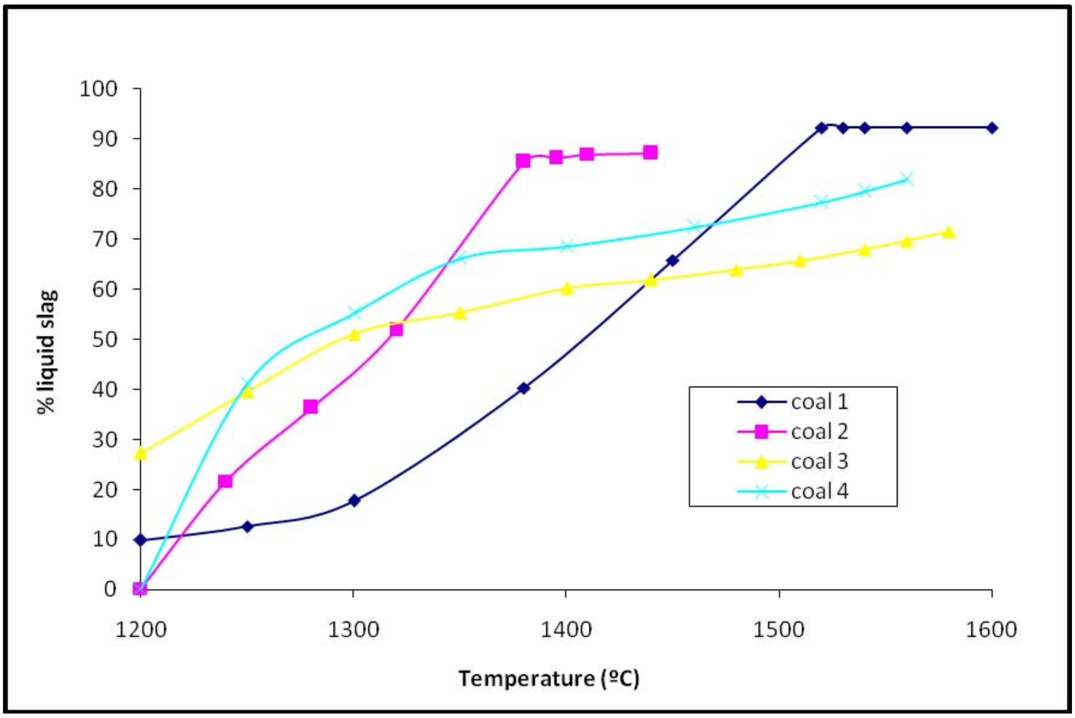


FigurE 4. Slag liquid fraction as a function of the temperature

Basically, the liquid slag fraction, both from ashes related to samples 1 and 2, grows steadily up to a plateau temperature, while liquid fraction from the other two coals (samples 3 and 4) has a lesser growing rate and shows no liquid fraction limit within the used temperature range.

In order to understand these behaviors, it is necessary to do a division and carry out an analysis considering each of the different system phases. For curves representing samples 1 and 2, it can be seen in Figure 4 the effect of higher content of silicon, with regard to the greater inclination of the curve %liquid slag / Temperature (ºC). It can be seen that the higher the amount of Si (as per the XRF analysis) the greater the amount of solid phase tridymite (see also Figure 5). With an increase in temperature, however, the amount of tridymite reduces because silicon is transferred to the liquid, as can be seen by increase in the amount of liquid slag. This is in agreement with the low softening temperatures measured for the silica-rich samples 1 and 2. The decomposition of silica happens for temperatures lower than for the other phases (in relation to mullite, for example).

For curves corresponding to samples 3 and 4 it can be seen in Figure 4 the effect of higher aluminum content in the lower slope of the curve %liquid slag / Temperature (ºC). Thus in respect to Al_2O_3 (as per the XRF analysis) a similar behavior was found: the higher the amount of alumina, the greater the amount of solid phase mullite (Figure 5). However, alumina is not so easily transferred to the liquid, since mullite is a more refractory phase. This is in agreement with the high softening temperatures measured for the alumina-rich samples 3 and 4.

Even after combining the coals into two different categories there are differences between the coals in the same category, due to differences in quantities of fluxing compounds (oxides of iron, sulphur, etc). Thus the special behavior of sample 2, which was determined by ash fusion tests and by viscosity tests, was also confirmed by the previsions of computational thermodynamics.

Figure 5 shows the amount of the most important phases (%mass) for the four coals as function of temperature. Through this figure it can be noted the modification in the proportion of the phases (which depends on composition of coals and temperature).

There are another solid phases which are not showed in this figure since they exist in lower amounts: Fe_2O_3, $KAlSi_2O_6$, $CaAl_2Si_2O_8$, Fe_2O_5Ti.

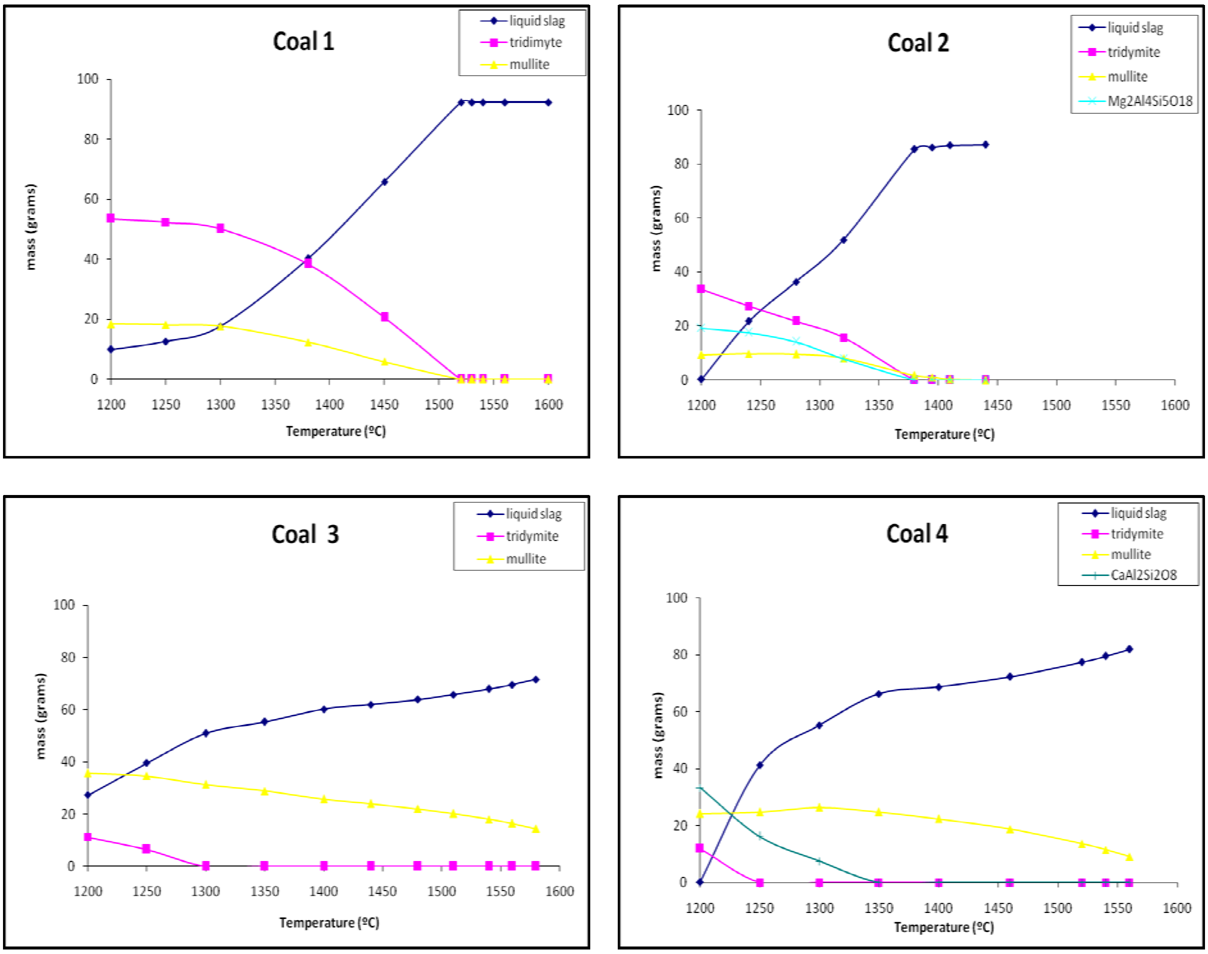


Figure 5. Amount of phases as function of temperature, for the four analised samples.

4 CONCLUSIONS

In the present work four types of coal ashes were characterized and analyzed regarding to the fluidity behavior. It was found that the analysis via computational thermodynamics provides insight into specific mineral interactions and slag formation.

There are, for these samples, different fluidity behaviors as described below:

- the coal ash 2 (sample 2) shows the lowest fusibility temperature and the lowest value of viscosity in the measured range of temperature;
- the coal ash 1 (sample 1) is the most slimy, since there is a long range T_f - T_a obtained by the ash fusion tests and also because of the high values of viscosity measured for this sample, even in temperatures close to 1600 ºC.
- the ashes generated by coals 3 e 4 (samples 3 and 4) have showed similar fluidity behavior, both of them with high softening temperatures (indicated by the fusibility test) and flow temperatures (viscosity test). However, before they turned fluids, it was observed a dramatic fall in the viscosity of these samples as function of a small increase in temperature.

There is a significant influence of the chemical and mineralogical composition on the physical behavior of fluidity of the coal ashes, where variations of the chemical elements are related to the formation of phases with very different properties. Essentially, high levels of quartz tend to impede the flow of ash while the high content of aluminum results in greater quantity of refractory phase mullite, which has got high temperature of melting, resulting in higher temperatures of softening and fluidity. The change in the proportion of these phases, depending on the composition of coal and temperature, was verified by computational thermodynamics.

Finally, the coal ash 2 presented the best performance for the technique of PCI, since it was fluid and with the lowest values of viscosity in lower temperatures, when compared to the others coal ashes.

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