Asian Journal of Chemistry; *Vol. 26, No. 6 (2014), 1583-1586*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17293

Melting Behaviour of Huainan Coal Ash in Reducing Conditions†

HANXU LI[1], YONGXIN TANG[2] and CHENGLI WU[1,*]

[1]School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, Anhui Province, P.R. China
[2]School of Science, Anhui University of Science and Technology, Huainan 232001, Anhui Province, P.R. China

*Corresponding author: Fax: +86 554 6668090; E-mail: chlwu2@163.com

Published online: 10 March 2014; AJC-14836

Computer-controlled scanning electron microscope analysis show that the mineral matter in Huainan coals are characterized by higher aluminosilicate clay minerals contents (more than 60 % of the total mineral matter in coal) together with quartz, which accounts for their higher ash flow temperatures, often higher than 1500 ºC. The transformation of mineral matter tested by XRD shows that, as temperature increasing from 1150 to 1450 ºC, quartz phases decrease sharply and anorthite contents show the tendency first increased greatly then decreased. Differences in peak intensity of mullite and anorthite reflect differences in phase concentration of the quenched slag fractions, which contribute to the difference of ash melting temperature. The addition of CaO at a low content around 8 % may increase the melting temperature of HN115 and HN119 coal ashes somewhat. With the increase of its addition, the melting temperature of ash initially decreases gradually, reaching its minimum value at the amount of CaO around 25 % and however increasing again with the further addition of CaO. This phenomenon is consistent with the theoretical thermodynamic equilibrium considerations.

Keywords: Huainan coal, Gasification, Melting behaviour, Flux.

INTRODUCTION

Mineral composition of coal play an important role in slag discharge in commercial gasification system[1,2]. In slagging gasifiers, the ash chemical and physical characteristics in coal and the slag viscosity *versus* temperature characteristics become very important in coal selection[3]. As the mineral matter controls the melting behaviour in high temperature gasification process[4], it is essential to know the proportion of each mineral matter in coal. The overall goal of this study is to investigate the fundamental knowledge of mineral matter characterization of Huainan coals for better understanding the ash melting behaviour under reducing condition in gasification.

EXPERIMENTAL

Twenty coal samples were ashed in air at 810 ºC for determination of the ash composition. The chemical compositions of the ash samples detected by Rigaku X-ray fluorescence and the melting temperatures of coal ash samples are presented in Table-1. Six typical coal samples were analyzed by JEM-5600 with CDU-LEAP SEM-EDX and computer-controlled scanning electron microscope. For computer-controlled scanning electron microscope analysis, three magnifications, 150 for the 22.0-211.0 mm, 250 for the 4.6-22.0 mm, 800 for the 0.5-4.6 mm were used to obtain the backscattered image of samples. The computer-controlled scanning electron microscope is used to measure the size, composition and abundance of mineral grains in the coal.

The melting test was carried out under a reducing condition of 60 % CO and 40 % CO_2. Calcium carbonate was used as flux and mixed with ash samples physically. A laboratory vertical gas-tight tube furnace apparatus was set up to heat the samples to high temperature in reducing condition (60 % CO and 40 % CO_2). About 1 g of ash samples were heated in the apparatus which was modified to allow ripid heating and quenching of ash samples. The sample was dropped in the furnace and reacted for 5 min at desired temperature range from 1050 to 1450 ºC and then was quenched into water. Quenched samples were examined by using Rigaku RINT X-ray powder diffractometry (XRD).

RESULTS AND DISCUSSION

Mineral matter composition in Huainan coals: Huainan coals mainly include the following groups: kaolinite, montmorillonite, quartz, pyrite, calcite, dolomite, unknown groups, *etc*. and other minor mineral matter (Fig. 1). The most abundant mineral matter in Huainan coals are those of the aluminosilicate

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

TABLE-1
CHEMICAL COMPOSITION (wt %) AND MELTING TEMPERATURE (°C) FOR THE COAL ASH SAMPLES (EXPRESSED AS wt % EQUIVALENT OXIDE, DRY BASIS)

Coal	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5	TiO_2	DT/	ST	FT
HN106	39.8	41.8	9.19	1.13	0.36	0.24	2.29	0.71	0.20	3.35	>1500	>1500	>1500
HN107	46.2	45.3	1.92	0.74	0.29	0.36	1.16	0.35	0.18	3.19	>1500	>1500	>1500
HN108	44.9	44.0	3.52	1.35	0.31	0.23	0.82	0.62	1.04	2.39	>1500	>1500	>1500
HN113	37.1	40.7	4.64	8.91	0.54	0.26	0.40	2.31	2.16	2.37	1492	>1500	>1500
HN114	55.1	29.7	3.37	6.98	0.50	0.2	0.55	1.78	0.17	1.22	1450	1500	>1500
HN115	42.3	34.5	6.17	8.55	1.00	0.21	0.76	3.20	0.55	2.24	1335	1360	1400
HN116	48.4	37.8	4.59	2.28	0.41	0.19	2.28	1.16	0.17	2.30	>1500	>1500	>1500
HN118	54.7	35.2	3.11	1.15	0.39	0.18	1.61	0.70	0.17	2.38	>1500	>1500	>1500
HN119	42.0	36.9	3.21	9.93	0.44	0.37	0.17	3.82	0.2	2.08	1434	1451	1480
HN120	50.3	36.9	3.70	2.58	0.44	0.20	2.24	1.36	0.13	1.79	>1500	>1500	>1500
HN121	52.0	38.2	3.50	1.50	0.44	0.13	1.10	0.49	0.14	2.09	>1500	>1500	>1500
HNC13	42.1	40.2	3.94	5.77	0.59	0.41	1.13	1.78	1.22	2.26	>1500	>1500	>1500
KL1	47.1	35.3	4.72	5.67	0.75	0.26	1.33	2.22	0.19	1.96	1450	1500	>1500
HX13C	49.2	38.6	3.35	2.73	0.31	0.29	1.04	1.37	0.74	1.89	>1500	>1500	>1500
HNP01	50.1	32.9	8.42	1.37	0.62	0.45	2.17	1.00	0.34	1.51	1425	1495	>1500
HNP09	45.0	44.7	2.67	1.33	0.2	0.22	1.04	0.63	1.02	2.66	>1500	>1500	>1500
HNP11	40.6	42.5	3.97	4.59	0.33	0.41	0.83	2.08	1.36	2.41	>1500	>1500	>1500
HW01	49.0	42.1	2.92	1.31	0.39	0.23	0.71	0.70	0.17	2.12	>1500	>1500	>1500
XM	43.8	27.7	10.7	6.85	0.14	0.00	1.53	7.00	0.15	1.38	1210	1250	1310
HNZ01	51.7	37.4	3.79	2.08	0.31	0.40	1.13	0.90	0.36	1.70	>1500	>1500	>1500

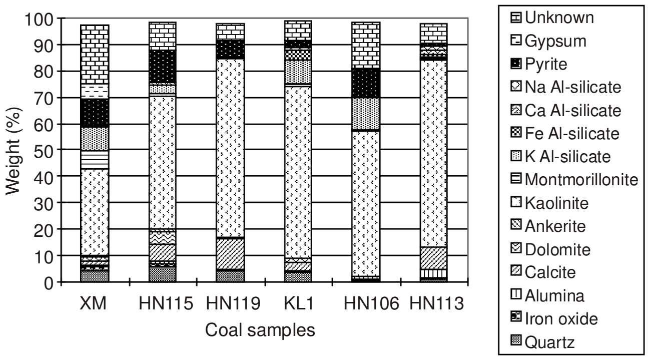

Fig. 1. Main mineralogical composition in six Huainan coals

clay minerals, together with quartz. They account for more than 60 % of the total mineral matter in coal. Quartz as the mineral matter in Huainan coals range from 1 to 7 %. The main carbonate mineral in Huainan coal is calcite [$CaCO_3$], but dolomite [$CaMg(CO_3)_2$] and ankerite [$Ca(Mg,Fe,Mn)(CO_3)_2$] are frequently associated with calcite. The contents of calcite and dolomite range from 0.16 % in HN106 to 11.57 % in HN119. Siderite [$FeCO_3$] is very low in Huainan coals. Another important of non-silicate mineral, pyrite, ranges from 0.73 % in HN113 to 12.25 % in HN115. Several other minerals, minor mineral matters, are found in the coals at low levels of abundance (< 1 %, total < 4 %); periclase, Na Al-silicate garnet, rutile, apatite and aluminosilicate. These minor minerals form ash particles with distinctive chemical compositions, but do not have great influence on ash behaviour. The key difference between HN115, XM coals and other high ash fusion temperature of Huainan coals is the content in the clay minerals, Pyrite and calcite. Low levels of kaolinite-type clays and high levels of calcite and pyrite in the HN115 and XM coals are beneficial to ash melting. It is suggested that the higher the kaolinite in Huainan coals show the tendency of the higher the ash fusion temperature. Therefore, the ash behaviour of Huainan coal in gasification will be controlled by the mineral group composition, mainly by kaolinite, pyrite and calcite, rather than by the properties of average chemical composition of the coal ash.

Mineral transformation of Huainan coal ashes at high temperature: Fig. 2 shows the main mineral phases change of HN115 coal ash in different temperature under a simulated gasification environment (60 % CO, 40 % CO_2). The behaviour of the ash sample at high temperature which is kept in the furnace for 5 min then quenched in the water bath is fairly complex. As temperature increased, thermal decomposition, transformation and interaction and phase change occurred among the components. With temperature increased to 1150 °C, hematite, lime, potassium meta disappeared and quartz, anhydrite decreased while mullite increased. Mullite, which is high fusion temperature phase, is derived from the kaolinite. The reason for anorthite and gehlenite formed is kaolinite (clay) reacted with alkali and iron compounds. From 1150 to 1350 °C, quartz phase decreased sharply and anorthite contents show the tendency first increased greatly then decreased. The formed mullite phase reach to the maximum at 1250 °C and show the slow decline tendency with temperature over 1250 °C. Above 1350 °C the major minerals identified are mullite and non-crystalline phase. The content of mullite formed in heating process is the main reason of high ash melting temperature of Huainan coals.

The XRD patterns obtained from the quenched ash samples for three Huainan typical coal ashes are quietly different at 1350 °C for 5 min under reducing condition (Fig. 3). The principal phases for HN115 and HN119 are mullite, anorthite, quartz and non-crystalline. The main phases for HN106 are mullite and non-crystalline components. Differences in peak intensity of mullite and anorthite reflect differences in phase concentration of the quenched slag fractions, which contribute to the difference of ash melting temperature. Fig. 3 also exhibits an amorphous hump maximum in 22-23° 2θ region for HN106 slag sample and in 24-25° 2θ region for HN115 and HN119 slag samples. The differences in the location of amorphous

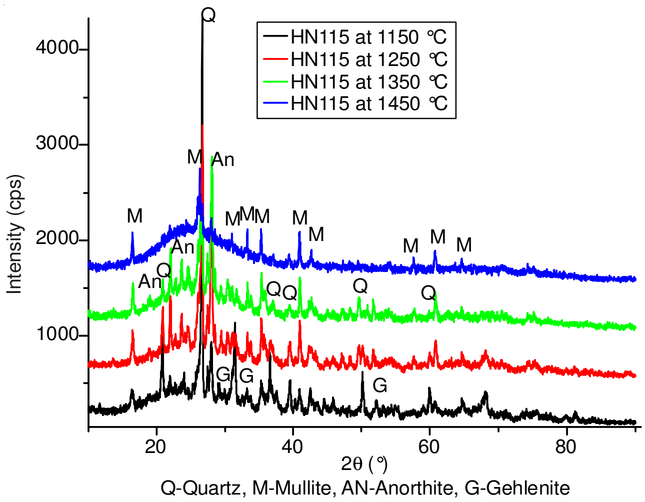

Fig. 2. XRD patterns of HN115 coal ash at different temperature under reducing atmosphere

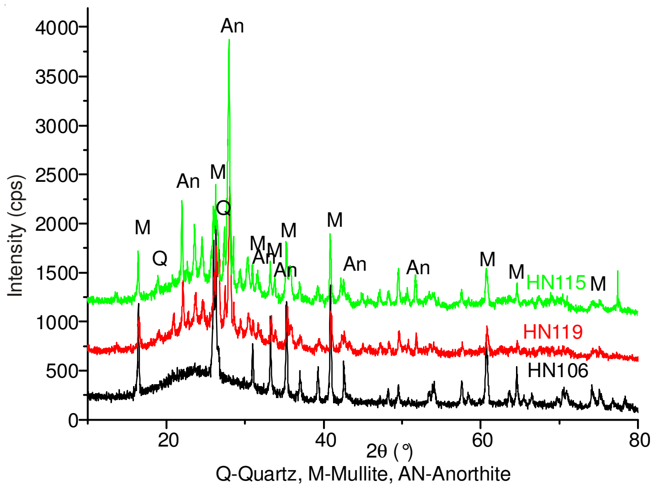

Fig. 3. XRD results of three Huainan coal ashes at 135 °C in reducing condition

hump maximum indicate the difference of glass types which may influence the ash melting temperature. For Huainan coal samples which have relatively high melting temperatures, the intensity of the diffraction lines at 1350 °C under reducing condition for mullite are high while the samples of relatively low melting temperature for anorthite are high.

FactSage calculation and analysis: The FactSage calculations were performed from 800 to 1600 °C. Fig. 4 shows clearly the weight percent of liquid phase as the function of temperature for six typical Huainan coal ash samples. The weight percentage of liquid phase formed during the heating process varied with coal ash samples over the temperature ranges. For HN115 and HN119, the initial liquid formed temperature is at 1000 °C. With the temperature increase, the weight percentage of liquid phase increases quickly to 75 % of the overall material for HN115 at 1400 °C and HN119 at 1450 °C, respectively which are quite fit for the tested ash flow temperature.

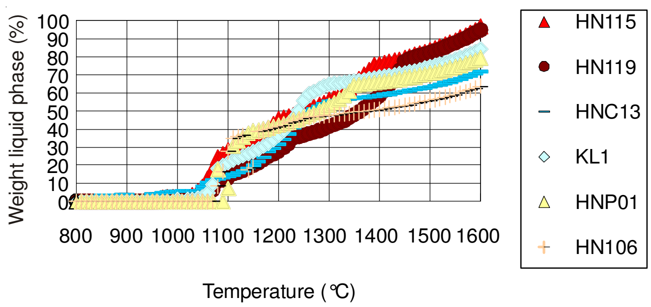

Fig. 4. Weight per cent of liquid phase for representative Huainan coal ash samples

Fig. 5 shows the main calculation results for ash transformation of HN115 coal with the temperature increase. The data shows that melilite (Ca, Na)$_2$(Al, Mg, Fe^{2+})(Si, Al)$_2$O$_7$, Feldspar (XAl$_{(1-2)}$ Si$_{(3-2)}$ O$_8$, quartz (SiO_2) mullite ($Al_6Si_2O_{13}$), cordierite

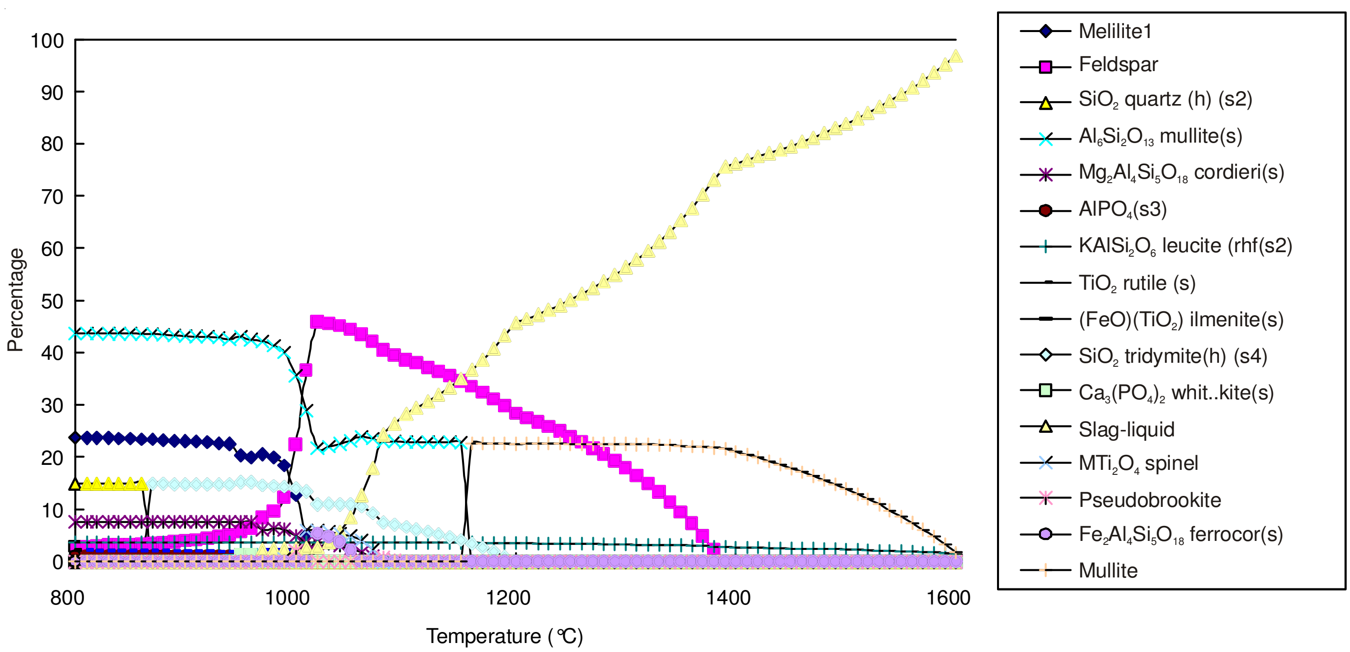

Fig. 5. Phase change of HN115 coal ash under reducing condition

($Mg_2Al_4Si_5O_{18}$), $AlPO_4$, leucite ($KAlSi_2O_6$), rutile (TiO_2), ilmenite (FeO)(TiO_2) was formed at 800 ºC As the temperature increase to 1000 ºC, liquid start to form. The formed feldspar phase has significant effect on the ash fusion characteristics. From 800 to 1000 ºC, the proportion of feldspar phase increase smoothly. From 1000 ºC, it increase sharply and reach to maximum at temperature 1020 ºC. As temperature over 1020 ºC, the feldspar phase and quartz decrease smoothly which results in a rapid increase in the proportion of liquid phase. Quartz disappeared at 1200 ºC and feldspar phase disappeared at 1400 ºC which has excellent agreement with the tested ash fusion temperature.

Effect of CaO on the ash fusion temperature of Huainan coals: In order to reduce the melting temperatures, limestone was added with several ashes at various equivalent levels. An equivalent CaO level of 8, 15, 20, 25, 30 and 42 % of ash weight were selected to estimate the impact of flux on the ash fusion temperature. It can be seen from Figs. 6 and 7 that, at a low content around 8 %, addition of CaO may increase the melting temperature of HN115 and HN119 coal ashes somewhat. With the increase of its addition, the melting temperature of ash initially decreases gradually, reaching its minimum value at the amount of CaO around 25 % and however increasing again with the further addition of CaO. This phenomenon is consistent with the theoretical thermodynamic equilibrium considerations. For HN106 and KL1, the ST of ash-CaO mixtures gradually decreased with the increasing CaO.

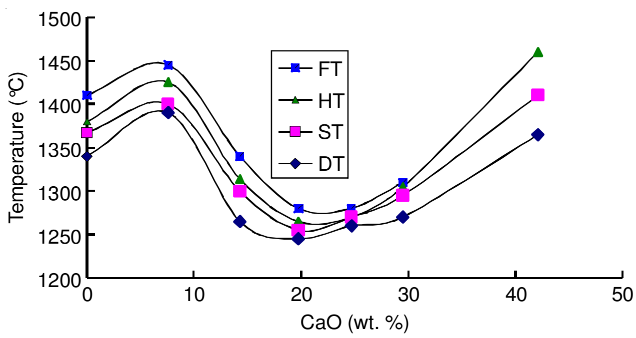

Fig. 6. Effect of CaO on the HN115 coal ash fusion temperature

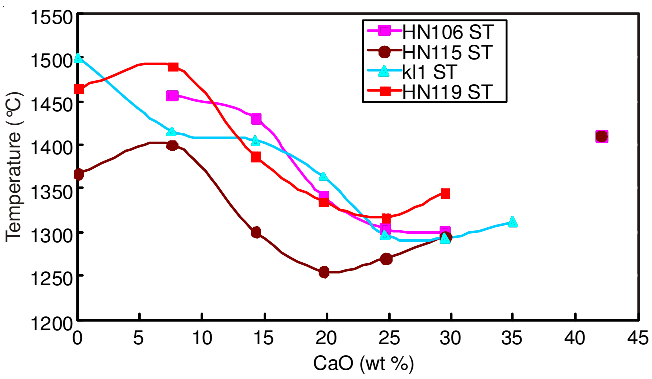

Fig. 7. Effect of CaO addition on the ash fusion temperature of Huainan coals

AFT measurements and the FactSage predictions: Two typical Huainan coals, HN115 with FT 1400 ºC and HN106 with FT higher than 1500 ºC, were selected for the comparison of tested FT and predicted FT with the addition of CaO flux. The predicted FT was defined as the temperature at which the formed liquid phase reaches to 75 % of total material. The comparison results are shown in Table-2. The results shows clearly the measured FT and the predicted FT are quite fit with maximum temperature difference less than 74 ºC which is within acceptable accuracy.

TABLE-2
COMPARISON OF THE TESTED FT AND THE PREDICTED FT BY FACTSAGE

Ash samples	Measured FT (ºC)	Predicted FT (ºC)	Temp. difference (ºC)
HN115	1400	1389	11
HN115 (CaO, 8 %)	1445	1451	6
HN115 (CaO, 15 %)	1340	1396	56
HN115 (CaO, 20 %)	1280	1302	22
HN115 (CaO, 25 %)	1280	1294	14
HN115 (CaO, 30 %)	1310	1384	74
HN115 (CaO, 42 %)	>1500	1481	–
HN106	>1500	>1600	–
HN106 (CaO, 8 %)	1470	1470	0
HN106 (CaO, 15 %)	1450	1418	32
HN106 (CaO, 20 %)	1360	1326	34
HN106 (CaO, 25 %)	1310	1288	22
HN106 (CaO, 30 %)	1310	1364	54
HN106 (CaO, 42 %)	1500	1512	12

Conclusion

The mineral matter analyses are characterized by higher aluminosilicate clay minerals contents (more than 60 % of the total mineral matter in coal) together with quartz, which accounts for their higher ash flow temperatures, often greater than 1500 ºC. The XRD results show that as temperature increasing from 1150 to 1450 ºC, quartz phases decrease sharply and anorthite contents show the tendency first increased greatly then decreased. Differences in peak intensity of mullite and anorthite reflect differences in phase concentration of the quenched slag fractions, which contribute to the difference of ash melting temperature. As limestone was added at a low content around 8 %, addition of CaO may increase the melting temperature of HN115 and HN119 coal ashes somewhat. With the increase of its addition, the melting temperature of ash initially decreases gradually, reaching its minimum value at the amount of CaO around 25 % and however increasing again with the further addition of CaO. This phenomenon is consistent with the theoretical thermodynamic equilibrium considerations.

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