Effect of the Ash from H₂-Rich Carbonaceous Materials on the Physicochemical Properties of Raceway Slag and Coke Reactivity

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The iron and steel industry is one of the most important sectors worldwide, and it has a great impact on the global economy; however, this sector is still highly dependent on fossil carbon. To decrease this dependency, approaches to partially replace the injected pulverized coal with secondary, highly reactive, renewable (biomass) and H₂-rich materials are studied. The injection of such materials is expected to significantly decrease the emitted CO₂ from blast furnaces. However, due to the different ash composition of these alternative materials (especially alkali and alkaline earth metals) compared to that of ordinary injected coal, these materials are expected to alter the raceway slag properties and affect the coke reactivity. Hence, the effect of the ash from different hydrogen-rich carbonaceous materials on the raceway slag physicochemical properties as well as coke reactivity is reported. The melting characteristics of the ash briquettes in contact with the coke and wettability of the melted ash on the coke surface are determined visually using an optical heating microscope. The effect of the ash on the coke reactivity is studied by means of thermogravimetry under a continuous flow of CO₂.

1. Introduction

Blast furnaces (BFs) dominate the ironmaking sector and are responsible for ≈70% of the iron production worldwide. BFs rely, mainly, on fossil coke and coal to extract and melt iron from its raw materials. The extraction of iron followed by steel making is an energy-intensive process that emits a substantial amount of CO₂. The production of one ton of steel is associated with the emission of ≈1.8 tons of CO₂.[1] Decreasing the carbon footprint is becoming a top priority for iron and steelmakers due to the commitment of governments to mitigate CO₂ emissions according to the Kyoto protocol and the European ambition to cut the CO₂ emissions by 2050 down to 80% of the 1990 emission levels.[2] Replacing coke and coal by H₂-rich carbonaceous materials (HCMs) is an important way to decrease the CO₂ emissions. The top charging of HCMs in BFs in the form of either lumps or agglomerates leads to problems related to their low mechanical strength and the high volatile matter compared with those of coke. The injection of HCMs through tuyeres, in contrast, is a straightforward way to utilize such materials in the BF iron-making process in the short to medium term. The present article focuses on the injection of HCMs (like biomass and waste plastic) into a BF and the subsequent effect of their ash on the raceway slag properties and coke reactivity.

For an optimal BF operation with injected carbonaceous materials, the whole amount of the injected material must be converted (combusted or gasified) as quickly as possible.[3] If the average blast velocity in the raceway is estimated to be 200 m s⁻¹, the transit time of the injected particles in the raceway could reach 20–30 ms. In such a limited amount of time, the injected particles are not completely combusted and a considerable amount of char escapes from the raceway region to reach the active coke zone. The injection of reactive hydrogen-rich materials, such as biomass or waste plastics, in this case not only decreases the emitted CO₂ due to the introduced H₂ but also enables an increase in the amount of injected materials and consequently reduces the coke consumption[4] which is, in addition to its high production cost, its production also a substantial amount of CO₂.

The injection of biomass and waste plastics (as HCMs) into BFs provides a flexible option for their utilization in large modern BFs. A high mechanical strength is not a prerequisite in this case. Other factors, such as the bulk density and calorific

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value, determine the maximum amount of the HCMs that can be injected without deteriorating the process performance. It has been reported that injection of 200–220 kg per tHM charcoal reduces the net CO2 emissions by ≈40%.[6] Moreover, injection trials using a specially designed injection rig have demonstrated that biomass exhibits a higher reactivity and higher combustion degree than those of pulverized coal (PC).[5,6] On the other hand, as plastics (except for polyvinyl chloride [PVC]) contain hydrogen and carbon, their injection has been proposed to be a substitute for reducing agents.[7] JFE Steel in Japan has reported the use of plastics in their BF since 1996. The use of plastics has been developed further by Bremer Stahlwerke in Germany, where more than 50,000 tons of plastics have been injected in their BFs.[8] The injection of “pure” waste plastic has been practised at several BFs in Germany, Japan, and Austria[7,9–11] with an injection rate of up to 60–80 kg per tHM. Upon injection of carbonaceous materials into a BF through the tuyeres, and during the course of their transport in the BF, they first lose their volatile content due to the rapid heating they are subjected to, and the released volatiles react with the atmosphere and combust. At the same time, the remaining char undergoes combustion with oxygen, and further in the process, the remaining char particles after combustion react with internally generated carbon dioxide.[12] The basic reactions that summarize these phenomena are given in Table 1.[13]

Ash, which is the inorganic portion of the char, remains in the raceway after complete char conversion. Ash fines might be trapped either in the raceway slag or the stagnant coke zone. The ash composition of plastics and biomass differs from that of coal (alkali content, basicity, etc.). Therefore, injecting plastics and biomass is expected to affect the coke zone. The ash composition was determined by a static heat and mass balance test. The samples were agglomerated into small briquettes (3 mm in height and 2 mm in diameter, see Figure 1) using a specially designed mould. The briquette was then centered on a flat coke plate and introduced to the hot zone of a horizontal tube furnace. The coke samples were made from commercial coke by grinding coke pieces down to the desired plate size. The two ends of the furnace are closed with transparent quartz glass to ensure that the samples are exposed to uniform temperature.

Five ash samples were studied, including ash from four HCMs (polyurethane [PU], torrefied sawdust [TSD], and two torrefied food residues (TF1 and TF2)) as well as ash from conventional PC. The ash of each sample was produced using a muffle furnace with a controlled atmosphere. The samples were heated up to 950 °C in a continuous flow of air until no further mass loss was observed (complete burnout). The wettability of the produced ash on the coke surface was studied with an optical dilatometer (Leitz Wetzlar, Germany) (Figure 1). The ash samples were agglomerated into small briquettes (3 mm in height and 2 mm in diameter, see Figure 1) using a specially designed mould. The briquette was then centered on a flat coke plate and introduced to the hot zone of a horizontal tube furnace. The coke samples were made from commercial coke by grinding coke pieces down to the desired plate size. The two ends of the furnace are closed with transparent quartz glass to enable the atmosphere control and imaging. An argon gas flow was maintained inside the furnace throughout the test. The sample was heated at a rate of 15 °C min⁻¹ up to 600 °C and thereafter at 10 °C min⁻¹ up to 1550 °C. The samples were kept at 1550 °C for 2 h. Imaging was carried out automatically according to preset parameters. The sample shape and contact-angle alteration were monitored by an analysis of the silhouette of the sample. Image recording and data analysis started at room temperature and continued throughout the heating step and the isothermal step.

The coke plates and residual ash samples after the wettability tests were furnace cooled and maintained for microstructural imaging using scanning electron microscopy (SEM, Gemini Zeiss Merlin). After SEM imaging, the coke plates were subjected to isothermal reactivity testing at 1000 °C for 1 h under a continuous flow of CO2 at flow rate of 200 mL min⁻¹ using thermogravimetric analysis (TGA, Netzsch), as shown in Figure 2.

The effect of the ash from the HCMs on the raceway slag composition was determined by a static heat and mass balance model that was developed in-house (MASMOD).[15] The melting interval and the viscosity of the slag were calculated using the Equilib module in FactSage 7.2 and the databases FactPS and FToxid.[16]

Table 1. Chemical reactions during the injection of carbonaceous materials.

| Reaction Type | Equation |
|---------------|----------|
| Homogenous reactions | VM + O2 → Products |
|            | CO + 0.5 O2 → CO2 |
|            | H2 + 0.5 O2 → H2O |
|            | CO + H2O → CO2 + H2 |
| Heterogeneous reactions | CO2 + H2 → CO + H2O |

Figure 1. Schematic of the heating microscope. 1) Light source, 2) sample carrier, 3) gas inlet and outlet, 4) furnace, 5) thermocouples, 6) sample, 7) reaction tube, 8) transparent ends, 9) camera.
3. Results and Discussion

The ash content of the studied materials and the chemical compositions can be seen in Table 2. The ash content varies significantly from one material to another, from as low as 0.5 wt% in case of the TSD to as high as 22.5 wt% in case of the food residue TF1. For the conventional injected material, PC, the ash content is ≈11 wt%. The ash composition, which is the main topic of interest in the present article, varies from a high to a moderately basic ash to an acidic ash, as in the case of the PC.

3.1. Effect of Ash on the Coke Properties

The effect of the ash from the HCMs on the coke properties was investigated through three ways: 1) By visual observations of the interactions of the ash and coke substrate, including the melting of the ash and its wettability; 2) by microstructural investigations of the coke surface after it interacted with the ash; and 3) by determining the effect of the residual ash on the coke reactivity.

3.1.1. Ash Melting and Wetting Behavior

The melting and wetting behavior of the pre-prepared ash on the coke surface as a function of temperature ($T$) and dwell time, the elapsed at $\approx1550$ °C ($D$) was determined and is given in Figure 3. The figure shows that the TSD ash melts after $\approx7$ min at 1547 °C. The ash of the food residue, TF1, does not melt, even after being held for 2 h at 1550 °C. Unlike TF1, the ash of the other food residue, TF2, melts at $\approx1280$ °C, whereas the PU ash melts at $1337$ °C. Similar to the ash from the TSD ash, the ash from the PC melts at $\approx1550$ °C.

The continuously recorded images of the shadows from the samples were further analyzed to determine the contact angle.
between the ash and coke substrate. The average values of the measured two contact angles as a function of time are given in Figure 4. The food residue, TF1, does not melt, and therefore shows no sign of wetting the coke substrate even after 100 min at 1550 °C. Two materials, TF2 and PU, tend to completely wet the coke surface after 100 min of heating. Among all the ash samples that became molten at 1550 °C, the PC ash was found to have the highest contact angle, and therefore the lowest wettability of the coke surface.

The differences in the wetting behavior (contact angle) among the different ashes are mainly due to the differences in the ash compositions. For a given ash sample, a continuous change in the contact angle upon heating is due to a continuous change in the composition that is either due to diffusion of some ash
species into the coke substrate or the interfacial reaction between the reducible oxides and coke as well as evaporation of low-boiling-point reduced components. The interfacial tension, contact angle, or wettability of the melted ash is strongly connected to its composition. It has been reported earlier that small changes in the composition significantly affect the contact angle and therefore the wettability. The present results indicate that in a BF, an ash with a decreased degree of wetting is preferred because this results in a limited interaction with the coke and therefore, less coke degradation. The ash from the PC shows lowest wettability to the coke among the other ash samples herein. However, the ash from the TSD shows the lowest variation in the contact angle among the test among the other ash samples herein. The contact angle for the ashes from the TSD and coke is limited, while the melts comprising the other ashes herein might substantially react with the coke and lead to significant coke degradation. In addition to the ash composition, the ash content in the HCMs is another important factor that has to be considered.

### 3.1.2. Microstructural Observations of the Coke Substrate

After the wettability tests, all coke substrates along with molten and penetrated ash were investigated with SEM. The SEM images show that coke plate that is exposed to the same heating cycle as that during the wettability tests but has not interacted with any ash maintains its original structure, as shown in Figure 5a. The images of the coke plates that have interacted with the ash, where ash briquettes were placed on the coke substrate and heated, exhibit a significantly worn out surface regardless of the type of ash, as shown in Figure 5. This figure shows also that the microstructure of the solidified ashes differs significantly; the microstructure varies from rounded droplets, as shown in Figure 5b–d, to needles, as shown in Figure 5e and to semi-cubes, as shown in Figure 5f. This difference is attributed to the difference in the ash composition.

### 3.1.3. Effect of Ash on the Coke Reactivity

As the reactivity (reaction rate with CO₂) is an important property of coke, the effect of the new ashes from the materials studied herein on the coke reactivity was studied at 1000 °C under CO₂ (200 mL min⁻¹). The coke substrate (plate, ≈200 mg) was placed on a pan and placed in a TGA, and the results are shown in Figure 6. The results are compared with coke that has not been in contact with any ash but was exposed to a similar heating cycle as that of the other coke samples.

Among the coke samples, the coke sample with the added ash from the food residue TF1 exhibits the highest reactivity and lowest resistivity to carbon gasification with more than 60 wt% mass loss during exposure to 100% CO₂ for 1 h at 1000 °C. The coke that did not interact with any ash shows the lowest reactivity followed by the coke that interacted with the ash from the PC, TSD, TF2, and then PU. Interestingly, the difference between the reactivity of that coke that did not interact with any ash and that of coke that interacted with ash from the PC is low. The differences in the reactivity (reaction rate) among the coke samples are attributed mainly to the ash composition.

The elements comprising the ash composition, especially the alkali and alkaline earth metals (AAEMs) and iron, are known to act as a catalyst during the gasification reactions of carbon. Studies showed that the reactivity of the char gasification can be correlated to the molar ratio of the catalytic ash, i.e., the ratio of the AAEMs to carbon. Other inorganic substances, such as silica, alumina and phosphates, on the other hand, decrease the reactivity of the char. Silica has been observed to reduce the reactivity by reacting with potassium to form a silicate, blocking the catalytic effect of potassium. Alumina has also been shown to deactivate the catalytic activity of potassium. Potassium phosphate has been observed to be inactive during the catalytic carbon gasification process. The complicated effects of various ash components are often expressed by an alkali index. The alkali index (A) is calculated by the following equation, where ash is wt% and each molecular formula is the mole fraction:

\[ A = \text{Ash} \times \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \]  

(1)
The alkali index calculated for all coke samples and the experimentally determined average rate of gasification are given in Table 3.

The estimated alkali indexes for the different ashes cannot explain the obtained reactivity results. This suggests that other factors, such as the wettability, ash distribution, and diffusion

Figure 5. SEM images of coke substrate after the heating microscope test: a) Coke substrate that has not been in contact with ash; b) Coke substrate that has been in contact with ash from the TSD; c) Coke substrate that has been in contact with ash from the TF1; d) Coke substrate that has been in contact with ash from the TF2; e) Coke substrate that has been in contact with ash from the PU; f) Coke substrate that has been in contact with ash from the PC.
in the porous coke structure, are very important and need to be considered. An extended reaction interface due to high wet-tability also promotes the reaction that increases coke degradation. This is very much connected to the ash content in a given HCM and its composition; therefore, pretreatment prior to injection to modify the ash composition or decreasing its net content might be required.

3.2. Effect of Ash on Slag Properties

By injecting HCMs into a BF, the properties of the formed slag, such as the viscosity and liquidus temperature, might change due to the changed ash composition. Such a change in the slag properties can affect the BF process. Therefore, thermodynamic calculations were conducted to determine the effect of the ash from the injected materials on the raceway slag viscosity and liquidus temperature. Calculations were carried out using the thermodynamic software FactSage 7.2. The chemical compositions of the slags that were predicted using the static heat and mass balance model MASMOD are given in Table 4.

The viscosity was calculated with the FactSage viscosity module. The calculations assumed that the system consisted of only molten phases. The following compounds in the slag were included: \( \text{SiO}_2, \text{Al}_2\text{O}_3, \text{CaO}, \text{MgO}, \text{MnO}, \text{Na}_2\text{O}, \text{K}_2\text{O}, \) and \( \text{TiO}_2. \) The slag compositions were normalized to 100% based on the compounds included in the viscosity calculation.

Figure 7 shows the viscosity of the formed slag as a function of the temperature. The figure shows how the viscosity changes when 80% of the PC is replaced by 20% of the HCMs. In most

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**Table 3.** Calculated alkali indexes and experimentally determined reaction rates.

| Ash origin | Alkali index | Average reaction rate [\% min^{-1}] |
|------------|--------------|-------------------------------------|
| TSD        | 2.11         | 0.33                                |
| TF1        | 0.13         | 0.71                                |
| TF2        | 0.64         | 0.39                                |
| PU         | 1.29         | 0.37                                |
| PC         | 0.03         | 0.26                                |
cases, the slag viscosity is comparable to that for the 100% PC injection case, with no significant difference. However, co-injection of 20% of the food residue results in a slag with a lower viscosity as a function of the temperature than that for when only PC was injected.

The melting range considers the range in which all the slag components convert from 100% liquid to 100% solid phases. All slag components except V$_2$O$_5$ were used in the calculations.

Figure 8 shows the melting interval for the various slags. The temperature of the first crystal varies between 1250 and 1630°C, whereas the temperature of the last melt varies between 820 and 930°C. The food residues, according to the calculations, give the narrowest melting interval herein. In most cases, mullite is the first phase to crystallize from the melt. The low viscosity and liquidus temperature values for the food residue’s ash

![Figure 7. Viscosity of the different slags.](image)

![Figure 8. Melting interval for the different slags.](image)

Table 4. Estimated slag compositions [wt%].

| Slag | Slag. bas. | CaO | MgO | SiO$_2$ | Al$_2$O$_3$ | TiO$_2$ | V$_2$O$_5$ | Na$_2$O | K$_2$O | S | P$_2$O$_5$ | MnO |
|------|----------|-----|-----|--------|------------|--------|----------|--------|-------|---|--------|-----|
|      | [kg per tHM] CaO/SiO$_2$ |
| PC$^{a)}$ Ref K | 34.62 | 0.08 | 4.79 | 1.35 | 58.48 | 27.49 | 0.15 | 0.1 | 0.38 | 1.53 | 5.1 | 0.43 | 0.21 |
| TSD$^{a)}$ 20/80 | 33.1 | 0.09 | 5.2 | 1.43 | 58.03 | 27.28 | 0.15 | 0.1 | 0.39 | 1.63 | 5.09 | 0.45 | 0.24 |
| 50/50 | 30.52 | 0.1 | 5.84 | 1.58 | 57.58 | 26.84 | 0.17 | 0.11 | 0.42 | 1.76 | 4.92 | 0.48 | 0.31 |
| 100/0 | 26.21 | 0.13 | 7.18 | 1.89 | 56.62 | 25.92 | 0.2 | 0.13 | 0.49 | 2.03 | 4.56 | 0.54 | 0.44 |
| TF$^{b)}$ 20/80 | 37.94 | 0.21 | 11.25 | 1.99 | 53.3 | 24.75 | 0.15 | 0.09 | 0.54 | 2.01 | 4.74 | 0.97 | 0.2 |
| 50/50 | 42.62 | 0.41 | 19.12 | 2.8 | 47.18 | 21.35 | 0.16 | 0.08 | 0.74 | 2.57 | 4.18 | 1.63 | 0.2 |
| 100/0 | 50.42 | 0.73 | 28.99 | 3.81 | 39.51 | 17.08 | 0.17 | 0.07 | 0.99 | 3.27 | 3.47 | 2.45 | 0.19 |
| TF$^{b)}$ 20/80 | 37.25 | 0.14 | 8.01 | 1.58 | 56.27 | 25.59 | 0.17 | 0.09 | 0.45 | 1.91 | 5.04 | 0.69 | 0.2 |
| 50/50 | 40.89 | 0.22 | 12.08 | 1.88 | 53.69 | 23.12 | 0.21 | 0.08 | 0.55 | 2.36 | 4.83 | 1.01 | 0.19 |
| 100/0 | 46.95 | 0.35 | 17.45 | 2.29 | 50.28 | 19.84 | 0.26 | 0.07 | 0.68 | 2.95 | 4.57 | 1.43 | 0.18 |
| PU$^{a)}$ 20/80 | 34.3 | 0.09 | 5.2 | 1.38 | 57.62 | 27.42 | 0.62 | 0.1 | 0.41 | 1.55 | 5.04 | 0.45 | 0.21 |
| 50/50 | 33.53 | 0.1 | 5.78 | 1.45 | 56.56 | 27.25 | 1.36 | 0.1 | 0.47 | 1.54 | 4.79 | 0.47 | 0.22 |
| 100/0 | 32.23 | 0.12 | 6.81 | 1.57 | 54.69 | 26.94 | 2.67 | 0.1 | 0.57 | 1.53 | 4.36 | 0.51 | 0.24 |

$^{a)}$Injection rate is 115 kg per tHM; $^{b)}$Injection rate is kept constant at 150 kg per tHM.
can be explained by the relatively high CaO and MgO content and low silica content. These results agree with the viscosity model for the iron BF slag that is proposed by Chen et al.\[20\].

4. Conclusion

In this article, the effect of the injection of HCMs, which could serve as alternative reducing agents for PC, on the coke and raceway slag physicochemical properties in a BF, was investigated. The following conclusions can be drawn: 1) The ash composition was found to have a significant effect on the reaction behavior between the ash and coke. The wettability of the ashes from the HCMs were in the following ascending order: PC < TSD < PU < TF2. 2) The reactivity of the coke was found to increase significantly after being in contact with the ash from the HCMs. Among these materials, the highest reactivity occurred after the coke was in contact with ash from the food residue (TF1). The estimated alkali index for the different ashes cannot explain the obtained coke reactivity results. This suggests that other factors, such as the wettability, ash distribution, and diffusion in the porous coke structure, are very important and need to be considered. 3) The viscosity and melting interval of a raceway slag varies depending on the ash composition of the injected material, replacement ratio, and temperature. However, the calculations show that the raceway adiabatic flame temperature was well above the melting interval for all slags.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

biomass, blast furnaces, injections, iron making, plastics

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