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Interactions between oxygen carriers used for chemical looping combustion and ash from brown coals

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ABSTRACT

Iron-based oxides are considered as potential oxygen carriers in coal chemical looping combustion. However, their redox or oxidation behaviour can be affected by coal mineral matters. The interactions between oxygen carriers and coal ashes depend strongly on the type of ash, which varies significantly in Australian brown coals.

We studied the interactions between two types of coal ash (silica-rich and iron and magnesium-rich) and two types of iron-based oxygen carriers (iron ore and industrial-grade ilmenite) via microstructural analysis of samples processed in reducing and oxidising atmospheres at 900 and 950 °C, respectively.

Both types of ash reacted locally with iron-based oxides, forming alumina silicates, spinels, magnesioferrites, and iron silicate phases as solid solutions or through liquid phase formation. These interactions can affect the oxidation and reduction kinetics of oxygen carriers. Our results show that iron-rich ash improves the oxidation and reduction kinetics of iron ore. It does not affect the reduction kinetics of ilmenite, but significantly increases ilmenite oxidation time. Silica-rich ash decreases oxidation rates of iron ore, but has less of an effect on the kinetics of ilmenite processing.

1. Introduction

Processing low-rank Australian brown coals by chemical looping combustion (CLC) allows coal to be used in a more environmentally friendly manner, because carbon dioxide (CO_2) gas emissions can be easily captured. In CLC, oxygen is delivered for coal combustion by solid oxygen carriers (OCs): typically, metal oxides. Supplying oxygen without air allows CO_2 to be captured easily because it not diluted by nitrogen. Mixed valency metal oxides can be used in CLC processes. During circulation between two interconnected fluidised beds, these oxides donate oxygen in the fuel reactor, and when oxidised, in the air reactor [1–2].To be effective, oxides must be highly reactive with the fuel, have high oxygen capacity and good mechanical strength, and be nontoxic. Industrial-grade, iron-based oxides such as iron ore and ilmenite ($FeTiO_3$) are low-cost materials often considered as OCs in CLC [3–6], especially where loss of materials is expected during circulation and separation of ash out of the system. The reactivity of iron ore and ilmenite have been extensively studied and compared with other Fe_2O_3-based OC [5–7]. Iron ore has been also tested in a commercial, coal-derived CLC unit with Chinese bituminous coal [8].

In recent studies of the combustion of Victorian brown coals with various OCs in CLC, coals were co-processed with CuO [9–10], Mn_2O_3 [11], and laboratory and commercial Fe_2O_3 and NiO powders [11–13]. These studies mainly focused on the reactivity of OCs in thermogravimetric analysers (TGAs) or fluidised bed reactors.

OC particles may interact with coal ash in CLC fuel and air reactors. This can cause deactivation, agglomeration, or attrition of the OCs. Even with the possible separation of the ash and OC particles due to differences in density, some solid–solid contact in the reactor is still expected [14–15]. The effect of different coal ashes on OCs in CLC depends on the ash content and mineralogy, experimental conditions, and OC composition [14–20]. Some interactions have been observed between ash and Fe_2O_3 OCs [16], while ilmenite is most resistant to reactions with individual common ash minerals [14]. The composition of coal ashes may also affect redox and oxidation kinetics [17–19] and char conversion rates [20]. Increased gas conversion rates have been seen for iron-based OCs in the presence of Ca-rich and Fe-rich coal ashes [17]. However, silica in ashes of sub-bituminous coal and anthracite reacts with $CuFe_2O_4$ in a redox cycle, forming stable Fe_2SiO_4 iron silicate, which reduces the activity of OCs in CLC [19].

Australian brown coals from the Latrobe valley typically have a low ash content. As the composition of minerals varies greatly in coals from different mines, we expect that the possible interactions of coal ashes with OCs could also vary for different brown coals. For example, when interactions of brown coal minerals with CuO were investigated for single and multi- CLC cycles, a strong interaction was observed for one type of coal during the reduction cycle, but another type of coal ash did not react with CuO [9].

In the present work, we investigate and describe the interactions between iron-based OCs and two types of Australian brown coal – high

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Table 1
Sample identification (ID) and materials ratio used in this study.

Oxygen carrier, OC		Brown coal ash 1 (Bca1) mixture		Brown coal ash 2 (Bca2) mixture	
Sample ID	Oxygen carrier	Sample ID	Bc ash1: OC (wt:wt)	Sample ID	Bc ash2: OC (wt:wt)
OC1	Iron ore	OC1-Bca1	1:5.7	OC1-Bca2	1:2.7
OC2	Ilmenite	OC2-Bca1	1:4.4	OC2-Bca2	1:2.1

Table 2
Chemical composition (wt.%) of oxygen carriers (OC) and brown coal ash (Bca), determined by X-ray fluorescence.

	Fe_2O_3	Al_2O_3	SiO_2	Mn_3O_4	MgO	CaO	TiO_2	Na_2O	K_2O	SO_3	BaO
OC1	96	1.3	2.3	0	0	0	0	0	0	0	0
OC2	46.8	0.6	0.5	1.5	1	0	50.1	0	0	0	0
Bca1	45.1	1.7	3.2	0.5	18.5	7.3	0.1	5.2	0.4	16.7	0.9
Bca2	3.6	10.3	76.7	0	2.2	1.1	0	1.8	0.4	2.8	0.1

iron and magnesium, and silica-rich – using different experimental techniques and thermodynamic modelling. We then discuss the mechanisms of possible reactions and their potential impact on oxidation and reduction kinetics.

2. Experimental

2.1. Materials preparation

Industrial-grade iron ore (OC1) and ilmenite (OC2) were used as raw materials for OCs. Both minerals were crushed to obtain particle sizes of <250 μm, and heat treated (calcined) in air in a muffle furnace at 900 °C. Brown coal ashes were prepared by ashing the coal samples at 780 °C for 20 h in a muffle furnace.

Ash and OCs were mixed and pelletised, followed by heat treatment in a tube furnace at 900 °C for 5 h under a neutral atmosphere (N_2 flow) and with a graphite lining in order to provide reducing conditions. Subsamples were taken for analysis, and the remainder of the samples were placed in alumina crucibles and heat treated in air at 950 °C for 5 h to recover the OC. Sample IDs and mixing ratios are listed in Table 1.

2.2. Materials analysis

Calcined ilmenite and iron ore, as well as their mixtures with brown coal ashes, were tested in a Thermogravimetric analysis (TGA) at 1 bar pressure in CO (at 900 °C) and in air (at 950 °C) to provide reducing and oxidising conditions, respectively. Before analysis, the materials were heated to the desired temperature in flushing nitrogen, and then the mass changes were recorded.

The bulk composition of coal ashes and OC composition were determined by X-ray fluorescence (XRF) according to the ASTM D3174-12 standard. Samples processed in the tube furnace were analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with electron probe microanalysis (EPMA). XRD analysis was performed on a Bruker D8 Advance Powder Diffractometer with Bragg–Brentano geometry at 40 kV, 30 mA, using Cu K_α radiation in conjunction with a graphite monochromator. Peaks and phases were determined using Bruker DiffracPlus Evaluation Software (Ver. 15.0.0).

SEM/EPMA of the processed OC-ash mixtures was performed using JEOL 8200 and JEOL JXA8530F electron probes. While iron is present as Fe^{2+} and Fe^{3+} in samples processed at different atmospheres, EPMA was used to obtain information on the total iron concentration only; the oxidation states of iron in various phases were not measured. For ease of presentation of XRF and EPMA results, all of the iron was recalculated to the ferric oxidation state.

2.3. Thermodynamic modelling

The thermodynamic phase equilibria package FactSage (version 6.4) was used to evaluate possible interactions between coal ash and OCs [21]. Databases used for calculations of compounds and solutions were FACT53 and FToxid.

FactSage calculations were performed according to the scheme shown in Fig. 1, where outputs of calculations in coal combustion conditions (inorganic species only) are used as input for calculations in oxidising conditions. This approach differs from previously published thermodynamic studies on the reaction of coal mineral matter with OCs [14,19], in which only individual minerals were considered in the reactions with OCs, thus ignoring possible interactions between ash minerals.

3. Results

3.1. Characteristics of starting materials

The chemical composition of OCs and brown coal ashes are listed in Table 2, and their phase compositions are shown in Fig. 2. According to the XRD results, calcined iron ore mainly contains an iron oxide in hematite form, with some aluminium and silica impurities. Iron ore sample OC1, processed in reducing conditions, consists of a mixture of magnetite (Fe_3O_4) and hematite (Fe_2O_3), with a very small fraction of wustite (FeO) (Fig. 2a). Only hematite was detected in the oxidised OC1 sample, as marked in Fig. 2b.

Iron and titanium oxides are the main components of ilmenite (Table 2). Small impurities of silica, magnesium and aluminium oxides (~2 wt%) were identified by XRF only. XRD analysis revealed that ilmenite, $FeTiO_3$, appears in OC2 after processing under reducing conditions, along with rutile (TiO_2) and small amounts of pseudobrookite (Fe_2TiO_5) (Fig. 2c). Calcined (as starting material) or oxidised (following the redox processing) OC2 contains pseudobrookite, as rutile and small amounts of hematite (Fig. 2d).

Fig. 3 shows backscattering images of a polished cross-section of a calcined iron ore sample (a, b) and ilmenite (c, d). Calcined iron ore, OC1, has areas that are more porous than other areas, while the microstructure of ilmenite looks uniform.

The chemical compositions of the two brown coal ashes (Table 2) as well as their phase compositions (Fig. 4) are very different. The main content of brown coal ash 1 (Bca1) is magnesioferrite ($MgFe_2O_4$), and possibly magnetite ($Fe(Mg)_3O_4$) and periclase (MgO), the XRD peaks of which overlapped with $MgFe_2O_4$. Other elements exist in ash as

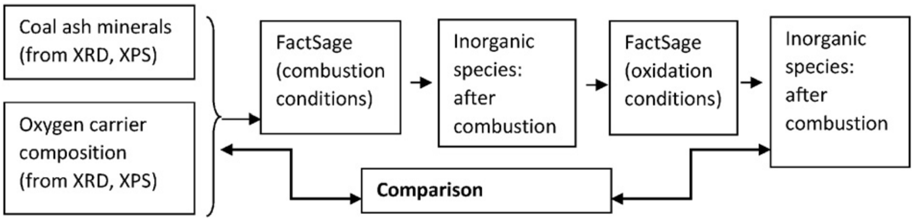

Fig. 1. Scheme of thermodynamic modelling calculations on oxygen carrier-brown coal ash (OC-Bca) mixtures. XRD = X-ray diffraction; XRF = X-ray fluorescence.