



Analysis and prediction of slag-induced corrosion of chromium oxide-free refractory materials during fusion of coal and biomass ash under simulated gasification conditions



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ABSTRACT

Four chromium oxide-free refractories based on spinel, alumina, and calcium aluminates are brought in contact with three ashes from coal and biomass with different base to acid ratios (B/A) and alkali contents under reducing atmosphere (simulated gasification). This investigation is performed in a lab-scale oven with a defined heat up to 1450 °C and a subsequent slow cool down to room temperature in H₂/Ar atmosphere over a period of 3–4 h. Afterwards sample sections are prepared and analyzed by optical microscopy and SEM/EDX. The slag infiltration pathways are identified and the formed mineral phases in the sections are localized by SEM/EDX mapping. A stepwise model of thermochemical calculations of the interacting species using the FactSage™ software package is applied to reproduce the slag progression inside of the different refractory materials and to predict the formed mineral phases by equilibrium state calculations. The corrosion mechanisms and corrosion depths are concluded from the comparison between experiment and thermochemical calculations. A comparably good agreement between both experiment and calculation is shown. Aim of the present study is the identification of promising candidates of environmentally friendly and cheap substitutes for the commercially used chromium oxide-based refractory materials as well as the development of related methodical approaches for the evaluation/prediction.

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1. Introduction

In high temperature gasification like entrained-flow process the mineral matter of solid fuels undergoes a fusion and, as a result, liquid slag is formed. These slag phases are found to act as corrosive media for refractories [1]. For the lining of entrained-flow gasifiers basically cooling screens are utilized. Ceramic refractory linings in most cases are rarely employed due to the high operation temperatures in the order of 1450 °C and lower lifetimes caused by slag-induced corrosion. Currently chromium oxide based materials are used as refractories in slurry gasifiers [1,2]. Recent developments have comprised chromium oxide-free refractories that could provide cheap and environmentally friendly alternatives [3–6] since a substitution of the refractory lining is attributed as major costs in gasifier operation [5]. The advantages of spinel-based refractories as materials and in interaction with slags are mentioned in Ref. [6] (see references therein): these have offered outstanding thermo-mechanical properties and good thermal shock resistance. Spinel-based materials are frequently used as steel lading linings where 20–25 wt.% of spinel are favored. For low spinel amounts

an increase of the corrosion is recognized while too high contents have led to a deeper infiltration since a reaction between slag and spinel is absent.

During the interaction between liquid slag and reactor lining a corrosion of the ceramic material occurs in terms of a dissolution of the refractory and/or mineral phase transformations inside the material caused by incorporated slag species [4,6]. It has to be noted that the principle corrosion mechanisms for combustion conditions are better understood [7] than for low oxygen partial pressures (gasification). A few detailed mechanisms, e.g. corrosion by alkali species or sulfides, are described for chromium oxide-free materials [8,9]. A selective infiltration of the refractory material and modifications of the respective microstructure are frequently found [1,4,6,10–14]. This interaction causes massive primary and secondary corrosion of the ceramic materials. In consequence, these processes are more intensively studied for commonly used chromium oxide-based materials for example in Refs. [11–13,15] instead of rarely applied chromium oxide-free ones. For chromium oxide-based materials the interaction with the slag has formed an iron-chromium spinel which on the one hand strongly decelerates a further slag penetration but on the other increases spalling [6].

The present study is focused on chromium oxide-free refractories and their respective mineral transformations which are induced by

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Nomenclature

B/A	base to acid ratio
AA	acidic ash
IA	intermediate ash
BA	basic ash
XRF	X-ray fluorescence analysis
DT	deformation temperature
ST	softening temperature
HT	hemispherical temperature
FT	flow temperature
SEM/EDX	scanning electron microscopy with energy dispersive X-ray spectroscopy
TOMAC	thermo-optical measurement system with atmosphere control
Traces	various oxides from Mn, Zn, Cr, Ni, Cu, V, Rb, Sr, Pb, Co, Zr, Mo etc.

the infiltration of liquid slag phases under simulated gasification conditions. For the description of the slag infiltration processes a step-wise thermochemical model with an adaption to the corrosion affinity is developed. A comparison between experiment and thermochemical calculation shall enable insights into slag progression and corrosion mechanisms as well as infiltration depth by means of a monitoring of significant mineral transformations.

2. Materials and methods

2.1. Materials

2.1.1. Ash samples

Three ash samples were utilized which are named as acidic, intermediate, and basic ash according to their base to acid ratio (B/A, calculated from Eq. (1) for oxidizing conditions due to ash production under combustion conditions). The acidic ash (AA) and intermediate ash (IA) originate from conventional coal power plants (fly ash), while the basic ash (BA) was achieved by low temperature ashing (450 °C, air) of a wood char from autothermal pyrolysis (pre-step of entrained-flow gasification). Afterwards all ashes were ground to a particle size $\leq 63 \mu\text{m}$. In Table 1 the ash composition determined by XRF and the respective base to acid ratios are listed.

$$\frac{B}{A} = \frac{\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MgO} + \text{CaO} + \text{Fe}_2\text{O}_3}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2} \quad (1)$$

2.1.2. Refractory materials

The four investigated refractory materials are based on magnesium aluminate spinel, corundum with titanium oxide, and calcium aluminate (see composition in Table 2) [6,16–18]. These refractory materials offer recognizable open porosities of 14.9 % (TTA1650), 15.5 % (AR78 MAC 1450), 18.1 % (AR78 AB 1500), and 24.4 % (CA₆ (Bonite)). They are environmentally friendly and cheaper than chromium oxide-based materials.

2.2. Methods

2.2.1. Chemical composition and ash fusion characteristics

The chemical composition of the ashes was determined by X-ray fluorescence analysis (XRF) using a S8 Tiger from Bruker with a rhodium radiation source. All species are given as oxides due to ashing under air. The characteristic ash fusion temperatures (DT, ST, HT, and FT) were determined with a heating rate of 10 K/min in a Leitz heating

Table 1

Composition and base to acid ratio (B/A) of the three utilized ash samples.

Species	Acidic ash (AA)	Intermediate ash (IA)	Basic ash (BA)
Mass fraction/wt.%			
Residual C	4.31	2.40	–
CO ₂	–	2.20	9.90
Na ₂ O	5.12	0.60	0.29
MgO	5.20	3.80	5.56
Al ₂ O ₃	18.40	2.44	8.07
SiO ₂	40.21	42.91	22.51
P ₂ O ₅	0.29	0.07	2.33
SO ₃	5.05	6.45	2.43
Cl	0.12	0.12	0.40
K ₂ O	3.39	0.19	6.72
CaO	9.43	27.00	27.89
TiO ₂	0.91	0.17	0.53
Fe ₂ O ₃	7.17	11.05	7.97
BaO	0.14	0.25	0.18
Traces	0.35	0.26	5.21
Sum	100.00	100.00	100.00
Base to acid ratio/–			
B/A (mass)	0.51	0.94	1.56
B/A (molar)	0.57	1.11	1.99

microscope by use of cylinders (3 mm in both diameter and height) from the $\leq 63 \mu\text{m}$ powder according to DIN 51730. During the measurements a reducing atmosphere (65 vol.% CO and 35 vol.% CO₂) was employed.

2.2.2. High-temperature corrosion

The high-temperature corrosion tests were performed in a special installation for thermo-optical measurements with atmosphere control (abbreviated as TOMAC, see schematic construction in Fig. 1). This oven is equipped with a window and a camera system to enable an in-situ monitoring of the ash melting and refractory wetting behavior. Ash cylinders with dimensions of 15 mm in diameter and approximately 10 mm in height pressed from the $\leq 63 \mu\text{m}$ powder were placed on refractory discs with a diameter of 50 mm and height of around 10 mm. In the corrosion test the system composed of ash and refractory was heated from room temperature to 800 °C by a heating rate of 20 K/min since in this range no significant mineral matter transformations can be expected. From 800 °C to 1450 °C the samples were heated by 10 K/min. The sample remains approximately 1 min at 1450 °C before cooling starts. This short time is sufficient to form new mineral phases since this process takes place immediately according to Vázquez et al. [19]. The choice of this final temperature is reasonable since entrained-flow gasification with a slag viscosity of 25 Pa·s is typically operated at process temperatures in the range of 1400–1500 °C [20, 21]. The whole heating and cooling process was executed under reducing atmosphere composed of 5 vol.% H₂ and 95 vol.% Ar at atmospheric pressure (1 atm) with a calculated value of $p_{\text{O}_2} \approx 10^{-14}$ – 10^{-9} atm at 1450 °C. During the heat up process the oven was purged by 300 ml/min of the reducing gas mixture. The wetted/infiltrated refractory was slowly cooled down from 1450 °C to room temperature inside the oven over a period of 3–4 h. After the TOMAC experiment polished sections of each sample system were produced for a further analysis by optical microscopy and SEM/EDX mapping.

2.2.3. Optical microscopy

The sections of all samples were studied by a stereo microscope using a 32-fold magnification. This investigation was performed to understand the infiltration path and depth of the slag as well as structural changes.

2.2.4. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)

The sample sections were further investigated by scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analyses in a

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