# A microscopic study of the precipitation of metallic iron in slag from iron-rich coal during high temperature gasification

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## ARTICLE INFO

## ABSTRACT

The behavior of iron in molten slag from iron-rich coal during high temperature gasification conditions was studied. The proportion of crystalline phase in the slag was measured by X-ray diffraction (XRD) and the microstructure of the slag was quantitatively analyzed by CCSEM. Metal ions in acid-digested slag samples were analyzed by ICP-AES. It was confirmed that the precipitation and settling processes of metallic iron in slag were significantly affected by both the atmosphere and the reaction temperature. In a strongly reducing atmosphere such as 10/90 (vol%) mixtures of $CO_2/H_2$, the Fe content of bulk slag was reduced due to the precipitation of metallic iron in molten slag below 1550 °C. The profile of the iron content of the slag was related to the dissolved oxygen transfer in molten slag. At temperatures higher than that of the equilibrium reaction of FeO (slag) = Fe (l) + [O] (slag), metallic iron is no longer precipitated and the slag becomes a homogeneous phase. In addition, some heavy metals showed the same behavior as iron in the strongly reducing atmosphere were extracted by 1M/HCl, which results in higher extraction rates for Fe, Mg, Zn, and Pb.

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## 1. Introduction

The integrated gasification combined cycle (IGCC) system is the most advanced technology for cleanly generating electricity from coal [1,2]. The performance of gasifiers is one of the key issues to the success of IGCC system. In recent decades, the entrained flow gasifiers are found increasing utilization for their good adaptability of feedstocks and producing tar-free gas. Additionally, the volume of waste is markedly reduced by means of coal ash being discharged from the gasifier as a slag. Two types of entrained flow processes are developed and commercialized in IGCC system: those with oxygen-blown gasifier and with air-blown gasifier. The oxygen-blown types were originally developed for use in chemical plants to produce higher concentration of synthesis gas. On the other hand, the air-blown type developed by Mitsubishi Heavy Industries in Japan is aimed at improving the thermal efficiency. This system has an advantage of decreasing auxiliary power consumption to 8% as compared with 10–15% for the oxygen-blown systems [3].

In the oxygen-blown gasifiers, crushed coal and oxygen are concurrently injected into the gasifier at high pressure. The temperature of the gasifier is sufficiently high (more than 1600 °C) to achieve efficient carbon conversion and completely melting of ash. The major components of synthesis gas consist of 30–60% CO, 25–30% $H_2$, and 5–15% $CO_2$ [4]. Iron compounds in ash are partially or fully reduced to elemental iron under such a strongly reducing condition and may cause problems with the slag after tapping; the oxygen-blown gasifier usually generates a slag with a distinct iron-rich phase in addition to the silicate phase [5,6]. By contrast, the air-blown gasifier consists of two-stage configuration: combustor (combustion) and reductor (gasification). It operates with a lower oxygen/coal ratio at the gasification zone and a higher oxygen/coal ratio at the combustion zone, as a result, the resultant slag is glassy and iron deposit was not observed in slag phase [7,8].

Iron is by far the most abundant heterovalent component in coal ash, and slag shows significant variation under different oxidation–reduction (redox) conditions. Therefore, it is expected that differences in gas composition give rise to slag with a wide range of physical, chemical, and structural properties (e.g., phase equilibrium, density, viscosity, and electrical conductivity). Iron behavior in ash/slag at high temperature gasification conditions has been studied from the points of chemical equilibrium [9,10]. On the other hand, the redox kinetics of iron (Fe) and the dissolved oxygen transfer in silicate melts with/without iron have been extensively studied in metallurgy fields [11–13]. However gasification process is a complex ensemble of chemical and

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physical phenomena: the temperature and atmosphere histories of slag in the gasifier are quite different from those in the blast furnace [14]. In addition, reducing conditions during gasification allow metals and metalloids to become embedded in the slag matrix. The release of heavy metals can pose a serious threat to ecological system [15].

In this paper, the precipitation of metallic iron in slag from iron-rich coal was studied under high temperature gasification conditions. In order to observe iron precipitation formation in slag, the concentration of $H_2$ and $CO_2$ of inlet gases was changed based on the equilibrium relationship between iron metal and oxides at high temperature. In addition, the effect of reducing atmosphere on the extraction of heavy metal produced in molten slag was also investigated for the purpose of evaluating the potential pollution after slag disposal.

## 2. Experimental

### 2.1. Samples

A typical iron-rich coal was used in this study, it was dried and pulverized to less than 120 μm prior to use. The proximate and ultimate analysis results of the coal are given in Table 1. The coal was ashed at 815 °C according to JIS M8812 [16], and the chemical composition of the resultant ash were analyze by X-ray florescence spectrometry (XRF, RIX 2100, Rigaku), the results are presented in Table 2, the concentration of major element are show as oxides. It indicates significant quantities of $Fe_2O_3$ and CaO in coal ash, as much as 18.4% and 19.0%, respectively.

### 2.2. Experimental apparatus and procedure

The slag was prepared using an electrical furnace with a maximum temperature of 1600 °C, as shown in Fig. 1. First, the fly ash was dried at 110 °C for 2 h. A 20-mm-diameter and around 10-mm-thick sample pellet was molded under a pressure of 40 MPa by a hydraulic molding press. The experimental temperature was varied from 1300 to 1550 °C and the melting time of the sample in the reaction zone was fixed at 10 min from the prediction of the average retention time of slag in the gasifier. The sample pellet was placed in an alumina crucible to make contact of only one surface with the mixture gas, and in addition the thickness of slag after melting was managed at about 6 mm which is to simulate the slag flow along the wall of the gasifier. The sample-laden crucible was initially placed at the upper position of a furnace. The furnace was heated up to 900 °C with $N_2$ atmosphere flowing, subsequently, the gas was changed to a mixture of $CO_2$/$H_2$ with the given volume fraction, 50/50 or 10/90. After the furnace was heated up to the specified temperature, the sample was dropped down to the react zone and was held for 10 min. After that, the sample was quickly raised to the top position of the furnace and instantly cooled down by $N_2$. The slag pellet was then divided into two parts for further analysis: one for use in XRD analysis and an acid resistance test, the other for microstructural observation.

#### Table 1
Proximate and ultimate analysis of samples (wt.%).

| | Proximate analysis (air-dry) | | Ultimate analysis, (dry and ash free) |
|---|---|---|---|
| Moisture | 12.58 | C | 73.05 |
| Ash | 1.58 | H | 5.11 |
| Volatile matter | 40.65 | O | 20.75 |
| Fixed carbon | 45.19 | N | 1.08 |
| Fuel ratio (FC/VM) | 1.11 | S | 0.01 |

#### Table 2
Chemical composition of the ash as oxides (mass%).

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | $SO_3$ | $TiO_2$ | MnO |
|---|---|---|---|---|---|---|---|---|---|
| 36.0 | 15.8 | 19.0 | 18.4 | 6.70 | 1.18 | 0.37 | 1.34 | 1.00 | 0.19 |
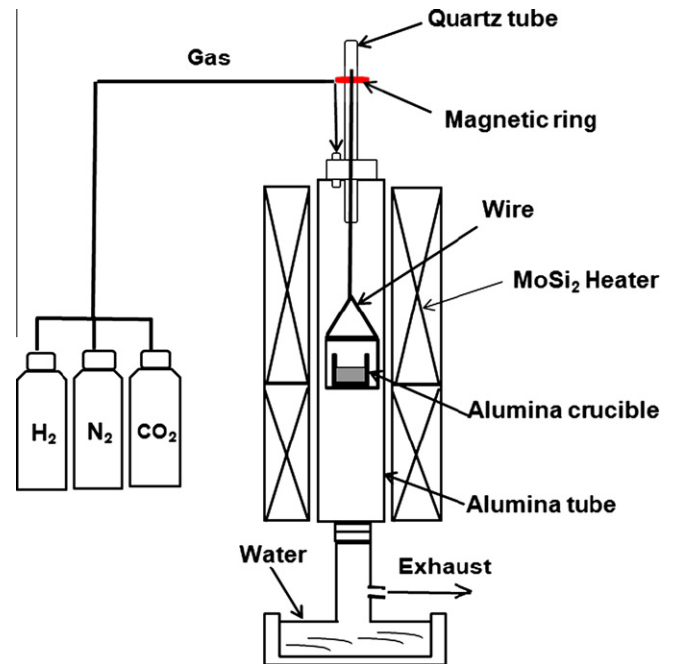


Fig. 1. Schematic of the experimental apparatus.

### 2.3. Characterization of the slag sample

The crystalline phases in the slag were measured by a powder X-ray diffractometer (XRD, RINT 2000, Rigaku) at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. The detector scanned over a $2\theta$ range of angles from 5 to 80° with a step size of 0.02°.

Microstructural observation was performed by scanning electron microscopy with an energy dispersive X-ray analyzer (SEM–EDX, JEOL-6510). The slag was mounted in liquid epoxy resin, then the solidified pellet was polished, and finally the surface was sputter-coated with carbon in a quick carbon coater (SC-701C, Sanyu Denshi Co., Ltd.). Because the backscattered electron (BSE) from metallic iron was stronger than that from the bulk slag in this study, a computer-controlled scanning electron microscopy (CCSEM) technique was employed to determine the visual structure, elemental composition, diameter, position, and shape factor of the precipitate in the slag [17].

The acid resistance test was performed according to JIS R 5202-1999 [18]. First, the slag were pulverized to less than 100 μm and dried at 105–110 °C for 2 h, and then they were digested to a liquid-to-solid ratio of 50 by 1M/HCl; this reaction was carried out in a warm water bath for 10 min. Finally, the leachant was filtered and the residue was evaluated by combusting the filter at 975 ± 25 °C. Extracts were diluted with deionized water and were examined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPS 1700VR) to characterize the release of metal species from the slag. The concentrations of metal species in the extracts, including the normal metals Ca, Mg, Si, Al, Fe, K, Na as well as the heavy metals Mn, Cd, Cr, Co, B, Cu, Zn, and Pb were determined.