

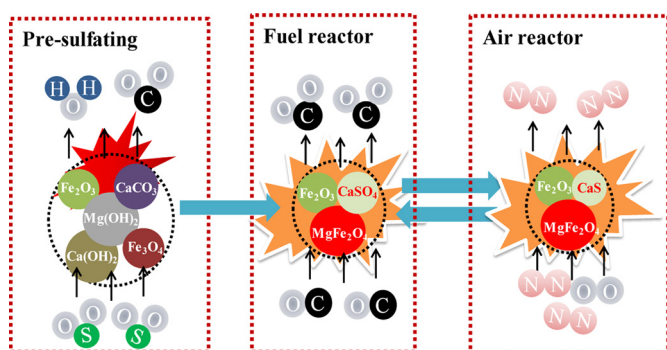


Full Length Article

Studies on steel slag as an oxygen carrier for chemical looping combustion

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GRAPHICAL ABSTRACT



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ABSTRACT

Chemical looping combustion (CLC) has been suggested as an energy-efficient method for clean combustion with inherent capture of carbon dioxide. The development of commercially available, less-costly, thermally-stable and good kinetics oxygen carriers is the first propriety in the CLC process. This study is the first to explore the use of steel slag, a typical metallurgical waste, as an oxygen carrier in CLC. The primary advantage of steel slag is its low cost because of its nature of the solid waste. Steel slag mainly contains two interested substances for oxygen transfer in CLC, iron oxides and calcium sulfate (after sulfation). The thermochemical analysis on pre-sulfating steel slag was conducted by the Aspen Plus software, and the experiments of the reduction of pre-sulfating steel slag were carried out using a thermogravimetric analyzer (TGA). Characterizations of used steel slag were carried out by X-ray diffraction (XRD). Results indicated that the pre-sulfating steel slag can be a proper and excellent oxygen carrier, whose reduction kinetics using model fuel gas (CO, carbon monoxide) was rapid at medium temperatures. Further investigations revealed that it is Ca-containing components (CaSO₄) in pre-sulfating steel slag that was mainly involved in the redox process using CO. Moreover, the reaction rate has increased by nearly 15 times as compared to that of the pure CaSO₄ at the same temperature. The conversion of CaSO₄ to CaS can be nearly complete. Higher temperatures were adverse to the stability of CaSO₄, leading the decomposition of CaSO₄, the degradation of its oxygen transfer capability and the increase of sulfur emissions. However, the use of steel slag rationally control the optimized reduction temperature to be 750 °C, when its kinetics can be maintained rationally at 100% conversion within 30 min and a stable oxygen transfer capability at 10.63 wt% with the minimized sulfur emissions. This finally validated steel slag as a promising oxygen carrier candidate.

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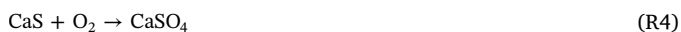
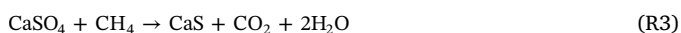
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1. Introduction

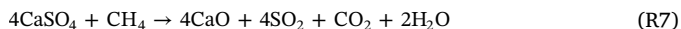
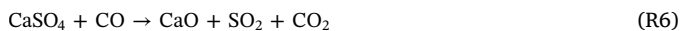
Chemical-looping combustion (CLC) is a promising alternative technology to the conventional combustion process. CLC transports oxygen using an oxygen carrier, avoiding fuel's directly contacting with air, by which CO₂ can be inherently separated [1–3]. It typically consists of two separate reactors: an air reactor and a fuel reactor [4]. Oxygen carriers circulate between these two reactors, releasing oxygen in the fuel reactor and capturing oxygen in the air reactor. In this way, the gas stream out of the fuel reactor consists of only CO₂ and H₂O, preventing mixing of air nitrogen. After the water condensation, the pure CO₂ can be obtained, preventing the involvement of the costly separation process [5,6].

One critical aspect in developing the CLC technology is to develop appropriate oxygen carriers in terms of cost, commercial availability and rational reactivity and thermal-stability [7,8]. The metal-based oxygen carriers, e.g. oxides of nickel, iron, copper, manganese, and cobalt, have attracted significant interest because of their higher reactivity [9–14]. The Fe-based oxygen carriers are most cheap, widely available and environmentally benign [15]. The recent focused Fe-based oxygen carriers involved natural ores and red mud waste, such as ilmenite (FeTiO₃) and hematite (Fe₂O₃), which can be potentially realistic commercial applications [16–18]. Both these two natural ores and industrial wastes showed sufficient reaction rate and good fluidizing properties [19–21]. The primary disadvantages of Fe-based oxygen carriers are their lower oxygen transfer capacity and incomplete combustion of fuels [22–24].

Alternatively, CaSO₄ became attractive as oxygen carriers due to being wide-accessible, less costly, but higher oxygen transfer capacity among many proposed materials [25,26]. The redox reactions of CaSO₄ in CLC can be expressed as (R1)–(R4):



Alstom is currently developing a 3MW_{th} Combustion-Gasification Chemical Looping unit based on CaSO₄ based oxygen-carrier for poly-generation of heat, electricity and hydrogen [27,28]. Abad introduced excellent results on the sulfated limestone and established the conceptual design of the CaSO₄-based CLC unit [29]. However, the limestone-starting CaSO₄ oxygen carriers were found conflict to balance higher reactivity [30] and sulfur release due to side reactions (R5)–(R10), which can also cause the loss of oxygen transfer capability of CaSO₄ [31].



The occurrence of side reactions are largely dependent on operating conditions, e.g. temperature and gas partial pressures. In the fuel-reactor, the side reaction is primarily the solid-solid reaction (R8) [32]. In the air reactor, the oxidation of CaS is also favored through reactions (R8) and (R10) at temperatures higher than 1000 °C [26],[33]. Overall, lower operational temperatures helped eliminating the SO₂ release, but the CaSO₄ reduction reactivity unexpectedly dropped [34], subsequently resulting in inefficient oxygen transfer.

Previous studies were carried out focusing on the enhancement of the oxygen transfer kinetics, the conversion efficiency and the

suppression of SO₂ release. Active additives were frequently used into CaSO₄. Ding et al. [35] proposed the binary mixture of natural anhydrite ore and iron ore as oxygen carrier, and found that its oxygen transfer capacity was kept constant in the CLC evaluation. Song et al. also used Fe₂O₃ as an additive to mix in CaSO₄ at different ratios, and found that added Fe₂O₃ acted as an intricate active phase to promote kinetics of coal gasification and also an active oxygen carrier constituent itself [36]. In their test, Fe₃O₄ was found the only reduction product. Li's work [37] revealed the catalytic effect of various iron based additives on the reduction of CaSO₄ to CaS and confirmed that Fe₂O₃ could effectively promote the reduction reaction.

Steel slag, a predominant industrial residues of metallurgical industries, mainly contains two meaningful substances, CaO and FeO [38] to the CLC process. These components of steel slag can be typical oxygen carrier base. The global production of steel slag in 2016 was estimated to be approximately 160–240 million tons. Significantly, its production in China accounted for approximately half of this global amount [39]. The current handling of massive steel slag is landfilled, leading not only the occupation of farmland also the contaminations of soil and groundwater resulted from leaching of certain potentially toxic elements. Therefore, the approaches to apply this massive solid waste, as the current case to be an oxygen carrier candidate, would greatly advance the development of less-costly oxygen carriers in the chemical looping process, also meaningful in alternative economic solid waste handlings.

The objective of this work was to explore the steel slag waste, with inherent having both constituents of calcium and iron, as an oxygen carrier in the CLC process. The thermochemical analysis on pre-sulfating steel slag was systematically conducted by Aspen Plus software. The kinetics experiment of the reduction of pre-sulfating steel slag and its product gas were carried out using a thermogravimetric analyzer (TGA) along with Mass Spectroscopy (MS). Its oxygen transportation capacity and cyclic and thermal stability during redox cycles were also carried out in TGA, referenced by the pure CaSO₄. Characterizations of used steel slags were conducted in their minerals compositions using X-ray diffractometric (XRD).

2. Material and methods

A representative steel slag particle was collected from the discharge line of the Ansteel Co., Ltd. The main elements involved are Ca, Fe, Mg, Si, as shown in Table 1. The diameter of raw steel slag was 3 mm.

The crystalline phase of the raw steel slag, pre-sulfating slag and used samples from different tests were characterized using X-ray diffraction techniques (XRD, a Bruker D2 Advance Phaser apparatus) with Cu target. The instrument settings were 30 kV and 10 mA, respectively. The scan rate was 3°/min from 10° to 80°. In addition, parts of XRD experiments were conducted to quantitative analysis mineral composition of the raw and pre-sulfating steel slag, using the scan step at 3°/min. The Rietveld method was used to quantitative calculation of mineral contents of the raw and pre-sulfating steel slag using 10% ZnO as internal standard sample [40].

The kinetics and cyclic redox experiments of pre-sulfating steel slag were conducted using a TG (Setsys Evolution TGA). Mass spectrometry (MS, Omnistar GSD320 mass spectrometer) was combined with TGA to analyze the evolved product gas, wherein argon was used as a carrying gas. The air and carbon monoxide (CO) were selected as oxidation and reduction atmospheres at flow rates of 140 ml/min. Between oxidation and reduction steps nitrogen blowing was applied. For each TGA test, the sample amount was 15 ± 0.1 mg.

Thermodynamic calculation was initially carried out to obtain the equilibrium composition in gas and solid phases based on minimization of Gibbs free energy using Aspen Plus V.7.2 software.

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