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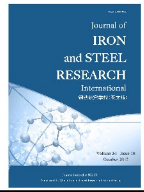

Recovery of iron and copper from copper tailings by coal-based direct reduction and magnetic separation

Chao Geng[1,2], Hua-jun Wang[1,*], Wen-tao Hu[1], Li Li[1], Cheng-shuai Shi[1]

[1] School of Civil and Resource Engineering, University of Science and Technology Beijing, Beijing 100083, China

[2] Key Laboratory for Solid Waste Management and Environment Safety, Ministry of Education of China, School of Environment, Tsinghua University, Beijing 100084, China

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ABSTRACT

A technique comprising coal-based direct reduction followed by magnetic separation was presented to recover iron and copper from copper slag flotation tailings. Optimal process parameters, such as reductant and additive ratios, reduction temperature, and reduction time, were experimentally determined and found to be as follows: a limestone ratio of 25%, a bitumite ratio of 30%, and reduction roasting at 1473 K for 90 min. Under these conditions, copper-bearing iron powders (CIP) with an iron content of 90.11% and copper content of 0.86%, indicating iron and copper recoveries of 87.25% and 83.44% respectively, were effectively obtained. Scanning electron microscopy and energy dispersive spectroscopy of the CIP revealed that some tiny copper particles were embedded in metal iron and some copper formed alloy with iron, which was difficult to achieve the separation of these two metals. Thus, the copper went into magnetic products by magnetic separation. Adding copper into the steel can produce weathering steel. Therefore, the CIP can be used as an inexpensive raw material for weathering steel.

1. Introduction

Copper is an important raw material in economic development, and increasing demands for the metal both in China and abroad have caused the copper industry to expand significantly in recent years. China is one of the most important copper producers and consumers throughout the world; the country produces a ton of refined copper for every nearly 2—3 tons of copper slag discharged. Thus, over 15 million tons of converter copper slags are produced each year[1]. The copper in these slags is preferentially recovered by flotation with a chemical agent. However, the residual solid wastes which are called copper tailings in this paper are still discarded as waste in large quantities. These copper tailings require large areas of land to store and reduce the area of usable farmland[2-4]. The construction and maintenance of copper tailing disposal sites has also increased the production cost of steelmaking plants. Even more problematic for environmental reasons is the release of chemical reagents, such as xanthate and alkaline oxides, from these storage sites, which could cause serious pollution of the soil and water[5,6].

Although the total iron content in copper tailings is relatively high, its recovery has not been developed because tailings contain large amounts of chemical reagents and are composed of a complex mixture of minerals. The particle size of ferrous minerals in copper tailings is usually small, and their compositions are also complicated[7-9]. Obtaining high-grade iron concentrate directly is difficult to achieve using traditional mineral processing techniques[10,11]. Coal-based direct reduction followed by magnetic separation has been demonstrated to be an effective method for iron recovery from solid wastes. Several researchers have investigated the production of direct reduction iron powder (DRIP) from red mud[12], iron ore tailings[13], vanadium tailings[14], cyanide tailings[15], oily hot rolling mill sludge[16], nickel metallurgical slag[17], blast furnace gas ash[18] and so on by using coal-based direct reduction followed by magnetic separation. In this process, solid wastes mixed with a reductant and additives are reduced to metallic iron, after which the roasted ores are ground and separated by mag-

* Corresponding author. Prof., Ph.D.
E-mail address: *wanghuajun@bjjzq.com* (*H.J. Wang*).

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netic separation to produce DRIP. The DRIP product obtained from this process generally contains more than 90 wt.% Fe and may be used as a substitute for steel scrap in electric arc furnaces for steelmaking[19].

Adding copper to steel can produce weathering steel with improved corrosion resistance, strength, fatigue resistance, weldability, and toughness[20,21]. The content of copper in weathering steel is generally less than 0.6 wt.%[22]. Because of its good resistance to atmospheric corrosion, weathering steel is widely used in ships, bridges, railways, pipeline, and other important areas[22,23]. The present work thus aims to recover iron and copper simultaneously from copper tailings by using the coal-based direct reduction-magnetic separation technique. Here, copper and iron minerals are reduced. After grinding and magnetic separation, copper-bearing iron powders (CIP) are obtained. This CIP could be used as an inexpensive raw material for smelting weathering steels. In this study, the effects of reduction conditions, such as additive and reductant ratio, reduction time, and reduction temperature, on the quality of the CIP produced were investigated.

2. Experimental

2.1. Materials

The copper tailings used in the study were residual slags obtained after copper recovery from copper slag by flotation. Multi-element analysis results of the copper tailings are shown in Table 1. The total iron content of the slag was approximately 42.20%, and the tailings included about 0.39% Cu. The copper tailings in the experiments were ground to 80 wt.% passing 0.074 mm. The index of basicity, $R=(w_{CaO}+w_{MgO})/(w_{SiO_2}+w_{Al_2O_3})$, was 0.29, which indicated that the copper tailings could be considered as acid slag.

Table 1
Multi-element analysis of copper tailings (mass%)

TFe	Cu	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O
42.20	0.39	32.66	3.20	4.46	5.93	0.47	0.33
MnO	**TiO_2**	**Pb**	**Zn**	**Co**	**P**	**S**	**As**
0.071	0.22	0.22	1.55	0.011	0.074	0.39	0.07

The X-ray diffraction (XRD) pattern of the copper tailings is shown in Fig. 1. The main iron minerals in the slag include fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). Peaks of copper minerals are not detected in the tailings, likely because of their low copper content. The gangue mineral is hedenbergite. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) images of the copper tailings are illustrated in Fig. 2. Fig. 2(a) shows the SEM image of the copper tailings and Fig. 2(b-e) provides detailed EDS analyses of points 1-4 in Fig. 2(a). The main copper mineral is copper matte (Fig. 2(b)), most of which is dispersed in the fayalite (Fig. 2(c)), magnetite (Fig. 2(d)), and hedenbergite (Fig. 2(e)) as small beads. These results illustrate the difficulty of recovering copper and iron through traditional separation processes.

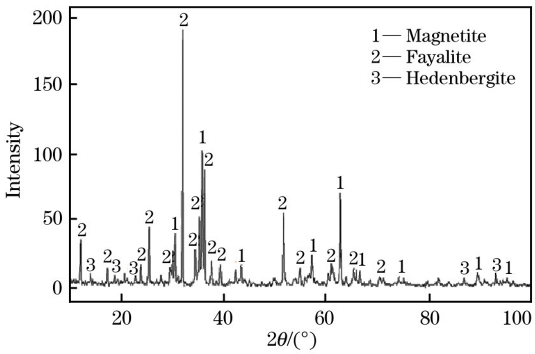

Fig. 1. XRD pattern of flotation tailings.

Bituminous coal was used as the reductant. The industrial analysis results of the bitumite show contents of 56.41% fixed carbon, 30.12% ash, 11.62% volatile matter, and 1.85% moisture. The bitumite was crushed into particles under 2 mm, and limestone, as an additive, was crushed into particles under 0.5 mm. The composition analysis of the limestone is shown in Table 2.

2.2. Principles

For copper tailings, the purpose of coal-based direct reduction is to reduce ferrous minerals and copper mattes to metallic iron and metallic copper, respectively. The reaction mechanism is expressed via the following equations[24,25]:

$$C(s)+CO_2(g)=2CO(g) \tag{1}$$

$$Fe_3O_4+CO(g)=3FeO+CO_2(g) \tag{2}$$

$$FeO+CO(g)=Fe+CO_2(g) \tag{3}$$

$$Fe_2SiO_4+CaCO_3+CO(g)=2Fe+CaSiO_4+2CO_2(g) \tag{4}$$

$$Fe_2SiO_4+2CO(g)=2Fe+SiO_2+2CO_2(g) \tag{5}$$

$$CuS+CO(g)+CaCO_3=Cu+CaS+2CO_2(g) \tag{6}$$

The calculated thermodynamic results for Eqs. (1)-(6) are shown in Fig. 3 to reveal the relationship between ΔG^θ and temperature. The overall reduction rate for coal-based direct reduction was revealed to be mainly controlled by the gasification reaction rate, i.e., the Boudouard reaction (Eq. (1))[26]. Taking Eq. (2) as an example, the relationship between reduction rate and other pertinent parameters is shown in Eq. (7)[25]:

$$t_R=\frac{R'}{A\exp(-E_0/RT)K\times M_c}+\frac{r_0\rho_0}{3D_e}[1/2-1/3R'-1/2(1-R')^{2/3}] \tag{7}$$