Research Article

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Kinetics of Iron Removal From Ti-Extraction Blast Furnace Slag by Chlorination Calcination

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Abstract: In this research, ammonium chloride was used to calcine Ti-extraction blast furnace slag (EBFS) with the aim of removing iron from it. The influences of calcination temperature, ammonium chloride to EBFS mass ratio and particle size on the rates of iron removal were investigated. The results show that the rate of iron removal increased to almost 100% with increases in calcination temperature and the NH₄Cl to EBFS mass ratio, but decreased with increases in particle size. Iron is removed in the form of ferric chloride gas, and ammonium chloride can be recycled by recrystallization after decomposition. The badgassarrym model was used to describe the calcination process at temperatures below 261°C, which was controlled by nonisothermal crystallization. The reaction kinetic equation was obtained and the apparent activation energy was 67.21 kJ/mol. Ferric chloride reaction product existed in the calcined slag in an amorphous solid state. The shrinking core model was used to describe the calcination process at temperatures above 261°C, which was controlled by surface chemical reactions. The reaction kinetic equation was obtained and the apparent activation energy was found to be 42.05 kJ/mol.

Keywords: Ti-extraction blast furnace slag; iron removal; chlorination calcination; kinetics

1 Introduction

In Panzhihua, China, over 60 million tons of Ti-bearing blast furnace slag (TBFS) is produced. It causes severe environmental problems such as groundwater contamination via the leaching of hazardous heavy metals, while particulates are emitted into the surrounding air [1]. At present, high-temperature carbonization-low-temperature chlorination is the main process used to utilise TBFS [2]. This process has a high titanium extraction rate; however, it produces a chlorine-containing waste residue called Ti-extraction blast furnace slag (EBFS), which is difficult to treat and can cause serious environmental pollution.

After chlorine removal, EBFS is mainly used to produce low-value-added products such as cement mortar admixtures [3] and bricks [4-5]. Based on its complex composition and amorphous phase structure, our research group used EBFS to produce glass-ceramics with good properties [6-7]. The chloride component escapes from EBFS during a calcination process; however, deleterious impurities can remain, usually in the form of iron compounds, which can discolor glass-ceramic products. This limits the commercial applications of glass-ceramics. Therefore, it is necessary to remove iron from EBFS before using it in glass-ceramics. Iron can be removed by two methods including: 1) a physical separation process that aims to remove iron-containing minerals, and 2) chemical treatment that dissolves iron compounds bonded at the surface or existing as mineral grains [8]. The appropriate method for the removal of iron from an industrial solid waste depends on its mineralogical form and iron distribution.

Based on a mineralogical study of EBFS, this work aims to investigate the iron removal from EBFS by ammonium chloride calcination. The iron component in EBFS reacts with ammonium chloride to form ferric chloride, which escapes from the slag in a gaseous state at a certain temperature. The process conditions, such as calcination temperature, mass ratio of NH₄Cl to EBFS and particle size, were assessed. Furthermore, the
chlorination calcination kinetics of iron was studied, which can provide a theoretical guide for future process optimization and industrial applications.

2 Materials And Methods

2.1 Mineralogical analysis of EBFS

Samples of EBFS were collected from Panzhihua Iron and Steel Co. Ltd., Sichuan, China. X-ray Fluorescence (XRF) was used to analyse the chemical components of EBFS, X-ray Diffraction (XRD) was used for mineral phase analysis, X-ray Photoelectron Spectroscopy (XPS) was used for valence analysis of the iron in EBFS, Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) was used to analyse the morphology and iron distribution of EBFS, and Thermogravimetric Analysis-Differential Scanning Calorimetry (TG-DSC) was used for thermal stability analysis.

2.2 Process of calcination with ammonium chloride

Calcination was carried out in a furnace with programmed temperature control. Firstly, a certain amount of ammonium chloride was put into a 10 g EBFS sample and stirred in a 100 mL ceramic crucible, which was then placed in the furnace. The experiments were repeated under various experimental conditions. The process design is represented in Table 1. After being calcined, The calcined product obtained below 260°C was leached in water to obtain the leached product. The leached product and the calcined product obtained above 261°C was characterized by XRF. The % iron removal (R) was calculated according to Equation (1):

\[ R = \frac{m_1}{m_2} \times 100\% \]

where \( m_1 \) and \( m_2 \) are the masses of \( \text{Fe}_2\text{O}_3 \) in the EBFS and calcined product or leached product, respectively.

Ethical approval: The conducted research is not related to either human or animal use.

Table 1: Design of the experiment.

| Parameters            | Levels   |
|-----------------------|----------|
| Time (min)            | 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60 |
| Temperature (°C)      | 180, 220, 260, 290, 310, 335, 350 |
| Mass ratio of \( \text{NH}_4\text{Cl} \) to EBFS | 1.0, 1.5, 2.0, 2.5 |
| Average particle size (µm) | 300, 200, 100, 74 |

Table 2: Chemical composition of EBFS samples (%).

| CaO | SiO₂ | Al₂O₃ | TiO₂ | MgO | Fe₂O₃ | Cl   | SO₃  |
|-----|------|-------|------|-----|-------|------|------|
| 32.45 | 27.72 | 13.37 | 8.68 | 7.62 | 4.39  | 2.96 | 0.84 |
| MnO | K₂O | Na₂O | BaO | SrO | P₂O₅ | ZrO₂ | Y₂O₃ |
| 0.81 | 0.67 | 0.26 | 0.1 | 0.06 | 0.04  | 0.03 | 0.01 |

3 Results And Discussion

3.1 Characterization of EBFS samples

The loss on ignition (LOI) of EBFS was 12.92%. On the basis of the XRF results, it contained 4.39% \( \text{Fe}_2\text{O}_3 \) (Table 2). XRD of the EBFS (Figure 1) shows that the main diffraction peaks are \( d_{\text{111}}=2.49 \text{ Å} \), \( d_{\text{200}}=2.16 \text{ Å} \), \( d_{\text{220}}=1.52 \text{ Å} \) and \( d_{\text{311}}=1.30 \text{ Å} \), which are characteristic peaks of its titanium carbide (TiC) (reference code: 00-032-1383) [9]. Besides, there are some amorphous substances in EBFS, the chemical bond in amorphous compounds is easier to break and synthesize than that in the crystal of the same substance. So the EBFS sample had high reactivity [10]. XPS was used to characterize the Fe oxidation state (Figure 2). The supported \( \text{Fe}_2\text{O}_3 \) was characterized by a spin-coupled doublet for curve fitting of \( \text{Fe}_{2p_{3/2}} \) and \( \text{Fe}_{2p_{1/2}} \) at 712.2 eV and 725.6 eV, respectively [11-12]. The supported \( \text{FeO} \) was characterized by a spin-coupled doublet for curve fitting of \( \text{Fe}_{2p_{3/2}} \) and \( \text{Fe}_{2p_{1/2}} \) at 711 eV and 723.7 eV, respectively, which indicates that both \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) species were present in the EBFS [13]. Figure 3 shows the SEM-EDS determined distribution of iron in the EBFS samples. The EBFS particles had no specific morphology and could be divided into two types: those with smooth and dense surfaces, and those with rough and loose surfaces. Surface scanning analysis indicates that the distribution of iron was very dispersed. Hence, it would be difficult to remove iron by beneficiation and a chemical method would be better.
3.2 Effect of experimental conditions on iron removal

3.2.1 Effect of calcination temperature

The mixture of NH₄Cl and EBFS was calcined at 180, 220, 260, 290, 310, 335 and 350°C for 1 h, with the mass ratio of NH₄Cl to EBFS and the particle size of EBFS held at 1.8:1 and 250 μm, respectively. The results shown in Figure 4 revealed that temperature had a strong influence on the iron removal rate, which was > 60% at temperatures > 335°C. Figure 5 shows the TG-DSC diagram for the mixture of NH₄Cl and EBFS, which has four endothermic peaks and two mass-loss regions from 170–350°C. The DSC curve of the mixture shows two small endothermic peaks at 172.1°C and 210.9°C due to the reaction of solid ammonium chloride with iron components in the EBFS. The DSC curve also shows a sharp endothermic peak at 261.1°C due to ammonium chloride being decomposed into ammonia and hydrogen chloride, resulting in a mass loss of 17.2% [14]. The DSC curve shows a small endothermic peak at 310.2°C due to the reaction of gaseous hydrogen chloride with iron components in the EBFS that formed ferric chloride gas, resulting in a mass loss of 5.2%. The reaction temperature is slightly lower than the thermodynamic calculation temperature of the reaction between Fe₂O₃ and HCl. It may be that other components in EBFS play a catalytic role in the reaction [15]. Therefore, an increase in the removal rate with increases in temperature could be attributed to a change of the state of the calcination additives leading to an increase in the reaction area between EBFS and the calcination additives.

3.2.2 Effect of the NH₄Cl to EBFS ratio

The effect of increasing the mass ratio of NH₄Cl to EBFS on iron removal is shown in Figure 6, with the calcination temperature and average particle size held at 335°C and 250 μm, respectively. An increase in the NH₄Cl to EBFS mass ratio was observed to have some influence on the iron removal rate. At low ratios, the NH₄Cl decomposed less hydrogen chloride gas, resulting in a low overall concentration of hydrogen chloride in the reaction system. Meanwhile, an increase in the ratio contributed to an increased concentration of hydrogen chloride gas in the reaction system, thus increasing the reaction rate of calcination additives and iron-containing particles in the EBFS.
3.2.3 Effect of particle size

The influence of average particle size fractions on the removal rate of iron is shown in Figure 7, with the reaction temperature and mass ratio of NH$_4$Cl to EBFS held at 335°C and 2.0:1. The results indicate that iron removal rates increased with decreases in the EBFS particle size. A decrease in particle size would contribute to an increase in the specific surface area, leading to much-improved heat and mass transfer rates and facilitating faster liberation of the iron component [16].

3.3 Phase analysis of calcined products and condensed products

As seen in the XRD patterns of the calcined product at 220, 260, 335 and 350°C with the mass ratio of NH$_4$Cl to EBFS and the particle size held at 1.8:1 and 250 μm in Figure 8, comparing with XRD of EBFS (Figure 1), the number and the intensity of the diffraction peaks of titanium carbide (TiC) decreased until they disappeared after calcination. The diffraction peaks of ammonium chloride appeared in the calcined products at 220 and 260°C. However, there is no diffraction peaks of ammonium chloride in the calcined products at 335 and 350°C. This is consistent with the
TG-DSC result (Figure 5) that ammonium chloride being decomposed into ammonia and hydrogen chloride when the temperature is higher than 261°C. This phenomenon shows that ammonium chloride will not remain in the calcined product when the calcination temperature is higher than 261°C, which is beneficial to the application of EBFS after iron removal. There are no diffraction peaks of ferric chloride in calcined product. The reason is that ferric chloride is gaseous when the calcination temperature is higher than 310.2°C, and ferric chloride may exist in amorphous state when the temperature is less than 310.2°C.

Gas produced by calcination of EBFS at 335°C, and the products of gas condensation show three distinct color ranges on the wall of quartz tube (Figure 9). The XRD pattern of the condensed products in three color ranges shown in Figure 9A, B, C revealed that white condensed product was calcination additive ammonium
chloride which is formed by hydrogen chloride gas and ammonia gas decomposed from ammonium chloride, yellow condensed product was the mixture of ammonium chloride and ammonium aqua iron chloride, brown condensed product was iron chloride hydrate. This phenomenon shows that iron can be successfully removed by calcination with ammonium chloride. Iron exists in the form of ferric chloride and can be recovered by condensation, the calcination additives ammonium chloride can also be recycled by recrystallization after decomposition.

### 3.4 Calcination kinetics analysis

#### 3.4.1 Temperatures less than 261°C

Ammonium chloride is solid at calcination temperatures lower than 261°C, so the chlorination reaction is a solid-solid reaction that forms a solid phase. The typical rate-controlling step of solid-solid reaction are the interfacial chemical reaction, diffusion control and nonisothermal crystallization process. The step with the highest kinetic resistance is the rate controlling step [17-18]. Table 3 shows the integrated rate equations. Experimental data obtained at 180, 220 and 260°C were compared with the three models, with the results shown in Figure 10 [19-21]. It can be seen that the plots of ln[-ln(1-\(r_{Fe}\))] had a very good linear relationship with ln(t), with a fitting degree higher than 0.9. This indicates that the calcination rate was controlled by regional nucleation reactions, the most appropriate reaction model is the bagdasarrym model [19].

The reaction rate constant ln(k) and its model equation at different temperatures are presented in Table 4. According to the kinetic equation, we can know that when \(n = 1\), the number of growth directions of the product nucleus is \(\alpha = 0\). So, it can be judged that the chlorination calcination reaction is completed in one step and the chlorination product is amorphous at temperatures < 261°C [22]. This is consistent with the conclusions of the experiment—that ferric chloride in the calcined product obtained at < 261°C is in an amorphous phase. The relationship between reaction rate and temperature is well established and can be modelled with the Arrhenius equation, as expressed below.

\[
kr = A e^{-\frac{E_a}{RT}}
\]

\[
\ln kr = -\frac{E_a}{RT} + \ln A
\]

Table 3: Integrated rate equations for the solid-solid reaction.

| Rate-controlling step                          | Rate equation                                      |
|------------------------------------------------|---------------------------------------------------|
| Interfacial chemical reaction                 | \((1-r_{Fe})^{1/3} - kr_1t\)                      |
| Diffusion control                             | \(1-2r_{Fe}/3-(1-r_{Fe})^{2/3} = kr_2t\)          |
| Nonisothermal crystallization                 | \(\ln[-\ln(1-r_{Fe})] = \ln kr_3 + \ln t\)       |

Table 4: Parameters of ln[-ln(1-\(r_{Fe}\))] vs ln(t) obtained at temperatures of 160°C, 200°C and 230°C.

| Temperature (°C) | Apparent rate constant ln(k) | Fitting equation                |
|------------------|------------------------------|--------------------------------|
| 180              | -8.40582                     | \(\ln[-\ln(1-r_{Fe})] = -8.40582 + 1.31927 ln t\) |
| 220              | -7.02595                     | \(\ln[-\ln(1-r_{Fe})] = -7.02595 + 1.37603 ln t\) |
| 260              | -5.72542                     | \(\ln[-\ln(1-r_{Fe})] = -5.72542 + 1.27014 ln t\) |

where \(kr\) is the rate constant, \(A\) is the frequency factor, \(E_a\) is the apparent activation energy (J/mol), \(R\) is the molar gas constant \((R = 8.314 J/mol)\) and \(T\) is the thermodynamic temperature.

The corresponding relationship between ln\(kr\) and \(1/T\) is shown in Figure 11. The apparent activation energy of iron removal is estimated to be 67.21 kJ/mol according to the slopes of the straight lines in Figure 11, with \(A\) estimated as is \(12.23 \times 10^3\) according to the intercept. Therefore, the semi-empirical kinetic equation is

\[
\ln[-\ln(1-r_{Fe})] = \ln 12.23 \times 10^3 e^{-\frac{67210}{RT}} + \ln t
\]

where \(r_{Fe}\) is the fraction of Fe removed, \(R\) is the molar gas constant \((R = 8.314 J/mol)\), \(T\) is the calcination temperature (K), \(t\) is the reaction time (min).

Because the ferric chloride calcined product is in an amorphous solid state at calcination temperatures below 261°C, solid ferric chloride cannot escape from the reaction system to achieve the purpose of iron removal. Hence, the dynamics of different \(\text{NH}_4\text{Cl:EBFS}\) mass ratios and EBFS particle sizes at calcination temperatures below 261°C are not discussed.

#### 3.4.2 Temperatures above 261°C

Ammonium chloride decomposes into ammonia gas and hydrogen chloride gas at calcination temperatures higher than 261°C. The reaction product, ferric chloride, is a gas at this temperature, so the reaction between hydrogen chloride and the iron component of EBFS is a solid-gas
reaction. Because EBFS particles have dense surfaces, which can be considered as non-porous particles, and the iron-containing particles gradually shrink during calcination, so the most appropriate reaction model is the shrinking core model [23-25]. In the chlorination calcination system, the ferric chloride gas is formed by chlorination of iron-containing minerals. Because the iron-containing minerals are widely distributed and the total iron content in EBFS is relatively low, the release of ferric chloride gas does not have a significant impact on the morphology of the EBFS particles. This results in the calcination process being controlled by diffusion through the EBFS particle layer or chemical reactions at the surfaces of the EBFS particles [17]. Integrated rate equations for the shrinking core model are shown in Table 5 [20].

The linear regression analysis of experimental data obtained at temperatures of 290, 310, 335 and 350°C using the equations in Table 5. Figure 12 compares the plots of 1 − (1 − \( r_{Fe} \))^{2/3} and 1 − (1 − \( r_{Fe} \))^{1/3} versus time at calcination temperatures of 290, 310, 335 and 350°C with a NH₄Cl to EBFS mass ratio of 1.8:1 and average particle size of 250 μm. The results show that there are very good linear relationships in the plots of 1 − (1 − \( r_{Fe} \))^{1/3} vs time.

Figure 10: Comparison between plots of (a) (1 − \( r_{Fe} \))^{2/3} − 1 and (b) 1 − 2\( r_{Fe} /3 \) − (1 − \( r_{Fe} \))^{2/3} vs time, (c) \ln[−\ln(1 − \( r_{Fe} \))] vs lnT.

Figure 11: Arrhenius plot between \( \ln r \) and 1/T for the calculation of activation energy. The values of \( K \) were calculated by using the bagdasarry model.
This indicates that the calcination rate was controlled by chemical reaction. Fitting the experimental data presented in Figures 6–7 with chemically-controlled model. The fitting results of the model to the experimental data is shown in Figure 13. The reaction rate constant and its fitting equation are presented in Table 6.

The apparent rate constant $k_r$ is affected by the calcination temperature, concentration of calcination additives and EBFS particle radius. The empirical formulas can be established as per Eq. (4) [26]. Therefore, the apparent rate constant can be calculated by the relationships between $k_r$ and each factor.

$$k_r = \frac{kC_0M}{\rho r_0}$$

Where $k_r$ is the apparent rate constant, $k$ is the reaction rate constant, $C_0$ is the concentration of hydrogen chloride gas, $M$ is the molecular weight of solid reactant, $r_0$ is the initial radius of solid reactant, and $\rho$ is the density of solid reactant ($\rho = 1.8944$ g/cm$^3$).

The relationship between $k_r$ and calcination temperature obeys the Arrhenius equation as expressed in Reactions (2) and (3), with the results shown in Figure 14a. The apparent activation energy of iron removal is calculated to be 42.05 kJ/mol, the relationship between $k_r$
and $T$ can be expressed as per Equation (5). It is generally believed that high values of activation energy (>40 kJ/mol) indicate chemical control, whereas values <20 kJ/mol imply diffusion-controlled processes [18-27-28], so the calcination rate was controlled by chemical reaction.

$$kr = 55.65e^{-42051/RT} \quad (5)$$

Equation (4) shows that the apparent rate constant $kr$ is positively proportional to the concentration of calcination additives. The concentration of hydrogen chloride gas can be calculated by the mass ratio of NH$_4$Cl to EBFS. When $\frac{KM}{\rho r_0}$ is regarded as a constant, $A_1$, Equation (4) can be transformed into:

$$\ln k_r = \ln C_0 + \ln A_1 \quad (6)$$

The plot of $\ln kr$ versus $\ln C_0$ is shown in Figure 14b. The slope of the fitting line is 0.86725, so the relationship between $kr$ and $C_0$ is:

$$kr = A_1 C_0^{0.86725} \quad (7)$$

The radius of EBFS can be calculated by its particle size. When $\frac{KM}{\rho r_0}$ is regarded as the constant $A_2$, Eq. (4) can be transformed into:

$$\ln k_r = \ln A_2 - \ln r_0 \quad (8)$$

The plots of $\ln k_r$ versus $\ln r_0$ are presented in Figure 14c. The slope of the fitting line is 0.61079, so the relationship between $kr$ and $r_0$ can be written as:

$$kr = \frac{A_2}{r_0^{0.61079}} \quad (9)$$

**Figure 14:** Relationships between $\ln kr$ and $1/T$, $\ln(C_0)$, and $\ln r_0$: (a) Arrhenius plot of the calcination process at 290, 310, 335 and 350 °C; (b) relationship between $\ln k_r$ and $\ln(C_0)$; and (c) relationship between $\ln k_r$ and $\ln r_0$. 

![Arrhenius plot](image)
The relationships between the three factors and $kr$ are established in Eqs. (5), (7) and (9). The semi-empirical kinetic equation can be obtained by synthesizing the three relationships.

$$k_r = \frac{kC_0M}{r_0} = \frac{kC_0 \cdot 0.06725}{r_0^{0.61079}} = \frac{C_0 \cdot 0.06725}{r_0^{0.61079}} A_3 \int \frac{e}{RT}$$

$$= \frac{C_0^{\frac{0.06725}{r_0^{0.61079}}}}{r_0^{0.61079}} A_3 \int e^{-42051} \int \frac{1}{RT}$$

Where $A_3$ is a frequency factor, and $A' = \frac{MA_3}{p}$.

The Arrhenius equation obtained from Figure 14a is $kr = 55.65 e^{\frac{0.06725}{r_0^{0.61079}}}$, then $A' = \frac{0.06725}{0.61079} = 55.65$.

Substituting $C_0 = 4.68\text{ mol/L}$ and $r_0 = 100 \times 10^{-6} \text{ m}$ gives $A' = 5.26 \times 10^3$. Therefore, the semi-empirical kinetic equation is

$$1 - (1 - r_{Fe})^{3/2} = 5.26 \times 10^{-2} \times \frac{C_0^{0.06725}}{r_0^{0.61079}} \times e^{-42051} \int \frac{1}{RT} \times t$$

where $r_{Fe}$ is the fraction of Fe removed, $C_0$ is the concentration of hydrogen chloride gas, $r_0$ is the initial radius of solid reactant, $R$ is the molar gas constant ($R = 8.314 \text{ J/mol}$), $T$ is the calcination temperature (K), $t$ is the reaction time (min).

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