Recovery of Soluble Potassium from Electric Arc Furnace Dust of Manganese Alloy Production: Characterization and Water Leaching Kinetics

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As an environmentally hazardous waste, electric arc furnace (EAF) dust had a potential to provide a wider resource of potassium if recycled due to high potassium content. In this study, the chemical and mineralogical characteristics of the EAF dust, especially the existing state of potassium, were analyzed. The results showed that the dust consisted dominantly of manganese oxides (Mn3O4, MnO, MnO2) and manganese silicate (MnSiO3). The K element existed in the dust was in the form of potassium permanganate (K2Mn4O8, insoluble) and potassium sulfate/sulfite (soluble). Then the soluble potassium salts in the dust were recovered by water leaching and crystallization. The recovery ratio of K reached 88.2%, and the products K2SO4 and KCl with the K2O content of 65.25% were obtained. During leaching, the Mn2+ and Mn4+ components were reduced to Mn2+ by sulfide (S2−) or sulfite (SO32−), and the S2− and SO32− components were oxidized to SO42−. The leaching kinetics was studied by the specific electrical conductivity method. The apparent activation energy was 7.76±0.65 kJ/mol, suggesting that the rate controlling step of leaching process was the diffusion of K+ through the diffusion layer.

KEY WORDS: metallurgical dust; ferromanganese and silicomanganese alloy; industrial solid waste; recycling; potassium recovery; leaching kinetics.

1. Introduction

Ferromanganese and silicomanganese alloy are a widely used deoxidizing agent for steelmaking, which is produced by carbothermal reduction of oxide ores in electric arc furnaces. As an environmentally hazardous by-product, electric arc furnace (EAF) dust of ferromanganese and silicomanganese production units is formed from volatiles and fines and collected by dedusting of the off-gas from manganese alloy smelting furnaces. The amount of dust and sludge from dry and wet off-gas cleaning is estimated to be about 120 kg per ton of ferromanganese and silicomanganese alloy production.1) Storage of EAF dust presents a long-term environmental concern.

A usual way to treat the EAF dust is returning it into electric arc furnace to reuse Mn and Si. However, a great amount of other elements, such as K, Na and Zn, are also reused in the recycle, which is harmful for normal operation of electric arc furnace.2) Many investigations on recycling of valuable components from EAF dust were carried out. Ghafarizadeh3) studied recovery of manganese from EAF dust by reductive leaching in sulfuric acid with oxalic acid as reducing reagents. Over 90% of manganese, in the form of MnSO4, was leached out. Ordiales4) suggested a cold agglomeration process using Portland cement and calcium aluminate refractory cement in order to transform manganese dust into a secondary raw material for the ferromanganese production. Shen and Hamano5–7) proposed a Zn removal method by reduction-volatilization in order to recycle EAF dust back into manganese smelting furnace based on the analysis of zinc balances. Zinc oxide was reduced by tar to zinc vapour above 800°C and evaporated into the off-gas. Kim8) suggested that the reduction-volatilization of zinc from EAF dust conformed to the shrinking-core kinetics model controlled by surface chemical reaction with the activation energy of 173 kJ/mol. In addition to Mn and Zn, the EAF dust from silicomanganese production contains up to > 15% potassium.8) However, the extraction of K from the EAF dust has rarely been reported. Since the reserve of soluble potassium ore was short in China, it would provide a wider resource of potash fertilizer for agricultural use if this K-bearing solid waste could be efficiently utilized.

Therefore, the aim of this work was to investigate the feasibility to recovery of potassium from EAF dust. The chemical and mineralogical compositions of the EAF dust, especially the existing state of potassium, were identified. Then the soluble potassium salts in the dust were recovered by water leaching and crystallization. Evolution of Mn valence state during leaching was analyzed by XPS. Finally, the leaching kinetics of soluble potassium salts was examined by in-situ specific electrical conductivity method, and
the activation energy of leaching was determined.

2. Experimental Section

2.1. Materials and Characterization

The electric arc furnace (EAF) dust used in the experiments was provided by Ordos Metallurgy Group Corporation in Inner Mongolia, China. The dust samples were collected from the furnace off-gas dry scrubbers installed in an electric arc furnace gas cleaning system. All the samples were dried at 110°C for 24 h.

2.1.1. Granulometric Analysis

The granulometric distribution analysis of the EAF dust was performed by using a laser particle size analyzer (Mastersizer 2000, Malvern, UK). In order to eliminate the variation of particle size by water solubility, absolute ethyl alcohol was used as a dispersing medium.

2.1.2. X-ray Powder Diffraction and X-ray Fluorescence

X-ray diffraction (XRD, X’Pert PRO MPD, PANalytical, The Netherlands) was used to identify the mineralogical (phase) composition of the EAF dust. The X-ray diffraction data were collected in a broad 2θ range using Cu-Kα radiation (45 kV, 40 mA) with a step size of 0.02° and a scanning speed of 6°/min. The mineral element composition (in oxide form) of the EAF dust was detected using X-ray fluorescence (XRF, AXIOS-MAX, PANalytical, The Netherlands).

2.1.3. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS, AXISULTRA-DLD, Shimadzu, Japan) was performed to determine the valence state of Mn in the EAF dust. The Al Kα (1 486.6 eV) line was used for the X-ray source. The peak positions for binding energy of samples were corrected by considering the charging effect. A binding energy of 284.7 eV was assumed for the C 1 s peak maximum in correcting for surface charging. XPSPEAK 4.1 software was used for fitting and deconvolution of Mn 2p3/2 spectrum.

2.1.4. Scanning Electron Microscopy

Scanning electron microscopy (SEM, Quanta 250, FEI, USA) with X-ray energy dispersive spectrometry (EDS, Systemsix, Noran, USA) was employed to analyze the microstructure, morphology and chemical composition of EAF dust. The same samples were also subjected to the element distribution analysis through X-ray mapping analysis via SEM.

2.2. Methods

2.2.1. Water Leaching and Crystallization

In order to evaluate the feasibility of recovering the soluble K, the EAF dust samples were leached by deionized water at 30°C for 1 h in a Jacketed PMMA (Poly(methylmethacrylate)) reactor. The solid-liquid ratio and the stirring speed were 1:10 (g/ml) and 300 rpm, respectively. Then the leaching solution containing the soluble K salt was separated by filtration. After filtration, the leaching residual was separated and dried at 110°C for 24 h. The filtrate was concentrated and crystallized by evaporation at 80°C. The chemical and phase compositions of the crystal substance and the leaching residual were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 3000, Perkin-Elmer, USA), XRD and XRF. The valence state of Mn in the leaching residual was determined by XPS.

2.2.2. Water Leaching Kinetics

In order to investigate kinetics of leaching, it was necessary to determine the K+ concentration in the solution as a function of time. However, great errors would be produced by intermittent sampling because the dissolution process of the dust was very fast. In dilute solution, the specific electrical conductivity was proportional to the concentration of solution. Therefore, in this study the specific electrical conductivity was equivalent to the K+ concentration for the calculation of leaching kinetics. The electric conductivity was measured using an in situ electric conductivity meter (DDS-11A, INESA, China). For a typical test, about 20 g of the dust sample was added into deionized water in a 100 ml flask (solid-liquid ratio 1:5 g/ml) at different temperatures of 28, 38, 45, and 50°C. The stirring speed was 300 rpm. The electrode of the electric conductivity meter was inserted into the solution directly during the leaching process. Then the data of the electric conductivity as a function of leaching time were recorded for kinetics evaluation.

3. Results and Discussion

3.1. Characterization of the EAF Dust

3.1.1. Fundamental Characteristics of the EAF Dust

The chemical composition of the EAF dust as determined by XRF is shown in Table 1. The chemical composition of the EAF dust was dominated by Mn (26.6%) and Si (22.4%). Ca, Al, Mg, Na, and Zn ranging from 2–5% originated from flux, manganese ores, and coke in which these elements occurred as impurities. It should be noted that the contribution of K was high (about 22%) in the dust. The source of potassium may be potassium aluminosilicate (mainly K-feldspar) in silica. K-feldspar was abundantly widespread in earth crust and usually existed as impurity in many minerals, especially in silica. Therefore, manganese ore or silica had a certain amount of K-feldspar, which depended on the geological deposition conditions. The K content in EAF dusts was affected by the content of K compounds in the gangue. Potassium in K-feldspar was partially reduced in the electric arc furnace (>1500°C) and more easily volatilized than other metal elements in the dust due to the relatively low melting point. The potassium compounds were evaporated and left the furnace by the top gas and were then condensed into fine particles during de-dusted by a gas-cleaning process.

Table 1. Chemical analysis of the EAF dust used in this study (in oxide form).

<table>
<thead>
<tr>
<th>Component</th>
<th>MnO</th>
<th>SiO2</th>
<th>K2O</th>
<th>SO3</th>
<th>CaO</th>
<th>Al2O3</th>
<th>MgO</th>
<th>Na2O</th>
<th>ZnO</th>
<th>Cl</th>
<th>Fe2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%)</td>
<td>26.62</td>
<td>22.43</td>
<td>22.00</td>
<td>8.57</td>
<td>4.61</td>
<td>3.87</td>
<td>3.05</td>
<td>2.55</td>
<td>2.13</td>
<td>1.66</td>
<td>1.20</td>
</tr>
</tbody>
</table>

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precipitator. Therefore, K was concentrated in the dust.

The mineralogical composition of EAF dust was determined by XRD analysis. As shown in Fig. 1, the major phases were hausmannite (Mn$_3$O$_4$), pyrolusite (MnO$_2$), manganosite (MnO) and pyroxmangite (MnSiO$_3$). The presence of Mn and Si can be associated with manganese oxide ores and silica, which were raw materials added for alloy production. In the electric arc furnace (> 1500°C), manganese were evaporated in the form of metal vapor, due to the higher vapor pressure of manganese (0.01 atm) on the ferroalloy. The volatilization of Si was attributed to the formation of gaseous SiO$_2$, which generated by the reduction of SiO$_2$ with coke. Therefore, the Mn and Si element were evaporated and collected as fine dusts. The major K-containing phases were detected as potassium permanganate (K$_2$Mn$_4$O$_8$), arcanite (K$_2$SO$_4$), and sylvite (KCl). Other phases bearing K and S with the low concentrations, such as dipotassium sulfite (K$_2$SO$_3$) and potassium sulfide (K$_2$S), could also be present in this sample. The sulfide (S$^{2-}$), sulfite (SO$_3^{2-}$) and sulfate (SO$_4^{2-}$) originated from the S element in the coke.

The granulometric distribution analysis of the EAF dust was performed by using a laser particle size analyzer. As shown in Fig. 2, the particle size distribution of the EAF dust was heterogeneous with two major size fractions: a coarser grained portion (1.29–5.03 μm) and a finer part (0.33–1.29 μm), where 90% of particles are below 2.83 μm. The mean particle size was 1.28 μm. Such an irregular granulometric distribution was probably due to agglomeration of the fine particles.

3.1.2. Existing State of Potassium in the EAF Dust

SEM/EDS analysis was performed to further investigate the existing state of K salt in the EAF dust. It was observed that the morphology of the dust sample roughly divided into two types of particles. According to EDS analysis (Fig. 3), the spherical particle (Point 1) mainly contained K (4.79%), Mn (19.48%), O (70.14%) with a little Si (5.60%), where the atomic ratio of K: Mn was about 1:4. There was hardly any S and Cl element detected. Combined with XRD analysis, the K element was in the form of K$_2$Mn$_4$O$_8$. The phases in the Mn-rich particle mainly consisted of K$_2$Mn$_3$O$_8$ and Mn–Si compounds. The irregular particle (Point 2) mainly contained K (12.98%), S (5.33%), O (79.87%) with a very little Mn (1.82%), where the atomic ratio of K: S was about 2:1. There was hardly any Cl element detected in the potassium salts. The valence state of S element cannot be determined by EDS. Thus, it was inferred that the K-rich particle probably consisted of the mixture of K$_2$SO$_4$ and K$_2$SO$_3$, which was soluble in water. As shown in Fig. 3, the distribution of soluble and insoluble components in the EAF dust was dispersive and separated, rather than embedded each other. Therefore, it was beneficial to the dissolution and diffusion of the soluble K salts during leaching.

3.2. Recovery of the Soluble Potassium from the EAF Dust

3.2.1. Characterization of Water Leaching Product

To investigate recovering of the soluble K salt, the EAF dust samples were leached by deionized water (solid-liquid ratio 1:10, g/mL) at 30°C. After filtration, the filtrate was concentrated and crystallized. The XRD patterns of the EAF dust and the leaching residual are shown in Fig. 4. It was observed that the soluble potassium phases (K$_2$SO$_4$, KCl, K$_2$SO$_3$ and K$_2$S) existed in the EAF dust, whereas their peaks disappeared in the leaching residual. In the crystal substance, the main compositions were K$_2$SO$_4$ and KCl. However, there was hardly any sulfide (S$^{2-}$) or sulfite (SO$_3^{2-}$) in the potassium salts. It was because that the
S\(^{2-}\) and SO\(_3\)\(^{2-}\) components were oxidized to SO\(_4\)\(^{2-}\) during leaching. The reaction mechanisms would be discussed in detail in the following section.

In the leaching residual, Mn (37.72%) and Si (30.92%) were dominant, whereas little S and Cl elements were detected (Table 2). This result suggested that most of the soluble K salt in the EAF dust was dissolved in water after leaching. The S and Cl elements are primarily from the geological deposition conditions, the coal type and coking process. The S element is one of the major impurities in manganese ore (<0.2%) and coke (<0.7%). In addition, at present some waste plastics were added with coal for co-coking process, resulting in an increase of the Cl content in the coke. Therefore, when the manganese ore and coal with high S and Cl content was used, S and Cl elements can be introduced in EAF dust. However, a little K (7.72%) still existed in the leaching residual. It was because of the insolubility of potassium permanganate (K\(_2\)Mn\(_4\)O\(_8\)).\(^{12}\) XRF analysis showed that the K content in the crystal substance was 65.25 wt% (in K\(_2\)O) and reached a superior grade (55%) used in fertilizer\(^{13}\) (Table 3). According to the K content (K\(_2\)O) before and after leaching, the recovery ratio of K was estimated as 88.2%. Therefore, the soluble K salt can be effectively separated from the EAF dust through leaching by water. In fact, K\(_2\)SO\(_4\) can be used directly to make fertilizer by mixing with other raw materials. However, some Cl and F elements existed in the K salts (Table 2), which were harmful to soil. Thus, the K salts containing Cl and F should be transferred into K\(_2\)SO\(_4\), and Cl and F were removed before used for fertilizer production. The K salts recovered from EAF dusts were served as just primary raw materials for fertilizer plant, rather than the final products.

The EAF dust used in this study was from Inner Mongolia of China. In 2015, the yield of Mn–Si alloys in this region was about 1.35 million tons/year.\(^{14}\) The amount of EAF dusts was about 100 kg per ton of Mn–Si alloy production, which was estimated to be about 135 000 tons/year. Assuming that the K content (K\(_2\)O) in EAF dusts was an average of 10%, the amount of K\(_2\)O recovered was 13 500 tons/year theoretically. In 2015, the yield of potash fertilizer (K\(_2\)O) in Inner Mongolia of China was about 36 000 tons/year,\(^{15}\) which was equal approximately with the demand of fertilizer. Therefore, if all the EAF dusts from Mn–Si production were used for potassium recovery, the contribution of recovered potassium was up 37.5% of the demand for fertilizer. As a result, the EAF dusts could provide a potential resource of potash fertilizer if this K-bearing waste dust could be efficiently utilized. This way could be useful to relieve to some extent serious lack of potassium fertilizer in China.

### Table 2. XRF analysis of the crystallized substance of leaching solution (in oxide form).

<table>
<thead>
<tr>
<th>Component</th>
<th>K(_2)O</th>
<th>SO(_3)</th>
<th>Na(_2)O</th>
<th>Cl</th>
<th>F</th>
<th>MgO</th>
<th>CaO</th>
<th>SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%)</td>
<td>65.25</td>
<td>18.31</td>
<td>6.91</td>
<td>6.04</td>
<td>1.16</td>
<td>0.75</td>
<td>0.51</td>
<td>0.45</td>
</tr>
</tbody>
</table>

### Table 3. XRF analysis of the leaching residual of the EAF dust (in oxide form).

<table>
<thead>
<tr>
<th>Component</th>
<th>MnO</th>
<th>SiO(_2)</th>
<th>K(_2)O</th>
<th>CaO</th>
<th>Al(_2)O(_3)</th>
<th>MgO</th>
<th>ZnO</th>
<th>PbO</th>
<th>Fe(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt%)</td>
<td>37.72</td>
<td>30.97</td>
<td>7.72</td>
<td>6.09</td>
<td>5.33</td>
<td>4.12</td>
<td>3.43</td>
<td>1.91</td>
<td>1.63</td>
</tr>
</tbody>
</table>
that the average oxidation degree of manganese decreased due to water leaching. It was inferred that part of Mn\(^{4+}\) and Mn\(^{3+}\) was reduced to Mn\(^{2+}\). As shown in Fig. 4(a), the high oxidation state Mn phase were K\(_2\)Mn\(_4\)O\(_8\) (Mn\(^{3+}:\)Mn\(^{4+}\)=1:1) and MnO\(_2\) (Mn\(^{4+}\)), the low oxidation state Mn phase were Mn\(_3\)O\(_4\) (Mn\(^{2+}:\)Mn\(^{3+}\)=1:2) and MnO (Mn\(^{2+}\)). The change of MnO (Mn\(^{2+}\)) phase was little. The peaks of MnO\(_2\) disappeared, whereas that of Mn\(_3\)O\(_4\) increased after leaching. Therefore, it was inferred that the decrease of the Mn oxidation state was attributed to the reduction of K\(_2\)Mn\(_4\)O\(_8\) and MnO\(_2\) to Mn\(_3\)O\(_4\). In alkaline conditions, the Mn\(^{3+}\) and Mn\(^{4+}\) components were reduced to Mn\(^{2+}\) by sulfide (S\(^{2−}\)) or sulfite (SO\(_3\)\(^{2−}\)), and the S\(^{2−}\) and SO\(_3\)\(^{2−}\) components were oxidized to SO\(_4\)\(^{2−}\). Based on the analysis above, the possible reactions were listed as:

\[
3\text{K}_2\text{Mn}_3\text{O}_8 + 5\text{SO}_3^{2−} + 3\text{H}_2\text{O} = 4\text{Mn}_2\text{O}_4 + 5\text{SO}_4^{2−} + 6\text{K}^+ + 6\text{OH}^−
\]

\[
12\text{K}_2\text{Mn}_4\text{O}_8 + 5\text{S}^{2−} + 12\text{H}_2\text{O} = 16\text{Mn}_2\text{O}_4 + 5\text{SO}_4^{2−} + 24\text{K}^+ + 24\text{OH}^−
\]

### 3.3. Leaching Kinetics Analysis

#### 3.3.1. Kinetics Models

During the leaching process, the EAF dust contacted with water. The soluble substances in the dust dissolve in water, while the insoluble substances suspended in the leaching solution. Therefore, leaching of EAF dust was a dissolution process of the soluble substances (mainly K\(_2\)SO\(_4\)), which was controlled by diffusion. In leaching process the soluble substances diffused from solid surface to solution as shown in Fig. 6. The distance from particle surface to the bulk solution was the diffusion layer. The rate of dissolution was equal to that of diffusion. For steady state diffusion, the relationship between diffusion rate and concentration gradient can be expressed by Fick equation:18)

\[
\frac{dn}{dt} = -DA \frac{dc}{dx} \quad \text{(1)}
\]

\[
C = \frac{n}{V} \quad \text{(2)}
\]

where \(dn/\text{dt}\) is diffusion rate (mol/s), \(n\) is the amount of soluble substances (mol), \(t\) is time (s), \(D\) is diffusion coefficient (m\(^2\)/s), \(A\) is surface area of soluble substances (m\(^2\)), \(V\) is the volume of solution (m\(^3\)), \(C\) is the concentration of soluble substances in liquid phase (mol/m\(^3\)), \(dC/dx\) is the concentration gradient (mol/m\(^4\)). Substitute Eq. (2) into Eq. (1), thus:

\[
\frac{dc}{dt} = \frac{DA}{V} \frac{dc}{dx} \quad \text{(3)}
\]

Assuming the concentration of soluble substances in the diffusion layer was as a linear function of the distance from particle surface to the bulk solution, Eq. (3) can be expressed as

\[
\frac{dc}{dr} = -\frac{DA}{V\delta} \frac{n-C_s}{C_t-C_s} \quad \text{(4)}
\]

Table 4. Fitting parameters obtained from XPS spectra of the EAF dust before and after leaching.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Valence</th>
<th>Binding energy (eV)</th>
<th>Peak area (−)</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before leaching</td>
<td>Mn(^{2+})</td>
<td>640.35</td>
<td>3 688.651</td>
<td>18.73</td>
</tr>
<tr>
<td></td>
<td>Mn(^{3+})</td>
<td>641.63</td>
<td>9 384.466</td>
<td>47.64</td>
</tr>
<tr>
<td></td>
<td>Mn(^{4+})</td>
<td>642.85</td>
<td>6 624.253</td>
<td>33.63</td>
</tr>
<tr>
<td>After leaching</td>
<td>Mn(^{2+})</td>
<td>640.45</td>
<td>5 063.288</td>
<td>21.86</td>
</tr>
<tr>
<td></td>
<td>Mn(^{3+})</td>
<td>641.61</td>
<td>10 447.23</td>
<td>45.10</td>
</tr>
<tr>
<td></td>
<td>Mn(^{4+})</td>
<td>642.83</td>
<td>7 651.958</td>
<td>33.04</td>
</tr>
</tbody>
</table>

Fig. 5. XPS spectra of Mn\(_{2p3/2}\) of the EAF dust before and after leaching.

Fig. 6. Schematic of the dissolution and diffusion of K\(^+\) during leaching.

3MnO\(_2\) + 2SO\(_3\)\(^{2−}\) = Mn\(_2\)O\(_4\) + 2SO\(_4\)\(^{2−}\)

6MnO\(_2\) + S\(^2−\) = 2Mn\(_2\)O\(_4\) + SO\(_4\)\(^{2−}\)
where $\delta$ is the thickness of diffusion layer (m), $C_i$ is the concentration of soluble substances in the dust (mol/m$^3$).

The preliminary experiments indicated that the dissolution rate of K salts in the dust was very fast, and the solution equilibrium could reach in a short time. In dilute solution, the specific electrical conductivity was proportional to the concentration of solution.\textsuperscript{19}

\[ \kappa \propto C \]

Therefore, the dissolution kinetics model can be expressed by:

\[ \frac{d\kappa}{dt} = \alpha (\kappa_i - \kappa) \]

\[ \alpha = \frac{DA}{V\delta} \]

where $\kappa_i$ and $\kappa$ refer to the specific electrical conductivity (mS/cm) of the particles in the interface and solution, respectively. $\alpha$ is the dissolution rate constant (s$^{-1}$), which is a function of temperature. If the dissolution process was considered as a reaction, the dissolution rate constant was described by the Arrhenius equation:\textsuperscript{20}

\[ \alpha(T) = \alpha_0 \exp \left( \frac{-E}{RT} \right) \]

By taking the logarithm and rearranging it, its form is changed to:

\[ \ln \alpha(T) = \ln \alpha_0 - \frac{E}{RT} \]

where $R$ is the gas constant (8.314 J·mol$^{-1}$·K$^{-1}$), $\alpha_0$ is the pre-exponential factor, $E$ is the apparent activation energy of leaching (kJ/mol).

According to Eq. (6), the dissolution rate constant [$\alpha(T)$] can be obtained from the slope of linear regression of $d\kappa/dt$ and $\kappa$ at different temperatures. Then by plotting $\ln \alpha(T)$ versus the reciprocal of reaction temperature ($1/T$) according to Eq. (9), the apparent activation energy and pre-exponential factor can be obtained by the slope and the intercept of linear regression, respectively.

3.3.2. Model Evaluation

In order to evaluate the kinetics model and the rate-controlled mechanism, the kinetics data ($\kappa$ versus $t$) were needed. Thus, the effect of the leaching time on the specific electrical conductivity was examined from 28 to 50°C (Fig. 7(a)). The results indicated that the specific electrical conductivity increased with the leaching time. The specific electrical conductivity increased rapidly from 0 to 15 s and reached a maximum at about 25 s at all leaching temperatures. In our preliminary experiments, the specific electrical conductivity of solution was measured in different concentrations of K$_2$SO$_4$ ($C_s$). The results indicated a good linear relation between $\kappa$ and $C_s$ in the K$_2$SO$_4$ concentrations <0.1 mol/L (Fig. A1). Because the Na$^+$ and Ca$^{2+}$ concentrations were very low, the specific electrical conductivity of solution was attributed to the soluble K salt and was represented by the concentrations of K$^+$ in this work. Substituting the data of the specific electrical conductivity into Eq. (6), the values of $d\kappa/dt$ can be calculated. According to Eq. (12), the values of dissolution rate constant, $\alpha(T)$, were determined from the slope obtained a regression line by plotting $d\kappa/dt$ versus $\kappa$ at different temperatures as shown in Fig. 7(b). The values of $\ln \alpha(T)$ also were calculated by taking the logarithm of $\alpha(T)$. Subsequently, the apparent activation energy and pre-exponential factor were obtained from the slope and intercept by linear regression of $\ln \alpha(T)$ with the reciprocal of reaction temperature ($1/T$) in the Arrhenius equation (Eq. (9)).

According to the data from Fig. 7(a), the plot of $d\kappa/dt$ with $\kappa$ at different temperatures is depicted in Fig. 7(b). The value of $\alpha(T)$ was obtained from the slope of a linear regression between $d\kappa/dt$ and $\kappa$. The dissolution rate constants at different temperatures calculated in Fig. 7(b) were listed in Table A1. Regression analysis showed that the correlation coefficients for all the fittings were $>0.99$, which supported a good linear relation between $d\kappa/dt$ and $\kappa$. Therefore, it was
indicated that our assumption about the diffusion-controlled model for leaching was reasonable. Then the value of \(-E/R\) was obtained from the slope of a linear regression between \(\ln(kT)\) and \(1/T\). The correlation coefficient was 0.993. The apparent activation energy \((E)\) was calculated as 7.76 ± 0.65 kJ/mol (Fig. 7(c)), which was closed to the result of leaching KCl and K2SO4 in sintering dust (11.46 kJ/mol).21 Because the \(E\) value of leaching was < 10 kJ/mol, this result also suggested that the assumption of the diffusion rate-controlling step was reasonable. According the kinetics analysis above, the rate-controlling step of water leaching was external diffusion (the diffusion of \(K^+\) through the diffusion layer). Therefore, the measures to enhance external diffusion would be beneficial to improve the recovery ratio of K. Considering the feasibility and economy, the recovery ratio of K was >90% when the particle size, leaching temperature, stirring speed, solid-liquid ratio were selected as < 10 \(\mu\)m, 50°C, 300 rpm, 1:5 g/ml, respectively.

4. Conclusions

In this paper, based on the chemical and mineralogical characterization, the process of recovering soluble K salt from the EAF dust by water leaching was investigated. The following conclusions can be drawn:

1) The EAF dust had a heterogeneous size distribution (0.33–5.03 \(\mu\)m) with a mean particle size of 1.28 \(\mu\)m. The chemical composition of the dust was dominated by Mn (26.6%), Si (22.4%), and K (22.0%). The Mn and Si phases were mainly manganese oxides (MnO, MnO2) and manganese silicate (MnSiO3). The K element existed in the dust was in the form of potassium permanganate (K2Mn4O8, insoluble) and potassium sulfate/sulfite (soluble).

2) The soluble potassium salt was recovered by water leaching and crystallization, and the recovery ratio of K reached 88.2%. During leaching, the Mn3+ and Mn4+ components were reduced to Mn2+ by sulfide (S2−) or sulfite (SO32−) and the S2− and SO32− components were oxidized to SO42−. Thus, the compositions in the crystallization product were mainly K2SO4 and KCl with the K2O content of 65.25%.

3) The kinetics of leaching of soluble potassium salts was examined by in-situ specific electrical conductivity method. The apparent activation energy was 7.76 ± 0.65 kJ/mol, suggesting that the rate controlling step of leaching process was the diffusion of \(K^+\) through the diffusion layer. The assumed reaction mechanism was in good agreement with the experimental observations.

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REFERENCES


Appendix

Details about the diffusion rate constants of leaching and the relationship between the specific electrical conductivity and the concentration of K2SO4 solution are given in Table A1 and Fig. A1.

![](image)

**Fig. A1.** Specific electrical conductivity as a function of the concentration of K2SO4 solution.

<table>
<thead>
<tr>
<th>Concentration of K2SO4 solution (mol/L)</th>
<th>Electrical conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.01</td>
<td>0.0</td>
</tr>
<tr>
<td>0.05</td>
<td>2.5</td>
</tr>
<tr>
<td>0.1</td>
<td>5.0</td>
</tr>
<tr>
<td>0.5</td>
<td>25.0</td>
</tr>
<tr>
<td>1.0</td>
<td>50.0</td>
</tr>
</tbody>
</table>

**Table A1.** Diffusion rate constant \(k\) at different leaching temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(1/T \times 10^3) (K(^{-1}))</th>
<th>(k(T))</th>
<th>(\ln(k(T)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>3.0945</td>
<td>0.2507</td>
<td>-1.3834</td>
</tr>
<tr>
<td>311</td>
<td>3.1431</td>
<td>0.2413</td>
<td>-1.4219</td>
</tr>
<tr>
<td>318</td>
<td>3.2139</td>
<td>0.2206</td>
<td>-1.5114</td>
</tr>
<tr>
<td>323</td>
<td>3.3206</td>
<td>0.2042</td>
<td>-1.5889</td>
</tr>
</tbody>
</table>