Separation of Chlorides from EAF Dust

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Abstract: To utilize waste EAF dust for high-value applications, such as in construction materials and ceramics, the significant problem of the release of chlorides in the inorganic phase must be solved. An environmentally safe and economically efficient leaching process to extract chlorine elements is proposed in this paper. We found that the application of polar organic solvents can, in part, complement conventional wet methods. Among the test solvents (methanol, ethanol, and acetone), methanol was the most optimal for removing the chlorines when diluted with 10% (v/v) pure water.

Keywords: EAF dust, chlorine compounds, extraction, organic solvent, Mohr titration

Introduction

There are two types of steel manufacturing processes: a blast furnace using iron ores and an electric arc furnace (EAF) using recycled iron products; the latter is used more frequently worldwide because of economic incentives. Thus, in Korea, the number of EAF facilities has steeply increased; currently, they occupy more than 95% of the domestic steel production market. However, the EAF steelmaking process discharges a large volume of waste dust. Because this dust contains various heavy metal elements, it is defined as a hazardous solid waste by the national legislation. Thus, landfilling of this waste in general dumping sites has been banned.

Although a few desirable treatment methods, such as permanent stabilization or recovery of valuable metal elements, have been presented, high cost has limited their practical application. The most frequent utilization of the waste is as packing materials of ascon in road paving and as concrete additives [1]. However, additional problems occur when the waste packing materials become exposed to the air, e.g., on an abraded road, which may result in secondary environmental impact, including soil contamination, air, and water pollution.

In addition to the heavy metals, immobilized chlorine ions present in free chlorides must be critically treated to enlarge the number of uses of this waste. Once chlorine elements are released into the air, they may cause acid rain, which eventually results in erosion and blazing of concrete, and furthermore facilitates corrosion of iron reinforcing structures in constructions, which finally leads directly to deterioration of physical resistance. In addition to other potential hazards, many efforts have been made to reduce the chlorine content of the waste. One of the simpler methods to remove the chlorine from the EAF dust is leaching by water, but this process discharges a large volume of waste water with the sludge. The dust deeply wetted during the washing process must be dried before any practical application as a cement additive [2,3]. A few of the conventional drying methods usually have high cost and depend absolutely on the dust’s properties [4]. In accordance, in this present study, we attempted to apply a semi-drying method by using organic solvents, which can afford an economical advantage, having high polarity: alcohols and acetone. We used them either as pure solvents or as solutions mixed with a minimum amount of water.

Experimental

Dust Preparation

The test dusts used in this study were received as the
result of two different processes of a major domestic steel company: sintered dust (dust-A) and mini-mill dust (dust-B). The elemental compositions of the dusts were analyzed by energy dispersive X-ray (EDX) spectroscopy and the results are summarized in Table 1. Crystalline structures, focusing on the chlorine compounds analyzed by the X-ray diffraction (XRD), are displayed in Figure 6. It displays major peaks for AlOCl₂, SiCl₄, and KCl for dust-A, but not significant crystalline structures appear for dust-B, except AlOCl₂ and KCl.

Besides iron oxides, calcium, aluminum, and silicon oxides were ubiquitous in both dust samples. For the experimental work, raw dust particles were ground by ball-milling and sieved with a stainless mesh (Tyler # 120) because fine mode particles are apt to provide better contact between solids and liquids. However, if the particles are too fine, they may become difficult to handle and the process will lose its economic advantages. The collected dust was dried at 110°C for 24 h in a vacuum oven and then reserved in a desiccator filled with silica gel until required for test extraction.

**Table 1. Compositions of Dust Samples (wt%)**

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Pb</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust A</td>
<td>4.23</td>
<td>33.41</td>
<td>0.63</td>
<td>0.28</td>
<td>1.72</td>
<td>4.61</td>
<td>1.43</td>
<td>5.84</td>
<td>7.26</td>
<td>9.01</td>
<td>30.31</td>
<td>0.32</td>
<td>0.95</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dust B</td>
<td>-</td>
<td>27.77</td>
<td>3.05</td>
<td>1.38</td>
<td>0.51</td>
<td>0.68</td>
<td>0.21</td>
<td>0.51</td>
<td>0.49</td>
<td>3.41</td>
<td>37.46</td>
<td>-</td>
<td>0.49</td>
<td>2.02</td>
<td>22.03</td>
</tr>
</tbody>
</table>

Figure 1. Schematic diagram of the test extraction process.

The efficiency of the solvent washing process could be evaluated finally from the concentration of residual chlorine compounds.

Figure 1 depicts the extraction process; a 500-mL flat-bottom flask was placed on a magnetic heating plate that was able to be adjusted for its temperature and agitation intensity. A thermocouple inserted into the glass reactor indicated the reaction temperature. The reactor was sealed with a thin para-film to prevent loss due to evaporation of the organic solvents during mixing.

**Results and Discussion**

This study focused on the removal efficiency of chlorides in EAF dust by applying various extraction solvents and washing conditions. The separation efficiency was defined as the ratio of extracted Cl elements in a liquid phase to the intrinsic amounts of chlorides in the dust.

**Effect of Solvent Dilution**

Figure 2 shows the effect of diluting each solvent with distilled water. Extraction was continued for 20 min. As can be seen from Figure 2, the addition of water obviously enhanced the extraction efficiency; better separation was achieved in pure methanol than in pure ethanol or acetone at a low dilution rate. In particular, for dust-A, >80% of the chlorine elements were removed by a 90% (v/v) methanol solution. This result was confirmed through the XRD analysis shown in Figure 6. When the dilution rate was 0.2, i.e., mixed with 20% (v/v) of additional water, the removal rate increased to 95%. The other two solvents showed a similar tendency in their extraction efficiencies: steep increases of the removal rates at high water content, which reached up to 97% at 50% (v/v) dilution. This result, however, might be due mainly to the
added water, rather than the organic solvent. The high polarity of water has great potential to extract chlorine from aqueous slurry solutions. Thus, chlorine extraction could not but depend greatly on the water content. In practice, more than 99% of chlorine elements disappeared when samples were washed with pure water, which was reconfirmed quantitatively by ion chromatography (Alltech, USA). Although methanol was best among the three solvents used in this work, it is more toxic than the other two solvents. Therefore, the addition of methanol must be applied with caution for any practical processes.

Meanwhile, dust-B showed a similar tendency in its extraction efficiency, but it was affected by the dilution rate to a relatively lower extent. The chlorine concentration that remained in the dust after washing often with 80% solvent was about 2000 ppm, and it decreased to 1200 ppm when using 50% (v/v) solvent. When comparing these two plots (Figure 2), we observe that the washed dust still held more than 1000 ppm of Cl even though water was added at up to 50%. In general, marketable EAF dust should contain chlorides at no more than 1000 ppm. Thus, to meet practical demand, multi-stage treatment must accompany any additional processes.

The extraction time was also investigated and the results are summarized in Figure 3. The test extraction times varied from 5 to 30 min, but they did not greatly affect the efficiency. In contrast, the extraction efficiency depended more on how well the dust was wetted by the vigorous stirring. Anyhow, sufficient time must be allocated to allow frequent and accurate contact between the dust particles and the solvent. Because the extraction time is closely related to the economic feasibility of a practical process, a more comprehensive assessment of the economic value must be made prior to applying the real process design.

Under the agitation applied in this study, we found that while the washing time did not affect significantly the release of chlorine compounds from dust-A, the removal efficiency increased consistently with time for dust-B in all solvents. Penetration of liquid solvent into the particles depends on the characteristics of the solid dust. The chemical structure of the chlorides in the dust particles may also influence the leaching behavior. In accordance, because the potential of extraction varies with the formation of intrinsic dust, a more profound investigation on the chemical bonding or structure of the chlorides is required to determine the optimum extraction conditions for each dust.

Effect of Repeated Washings

Figure 4 presents the experimental results of a study performed to determine how to maximize the treatment
efficiency by minimizing the addition of water. Dust samples were washed repeatedly up to 3 times using a fresh solvent with 10% (v/v) dilution for each 20-min extraction. Figure 4 shows a very obvious difference between dust-A and dust-B. As mentioned above, while the effectiveness of methanol was quite clear in dust-A relative to the other solvents, the differences between the solvent types was relatively low in dust-B. The second washing led to more than a 20% enhancement in Cl removal for dust-A, and 10% for dust-B, for every solvent. Ethanol and acetone still showed low efficiencies (maximum about 40%) in dust-A despite repeated washings with fresh solvent. Washings repeated several times could result in more chlorine extraction from dust-B. In particular, washing three times with acetone approached an efficiency as high as that of methanol, which suggests the possibility of substituting a less-toxic solvent for methanol.

Although it was not stated earlier in this paper, 80% (v/v) acetone could wash out more than 90% of chlorine elements from dust-A when washing twice. The mixtures of 70% (v/v) acetone and 70% (v/v) methanol showed nearly 90% removal from dust-B. We also found that washing five times did not increase the removal efficiency any further. As a consequence, optimum operations conditions should be chosen by considering the practical feasibility between the drying of the dust, the environmental safeness, and the economic cost of repeated washing.

**Effect of Solvent Volume**

The removal efficiency was examined according to the volume of the extracting solution. We had expected that contact between the particles and solvent for a given mixing time and under the same stirring conditions would be increased when using a greater volume of solution. Additionally, the solvent might be able to penetrate more deeply into the dust particles and finally extract more chlorine elements out of the EAF dust. The test was performed using volumes of each solvent of 50 to 300 mL to ascertain the absolute amount of the solution that could affect the chlorine extraction.

The extraction efficiency was tested by using only the 90% solution, and the results are summarized in Figure 5. The experiments showed that methanol was the best choice, providing a maximum extraction of 98% with a 300-mL solution for dust-A and 86% for dust-B. Again, ethanol and acetone revealed low extraction efficiencies. According to the reference test, one of the simplest methods to recover the used solvent is distillation, but distillation usually comes at a high cost, and, thus, the economic value will drop upon increasing the applied volume. In practice, as a result of the distillation test, the recovery rate was less than 90% with a maximum purity of 98%, which varied with the dilution rate.
XRD Observations

Figure 6 displays a few selected XRD patterns obtained after applying the extraction condition. Analysis was performed using the samples obtained after single washings. Many peaks appeared for metallic compounds, and some indicated metal chlorides, such as KCl, AlOCl₂, and SiCl₄ for dust-A, and KCl and AlOCl₂ for dust-B. As can be seen from the diffractograms, while no significant change in the abundances of metal oxides and compounds occurred after solvent washings, reduction of the peaks for the chlorine compounds was comparatively apparent. The decreases in peak height imply the partial disappearance of chlorine elements. In particular, we also could visually ascertain that the 90% (v/v) methanol solution [Figure 6, i-(b)] was more effective than 70% (v/v) acetone.

Other metallic elements might not be leached using only polar organic solutions, so additional processes may be required for the recovery of potentially hazardous heavy metals if the waste dusts are to be used for more environmentally safe purposes.

Conclusions

Pure or diluted solvents (methanol, ethanol, and acetone) were applied to the extraction of chlorine elements from EAF dusts. The extraction ability of the organic solvents was related closely to their polarity and solubility of ionic phases. Amongst the test solvents, methanol was the most effective because of its high polarity, which is useful when dissolving ionic materials, and this solvent diluted with water resulted in more than 90% extraction efficiency. Repeated washings and/or using a high volume of the solvent also led to better extraction. XRD observations confirmed the extraction of chlorine compounds by revealing an evident reduction of the signals of the chlorides. Recovery of the organic solvents used is very important in order to achieve any economic benefits from this process. Two purification processes, distillation and adsorption using activated carbon and ion exchange resin, are now on peer tests.

References