Separation and Recovery of Valuable Metals from Automobile Shredder Residue (ASR) Fly Ash by Wet Processing

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The amount of automobile shredder residue (ASR) reaches 0.6-0.7 million tons per year in Japan, approximately. One of the effective processes to reduce the amount of ASR was the incineration process, generally carried out in smelting and refining plant. During the process, however, large amounts of ASR fly ash containing chloride (Cl) compounds and some valuable metals (e.g., copper, zinc) were produced. In this contribution, the recycling of copper, zinc and Ca/Na chloride compounds from ASR fly ash was investigated by using a process consisting of cementation, sulfide precipitation and distillation. The experimental results showed that high-grade copper (metal and oxide) and zinc (sulfide) were separated with recovery rate > 97% from the HCl washing solution of ASR fly ash by cementation and precipitation. CaCl₂·9H₂O and NaCl were obtained from the washing solution of ASR fly ash by vacuum distillation.

Key Words: Recycling, Automobile Shredder Residue (ASR), Fly Ash, Cementation, Sulfurization

1. Introduction

In Japan, a new law to strengthen the treatment of the End of Life Vehicles (ELVs) has started on 1st January 2005. Recently, the amount of automobile shredder residue (ASR) approximately reaches 0.6-0.7 million tons per year in Japan. Some recycling and reducing treatments for the ASR were conducted in many industrial fields including the automobile making, shredder and dismantling, and smelting/refining of ferrous and non-ferrous metals [1-28].

It is well known that the ASR contains useful metals and organics/inorganics, such as copper, zinc, lead and rubber, plastics, sponge, glass, respectively [1-19]. Although the primary processes for the recycling of the ASR were mainly composed of dry separation and/or dismantling process [20-28], in many recycling processes the thermal treatment or incineration was widely used to recover the valuable metals and energy by an environmentally friendly production and management [1-19]. In these processes, large amounts of ASR fly ash containing chloride (Cl) compounds and some valuable metals (e.g., copper, zinc) were produced, particularly in the smelting and refining plant, becoming important secondary resources in consideration of the environmentally sustainable development of society.

On the other hand, it was infeasible to apply the ASR fly ash into the smelting processes directly, because in the fly ash the content of metals was relatively low and the high concentration of chlorine will damage the plant equipments also. In order to decrease the Cl content in the ASR fly ash to a reasonable level for an industrial application and ensure an eco-friendly process, a practical process to concentrate the useful metals including Cu and Zn and an effective de-chlorination process to remove the Cl from the fly ash have to be considered. From a viewpoint for the comprehensive utility of resources and environmental protection, both the process to recover metals e.g., Cu and Zn and the technology to remove and immobilize the chlorine (Cl) from ASR fly ash are quite necessary to avoid the diffusion of Cl into the environment.

In this contribution, the recycling of copper and zinc from the HCl leaching solution of ASR fly ash was investigated by using a process composed of cementation, sulfide precipitation [29-30]. A solid Ca/Na chloride mixture was also recovered by distilling water from the solution after separation of Cu and Zn. Some new results regarding to the effective conditions were revealed and a treatment procedure for industrial application was suggested also.

2. Experiments

2.1 Samples

In this case, the ASR fly ash of the following properties was used for study. The chemical compositions were listed in Table 1. These data was obtained by chemical method using acidic and alkaline dissolution to decompose the samples and Inductively Coupled Plasma (ICP spectrometry, Seiko Instrument, Inc. SPS 3000) to determine the contents of metals. The contents of Cu, Ca and Zn were 10.6%, 8.9% and 2.8%, respectively. As shown
in Figure 1, the X-Ray Diffractometry (XRD, JEOL, JDX-3530) results suggested that the main phase of the ASR fly ash was CuO, SiO₂ and CaO. Additionally, the undersize fraction of the sample at 400 mesh (37 μm) was 85.1% and a natural pH of the suspension was 3.8.

2.2 Experimental procedure

Firstly, HCl and NaOH were used to adjust the pH, because the natural pH of ASR fly ash suspension was in acidic region (pH 3.8), and the dependence of metal dissolution on pH was also obtained by using ICP analysis, where the pulp density was 50 gram dry-ASR per liter solution. According to the results from Figure 2, pH 1.5 was determined to achieve a relatively high dissolution of the metals (74.6%, 60.0% and 76.9% for Cu, Zn and Ca, respectively) and to control the Fe and Pb dissolution at a low level as possible as we can and also the Cl content derived from HCl solution. The detail experimental procedure was shown in Figure 3 further.

Secondary, the metal recovery processes from washing/leaching solution of ASR fly ash (pH 1.5, shown in Figure 2) were performed according to following steps: cementation, sulfurization and distillation process.

The cementation and sulfurization were used to recover the Cu and Zn from washing solution with pH 1.5. Cementation was an ion exchange phenomenon in solution, and could be explained by standard electrode potential. In solution the metallic aluminum (Al) scrap plate can reduce the dissolved Cu ion (Cu²⁺) to Cu (Cu⁰), because in the strong acidic regions, the standard electrode potential (i.e. E°) of Cu is more positive than that of Al. In fact, the E° of Al is of negative value [31,32], while E° of Cu is positive. Therefore, the reaction of cementation can be expressed as equation (1).

\[ 2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu \]  \hspace{1cm} (1)

Generally, in order to achieve a high productivity of Cu, the reaction time for the cementation was determined to be 180 minutes (see Figure 8 also), after Al plate was added to the leached solution.

Sulfurization was carried out to recover Zn from the solution after cementation with NaSH (1 wt% aqueous solution). The sulfurization time was 90 minutes. In this sulfurization process, the sulfurized compound of Zn was produced in the form of precipitate, and can be separated by filtration.

Finally, the solution from sulfurization step was neutralized to pH 7.5 by adding NaOH to remove the Fe and Al ions by precipitation. The calcium and sodium chlorides were obtained by distilling the water from the remnant solution at 120°C in a rotary evaporator.

| Table 1 Compositions of ASR fly ash (wt%) |
|---|---|---|---|---|---|---|---|
| Fe | Ca | Pb | Zn | Al | Si | K | Cu | Na | Cl |
| 6.2 | 10.6 | 1.8 | 2.8 | 8.2 | 15.8 | 1.0 | 8.9 | 1.8 | 11.1 |

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\text{Figure 1} \quad \text{XRD pattern of ASR fly ash.}
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\text{Figure 2} \quad \text{Relationship between metal extraction and the pH of the ASR fly ash suspension.}
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\text{Figure 3} \quad \text{Experimental procedure for the metal recovery from ASR fly ash.}
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3. Results and Discussions

3.1 Recovery of Cu by cementation and comparison with sulfurization

The Cu and some valuable metal ions were dissolved in the washing (leaching) solution of the ASR fly ash with pH 1.5 (Figure 2). Cementation and sulfurization process were compared to recover Cu. At first, to obtain the sulfurized precipitate of Cu from the washing solution, the effect of sulfurization with addition of NaSH(aq) was investigated. The results were shown in Figure 4. It revealed that the concentration of Cu ion surely decreased with the concentration of NaSH, although the concentration of Ca was almost kept constant. The initial concentrations of Cu and Ca ion are both 3.4x10^3 mg per dm^3, approximately. The formed precipitate was sulfurized Cu (i.e., CuS) according to the XRD analysis. The grade and recovery of Cu (as a precipitated CuS) from the washing solution of ASR fly ash were 60.0% and 90.1%, respectively. On the other hand, as impurity ions, Pb and Zn can be kept at constant concentrations in the full NaSH concentration range under the present experimental conditions. This result was explained by the relationship between solubility of sulfurized precipitate (log[M^{2+}]) and concentration of S^{2-} (log[S^{2-}]) as shown in Figure 5 [33]. The results in Figure 5 showed that CuS has lower solubility than PbS, ZnS and FeS, even in the low concentration range of S^{2-} ion. This suggested that the Cu ion could be primarily and selectively precipitated by sulfurization, while Pb, Fe and Zn ions could be mostly maintained in the solution. However, another important issue has to be considered to recover metals from the washing solution effectively. In present experiment, the sulfurized precipitate was difficult to be filtered because of the fine size of particles.

In order to overcome the shortcoming of selective precipitation in the sulfurization process, a cementation process was chosen as an alternative method to recover the Cu from a washing solution of ASR fly ash. The basic principle of cementation process was based on the reaction (1), where Cu ion in the washing solution can be replaced to form metallic Cu. In this case, we used Al scrap plate to replace Cu.

Figure 6 showed the dependence of Cu concentration on the addition of Al scrap plate. The results showed that Cu and Pb concentrations in the washing solution were decreased with the additional amount of Al scrap to the solution. On the other hand, the concentrations of Ca, Zn, Fe were almost kept constant at their initial levels.

It is obvious that Cu could be selectively recovered from the washing solution, which was obtained by washing the ASR fly ash suspension (pH1.5), according to the difference of standard electrode potential (E°) of the metals. The E° of Cu is of positive value in acidic region, while the E° of Zn, Ca, Fe and Al are of negative values comparing with Cu (Al^{3+}: -1.66, Zn^{2+}: -0.76, Fe^{2+}: -0.44, Cu^{2+}: +0.34, Vat pH10) [31,32].

The results in Figure 6 also indicated that Cu contained in the washing solution was recovered almost completely by cementation by using Al scrap. The concentration of Cu in the remnant solution was decreased from 3.5x10^3 mg/dm^3 of the initial concentration to
1.2 mg/dm$^2$, where the added amount of Al scrap plate was 0.038 mol/dm$^3$. Moreover, the recovery product was composed of metallic Cu and Cu$_2$O according to the XRD analysis results as shown in Figure 7. Under this condition, the grade and recovery rate of Cu reached 90.0% and 97.8%, respectively.

Finally, the influence of reaction time on the recovery of Cu by sulfuration and cementation from the washing solution of ASR fly ash was compared as shown in Figure 8. It is illustrated that the reaction rate of sulfuration was slightly faster than that of cementation. In the case of cementation, it is probable that a longer time to dissolve the Al scrap into the washing solution at pH 1.5 than that in the sulfuration process was required.

In the cementation process, the concentration of Cu was gradually decreased with time on stream from average initial concentration of about 3.5x10$^3$ mg/dm$^3$. Three hours were required to achieve a high recovery rate of the Cu with high grade from the washing solution of ASR fly ash (Figure 8). The grade and recovery rate of the Cu from the cementation process was distinctly higher than that from the sulfuration process.

3.2 Recovery of Zn by sulfuration and chloride compounds by distillation

After the cementation (pH of the washing solution was ca. 2.0), a sulfuration process was investigated to recover Zn from the solution by adding NaSH(aq). Figure 9 shows the effect of pH in the solution after NaSH sulfuration on the dissolution of Zn ion. The results revealed that the concentration of Zn in the solution after the sulfuration decreased with pH. Especially, the concentration of Zn at pH 3.2 was remarkably decreased from an initial value of 5.9x10$^2$ mg/dm$^3$ to 1.8 mg/dm$^3$ due to the formation of sulfurized precipitate. In this case, the recovered product was determined to be ZnS by the XRD analysis as shown

![Figure 7](image1.png) XRD pattern of Cu recovered by cementation.

![Figure 8](image2.png) Dependence of the concentration of Cu on reaction time of sulfuration and cementation (NaSH 0.06 mol/dm$^3$, Al scrap 0.04 mol/dm$^3$)

![Figure 9](image3.png) Effect of pH on the dissolution of Zn ion in washing solution after sulfuration by NaSH. (reaction time 30 min.)

![Figure 10](image4.png) XRD pattern of Zn recovered by sulfuration.
in Figure 10. The grade and recovery rate of Zn was 49.0% and 98.6%, respectively.

According to the experimental results, Cu and Zn can be almost completely separated with relatively high grade and recovery rate from the washing solution of the ASR fly ash (pH1.5), manifesting that the ASR fly ash can be reused as new resources of non-ferrous metals in smelting and refining plant.

In the following step, the remained metallic ions in the solution after the removal of Cu and Zn, such as Fe ion have to be removed also. After being neutralized to pH7.5 with addition of NaOH(aq), the solution and residue was separated by filtration. Fe ion was precipitated as hydroxide as shown in Figure 11.

The results in Figure 11 revealed that the concentration of Fe and Ca ions in the remnant solution was decreased with pH adjusted by NaOH. Especially, under the condition of pH > 7.5, most of the Fe was removed in the form of iron hydroxides from the remnant solution which was of an initial average Fe concentration of 2.0x10^2 mg/dm^3. At the same time, the Ca ion was also partially removed to some extent. We ascribe this to the co-precipitation of Ca(OH)_2 with the iron hydroxides precipitate and/or to the adsorption of the Ca ion onto the newly formed iron hydroxides.

It was confirmed that the concentration of the remained Ca after neutralization was around 2.8x10^2 mg/dm^3. In addition, the solution also contained small amount of Na ion. A distillation treatment by rotary evaporator was carried out to concentrate and further to immobilize the Ca, Na and Cl from the remnant solution via the form of chloride compounds. It was confirmed that CaCl_2 (9H_2O) and NaCl were the main components of solid separated from the final solution by vacuum distillation under the condition of 393K. The XRD patterns of recovered products were shown in Figure 12.

In this experiment, 9.1 g of total amount of chloride compounds were produced from the initial 50 g of ASR fly ash, and total recovery rate of Ca from the washing solution of ASR fly ash was over 80%. However, there is a doubt that the grade of the Ca contained in the final chloride compounds from this process was less than 43.9%. Therefore, further investigations are necessary to apply efficient processes to increase the purity of chloride compounds, in order to comply with the requirement for a practical use, although high recovery rate and grade of Cu and Zn from the washing solution of ASR fly ash has been already achieved by cementation and sulfurization.

4. Conclusions

In this study, a recycling process in terms of an ASR fly ash was developed to recover copper, zinc and Ca/Na chloride compounds, including cementation, sulfide precipitation and distillation. The experimental results were summarized as follows:

(1) By using cementation and sulfurization process, the grade and recovery rate of Cu are determined to be 90% and 97.8%, respectively. The Zn can be recovered in form of ZnS (XRD analysis) with a grade of 49% and a recovery rate of 98.6%. These manifest that the cementation-sulfurization process is more effective than flotation to concentrate the Cu and Zn from the ASR fly ash.

(2) Al scrap plate is effective to separate Cu and Zn by cementation. The grade and recovery rate of Cu is positively related to the addition of Al. With respect to Zn, a positive relationship between the grade and/or recovery rate with addition of NaSH has also been found.

(3) Vacuum distillation was found to be effective for the recovery of CaCl_2 (9H_2O) and NaCl from the remnant solution after separation of Cu and Zn. In addition, the chloride (Cl^-) ion can also be removed from the washing solution of ASR fly ash.

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References

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