

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

Table 1 Compositions of ASR fly ash (wt%)

Fe	Cu	Pb	Zn	Al	Si	K	Ca	Na	Cl
6.2	10.6	1.8	2.8	8.2	15.8	1.0	8.9	1.8	11.1

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 (37μm) 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 (pH3.8), 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, pH1.5 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

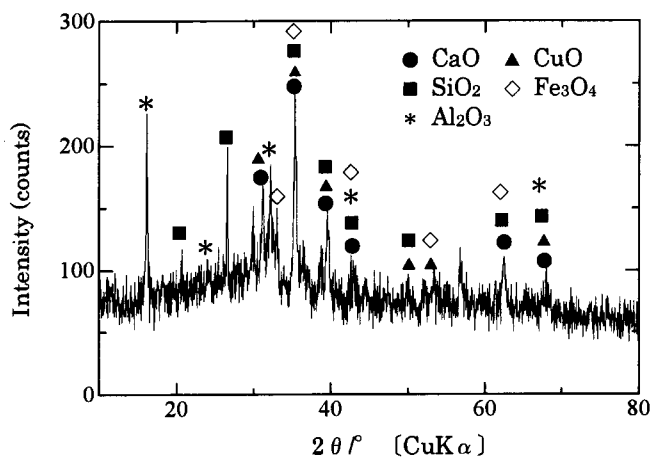


Figure 1 XRD pattern of ASR fly ash.

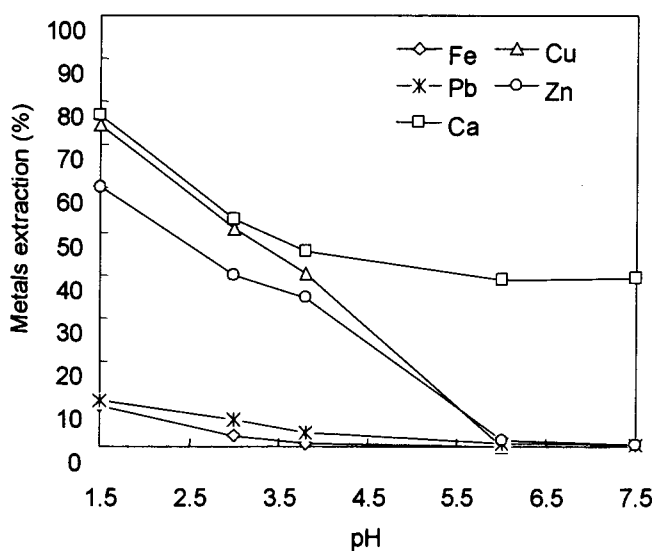


Figure 2 Relationship between metal extraction and the pH of the ASR fly ash suspension.

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 (pH1.5, 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 pH1.5. 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. E⁰) of Cu is more positive than that of Al. In fact, the E⁰ of Al is of negative value [31,32], while E⁰ of Cu is positive. Therefore, the reaction of cementation can be expressed as equation (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 (1wt% 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 pH7.5 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.

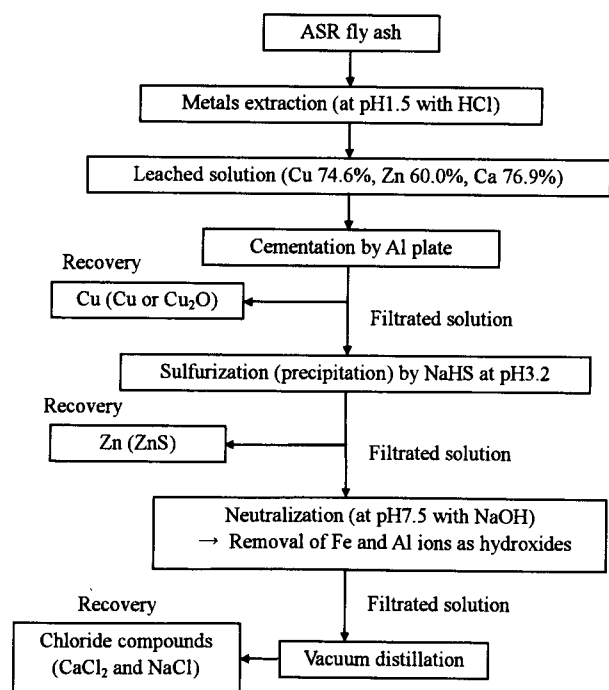


Figure 3 Experimental procedure for the metal recovery from ASR fly ash.

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 pH1.5 (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 3.4×10^3 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.

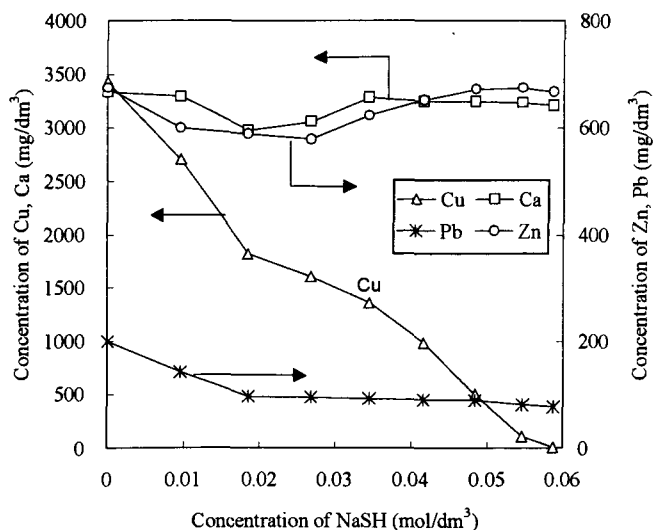


Figure 4 Dependence of the metal concentration (Cu, Ca, Pb and Zn) in washing solution on the addition of NaSH at initial pH1.5.

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^0) of the metals. The E^0 of Cu is of positive value in acidic region, while the E^0 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 pH0) [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 3.5×10^3 mg/ dm^3 of the initial concentration to

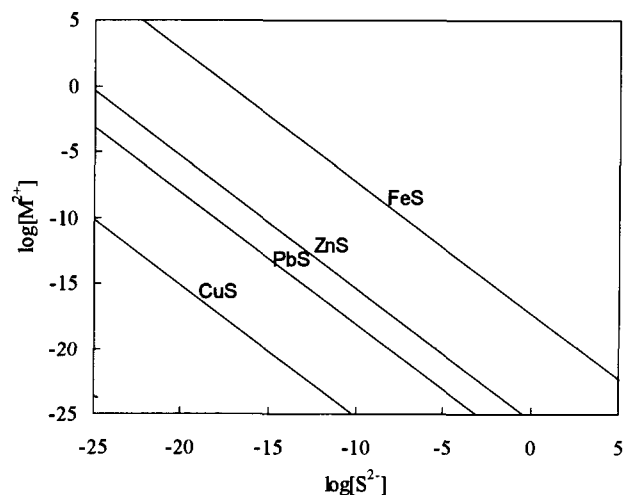


Figure 5 The relationship between the solubility of the sulfurized precipitate ($\log[M^{2+}]$) and the concentration of S^{2-} ($\log[S^{2-}]$) [31-33].

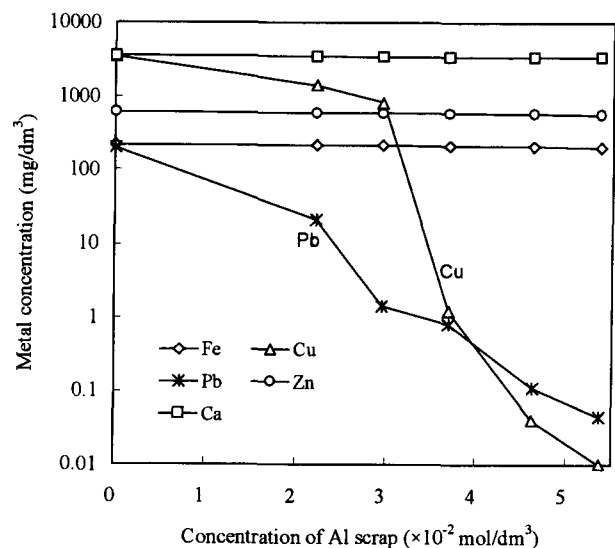


Figure 6 Dependence of Cu concentration on the addition of Al scrap plate. (pH1.5, reaction time 30 min.)

1.2 mg/dm^3 , 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_2O 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 sulfurization 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 sulfurization 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 sulfurization process was required.

In the cementation process, the concentration of Cu was gradually decreased with time on stream from average initial

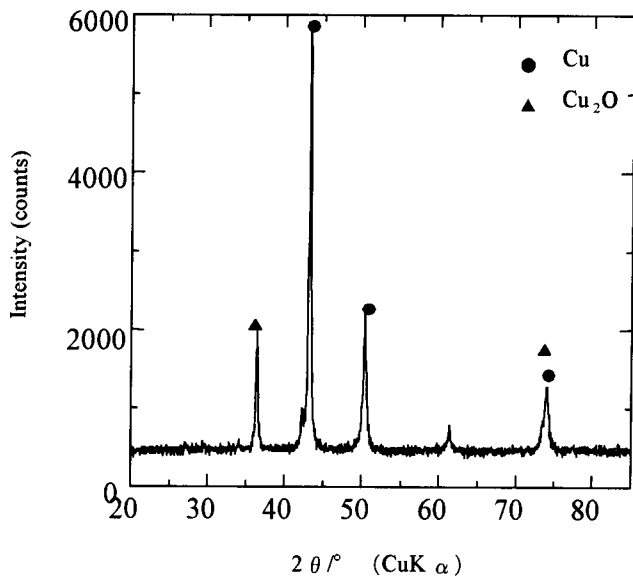


Figure 7 XRD pattern of Cu recovered by cementation.

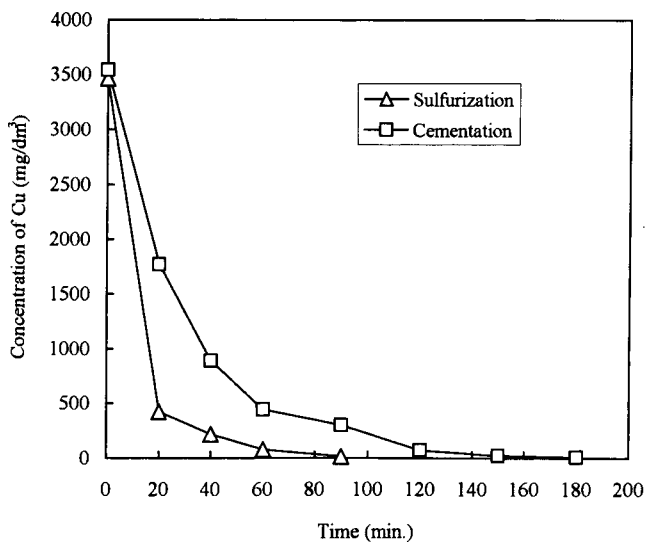


Figure 8 Dependence of the concentration of Cu on reaction time of sulfurization and cementation ($\text{NaSH } 0.06 \text{ mol/dm}^3$; Al scrap 0.04 mol/dm^3)

concentration of about $3.5 \times 10^3 \text{ mg/dm}^3$. 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 sulfurization process.

3.2 Recovery of Zn by sulfurization and chloride compounds by distillation

After the cementation (pH of the washing solution was *ca.* 2.0), a sulfurization 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 sulfurization on the dissolution of Zn ion. The results revealed that the concentration of Zn ion in the solution after the sulfurization decreased with pH. Especially, the concentration of Zn at pH 3.2 was remarkably decreased from an initial value of $5.9 \times 10^2 \text{ mg/dm}^3$ 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

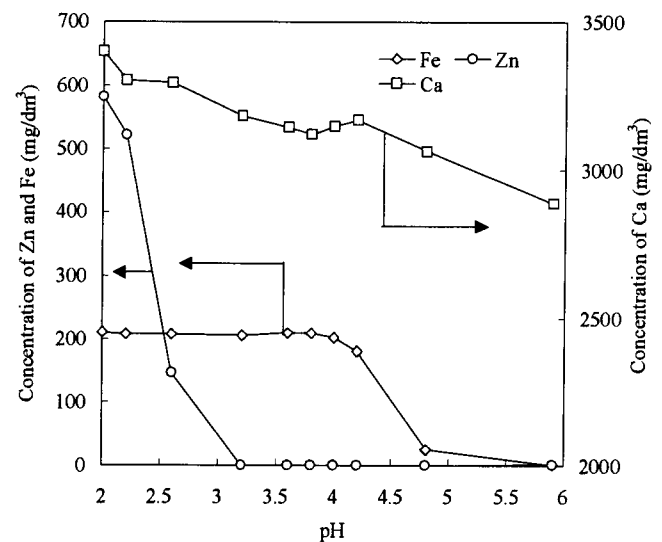


Figure 9 Effect of pH on the dissolution of Zn ion in washing solution after sulfurization by NaSH . (reaction time 30 min.)

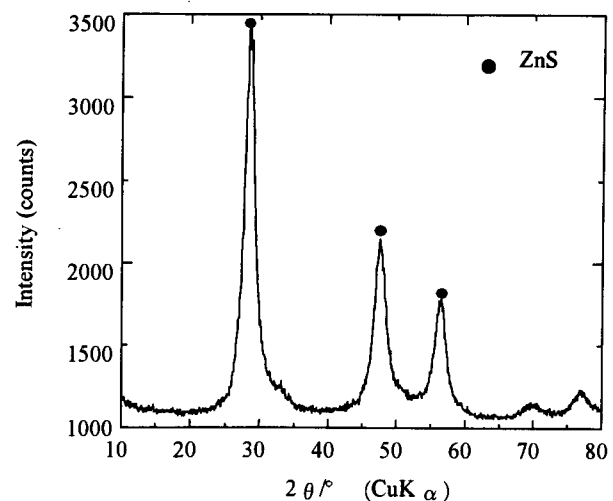


Figure 10 XRD pattern of Zn recovered by sulfurization.

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 $2.0 \times 10^2 \text{ mg/dm}^3$. At the same time, the Ca ion was also partially removed to some extent. We ascribe this to the co-

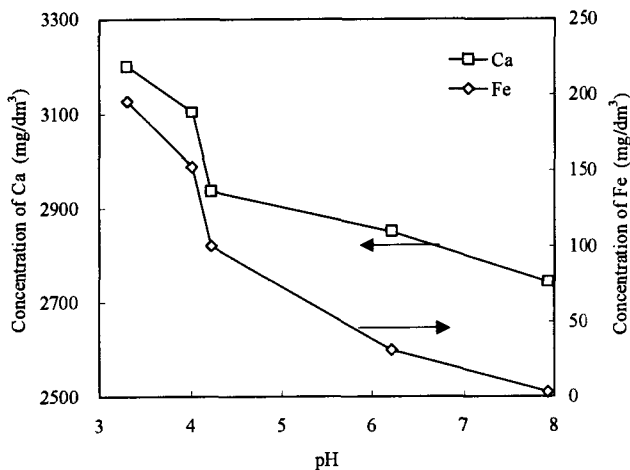


Figure 11 Relationship between the concentration of Ca, Fe and different pH of washing solution.

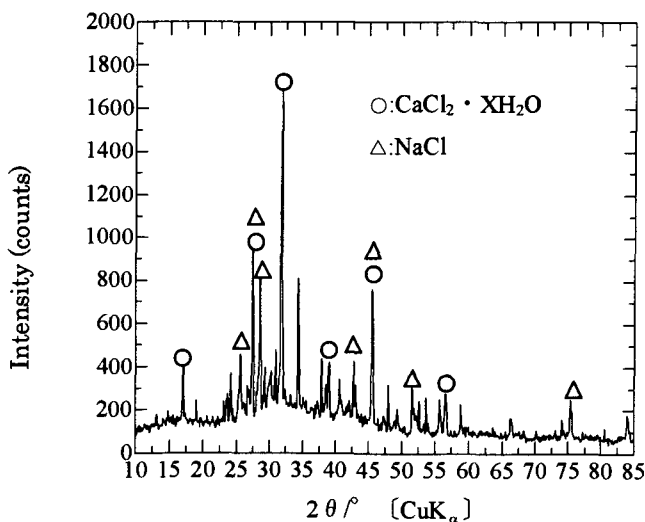


Figure 12 XRD patterns of chloride compounds recovered by distillation treatment carried out on a rotary evaporator.

precipitation of $\text{Ca}(\text{OH})_2$ 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 $2.8 \times 10^3 \text{ mg/dm}^3$. 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 $\text{CaCl}_2 \cdot 9\text{H}_2\text{O}$ 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 $\text{CaCl}_2 \cdot 9\text{H}_2\text{O}$ 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

- [1] Hamai, M., et al., "Study Concerning Combustion Characteristics of Gasified Shredded Dust -Evaluation of the ASR Gasification and Fusing System for Energy Recovery and Environmental Load Characteristics-, Proceedings of the 2000JASE Annual Congress, No.75-00, pp.17-20 (2000).

- [2] De Filippis, P., Pchetti, F., Borgianni, C. and Paolucci, M., "Automobile Shredder Residue Gasification", *Waste Manage. Res.*, Vol.21, No.5, pp.459-466 (2003).
- [3] Horii, M. and Iida, S., "Gasification and Dry Distillation of Automobile Shredder Residue (ASR)", *JSAE Rev.*, Vol.22, NO.1, pp.63-68 (2001).
- [4] Day, M., Cooney, J. D. and Shen, Z., "Pyrolysis of Automobile Shredder Residue : an analysis of the products of a commercial screw kiln process", *J. Anal. Appl. Pyrolysis*, Vol.37, No.1, pp.49-67 (1996).
- [5] Jean A.A., "Mixed Combustion of Automotive Shredder Residues with Municipal Solid Waste : a sound route to energy recovery from end of life vehicles", *Polym. Recycl.*, Vol.2, No.4, pp.291-297 (1996).
- [6] Nikko Mikkaichi Recycle Co., "Incineration Experiment on Shredder Dust of Used Motor", *Enbi-to-Porima*, Vol.38, No.5, pp.1-3 (1998).
- [7] Shibaïke, H., et al., "Shredder Dust Recycling with Direct Melting Process", *Iron Steel Inst. Jpn.*, Vol.40, No.3, pp.252-259 (2000)
- [8] Hino, J., et al., "Test of Metal Recovery from Shredder Dust utilizing Nonferrous Smelting Technology", *Proceedings of the Japan Society of Waste Management Experts Annual Congress*, Vo.9th, No.Pt.1, pp.468-470 (1998).
- [9] Takaoka, T., et al., "New Cycling Process for Automobile Shredder Residue Combined with Ironmaking Process", *Stahl Eisen*, Vol.123, No.11, pp.101-106 (2003).
- [10] Tsukimoto, E., et al., "Basic Investigation on the Utilization of Automobile Shredder Dust Dry Distillation Residue. -Recycling Techniques using Grinding by Wet Process and the Flotation of Carbon-, *Proceedings of the 2000JASE Annual Congress*, No.25-00, pp.13-16 (2000).
- [11] Ueno, I., et al., "Development of the Recycling Process of Automobile Shredder Residue by Coat-tar Based Oil Bath Treatment", *Tetsu-To-Hagane/J. Iron Steel Jap.*, Vol.88, No.10, pp.635-642 (2002).
- [12] Hino, J., et al., "Nonferrous Metal Smelting using Shredder Dust", *Shigen-to-Sozai*, Vol.113, No.12, pp.29-32 (1997).
- [13] Inoue, H., "Recycling of the Automobile Shredder Residue (ASR) for Recover of Metals and Energy", *Proceedings of the 2004JASE Annual Congress*, No.7-04, pp.1-5 (2004).
- [14] Hino, J., et al., "Recycling. Recovering Technology of Nonferrous Metals in Shredder Residue", *Shigen-to-Sozai*, Vol.113, No.12, pp.1043-1047 (1997).
- [15] Rausa, R. and Pollesel, P., "Pyrolysis of Automotive Shredder Residue (ASR) Influence of Temperature on the Distribution of Products", *J. Anal. Appl. Pyrolysis*, Vol.40-41, pp.383-401 (1997).
- [16] Roy, C. and Chaala, A., "Vacuum Pyrolysis of Automobile Shredder Residues", *Resources, Conserv. Recycl.*, Vol.32, No.1, p.1-27 (2001).
- [17] Winslow, G.R. and Adams, T.N., "Recycling Automotive Shredder Residue and Plastics using the CWT Thermal Process", *Global Plastics Environmental Conf. 2004-Plastics (GPEC2004)*, p.1-6 (2004).
- [18] Ueno, I., et al., "Development of New Recycling Process for ASR", *JSAE Rev.*, Vol.23, No.40 p.504-505 (2002).
- [19] Reuter, M.A., Pieterse, M.V. and Dalmijn, W.L., "Is the Pyrometallurgical Recovery of Inorganic Material an Option for Automobile Shredder Residue", *Proc. of the TMS Fall Extraction and Processing Conf.*, Vol.2, pp.1787-1797 (1999).
- [20] Izumikawa C., et al., "Test of Metal Recovery from Shredder Dust Incinerated Ash utilizing Mining Engineering", *Proceedings of the Japan Society of Waste Management Experts Annual Congress*, Vo.9th, No.Pt.1, pp.465-467 (1998).
- [21] Winslow, G.R., Liu, S.X., Yester, S.G., "Study of Plastic Material Recovery fom Automotive Shredder Residue", *SAE Special Publications (Design and Manufacture for the Environment)*, Vol.1342, p.11-18 (1998).
- [22] Kusaka, K., Iida, S., "Sorting, Compaction and Solidification Technologies for Automobile Shredder Residue (ASR)", *JSAE Rev.*, Vol.21, n4, p.549-554 (2000).
- [23] Kita, M., Oohashi, A., Okamura, Y., "Development of a Pre-Disposal Separating System for Automobile Shredder Residue", *Rev. of Automot. Eng.*, Vol.26, n2, p147-150 (2005).
- [24] Izumikawa, C., "Metal Recovery from Ash of Automobile Shredder Residue-Especially Focusing on Particle Shape", *Proceedings of TMS Fall Extraction and Processing Conferense*, Vol.2, p.1777-1786 (1999).
- [25] Sendjarevic, V., Pokorski, B., Klempner, D., Frisch, K.C., "Recent Developments in Shredder Downstream Separation Processes and Recycling Options for Automotive Shredder Residue", *SAE Special Publications (New Plastics Application for the Automotive Industry)*, Vol.1253, p.163-169 (1997).
- [26] Lanoir, D., Trouve, G., Delfosse, L., Froelich, D., Kassamaly, A., "Physical and Chemical Sharacterization of Automotive Shredder Residues", *Waste Manage. Res.*, Vol.15, n3, p.267-276 (1997).
- [27] Lee, C.H., Fan, K.S., Chang, T.C., "Resource Recovery and Recycling of Scrap Vehicles", *EM : Air and Waste Management Associations Magazine for Environmental Managers*, No.DEC, p.14-23 (1999).
- [28] Jody, B.J., Daniels, E.J., Pomykala, J.A.Jr., "Progress in Recycling of Automobile Shredder Residue", *TMS Annual Meeting, EPD Congress 1996*, p.585-592 (1996).
- [29] Shibayama, A., et al., "A Separation Process for Recycling Fly Ash from Incineration of Automobile Shredder Residue (ASR)", *Proceedings of the 2004JASE Annual Congress*, No.7-04, pp.6-10 (2004).
- [30] Shibayama, A., Otomo, T., et al., "Metal Recovery of Fly Ash from Automobile Shredder Residue Incineration by Wet Process", *Proc. of 5th Int. Conf. on Mater. Eng. for Resources (ICMR 2005 AKITA, Akita, Japan, 2005)*, B2-3, pp.161-165 (2005).
- [31] The Japan Institute of Metals, "Extarctive Metallurgy", pp.109-150 (1999).
- [32] P. Balaz, "Extractive Metallurgy of Activated Minerals (Process Metallurgy 10)", p.145-193 (2000).
- [33] *Nihon-Bunseki-Kagakukai ; Bunseki Kagaku Binran*, Maruzen, p.666 (2003).