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Characteristics and heavy metal leaching of ash generated from incineration of automobile shredder residue

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Abstract

Bottom and fly ash collected from automobile shredder residue (ASR) incinerator have been characterized in terms of particle size, compositions, and heavy metal leaching by the standard TCLP method. Two alternative methods were also examined for the treatment of heavy metals in ASR incinerator ash from the aspect of recycling into construction or lightweight aggregate material. It was remarkable that the concentration of Cu was very high compared to common MSWI bottom and fly ash, which was probably originated from copper wires contained in ASR. As a whole, the results of characterization of ASR fly ash were in good agreement with common MSWI fly ash in terms of particle size, pH, and water-soluble compounds. It was clearly found that heavy metals could be removed thoroughly or partly from ASR fly ash through acid washing with dilute HCl solution so that the remaining fly ash could be landfilled or used as construction material. It was also found that the amount of heavy metal leachability of lightweight aggregate pellet prepared with ASR incineration ash could be significantly decreased so that the application of it to lightweight aggregate would be possible without pre-treatment for the removal of heavy metals.

Keywords: ASR; Incineration; Ash; Lightweight aggregate; Heavy metals

1. Introduction

Automobiles are composed of a lot of parts made of various materials such as iron, nonferrous metals, plastics, and rubber, etc. and therefore, the end-of-life vehicle (ELV) may be one of the important resources of recycled materials. In the disassembling process of ELV, engines, doors, tires and liquid materials are mechanically separated through the disassembling machines and/or manpower. In some cases, seats and glass are also detached so as to reduce the volume and weight.

After the above-mentioned disassembling process, the remaining frame of ELV is pressed followed by the shredding. In most cases, iron scrap and nonferrous metals such as aluminum, copper and zinc, etc. are separated from the shredder products by magnetic separator (MS) and eddy current separator (ECS), respectively. During the shredding and separation of pressed vehicles, automobile shredder residue, so-called ASR, which is composed of a variety of plastics, fibers, rubber, and sponge, etc., is produced [1–3] and the majority of ASR is now treated by the landfill method. The landfill of such ASR materials would cause the severe environmental problems and the recent government regulations enforce the prohibition of ASR landfill because of the shortage of landfill sites as well as the environmental pollution. Accordingly, in recent years an attempt to incinerate ASR has been made as an alternative treatment method [4].

As far as the fraction of ASR materials in pressed vehicles is concerned, it is reported to account for about 30–35% of shredder product [5]. As stated previously, ASR is mainly composed of plastic, fiber, rubber and sponge, etc. and has a high potential for recycling as a source of thermal energy. Although incineration of ASR can generate thermal energy and reduce the volume of ASR sent to landfill, however, this still produces significant quantities of incinerator ash involving bottom and fly ash. The environmental advantage of incineration over landfill is even greater if incineration ash is recycled into new raw materials such as road construction or aggregate material [6–8]. A remaining problem is heavy metals pre-concentrated in bottom ash and particularly in fly ash. Fly ash collected from flue-gas is generally regarded as hazardous waste, and handled accordingly.

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As an instance, in order to be disposed of in ordinary landfills or possibly recycled, fly ash needs to be stabilized/solidified by suitable processes, generally based on the use of Portland cement [9–11]. The main drawbacks of such a process are the considerable increase in volume and weight of the residue. This means that the advantage of the incineration process is lost, and material is produced that might still be very hazardous for the environment, especially if the material breaks up. Moreover, another factor to be considered is the behavior of heavy metals contained in ASR incinerator ash, which may be essentially different in source or content from those in municipal solid waste incinerator (MSWI) ash.

In the present work, bottom and fly ash collected from ASR incinerator have been characterized in terms of particle size, compositions, and heavy metal leaching by the standard TCLP method. In addition, two alternative methods were also examined for the treatment of heavy metals in ASR incinerator ash from the aspect of recycling into construction or lightweight aggregate material.

2. Experimental

2.1. Materials

Two bottom ashes and four fly ashes were collected from the commercial incinerator of ASR, the capacity of 15,000 ton/year, located at Pohang, Korea. Table 1 shows the type of ash used in this work. Bottom ashes taken out from the water reservoir contained much water while fly ashes were of dry powder except semi-dry reactor ash. Bottom ash accounting for about 85% of total ash was a heterogeneous mix of ceramic materials such as brick, glass, ferrous and non-ferrous metals and other non-combustible inorganic and residual organic matter. All samples were sufficiently dried in vacuum oven at 105 °C.

Among those ashes, boiler ash #4 was selected to prepare the lightweight aggregate pellet by mixing with a lightweight filler and mineral binder. Expanded perlite, effective density of 0.18 g/ml and mean particle size of 150 μm, which was delivered by SK CMT Corp. in Korea, was used as a lightweight filler and bentonite, one of the clay minerals, was also used as a binding material.

2.2. Characterization of ash

The particle size distribution of the dried samples was analyzed by laser diffraction (Beckman Coulter LS-100) in the range from 0.04 to 2000 μm. Crystalline phases present in ash were determined by X-ray diffraction (XRD) using a Phillips PW 1830 diffractometer system with 40 mA and 40 kV, Cu Kα radiation. The pH of the as-received ashes was measured with a pH meter (Fisher Scientific accumet® model 20) by preparing a slurry of 10 wt% solid density in deionized water. The fraction of soluble compounds in ash was also determined by washing three times with deionized water.

Table 1
The type of ASR incineration ash generated from incinerator used in the work

Sample code	Classification	Generation part
Bottom #1	Bottom ash	Stoker grate
Bottom #2	Bottom ash	Stoker grate
Cyclone #3	Fly ash	Cyclone
Boiler #4	Fly ash	Boiler
SDR #5	Fly ash	SDR
Bag filter #6	Fly ash	Bag Filter

2.3. Preparation of lightweight aggregate pellet

Three materials, that is, boiler ash #4, lightweight filler and bentonite, were weighed and thoroughly mixed in a V-mixer of 5 l capacity in the laboratory. After 1 h mixing of those materials, the mixture was placed in a polyethylene vessel and kneaded with 3% carboxymethylcellulose (CMC) solution. The kneading was continued until a mix of uniform was achieved. The test pellet, 30 mm diameter and 30 mm height, was cast in a cylindrical mold with hand compaction only. The cast pellet was dried in a vacuum oven at 105 °C for 8 h and calcined at elevated temperatures up to 1,000 °C for 2 h.

2.4. Heavy metal leaching test

The batch test of heavy metal leaching from ash or lightweight aggregate pellet was conducted based on the standard TCLP (toxicity characteristic leaching procedures of US EPA) method [12]. In case of lightweight aggregate pellet, it was previously crushed and classified with a sieve, the aperture of 1 mm. The oversize product was re-crushed until all particles passed through a sieve. The weighed sample and leaching solution were mixed together in a polypropylene bottle and placed in an incubator adjusted to 25 ± 1 °C for 18 h with mechanical shaking of 30 rpm. After leaching of heavy metals, the material was filtered with filter paper and then metal concentrations (As, Cd, Cr, Pb, Cu) in the filtrate were determined by AA spectroscopy (Varian, SpectrAA 800) and ICP(Thermojarrell Ash, Polyscan 61E).

3. Results and discussion

3.1. Characterization of ash

The amount of heavy metals (As, Cd, Cr, Pb, and Cu) and chloride ion in ASR ashes used in the work was given in Table 2. It was remarkable that the concentration of Cu was very high compared to common MSWI bottom and fly ash [13]. Especially, the concentration of Cu was found to be more than 10,000 mg/kg in ASR bottom ashes, which was probably originated from copper wires contained in ASR. Moreover, the majority of Pb contained in ASR was believed to vaporize during incineration so that the content of Pb in bottom ash was less than 600 mg/kg. High concentration of chloride ion in SDR #5 and bag filter #6 would be due to the neutralization of HCl gas with slack lime in the semi-dry reactor.

Fig. 1 shows the particle size distribution of fly ashes, that is cyclone #3, boiler #4, SDR #5, and bag filter #6, respectively.

Table 2
The content of heavy metals (As, Cd, Cr, Pb, and Cu) and chloride ion in ASR ashes

Sample code	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Cl^- (mg/kg)
Bottom #1	12.3	<1	12.1	540	34,000	6,700
Bottom #2	10.7	<1	11.4	600	27,000	6,100
Cyclone #3	12	7	9.7	1,400	2,800	580
Boiler #4	38.4	110	10.2	12,000	3,400	8,500
SDR #5	10.7	16	6.5	4,700	1,200	156,000
Bag filter #6	20.4	105	5.4	9,600	4,600	243,000

The particle size distribution of two bottom ashes collected from the commercial incinerator of ASR was not measured because bottom ash was a severely heterogeneous mix in particle size, including some materials even more than 100 mm. As shown in the figure, the majority of particles in fly ash existed in the range of 2–1000 μm. It was found that the order of mean particle size was cyclone #3 > boiler #4 > SDR #5 > bag filter #6. Especially, very fine particles less than 0.4 μm are included in bag filter #6, which may be originated from the use of slack lime for semi-dry reactor.

According to our preliminary test in the laboratory, SDR #5 and bag filter #6 contained much water soluble compounds due to the addition of slack lime to neutralize the acidic gas like HCl while other ashes had the negligible amount of water soluble compounds. The weight loss of those ashes depending on the number of water washing was given in Fig. 2. It was found that SDR #5 and bag filter #6 lost their weight after water washing of three times by 41% and 73%, respectively. According to the X-ray diffraction analysis of those ashes, as shown in Fig. 3, the major constituent material of SDR #5 and bag filter #6 were observed to be $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$ and $CaCl_2 \cdot 4H_2O$, respectively. These calcium compounds would be generated through the reaction between hydrogen chloride and slack lime added in a semi-dry reactor. Moreover, the results of the X-ray diffraction analysis are in good agreement with the test of water washing in that bag filter #6 contains more water-soluble compounds than SDR #5. In addition, the pH value of ASR incineration ash appeared to be relatively high alkaline, especially in case of SDR #5 as shown in Table 3. As a whole, the results of characterization of ASR fly ash were in good agreement with common MSWI fly ash in terms of particle size, pH, and water-soluble compounds [9,14].

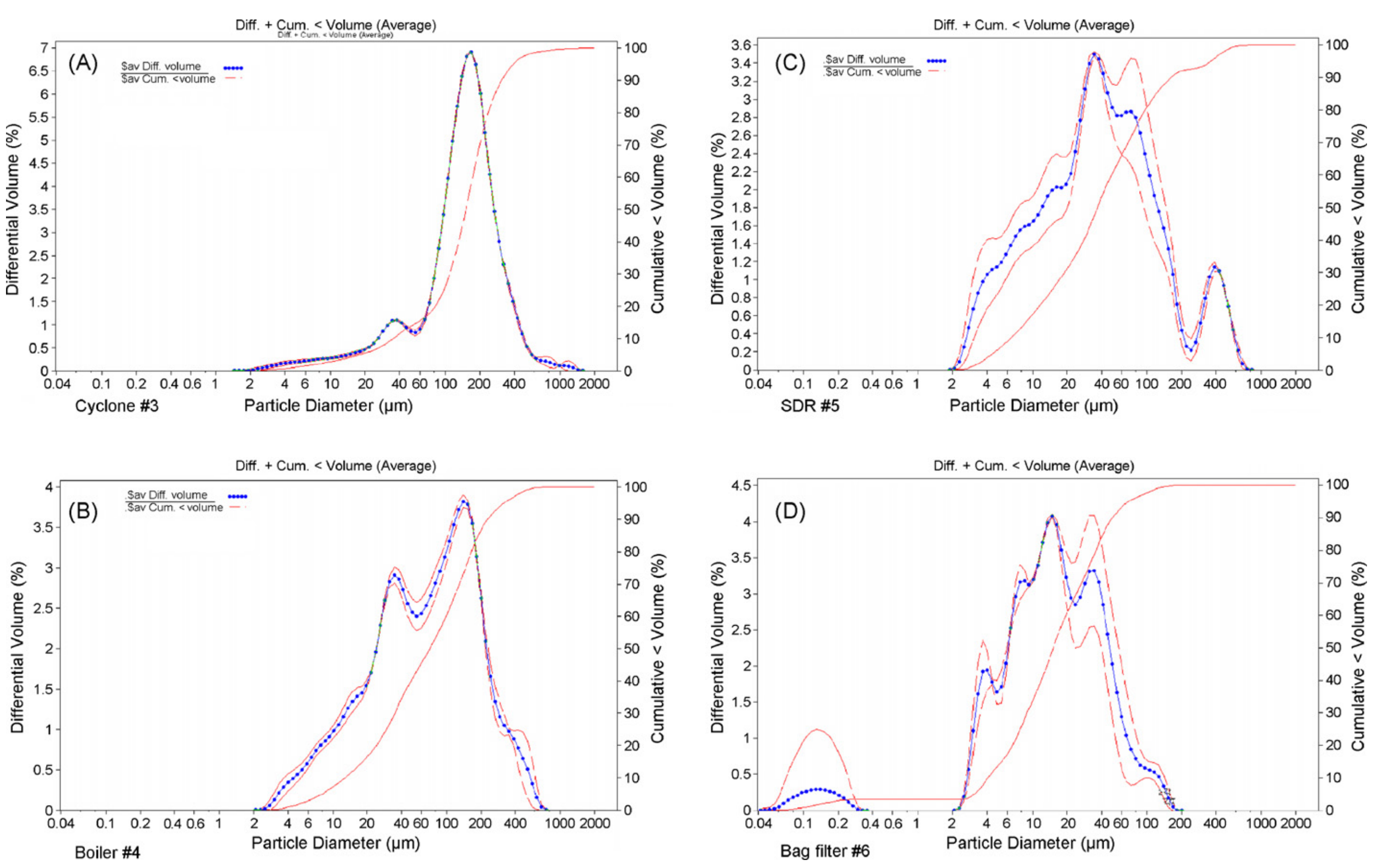

Fig. 1. Particle size distribution of ASR fly ashes used in the work.

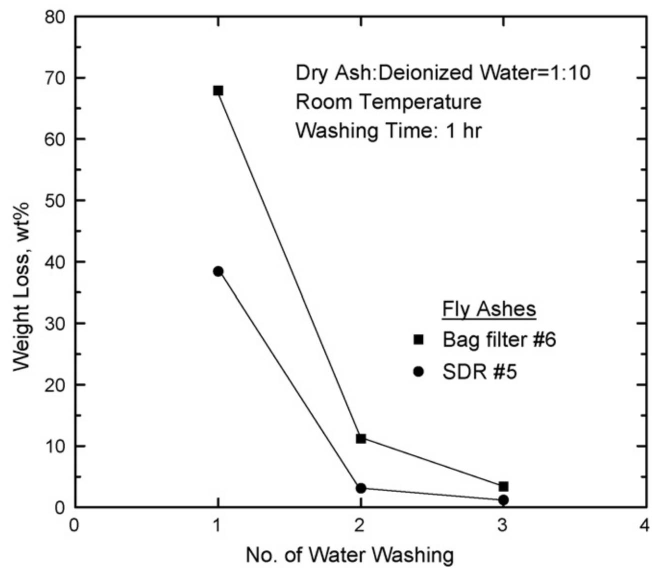

Fig. 2. Variation of weight loss with the number of water washing for fly ashes.

3.2. Heavy metal leaching test

Table 4 shows the results of metal leachability for ASR incineration ash determined by the standard TCLP method.

As shown in the Table 4, the amount of heavy metals leached out from ASR bottom and cyclone ashes was found to be lower level than the regulatory limit in Korea. Especially, it may be remarkable that the amount of Pb leached out from bottom ashes is very low compared to common MSWI ash [13]. Actually,

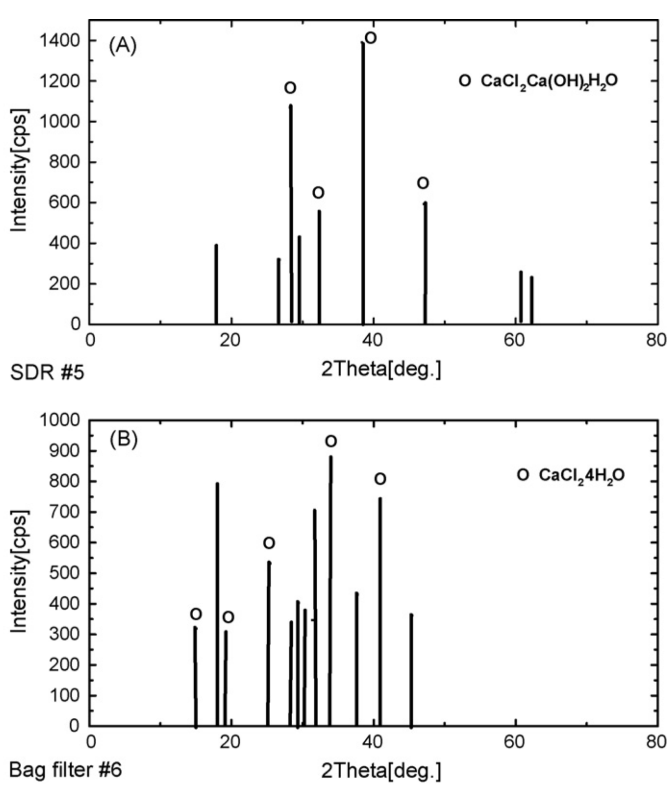

Fig. 3. XRD diffraction pattern of ASR fly ashes used in the work.

Table 3
The pH value of ASR incineration ash used in the work

Sample code	Bottom #1	Bottom #2	Cyclone #3	Boiler #4	SDR #5	Bag filter #6
pH	9.09	9.14	11.01	6.55	12.06	11.80

considerable amount of Pb leach from MSWI bottom ash may often require further treatment like aging process in order to use as road construction material. It can be concluded, therefore, that ASR bottom ash may be applicable to a raw material for road construction without further treatment for the removal of heavy metals. However, in case of fly ash such as boiler #4, SDR #5 and bag filter #6, it was found that Cd, Pb and Cu were considerably leached out so that the removal or stabilization process was essentially required prior to landfill or reuse as construction material. In this work, two alternative methods were examined for the treatment of heavy metals in ASR fly ash. Acid washing [15] of incineration ash is one of the conventional methods for the removal of heavy metals. However, acid washing has a drawback in that a great deal of wastewater containing metals leached out is inevitably produced. Another attempt has also been made for solidification of heavy metals by the production of lightweight aggregate with ASR fly ash.

The production of lightweight aggregate (LWA) represents a particularly attractive reuse application for ASR ash [6,7]. Most natural aggregates have particle densities of 2.4–2.8 g/cm^3, while LWA have particle densities of 0.8–2.0 g/cm^3. As a result, LWA are used for the production of lightweight concrete, lightweight blocks and other lightweight construction products and have additional benefits associated with low density such as high insulation and high thermal inertia. In this work, boiler #4 was used for the production of lightweight aggregate because other fly ash such as SDR #5 and bag filter #6 contained much soluble compounds.

Table 5 shows the results of heavy metal leachability after acid washing of boiler #4, SDR #5, and bag filter #6 for Cd, Pb and Cu. Two different concentrations of HCl solution, that is, dilute HCl solution of pH 1.3 and 0.24 N HCl, were used for acid washing of ASR fly ash. Acid washing was conducted at room temperature for 1 h with the solid density of 100 g/l. After acid washing, the slurry was filtered with filter paper and the resulted cake was washed three times with deionized water followed by drying at the vacuum oven at 105 °C in order to examine heavy metal leachability by the standard TCLP method.

As shown in Table 5, it was clearly found that heavy metals could be removed thoroughly or partly from ASR fly ash through acid washing with dilute HCl solution so that the remaining fly ash could be landfilled or used as construction material. According to our preliminary test, acid washing with more concentrated solution than 1 N HCl resulted in the nearly perfect dissolution of sample, especially in case of bag filter #6, indicating that acid washing was meaningless. As a whole, the removal of Pb available by the TCLP test was found to be relatively poor compared to Cd and Cu after acid washing.

Table 4
Results of metal leachability for ASR ash determined by the standard TCLP method

Sample Code	As (mg/l)	Cd (mg/l)	Cr (mg/l)	Pb (mg/l)	Cu (mg/l)	Final pH
Regulatory limit	1.5	0.3	1.5	3	3	-
Bottom #1	<0.05	<0.1	<0.05	<0.05	<0.02	3.79
Bottom #2	<0.05	<0.1	<0.05	0.1	0.40	3.84
Cyclone #3	<0.05	<0.1	0.14	<0.05	<0.02	3.78
Boiler #4	<0.05	6.26	<0.05	7.4	0.34	3.95
SDR #5	<0.05	0.16	<0.05	17.2	0.07	4.68
Bag filter #6	<0.05	0.44	<0.05	685	84.7	3.91

Table 5
Heavy metal leachability after acid washing of ASR fly ash

Metal	Sample code	Before washing (mg/l)	After washing (mg/l)	
			pH 1.3 HCl	0.24 N HCl
	Boiler #4	6.26	0.14	0.11
Cd	SDR #5	0.16	0.04	0.05
	Bag filter #6	0.44	0.01	0.09
	Boiler #4	7.4	2.0	4.1
Pb	SDR #5	17.2	3.7	1.5
	Bag filter #6	685	0.1	0.5
	Boiler #4	0.34	0.05	0.08
Cu	SDR #5	0.07	<0.02	<0.02
	Bag filter #6	84.7	0.30	0.08

On the other hand, heavy metal leachability for lightweight aggregate pellet prepared with boiler #4 was given in Table 6. As shown in the table, the density of pellet was increased with the fraction of fly ash because the fraction of lightweight filler material became relatively small. In addition, higher calcination temperature resulted in higher density of pellet due to shrinkage of pellet during calcination.

As far as heavy metals leached out from lightweight aggregate pellet were concerned, it was found that the amount of heavy metal leachability could be significantly decreased after the preparation of lightweight aggregate pellet. It may be ascribed to the solidification of heavy metals or conversion into insoluble compounds like oxide during the calcination of pellet at elevated temperature. It indicates that the application of ASR incineration ash containing some heavy metals to lightweight aggregate may be possible without pre-treatment for the removal of heavy metals. Accordingly, it could be concluded that the reuse of ASR incineration ash as construction materials such as lightweight aggregate had some advantages of minimizing the environmental pollution of heavy metals as well as reducing the volume of ash sent to landfill.

Table 6
Heavy metal leachability for lightweight aggregate pellet determined by the standard TCLP method

Calcination temperature	Mixing ratio (wt%) (ash:LWF*:bentonite)	Cd (mg/l)	Pb (mg/l)	Cu (mg/l)	Pellet density (g/ml)
600 °C	50:40:10	0.05	<0.2	<0.02	0.46
800 °C	50:40:10	<0.02	<0.2	<0.02	0.47
1,000 °C	30:60:10	<0.02	<0.2	<0.02	1.20
	50:40:10	<0.02	<0.2	<0.02	1.22
	70:20:10	0.07	0.46	<0.02	1.25
	90:0:10	0.20	2.01	0.05	1.34

* LWF = lightweight filler.

4. Conclusions

Characteristics and heavy metal leaching of ash generated from incineration of ASR, which was produced during the shredding and material separation of end-of-life vehicle, have been examined. Bottom ash accounted for approximately 85% of total ASR incineration ash and was a heterogeneous mix of glass, ferrous and non-ferrous metals and other non-combustible inorganic materials. It was remarkable that the concentration of Cu was very high compared to common MSWI bottom and fly ash, which was probably originated from copper wires contained in ASR.

The majority of particles in fly ash existed in the range of 2–1000 μm with the order of mean particle size of cyclone ash > boiler ash > SDR ash > bag filter ash. It was found that SDR ash and bag filter ash lost their weight after water washing of three times by 41% and 73%, respectively. As a whole, the results of characterization of ASR fly ash were in good agreement with common MSWI fly ash in terms of particle size, pH, and water-soluble compounds. The amount of heavy metals leached out from ASR bottom and cyclone ashes was found to be lower level than the regulatory limit. However, in case of fly ash such as boiler ash, SDR ash and bag filter ash, it was found that Cd, Pb and Cu were considerably leached out so that the removal or stabilization process was essentially required prior to landfill or reuse as construction material.

It was clearly observed that heavy metals could be removed thoroughly or partly from ASR fly ash through acid washing with dilute HCl solution so that the remaining fly ash could be landfilled or used as construction material. Nevertheless, the removal of Pb available by the TCLP test was found to be relatively poor compared to other metals after acid washing.

The density of lightweight aggregate pellet was increased with the fraction of fly ash because the fraction of lightweight filler material became relatively small and higher calcinations temperature resulted in higher density of pellet due to shrinkage of pellet during calcination. As far as heavy metals leached out from lightweight aggregate pellet were concerned, it was found that the amount of heavy metal leachability could be significantly decreased, indicating that the application of ASR incineration ash to lightweight aggregate would be possible without pre-treatment for the removal of heavy metals.

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References

[1] Y. Matsushita, T. Oka, T. Nagata, M. Endo, Recovery of automobile shredder residue at Nissan Oppama Plant, in: 4th International Automobile Recycling Congress, Mar. 10–12, Geneva, Switzerland, 2004, pp. 1–16.
[2] H. Spoel, The current status of scrap metal recycling, JOM (April 1990) 38–41.
[3] B. J. Jody, E. J. Daniels, P. V. Bonsignore, F. J. Dudek, Recycling of plastics in automobile shredder residue, U. S. DOE Report, DE90-011110 (1990) 1–5.
[4] J.K. Oh, H.Y. Lee, S.G. Kim, Evaluation and analysis of composition of shredder residue from end-of-life vehicle, J. Kor. Inst. Res. Recycl. 10 (2001) 34–41.
[5] W. S. Hubble, I. G. Most, M. R. Wolman, Investigation of the energy value of automobile shredder residue, U. S. DOE Report, DE87-013645 (1987) 7–14.
[6] D.S. Babu, K.G. Babu, T.H. Wee, Properties of lightweight expanded polystyrene aggregate concretes containing fly ash, Cem. Concr. Res. 35 (2005) 1218–1223.
[7] C.R. Cheeseman, G.S. Virdi, Properties and microstructure of lightweight aggregate produced from sintered sewage sludge ash, Res. Conserv. Recycl. 45 (2005) 18–30.
[8] C.R. Cheeseman, A. Makinde, S. Bethanis, Properties of lightweight aggregate produced by rapid sintering of incinerator bottom ash, Res. Conserv. Recycl. 43 (2005) 147–162.
[9] R. Fuoco, A. Ceccarini, P. Tassone, Y. Wei, A. Brongo, S. Francesconi, Innovative stabilization/solidfication processes of fly ash from an incinerator plant of urban solid waste, Microchem. J. 79 (2005) 29–35.
[10] J. Reich, C. Pasel, J.D. Herbell, M. Luckas, Effects of limestone addition and sintering on heavy metal leaching from hazardous waste incineration slag, Waste Manag. 22 (2002) 315–326.
[11] T.V. Gerven, J. Moors, V. Dutre, C. Vandecasteele, Effect of CO_2 on leaching from a cement-stabilized MSWI fly ash, Cem. Concr. Res. 34 (2004) 1103–1109.
[12] E.E. Chang, P.C. Chiang, P.H. Lu, Y.W. Ko, Comparisons of metal leachability for various wastes by extraction and leaching methods, Chemosphere 45 (2001) 91–99.
[13] Y. Matsuzawa, K. Mae, S. Kitano, S. Yoshihara, S. Ueno, J. Nishino, N. Kubota, Leaching behavior of heat-treated waste ash, Fuel 85 (2006) 401–409.
[14] H.P. Bipp, P. Wunsch, K. Fischer, D. Bieniek, A. Kettrup, Heavy metal leaching of fly ash from waste incineration with gluconic acid and a molasses hydrolysate, Chemosphere 36 (1998) 2523–2533.
[15] B.V. Bruggen, G. Vogels, P.V. Herck, C. Vandecasteele, Simulation of acid washing of municipal solid waste incineration fly ashes in order to remove heavy metals, J. Hazard. Mater. 57 (1998) 127–144.