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Elution of Metals from Fused Slags Produced from General Garbage

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Abstract

The reuse of fused slags obtained by treatment of incineration ash produced during the disposal of city garbage or sewage sludge as building materials such as bricks is attracting attention. In this study, we performed elution tests and investigated the physical properties and metal contents of such materials to establish their safety during use. We examined the physical and chemical characteristics of ten slags, which were produced using various methods. A check of the physical properties showed that there were no problems, and we concluded that reuse is possible. Tests showed that elution of toxic metals was low when water was used as the eluent. However, when acid and alkali were used, metal elution increased. Analysis of the eluates showed that arsenic was not eluted from any of the slags tested, and that high concentrations of manganese were present in all the slags.

Keywords: Fused slag; Toxic metal; Safety

Introduction

Many industrial products that would traditionally be disposed of are now being recycled to reduce environmental pollution and conserve resources. Various techniques for the recovery, processing, and reuse of materials have been developed. Recently, the safety of reusing such materials has been investigated. Waste materials such as city garbage are generated in great quantities. In Japan, most garbage is incinerated and the residue (incineration ash) is reclaimed. The residual capacities of disposal plants are gradually decreasing annually. Control of the amount of city garbage generated and recycling of incineration ash are necessary for environmental protection. Fused slags can be produced from incineration ashes, and such slags can be used to produce construction materials such as slabs for sidewalks [1]. These products are now being used in various practical applications, therefore it is necessary to better understand their safety. There are various types of melting furnaces and materials, e.g., sewage sludge, therefore the properties of the slags produced vary greatly depending on the location and season. Most investigations to date have focused on the physical aspects of their use, e.g., the density and durability of concrete products prepared from slag for use as building materials [2]. There are few reports on the chemical components of slag aggregates. The inorganic materials in slags are important. They do not decompose during fusion and remain largely intact in the end product. This is particularly important because metals can have toxic effects [3]. In this study, we investigated the safety of reusing fused slags as building materials. Elution tests were performed on ten fused slags, with different sampling points and produced using different methods, and their metal contents were determined.

Materials and Methods

Apparatus and reagents

Standard metal solutions of atomic absorption spectrometry (AAS) grade were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan), and distilled with 0.1 M nitric acid. Hydrochloric acid, hydrofluoric acid, and nitric acid (heavy metal analysis grade) were also obtained from Wako Pure Chemical Industries Ltd. All water used was purified using an Elix 3/Element A10 system (Merck-Millipore, Billerica, MA, USA). All other reagents were special grade and commercially available.

Ten slags produced using different fusing methods (e.g., coke bed, rotation, and surface), cooling methods (air and water), and materials (sewage sludge and city garbage) were used (Table 1).

The slags were decomposed using an Ethos TH microwave decomposition instrument (Milestone General, Kanagawa, Japan). The metal concentrations in the decomposition liquids and eluates were determined using an atomic absorption spectrometer (Z-6000, Hitachi, Ibaraki, Japan) with a graphite furnace. Five metals (chromium, manganese, arsenic, cadmium, and lead) were determined. The analytical conditions were optimized according to the manufacturer's instructions. All containers were soaked in 0.1 M nitric acid before use.

Metal contents

Slag (0.2 g) and hydrochloric, hydrofluoric, and nitric acids (2 mL each) were placed in a dedicated Teflon decomposition container and decomposed using a microwave decomposition instrument. The decomposition conditions were 120°C, 60 min, and 400 W. The device decompressed the container to 11 MPa. After decomposition the sample was transferred to another tube, centrifuged at 3000 rpm at room temperature for 5 min, and the supernatant was collected. Water was added to the residue and centrifugation was repeated. The metals in samples of the decomposition liquid (20 mL) were determined using AAS.

Metal elution tests

Elution tests were performed using the standard method [4]. Slag (3.5 g) was crushed with a pestle in a mortar and passed through two sieves of mesh 8.6 and 60 and fractioned into three parts. The medium granules (0.425-2 mm φ) were placed in a 50 mL conical flask, and

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water (35 mL) was added. The suspended solution was shaken using a mechanical shaker (200 min^{-1}, width 4 cm) at room temperature for 6 h. After shaking, the supernatant was filtered with a membrane filter (pore size 0.22 μm), and nitric acid was added to give 0.1 M acidity. The metals in the eluate were determined using AAS. Elution was also performed using pH 4 nitric acid and pH 10 potassium hydroxide as eluents, simulating acid rain and snow, and soil exudation liquids, although dissolution tests with an acid or alkali are not required by Japanese law. Each slag was tested in duplicate; it was checked that the control value was below the sensitivity (chromium <0.5 ppb; manganese <0.5 ppb; arsenic <5 ppb; cadmium <0.05 ppb; and lead <1 ppb).

Results and Discussion

Metal contents

The metal contents of the slags were converted into metal amounts (nanograms to milligrams) per gram of slag, based on the amount of decomposed slag, the decomposition liquid volume (20 mL), and the metal concentration in the decomposition liquid; the results are shown in Table 2. The manganese contents in all samples were about 0.1%. The chromium and lead levels in all samples were parts per million. The chromium content was highest in Slag II, about 0.6%. Arsenic was detected only in Slag VII. Cadmium was detected at the parts per billion level in the decomposition liquids of some samples, and the contents were high in Slags I, IV, and VIII.

Metal elution

Chromium was detected in the eluates from some samples, and the amount increased with increasing medium alkalinity at the pH values tested. When Slag II was eluted with water, the chromium concentration in the eluate was high (68.7 ppb, not shown in table); this exceeds the environmental quality guideline (<50 ppb; the environmental quality is judged based on hexavalent chromium, and most of the chromium in this case is hexavalent because of its solubility in alkali and ability to form oxyanions) [5]. Arsenic was not detected in the eluates. Cadmium was detected only in two eluates (Slags IV and IX), and the concentrations in alkali, water, and acid increased in this order. Manganese was detected for most slags and under most elution conditions; the concentration was higher under acidic elution conditions. This is probably because the number of oxyanions generated is small. Lead elution was confirmed only for some slags, and increased with increasing acidity. We suggest that the differences among metal concentrations in the eluates reflect the slag materials and preparation methods, and the type and chemical forms of the metals [6]. Although the metal elution differences among the slags are probably caused by the quality of the garbage used, the matrix could also be changed by the slag preparation methods (e.g., fusion and cooling). The amounts of some metals eluted from the slags increased when acid or alkali, rather than water, was used as the eluent.

Metal elution rates

The metal concentrations in the eluate compared with those in the decomposition liquid (i.e., the elution rate from the slag) are shown in Figure 1. Elution changed the slag properties such as the density. The slags that give high metal elution changes depend on the pH because the location and form of the metals in the slags differ, and this is reflected in the elution conditions. Similarly, the obtained values vary even for the same slag, showing that the sample components differ depending on the location. Cadmium elution from Slag IX was at least 14% under acidic conditions. The amount of cadmium in the slag was low, suggesting that the slag quality was not affected by elution. Because of the environmental effects of the release of toxic metals, acid washing (elution with an acidic solution) of ash products before their use as building materials is desirable (Figure 1).

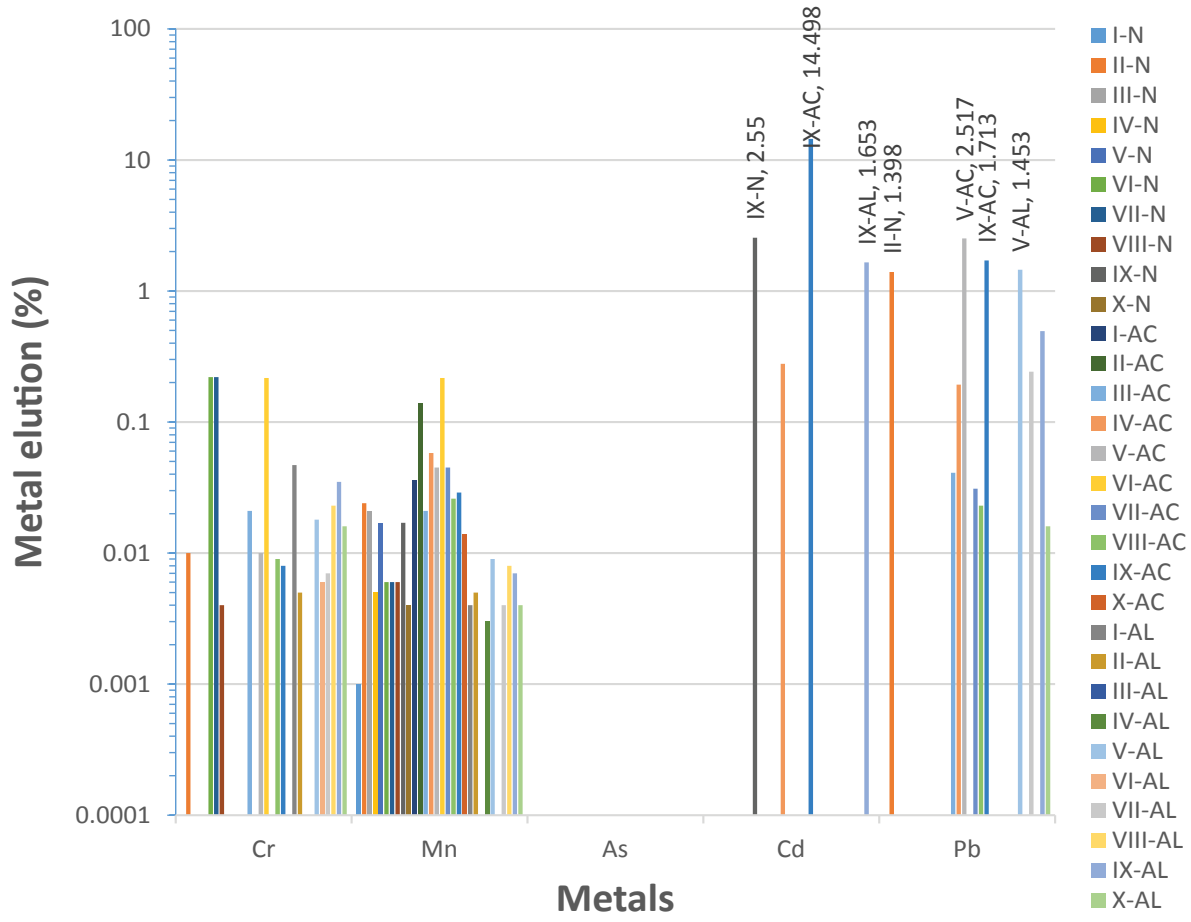
Slag	Source	Fusion	Cooling	Density (g/cm^3)	Water absorption (%)	Actual capacity (%)
I	Sewage sludge	Coke bed	Air	2.63	0.93	57.8
II	Sewage sludge	Coke bed	Water	2.97	0.38	1.59
III	Sewage sludge	Rotation	Water	2.43	1.55	52.0
IV	Sewage sludge	Surface	Water	2.56	0.31	51.2
V	City garbage	Arc	Water	2.68	0.16	62.8
VI	City garbage	Electric resistance	Air	2.68	0.02	62.7
VII	City garbage	Heat decomposition gasification	Water	2.89	0.49	57.7
VIII	City garbage	Kiln-type gasification	Water	2.77	0.35	63.4
IX	City garbage	Plasma	Water	2.82	0.16	56.0
X	City garbage	Surface	Water	2.71	0.82	54.9

Table 1: Fused Slag Types.

Slag	Chromium (μg/g)	Manganese (mg/g)	Arsenic (μg/g)	Cadmium (ng/g)	Lead (μg/g)
I	18.4	0.695	<0.5	387	26.9
II	6650	1.25	<0.5	<5	0.925
III	552	1.06	<0.5	36.7	32.7
IV	421	1.96	<0.5	406	8.31
V	161	1.66	<0.5	<5	7.53
VI	92.3	1.14	<0.5	<5	3.07
VII	1940	2.02	0.790	<5	54.6
VIII	349	1.02	<0.5	362	126
IX	230	1.27	<0.5	42.5	23.6
X	204	1.06	<0.5	36.7	238

Symbols are the same as in Table 1; Contents indicate the average of two measurements.

Table 2: Metal Contents of Crushed Slags.



N, neutral pH; AC, pH4; AL, pH10. The black bars show not determined or not calculated because the metal concentrations were less than the AAS determination limits. Only those with elution rates greater than 1%show the actual values on the bars.

Figure 1: Metal Elution Rates from Crushed Slags.

Conclusion

The safety of slags produced from general garbage was investigated. Although there was little elution of all metals tested when water was used as the eluent, higher concentrations of metals were eluted when acidic and alkaline solutions were used for the tests. The metal elution rates were low in many cases compared with the metal contents of the slags, but the eluted amounts might increase under severer conditions (e.g., pH, temperature, and time). This is an important point in the case of building materials because it is desirable that their physical properties do not change. It is also important in environmental terms because toxic metal elution is undesirable [7]. Elution tests were performed using a standard method, mainly with water as the eluent, and only a few metals (hexavalent chromium, arsenic, selenium, cadmium, lead, and mercury) were investigated. Few metal species were tested in this study; we were unable able to determine mercury and selenium levels. The tests did not take account of the changes in the physical properties of the slags caused by contact with rain or soil exudation liquids. Future studies of the long-term effects of elution by acids and alkalis, the chemical forms of the metals, and toxicity are required.

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