A Study on Safety Management Plan for Recycling of Medium-Contact Wastes via Ecotoxicity Assessment

Authors: Hong, Soo-Yeon, Yoon, Cheol-Woo, Yoon, Young-Sam, Kang, Jang-Hyun, and Jeon, Tae-Wan

Source: Environmental Health Insights, 16(1)

Published By: SAGE Publishing

URL: https://doi.org/10.1177/11786302221111872

A Study on Safety Management Plan for Recycling of Medium-Contact Wastes via Ecotoxicity Assessment

Environmental Health Insights
Volume 16: 1–14

DOI: 10.1177/11786302221111872

Soo-Yeon Hong[1], Cheol-Woo Yoon[1,2], Young-Sam Yoon[1], Jang-Hyun Kang[1] and Tae-Wan Jeon[1]

[1]Resource Recirculation Research Division, National Institute of Environmental Research, Incheon, South Korea. [2]Department of Environmental Engineering, In-Ha University, South Korea.

ABSTRACT: In South Korea, hazardous characteristics of wastes to be recycled are managed through the "Environmental Impact Assessment of Recycling" system. The ecotoxicity of medium-contact recyclable wastes, that is, those in contact with soil, groundwater, surface water, etc., is managed according to this system and is determined based on whether or not they exceed an ecotoxicity value (TU) of 2.0. The ecotoxicity of wastes is tested and determined by using pretreated eluate samples according to the Official Wastes Test Standard and applying the Official Water Pollution Process Test Standard. However, no ecotoxicity management limits are stipulated for medium-contact recycling using wastes in numerous other countries. This study aims to evaluate applicability and safety of the ecotoxicity test for wastes used in medium-contact recycling and establish an efficient management plan for hazardous characteristic wastes. Target wastes for the survey were selected based on the Wastes Control Act in South Korea. Nine types of waste were selected, which are representative types of wastes to which ecotoxicity is applied. In order to secure the representativeness of the target samples, a total of 45 samples were collected by selecting 5 cases each of the 9 waste types in consideration of the type of industry and amount of waste generated. Limit exceedance was calculated for each category of hazardous substances (leaching, total content), pH, and ecotoxicity of a total of 45 samples, and was found to increase in the order of leaching 2.22% < pH 9.09% < content 31.11% < ecotoxicity 37.21%. This indicates that the limit exceedance was maximum in the ecotoxicity category. Therefore, the application of ecotoxicity limit is efficient for identifying and comprehensively managing the environmental impacts of various types of hazardous substances contained in wastes from the perspective of comprehensive toxicity.

KEYWORDS: Hazardous characteristics, up-flow percolation method, ecotoxicity, hazardous waste, environmental impact assessment of recycling

RECEIVED: April 5, 2022. **ACCEPTED:** June 20, 2022.

TYPE: Original Research

FUNDING: The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This study was supported by the NIER funded by the Ministry of Environment (NIER-2020-03-01-005).

DECLARATION OF CONFLICTING INTERESTS: The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

CORRESPONDING AUTHOR: Cheol-Woo Yoon, Resource Recirculation Research Division, National Institute of Environmental Research, Seo-gu Hwangyong-ro 42, Incheon 22689, South Korea. Email: ooiuy@korea.kr

Introduction

In South Korea, the Environmental Impact Assessment of Recycling System (EIARS) was introduced for the safe recycling of wastes.[1] The EIARS prevents environmental pollution while allowing active recycling of wastes by surveying and predicting the impact of waste recycling on human health and the environment. Therefore, a system for managing hazardous characteristics during waste recycling has been established and operated. Hazardous characteristics are managed under 9 categories: corrosiveness, infectiousness, leaching toxicity, explosiveness, flammability, combustibility, oxidation, reaction with water, and ecotoxicity.[2,3] Among these categories, performing ecotoxicity tests is mandatory for medium-contact recycling of wastes, that is, recycling wastes for cover material, fill material, road base material, etc. by bringing the wastes in contact with soil, groundwater, or surface water. Ecotoxicity refers to the negative effect on living organisms immediately or after a certain period of exposure due to the biotoxicity or bioaccumulation of harmful substances released into the ecosystem. Ecotoxicity is determined by the exceedance of a TU value over 2, which indicates acute toxicity for *Daphnia magna Straus*.[1]

In South Korea, target wastes are pretreated by an up-flow percolation test method, and the eluate is used as a sample for *Daphnia magna Straus* acute toxicity test for assessing the ecotoxicity of medium-contact wastes. Thus, the pretreated eluate is tested to assess ecotoxicity by applying the Official Water Pollution Process Test Standard[4] and the Acute Toxicity Test Method for *Daphnia magna Straus* according to the Official Wastes Test Standard[5] in South Korea.

Previous research on the applicability of the ecotoxicity test for wastes in South Korea includes studies that applied the Acute Toxicity Test Method for *Daphnia magna Straus* to medium-contact recycling waste samples. Studies have also been done on recycling of coal ash,[6] and technical guidelines for environmental impact assessment for recycling inorganic wastes have been established.[7]

This study aims to evaluate the applicability of the ecotoxicity test for wastes used in medium-contact recycling in accordance with the Hazardous Characteristics Management System of the Wastes Control Act of South Korea. This study confirms the safety of medium-contact recycling and provides an efficient management plan for hazardous wastes. Furthermore, the management of each influencing factor by applying the ecotoxicity standard in an integrated manner can be beneficial for assessment and management of hazardous waste during recycling.

Table 1. Selected regulations on the types of wastes and relevant industries to be identified for hazardous characteristics.

TYPE OF WASTES	RELEVANT INDUSTRY	HAZARDOUS CHARACTERISTICS
1. Waste synthetic polymer compounds	A. Synthetic rubber manufacturing industry (20 301)	Flammability
	B. Synthetic resin and other plastic material manufacturing industry (20 302)	Flammability
2. Process sludge	A. Basic organic chemicals manufacturing industry (2011) ※ Excluding natural resin and wood chemicals manufacturing industry (20 112)	Oxidation, combustibility, flammability, corrosiveness, leaching toxicity
	B. Basic inorganic chemicals manufacturing industry (2012)	Oxidation, combustibility, flammability, corrosiveness, leaching toxicity
	C. Non-ferrous metal smelting, refining, and alloying manufacturing industry (2421)	Oxidation, corrosiveness, leaching toxicity
	D. Metal powder product manufacturing industry (25 911)	Oxidation, corrosiveness, leaching toxicity
3. Wastewater treatment sludge	A. Basic organic chemicals manufacturing industry (2011) ※ Excluding natural resin and wood chemicals manufacturing industry (20 112)	Leaching toxicity
	B. Basic inorganic chemicals manufacturing industry (2012)	Leaching toxicity
	C. Non-ferrous metal smelting, refining, and alloying manufacturing industry (2421)	Leaching toxicity
	D. Metal powder product manufacturing industry (25 911)	Leaching toxicity
⋮	⋮	⋮
17. Medium-contact recycling wastes	All industries	Ecotoxicity

Waste Ecotoxicity Management System

Hazardous characteristics of wastes in South Korea

The waste management plan in South Korea was modified with the revision of the Wastes Control Act, enacted on July 21, 2016. Previously, the waste recycling was only allowed as per purposes and methods of recycling stipulated by the law. Now, it allows recycling through an environmental impact assessment even if the purposes and methods of recycling are not specified by the law. Accordingly, the EIARS was introduced to determine whether target wastes could be recycled. With the introduction of the new recycling system, the Wastes Control Act expands the categories of hazardous characteristics of target recycling wastes to 9 as follows: corrosiveness, infectiousness, leaching toxicity, explosiveness, flammability, combustibility, oxidation, reaction with water, and ecotoxicity. These characteristics should be eliminated or alleviated during recycling to prevent hazards to human health or the surrounding environment.

The EIARS specified the application of the ecotoxicity category to wastes subjected to medium-contact recycling from January 1, 2018. Medium-contact recycling implies recycling wastes by bringing them into contact with soil, groundwater, or surface water, so that they can be used as cover material, fill material, road base material, etc. The evaluation of ecotoxicity was conducted in accordance with EIARS, Article 13-3(1) of the Waste Management Act.[8] Newly created wastes that exceed a certain scale (greater than 120 000 tons or 30 000 m^2) can be recycled.

Ecotoxicity is assessed by TU value, which when exceeds 2.0, indicates acute toxicity in *Daphnia magna Straus* according to the "Definition and Standard of Nine Hazardous Properties that must be Identified in Recycling" [Attachment 2]. A TU value of 2.0, which is considered the reference value for ecotoxicity, is obtained by statistically calculating the median effective concentration (EC_{50}), and dividing 100 by the EC_{50} value. The median effective concentration (EC_{50}) indicates the concentration at which 50% of the introduced test organisms are killed or immobilized.

The wastes and relevant industries that need to be evaluated for ecotoxicity are selected in accordance with the notification "A Few Types of Wastes and Relevant Industries that must be Verified as a Hazard"[9] (Table 1). "Types of Wastes" refers to the waste types that are highly likely to exhibit hazardous characteristics; a total of 17 types are stipulated. "Relevant Industries" implies industries that discharge wastes that are likely to exhibit hazardous characteristics. The classification numbers are indicated in parentheses based on the categories and subcategories classified in the Korean Standard of Industry Classification. According to this notification, ecotoxicity must be verified in all relevant industries when wastes are used for medium-contact recycling, and the corresponding limit must be met.

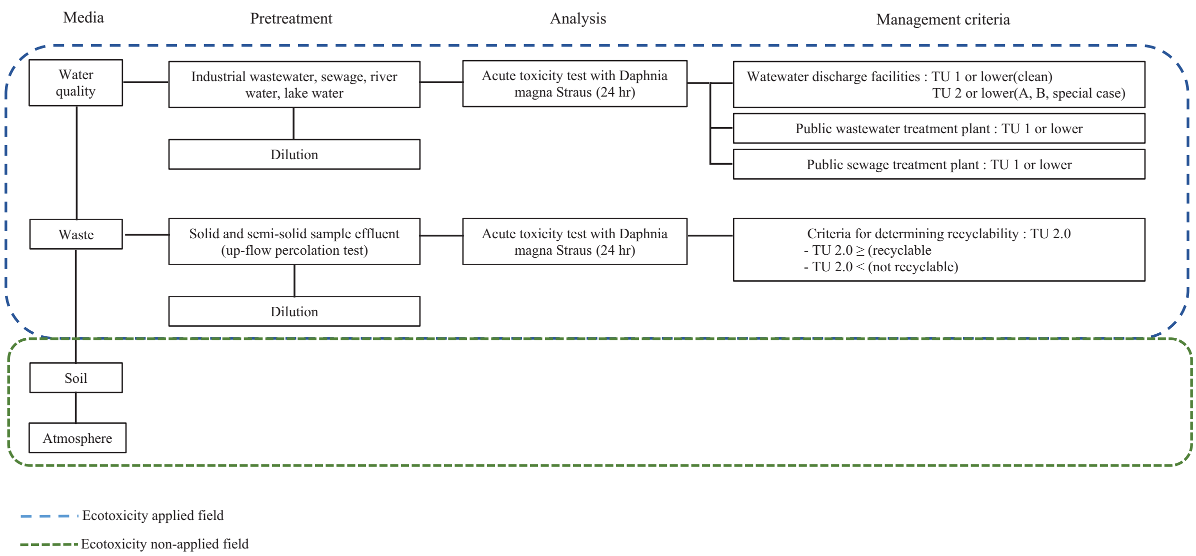


Figure 1. Waste ecotoxicity management system in South Korea.

Comparison of methods of status of ecotoxicity management for waste recycling

In South Korea, ecotoxicity limits are applied and managed for wastes and water quality, as shown in Figure 1. The test method of using *Daphnia magna Straus* in a pretreated solution is common between both analytical methods, differ in the pretreatment method. For the analysis of water quality, industrial wastewater, sewage, river water, and lake water are used as pretreated solutions. The eluate obtained from the up-flow percolation of solid or semi-solid waste is used as a pretreated solution of wastes.

In South Korea, the ecotoxicity limits are stipulated for medium-contact recycling using wastes, and the limits are managed based on whether TU exceeds 2.0.[10] In other countries, no ecotoxicity management limits are stipulated for medium-contact recycling using wastes. Table 2 shows the current status of the ecotoxicity management system in each country. The European Union and Basel Convention stipulate ecotoxicity for hazardous wastes but only as guidelines for waste characteristics. In the European Union, ecotoxicity is classified by the classification code HP14, and the ecotoxicity value of wastes is calculated using the equation specified in (EC) No. 1272/2008.[11] The hazards of corresponding wastes are determined by criteria based on HP14.[12] The ecotoxicity of hazardous wastes under the Basel Convention is classified as H12, and wastes are considered to be ecotoxic if the sum of the concentrations of individual hazardous substances exceeds the prescribed limits. The concentration of a substance is calculated as a percentage of the dry weight of the waste.[13] In the United States, ecotoxicity of industrial wastewater is managed through the Whole Effluent Toxicity (WET) testing.[14] Ecotoxicity is determined based on the total toxic effect of all pollutants contained in wastewater on aquatic organisms.[15]

Materials and Methods

Sample preparation

In South Korea, the Allbaro system is capable of managing the entire waste process (discharge, transport, and final treatment) in real time via Internet. Data in the Allbaro system were used to select target wastes and relevant industries to be surveyed according to the notification "A Few Types of Wastes and Relevant Industries that must be Verified as a Hazard."[9] Based on the types of recyclable wastes managed by the Waste Management Act, medium-contact recycled waste in South Korea were selected as the target. Medium-contact recycling waste selected according to the relevant notification include slags, stone and aggregate wastewater treatment sludge, coal ash, and incineration ash. In South Korea, industrial wastes are collected from one point without being subdivided by process stage. That is, the waste generated in the last step of the process is selected as the sampling point. Accordingly, in this study, waste generated in the final stage of the entire process was sampled as a sample through a step-by-step process. Table 3 shows details of the samples. To ensure representativeness of the target samples, the target survey companies based on their quantity of waste discharge. Thus, a total of 45 samples, with 5 samples from each waste type were selected from 28 industries, including thermal power generation industry.

Analysis method

In South Korea, limits for leaching of recyclable wastes are managed in accordance with the Standard of Harmful Substance Classified as Hazardous Waste in Annex 1 of the Enforcement Regulation of the Wastes Control Act.[16]

In South Korea, medium-contact recycling is possible only for general wastes that satisfy the leaching, total content, and ecotoxicity limits. Therefore, analysis items and methods were

Table 2. Current status of ecotoxicity management system in different countries/regions.

	SOUTH KOREA	EUROPEAN UNION	UNITED STATES	BASEL CONVENTION
Availability of ecotoxicity management	○	○	○	○
Applicable target for ecotoxicity	Recycling wastes	Hazardous wastes	Wastewater	Hazardous wastes
Testing method	Official Wastes Test Standard[5] ES 06151.1 (pretreatment) Official Water Pollution Process Test Standard[4] ES 04704.1b	(EC) No 1272/2008	40 CFR 136.3 WET (Whole Effluent Toxicity) Testing	Interim Guidelines on the Hazardous Characteristics H12: Ecotoxic
Determination method	*Daphnia magna Straus* Acute Toxicity Test	Waste hazards determined using the equation and criteria according to HP14 of the corresponding waste	Total toxic effect of all pollutants contained in wastewater on aquatic organisms	Waste considered to be ecotoxic if the sum of the concentrations of individual hazardous substances exceeds the limit; the concentration of substances represented as a percentage of waste dry weight
Determination criteria (management criteria)	Exceeds TU 2.0	- H420: ⩾0.1% - H410: ⩾0.25% - H411: ⩾2.5% - H400, H412, H413: ⩾25%	Lowest Toxicity Values from FIFRA Guideline Studies - Aquatic Acute Freshwater fish, Marine/estuarine fish: LC_{50} Freshwater invertebrate, Marine/estuarine crustacean, Marine/estuarine mollusks: EC50 - Aquatic Chronic: refer to Attachment 3, including NOAEC, etc.	- Acute Class 1, 2, 3: exceeds 25% - Chronic Class 1: exceeds 0.25% - Chronic Class 2: exceeds 2.5% - Chronic Class 3, 4: exceeds 25%
Notes	- Ecotoxicity standards proposed in hazardous characteristics of wastes	- Classification code: HP14 - Ecotoxicity determined based on the concentration of substances classified by hazard codes contained in waste - Stipulated as guidelines for waste characteristics	Whole Effluent Toxicity Methods Errata Sheet	- Classification code: H12 - Stipulated as guidelines for waste properties

applied to determine the exceedance of limits based on the legally stipulated test method and identified recyclable wastes. General wastes were tested according to the Official Wastes Test Standard[5] to determine their recyclability in terms of the waste leaching limit. In the case of the total content limit, the Official Soil Pollution Test Standard[7] was used to determine whether the wastes satisfied the Soil Contamination Warning Standard. In addition, for the ecotoxicity limit, samples were pre-treated according to the Official Wastes Test Standard[5] and analyzed according to the *Daphnia magna Straus* acute toxicity test method in the Official Water Pollution Process Test Standard.[4] Figure 2 shows the analysis items and methods based on each official test standard.

Analyses of leaching and total content of hazardous substances in wastes. Leaching test analysis of hazardous substances in wastes was conducted to determine the medium-contact recyclability of wastes and leaching toxicity of hazardous wastes. Seven items including As, Cd, Cu, Pb, Hg, Cr(VI), and CN managed in the Wastes Control Act were selected for the leaching test and analyzed according to the Official Wastes Test Standard.[5] According to the recycling standards in the Wastes Control Act, wastes can be recycled only when they meet the Soil Contamination Warning Standard. Therefore, the hazardous substances in wastes were analyzed through the total content test based on the Official Soil Pollution Test Standard,[7] and 10 items (As, Cd, Cu, Pb, Hg, Cr(VI), CN, Ni, Zn, and F) controlled by the Soil Contamination Warning Standard were selected for the analysis.

Ecotoxicity test. In this study, the ecotoxicity test was performed by selecting medium-contact recyclable wastes and applying

Table 3. Details of samples.

NO.	TYPE OF WASTE	RELEVANT INDUSTRY	NUMBER OF SAMPLES	COORDINATES
1	Slags (steel slags)	5 Industries, including steel and steelmaking	5	34.9331, 127.7361
2	Other slags	4 Industries, including other non-ferrous metal smelting, refining, and alloy manufacturing	5	36.9528, 126.7818
3	Stone and aggregate wastewater treatment sludge	3 Industries, including pulverized non-metallic mineral material manufacturing	5	37.146, 126.911
4	Coal ash (bottom ash)	Thermal power generation industry	5	37.4854, 129.1458
5	Waste stone powder sediments	4 Industries, including pulverized non-metallic mineral material manufacturing	5	37.5335, 127.938
6	Coal ash (fly ash)	3 Industries, including thermal power generation	5	37.1892, 129.3356
7	Incineration ash (bottom ash)	4 Industries, including craft paper and carton board manufacturing	5	35.4882, 129.3688
8	Incineration ash (fly ash)	2 Industries, including other non-classified textile product manufacturing	5	37.8409, 127.0079
9	Incineration ash (bottom ash and fly ash mixed)	3 Industries, including pulp manufacturing	5	37.3026, 126.771

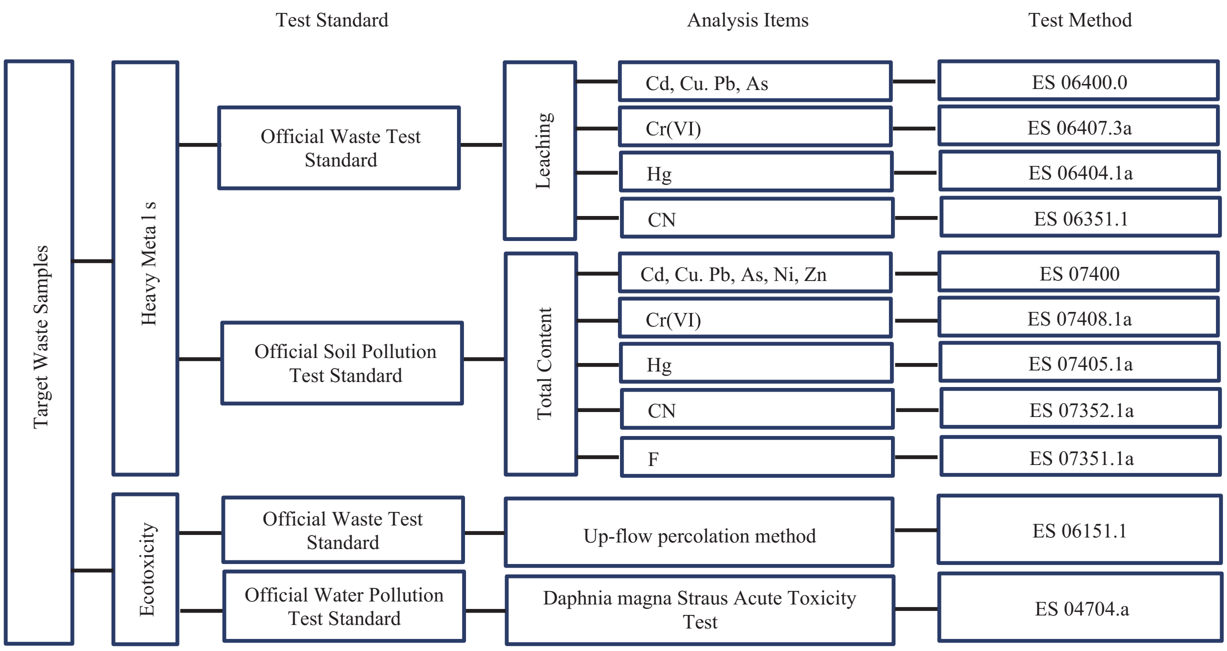
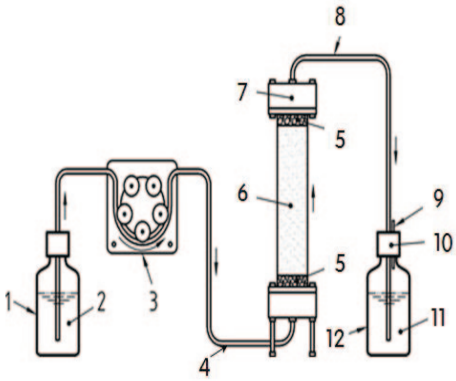


Figure 2. Methods of analysis applicable for each item in the samples.

the acute toxicity test method using *Daphnia magna Straus* to the eluate obtained through the up-flow percolation method. The test method was selected according to the criteria for determining the ecotoxicity stipulated in the Waste Management Act of South Korea.[8] Accordingly, *Daphnia magna Straus* was selected among organisms that could be tested for ecotoxicity. In addition, the dilution factor was determined according to the test method of ES 04704.1b.[4]

Pretreatment. In the up-flow percolation method (Figure 3), the liquid:solid ratio was set to 1:2, and the column was 100% filled with a waste sample. The glass tube was filled with the sample, and the eluant was passed through at a constant flow rate. The collected eluate was filtered through a 0.45-μm membrane filter. The test was conducted in accordance with the Official Wastes Test Standard ES 06151.1.[5]

Acute toxicity test using Daphnia magna *Straus.* The ecotoxicity test was performed by diluting raw water (100%) at dilution ratios of 50%, 25%, 12.5%, and 6.25%, placing 5 test organisms in 4 repetitions for each concentration, and observing the immobilization or death 24 hours later, to calculate the EC_{50} values of the raw water and diluted samples. For the *Daphnia magna Straus* toxicity test, the column eluate was diluted with



1.Storage container
2. Eluant
3. Pump
4. Bottom tube
5.Quartz layer
6. Glass column (sample filling layer)
7.Glass column stopper
8. Top tube
9. Ventilator
10. Collection container stopper
11. Effluent
12.Collectioncontainer

Figure 3. Schematic representation of the up-flow percolation process.

Culture and subculture the Daphnia magna Straus community

↓

Check the status of samples
(e.g., water temperature, pH, and residual chlorine)

↓

Prepare samples
(100%, 50%, 25%, 12.5%, 6.25%)

↓

Exposure the Daphnia magna Straus to samples of each concentration
(Use young individuals less than 24 h of age)

↓

Calculate the result after observing swimming inhibition and lethality

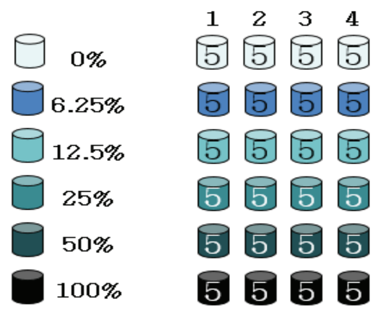


Figure 4. Procedure for *Daphnia magna Straus* toxicity test to obtain acute toxicity.

the culture solution in a 50-mL beaker to prepare samples at 100%, 50%, 25%, 12.5%, and 6.25%. After exposing 5 young *Daphnia magna* Strauss individuals that were less than 24-hour-old per beaker, the toxicity were calculated by observing immobilization or death 24 hours later. As shown in Figure 4, the test was performed in accordance with the Official Water Pollution Process Test Standard[4] ES 04704.1b and the Acute Toxicity Test Method of the *Daphnia magna Straus*.[5]

The TU value was calculated using the Probit and Trimmed Spearman–Karber (TSK) programs. Probit is a statistical program used when there are at least two 1% to 99% lethality datasets, excluding killed and immobilized *Daphnia magna* Straus individuals at concentrations of 0% and 100%. TSK is a statistical program used when there is one or more 1% to 99% lethality datasets for killed and immobilized *Daphnia magna Straus* individuals at concentrations of 0% and 100%. The ecotoxicity value is calculated by determining the median effective concentration (EC_{50}) value and dividing 100 by the EC_{50} value.

$$\text{Ecotoxicity Value (TU)} = \frac{100}{EC_{50}}$$

Results and Discussion

Analyses of hazardous substances

The leaching limit for hazardous substances (items and management standards) contained in designated wastes are managed in accordance with Annex 1 of the Enforcement Regulation of the Wastes Control Act.[16] The limit for the total content of a hazardous substance is divided into Areas 1, 2, and 3 depending on the use of land in the Soil Contamination Warning Standard.[7] According to regulations for the construction and management of spatial information, Area 1 includes residential land, school land, parks, and playground facilities for children (only applied when installed outdoors). Area 2 includes forests, salt fields, warehouses, rivers, and sports sites. Area 3 includes plant sites, parking lots, gas station sites, roads, railroads, and embankments. Table 4 shows the hazardous substance management standards for Areas 1, 2, and 3 based on the designated wastes and the Soil Contamination Warning Standard.

The management items and their corresponding standard values of soil for medium-contact recycling of waste in South

Table 4. Hazardous substance management standards and quantitative limits for different analysis items for medium-contact recycling of wastes.

ITEM	LEACHING		TOTAL CONTENT			
	STANDARD FOR HAZARDOUS SUBSTANCES IN DESIGNATED WASTES ($MG\,L^{-1}$)	QUANTITATIVE LIMIT	SOIL CONTAMINATION WARNING STANDARD ($MG\,KG^{-1}$)			QUANTITATIVE LIMIT
			AREA 1	AREA 2	AREA 3	
CN	1	0.01	2	2	120	0.2
Cr	-	0.01	-	-	-	-
Cr(VI)	1.5	0.01	5	15	40	0.5
Cu	3	0.008	150	500	2000	1.0
Cd	0.3	0.002	4	10	60	0.10
Pb	3	0.04	200	400	700	1.5
As	1.5	0.004	25	50	200	1.50
Hg	0.005	0.0005	4	10	20	0.05
Zn	-	-	300	600	2000	1.0
Ni	-	-	100	200	500	0.4
F	-	-	400	400	800	10

Korea are as shown in Table 4. However, regulatory items and management standards are globally diverse. Furthermore, Antoniadis et al[17] calculated the risk index based on the highest allowable limit value in soil as trace elements in soil can have toxic effects on plants and humans, which demonstrates the need to reduce the diversity of regulatory limits in each country.

Results of leaching analysis. Figure 5 shows the analysis results of 45 ecotoxic waste samples. Results show ranges for different items as follows: As: not detected (ND)–0.007 $mg\,L^{-1}$; Cd: ND–8.113 $mg\,L^{-1}$; Cu: ND–0.568 $mg\,L^{-1}$; Pb: ND–10.18 $mg\,L^{-1}$, and Cr(VI): ND–0.20 $mg\,L^{-1}$. Hg and CN were not detected. A study by Singh et al show that the trace elements Mn, Mg, Cr, Zn, Ni, Pb, Fe, and Cu are the most abundant, while Hg, Mo, and Co are the least abundant based on leaching of fly ash and bottom ash.[18] It was found that 43 of 45 samples satisfied the standard for hazardous substances in designated wastes. Additionally, Cd was detected at 8.113 $mg\,L^{-1}$ in other unclassified incineration ash (fly ash) samples from the textile manufacturing industry, while Pb was detected at 10.18 $mg\,L^{-1}$ in the incineration ash (bottom ash) samples discharged from the business facility maintenance service industry; these exceed the designated waste management limits.

Results of total content analysis. Figure 6 shows the results of the total content analysis, which show ranges for different items as follows: As: ND–93.14 $mg\,kg^{-1}$; Cd: ND–138.47 $mg\,kg^{-1}$; Cu: ND–23 366.7 $mg\,kg^{-1}$; Pb: ND–3323.1 $mg\,kg^{-1}$; Hg: ND–56 $mg\,kg^{-1}$; CN: ND–141.2 $mg\,kg^{-1}$, Cr(VI): ND–4.4 $mg\,kg^{-1}$; F: ND–61 861 $mg\,kg^{-1}$. Among the 9 target wastes, 5 types of wastes, including 3 types of incineration ash (bottom ash, fly ash, and a mixture of bottom ash and fly ash), steel slags, and other minerals exceeded the Soil Contamination Warning Standard. The 8 items that exceeded the Soil Contamination Warning Standard were As, Cd, Cu, Pb, Zn, Ni, CN, and F.

The samples exceeding the Soil Contamination Warning Standard were identified to be incineration ash, slags, and other minerals, and 9 of 15 incineration ash samples exceeded the total content limits. Heavy metals that exceeded the limits were Cu, Cd, Pb, Zn, and Ni, which were detected in high amounts in incineration ash. A study by Monika Czop analyzed the heavy metal concentrations in fly ash and bottom ash that are formed during thermal decomposition of urban solid wastes, which were in the order of Ba > Zn > Pb > Cu > Cd. Fly ash had elemental concentrations in the following order: Ba > Zn > Pb > Ni > Cu, while other metals such as Cd, Cr, Co, Fe, and Mn were below the detectable limit. The bottom ash had elemental concentrations in the following order: Ni > Cr > Pb > Cd, while other metals such as Zn, Cu, Co, Fe, and Mn were below the detectable limit.

Among the 45 target wastes for ecotoxicity analysis, 14 samples exceeded the Soil Contamination Warning Standard, which indicates that special care is needed to prevent adverse environmental effects when wastes are medium-contact recycled for removal of hazardous substances.

PH Analysis

Figure 7 shows the average pH value of the waste types. The pH of steel and other slags, stone, and other aggregate wastewater treatment sludge, waste stone powder sediments, coal ash (bottom ash), coal ash (fly ash), incineration ash (bottom ash),

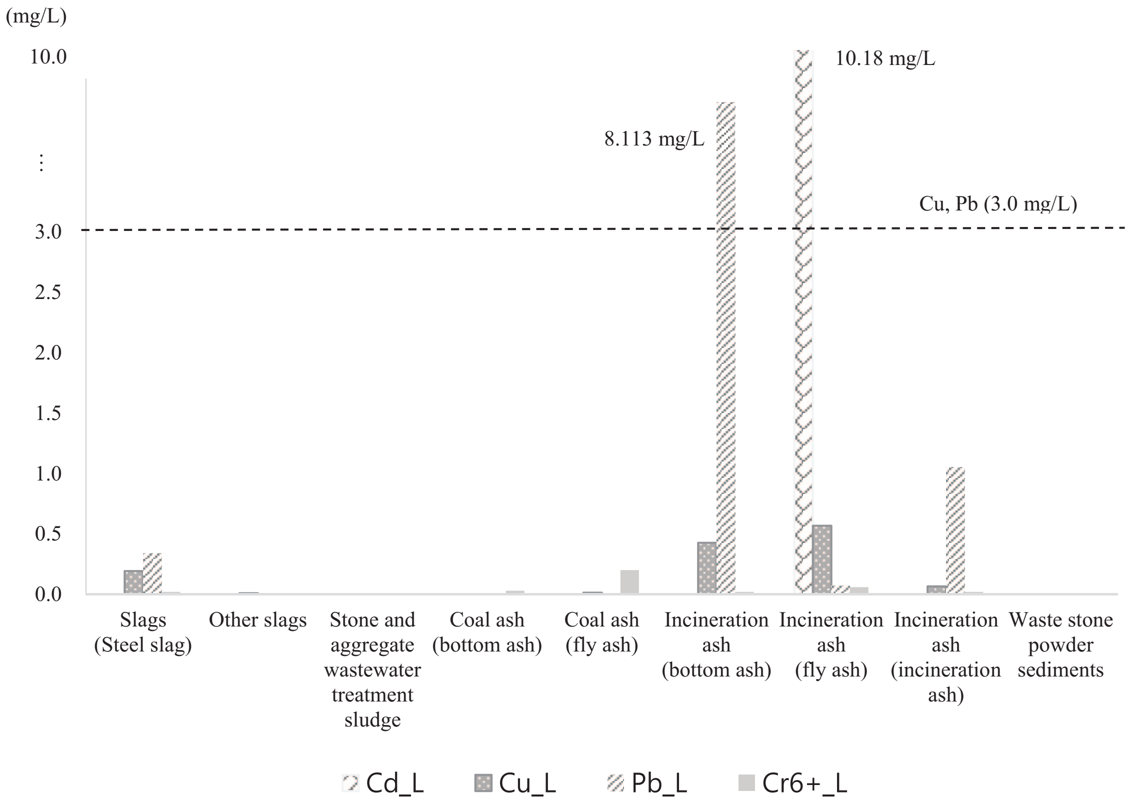


Figure 5. Results of leaching analysis.

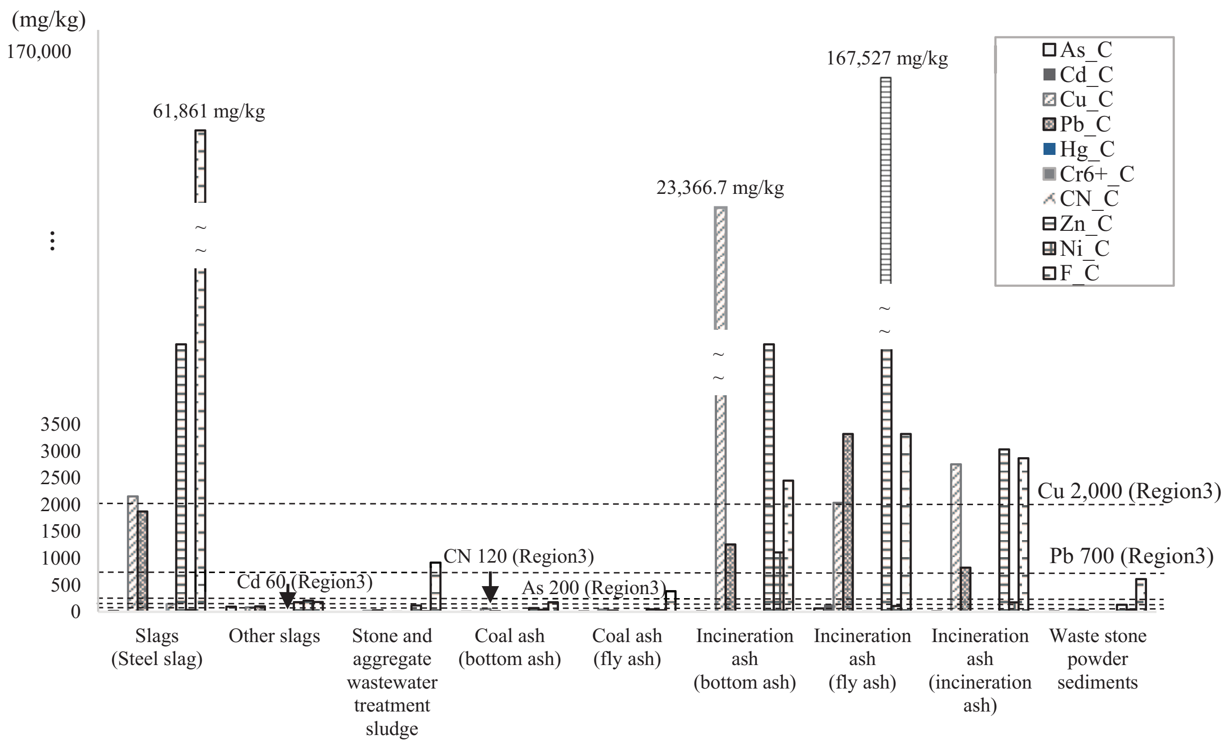


Figure 6. Results of total content analysis.

and incineration ash (bottom ash + fly ash) had a pH of 12.1, 6.5, 8.8, 8.1, 10.2, 12.7, 10.7, and 12.2, respectively. According to a study by Risdanareni et al[19] when solid household wastes are incinerated, bottom ash contains mainly Ca (23.81%), Cl (5.44%), and heavy metal compounds (Σ 11.27 g/kg), while fly ash contains a high amount of Cl (7.22%) and heavy metals (Σ 7.83 g/kg), which results in an alkaline pH for the corresponding samples. Dahl et al[20] suggested that ashes have strong

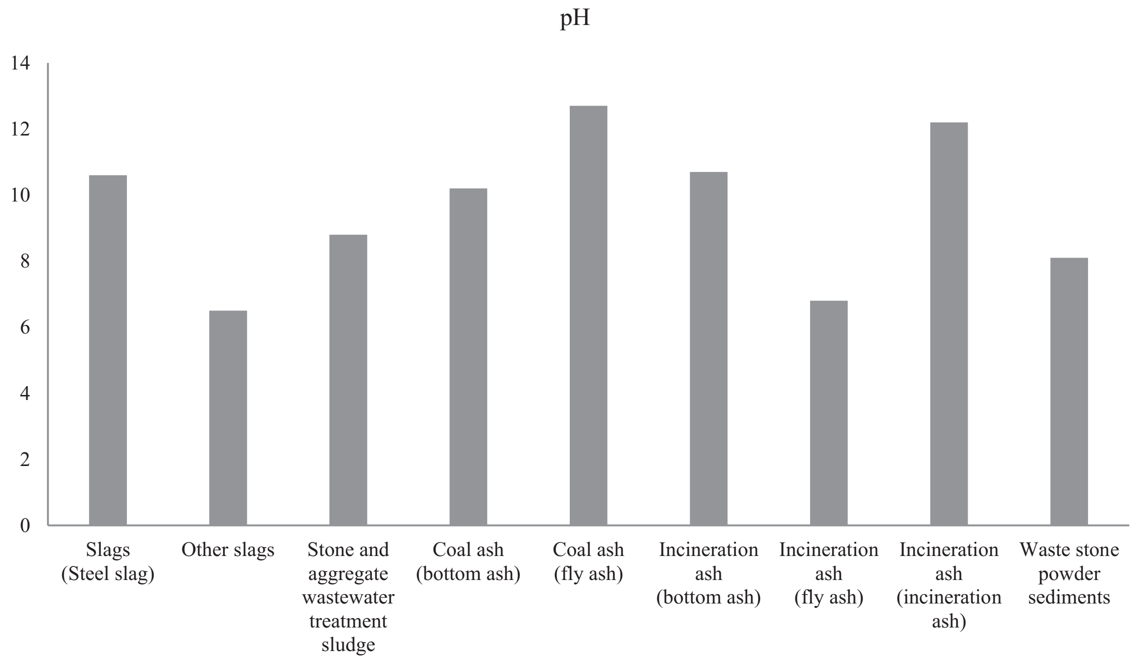


Figure 7. Results of pH measurements (average values).

alkalinity with a pH 11.9 to 12.6. Furthermore, the samples classified as combustion residues (fly ash and bottom ash) in this study exhibited alkalinity with an average pH of 10.2 to 12.7. The average pH of incineration ash (fly ash) was 6.8, while the pH of one of the 5 samples could not be measured because the sample absorbed water during sample preparation according to the Official Wastes Test Standard.[5]

Results of ecotoxicity analysis

For the ecotoxicity survey, the analysis of hazardous characteristics of 45 target wastes were performed. Results in Figure 8 show that 16 samples were ecotoxic as they exceeded the reference ecotoxicity value of TU 2.0. This includes 9 cases of incineration ash (fly ash, bottom ash, fly ash and bottom ash mixture; 5 cases with a TU value of 2.7-7.4, and 4 cases exceeding a TU value of 16.0), 5 cases of steel slags (3 cases with a TU value of 2.8-15.0 and 2 cases exceeding a TU value of 16.0), and 2 cases of coal ash (exceeding a TU value of 16.0). Samples of other slags, waste stone powder sediments, and stone and aggregate wastewater treatment sludge were determined to be non-ecotoxic as they did not exceed the TU value of 2.0. A total of 2 samples, that is, one each of coal ash (fly ash) and incineration ash (fly ash), were not analyzed for ecotoxicity as the up-flow percolation could not be performed due to the hydration reaction of the high quantity of the CaO component in them.

Conditions Affecting Ecotoxicity

Influential factors

The influencing factors for ecotoxicity were identified based on the results of the ecotoxicity analysis. Wang focused on the factors influencing metal toxicity affecting aquatic organisms. Abiotic factors include organic substances, pH, temperature, alkalinity and hardness, inorganic ligands, interactions, and sediments, and these can substantially alter metal toxicity in the aquatic environment.[21] Among these factors, toxic factors affecting pH and heavy metals were also identified. Therefore, the correlation between pH and exceedance of heavy metal limits (leaching and total content) with ecotoxicity was determined for 15 of the 45 target survey samples that exhibited ecotoxicity.

Among the 16 samples that exhibited ecotoxicity, 4 samples (including coal ash (fly ash), incineration ash (fly ash), incineration ash (bottom ash), and steel slags), exceeded the pH limit of 12.5. Additionally, the samples that did not exceed the heavy metal leaching and total content limits, but exhibited ecotoxicity with pH 11.7 to 12.8 (strong alkaline), indicating that pH has a significant effect on ecotoxicity. A study by El-Deeb Ghazy et al[22] also demonstrated that beyond the pH range of 4.55 to 10.13 *Daphnia magna Straus* was be affected.

Four out of 16 ecotoxic samples were confirmed to be within the heavy metal leaching and total content limits, and 2 samples exceeded the leaching limit in the Cd and Pb categories. Furthermore, 12 samples exceeded the total content limit for Cd, Cu, Pb, Zn, NI, CN, and F.

In terms of ecotoxicity factors, no tendency was observed between pH and the items exceeding the heavy metal limits. However, Cd, Zn, Ni, Pb, and Cu affected ecotoxicity. Pérez and Hoang[23] performed Ni only and Ni + Cd mixed toxicity tests for *Daphnia magna* Straus with Ni alone at concentrations of 20, 40, 80, 100, 120, 140, and 160 mg/L and in increments with a constant Cd concentration of 1.5 mg/L. They found that 1.5 mg/L of Cd was found to be highly toxic to *Daphnia*

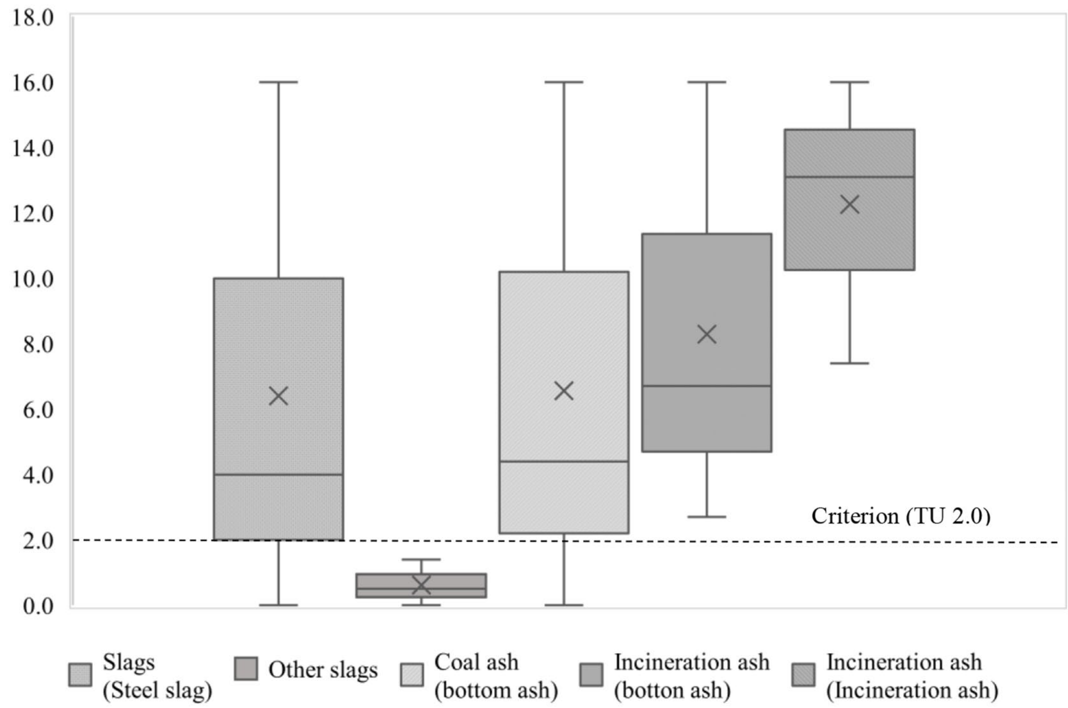


Figure 8. Results of the ecotoxicity analysis.

magna Straus. Ni contributes to the toxic effect of Cd at concentrations higher than the optimal range (>80 mg/L). Nguyen et al[24] showed that the effect of metals and mixed compounds on *Daphnia magna* Straus was in the order of bisphenol A (BP A) + Cd > BPA + Pb + Cd > BPA + Pb. Therefore, Cd alone or when mixed with other substances appears to be toxic.[24] Moreover, 7 out of 9 incineration ash samples that exhibited ecotoxicity commonly exceeded the limit in the Pb, Cu, and Zn categories. Cooper et al[25] showed that the toxicity of the binary and ternary mixtures of Pb, Cu, and Zn were more toxic than that of single metals. Ali et al[26] comprehensively reviewed different aspects of heavy metals as hazardous materials with a focus on their environmental persistence, toxicity in living organisms, and bio-accumulative potential, and suggested that the most hazardous and environmentally relevant heavy metals and metalloids are Cr, Ni, Cu, Zn, Cd, Pb, Hg, and As.

Limit exceedance

Table 5 summarizes the calculated exceedance values of hazardous substance limits depending on the waste samples. To understand the overall trend and influencing factors of the 45 waste samples, the calculated total limit exceedance values for hazardous substances (leaching and total content), pH, and ecotoxicity were compared. The exceedance of ecotoxicity was the highest at 37.21%. Most samples that exceeded the heavy metal and pH limits also exhibited ecotoxicity, but some samples that satisfied these limits still exceeded the ecotoxicity limit. Most of the samples exceeding heavy metal and pH standards expressed ecotoxicity. In addition, some samples that met the criteria exceeded the ecotoxicity criteria. These results show that ecotoxicity can be caused unknown hazardous substances.

Validity

Several countries have developed and used the whole effluent assessment of toxicity of discharged water since the 1970s. However, the effects of unknown chemicals are still observed even after sewage and wastewater are discharged in compliance with emission allowance standards. Most of the countries have introduced an ecotoxicity management system using living organisms to understand the environmental impact of these unknown chemicals. Accordingly, to overcome the limitations of water quality evaluation by unknown chemicals in Korea, an ecotoxicity management system was introduced to comprehensively manage the water quality of industrial wastewater.[27] In addition to discharged water, Korea also applies an ecotoxicity management system during medium-contact recycling, when water comes into contact with waste. The validity of this can be judged based on the leaching of unknown harmful substances into soil, ground and surface water.[28] As per the Ministry of Environment of South Korea, it was reasonable to include ecotoxicity items in a realistic management plan to prevent release of unknown harmful substances in the environment. Moreover, various industries generate ecotoxic wastes that can be medium-contact recycled in South Korea. Therefore, the hazardous characteristics system of South Korea that manages medium-contact recycling of wastes generated from various industries for ecotoxicity is believed to be appropriate.

Table 5. Limit exceedance values of samples.

SAMPLE	LEACHING	TOTAL CONTENT (EXCEEDING ITEM)		PH	TU
Total limit exceedance (%)	2.22	31.11		9.09	37.21
Incineration ash (bottom ash) 1	×	○	(Cu)	×	○
Incineration ash (bottom ash) 2	×	○	(Cu, Pb, Zn, Ni, F)	×	○
Incineration ash (bottom ash) 3	×	○	(Cd, Cu, Pb, Zn, Ni)	×	○
Incineration ash (bottom ash) 4	×	○	(Cu, Pb, Zn, Ni, F)	×	○
Incineration ash (bottom ash) 5	○	○	(Cd, Cu, Pb, Zn)	×	○
Incineration ash (fly ash) 1	○	○	(Cd, Cu, Pb, Zn, Ni, F)	-	○
Incineration ash (fly ash) 2	×	○	(As, Cd, Cu, Pb, Zn)	×	-
Incineration ash (fly ash) 3	×	×		×	×
Incineration ash (fly ash) 4	×	×		×	×
Incineration ash (fly ash) 5	×	×		×	×
Incineration ash (bottom ash + fly ash) 1	×	○	(Cd, Cu, Pb, Zn, Ni, F)	×	○
Incineration ash (bottom ash + fly ash) 2	×	×		○	○
Incineration ash (bottom ash + fly ash) 3	×	○	(Cd, Cu, Pb, Zn)	×	○
Incineration ash (bottom ash + fly ash) 4	×	×		×	×
Incineration ash (bottom ash + fly ash) 5	×	×		×	×
Limit exceedance (%)	2.22	20.00		2.27	20.93
Coal ash (bottom ash) 1	×	×		×	×
Coal ash (bottom ash) 2	×	×		×	×
Coal ash (bottom ash) 3	×	×		×	×
Coal ash (bottom ash) 4	×	×		×	○
Coal ash (bottom ash) 5	×	×		×	×
Coal ash (fly ash) 1	×	×		○	-
Coal ash (fly ash) 2	×	×		○	○
Coal ash (fly ash) 3	×	×		×	×
Coal ash (fly ash) 4	×	×		×	×
Coal ash (fly ash) 5	×	×		×	×
Limit exceedance (%)	0.00	0.00		4.55	4.65
Slags (steel slags) 1	×	×		×	○
Slags (steel slags) 2	×	○	(CN, F)	○	○
Slags (steel slags) 3	×	○	(Cu, Zn)	×	○
Slags (steel slags) 4	×	○	(Cu, Pb, Zn)	×	○
Slags (steel slags) 5	×	○	(CN)	×	○

(Continued)

Table 5. (Continued)

SAMPLE	LEACHING	TOTAL CONTENT (EXCEEDING ITEM)		PH	TU
Other slags 1	×	×		×	×
Other slags 2	×	×		×	×
Other slags 3	×	○	(As)	×	×
Other slags 4	×	×		×	×
Other slags 5	×	×		×	×
Limit exceedance (%)	0.00	11.11		2.27	11.63
Stone aggregate wastewater treatment sludge 1	×	×		×	×
Stone aggregate wastewater treatment sludge 2	×	×		×	×
Stone aggregate wastewater treatment sludge 3	×	×		×	×
Stone aggregate wastewater treatment sludge 4	×	×		×	×
Stone aggregate wastewater treatment sludge 5	×	×		×	×
Waste stone powder sediments 1	×	×		×	×
Waste stone powder sediments 2	×	×		×	×
Waste stone powder sediments 3	×	×		×	×
Waste stone powder sediments 4	×	×		×	×
Waste stone powder sediments 5	×	×		×	×
Limit exceedance (%)	0.00	0.00		0.00	0.00

○, Above limit; ×, Below limit; Blank: No test.

Framework

The flowchart for integrated management to which ecotoxicity is applied is shown in Figure 9. In South Korea's Waste Management Act, only wastes within the management criteria for 3 items (leaching, total content, hazardous characteristics) and management standards can be recycled in a media contact type. On the other hand, since waste exceeding these standards cannot be recycled, it is disposed of as landfill. Therefore, Figure 9 (management system applying ecotoxicity in medium-contact recycling) is a system for efficiently managing hazardous waste. It is to be managed from the point of view of integrated toxicity (integrated management of harmful factors) by applying ecotoxicity standards to wastes that can be recycled in a medium-contact type.

Conclusion

The pretreated solutions from the up-flow percolation test performed on waste samples are applied to the acute toxicity test using *Daphnia magna Straus* to evaluate the ecotoxicity of wastes in South Korea. In this study, the applicability of ecotoxicity was assessed for medium-contact recycling of wastes. We found that 16 out of 45 samples were ecotoxic wastes, and accounted for approximately 37% of the total. Among them, 3 samples were within the hazardous substance management limits but were considered to exhibit ecotoxicity as their pH value mainly affected *Daphnia magna* Straus. Analysis of the total limit exceedance for hazardous substances (leaching and total content), pH, and ecotoxicity indicated that the exceedance was 2.22% for leaching, 31.11% for total content, and 37.21% for ecotoxicity, which was the highest.

In this study, an efficient management plan for hazardous wastes was proposed through applicability assessment of the ecotoxicity test on medium-contact recycled waste samples. First, the plan comprehensively manages hazardous factors by applying strict ecotoxicity limits. Second, the information regarding wastes that can be medium-contact recycled is accumulated through research. Based on this, environmental impacts such as the interaction between pollutants are understood and it is believed that hazardous wastes can be efficiently managed from the perspective of comprehensive toxicity.

However, this research paper presents 2 limitations as follows: First, ensuring representativeness for the management of hazardous wastes was limited in this study. Therefore, further research that expands the scope of medium-contact recyclable wastes and relevant industries is necessary. Second, further

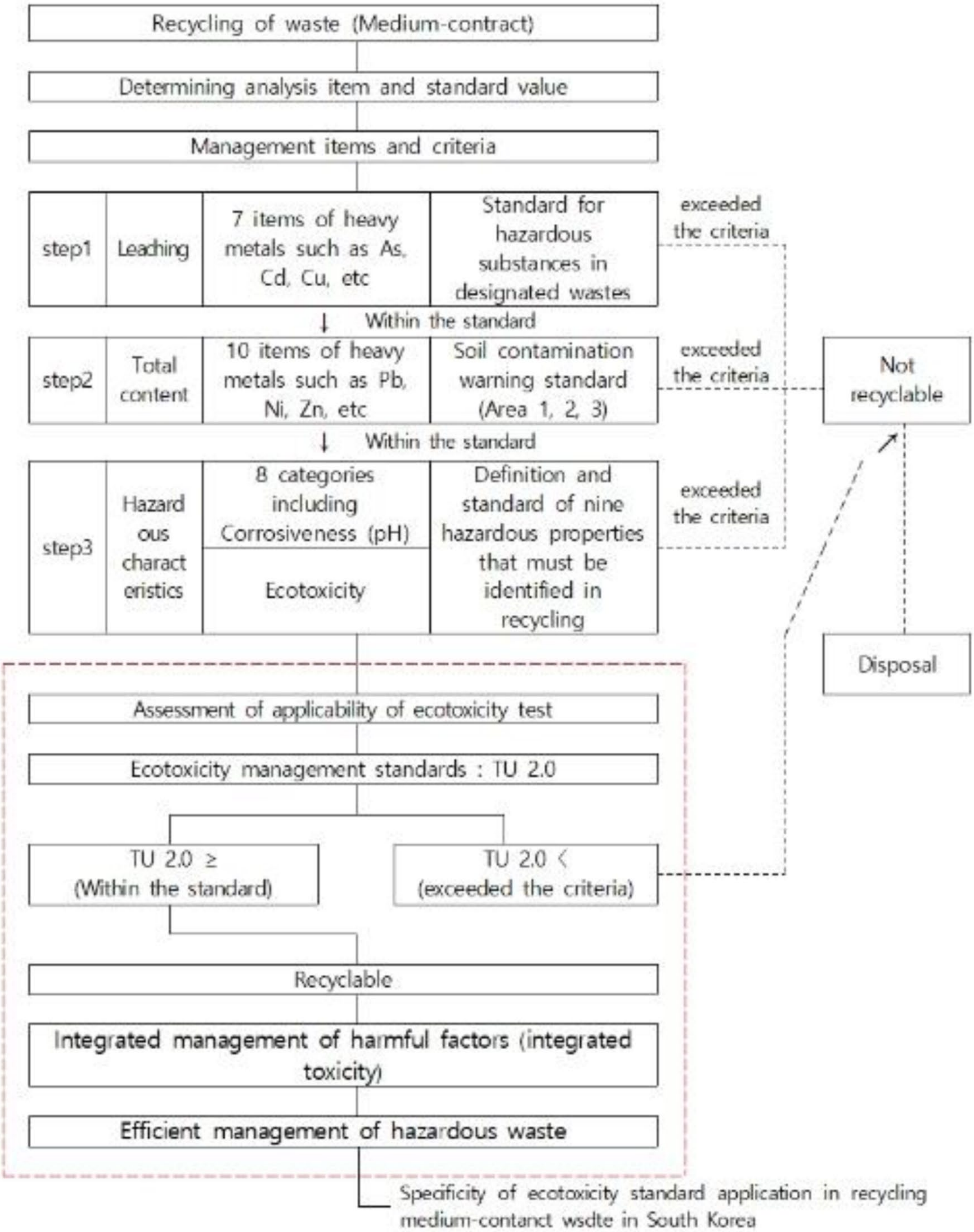


Figure 9. Management system applying ecotoxicity in medium-contact recycling.

studies on the applicability of the ecotoxicity reference value and test method for medium-contact recycling of wastes are required. Additional ecotoxicity tests using organisms other than *Daphnia magna Straus* should be investigated to develop a revised plan for the ecotoxicity reference value and test method for medium-contact recycling of wastes.

The method of comprehensively managing each influential factor by applying ecotoxicity limits in determining hazardous wastes will be useful from the perspective of recycling during waste management. In countries with inadequate waste recycling management systems, this method can provide an effective framework to prepare a management system for recycling (hazardous/non-hazardous) wastes.

Author Contributions

S.-Y.H. conceived the idea and collected the data, and played a major role. The authors (C.-W.Y., J.-H.K., T.-W.J., and Y.-S.Y) contributed to data analysis, writing, and editing the document. C.-W.Y. gave valuable ideas for the manuscript. C.-W.Y. and S.-Y.H. revised the manuscript. Finally, the authors read and approved the final version to be published and agreed on all aspects of this work.

REFERENCES

1. Um N, Kang YY, Kim KH, Shin SK, Lee Y. Strategic environmental assessment for effective waste management in Korea: a review of the new policy framework. *Waste Manag*. 2018;82:129-138.
2. Yoon CW, Yoon YS, Hong SY, Jeon TW, Shin SK. Hazardous characteristics of dust waste from metal manufacturing industries in South Korea. *Waste Manag Res*. 2021;39:1471.
3. Yoon CW, Kim MJ, Park YS, Jeon TW, Lee MY. A review of medical waste management systems in the Republic of Korea for hospital and medical waste generated from the COVID-19 pandemic. *Sustainability*. 2022;14:3678.
4. National Institute of Environmental Research. *The Official Water Pollution Process Test Standard in South Korea*. National Institute of Environmental Research Notification No. 2022-12. 2022. Accessed March 9, 2022. https://law.go.kr/admRulLsInfoP.do?admRulSeq=2100000209158
5. National Institute of Environmental Research. *The Official Wastes Test Standard in South Korea*. National Institute of Environmental Research Notification No. 2021-95. 2021. Accessed March 9, 2022. https://law.go.kr/admRulLsInfoP.do?admRulSeq=2100000206946
6. National Institute of Environmental Research. *The Study on Recycling Availability and Use Expansion of Coal Ash*. 2014. Accessed February 27, 2022. https://ecolibrary.me.go.kr/nier/#/search/detail/5591686
7. National Institute of Environmental Research. *The Official Soil Pollution Test Standard in South Korea*. National Institute of Environmental Research Notification No. 2018-53. 2018. Accessed March 9, 2022. https://law.go.kr/LSW/admRulLsInfoP.do?admRulSeq=2100000171830
8. Ministry of Environment. *Wastes Control Act, Article 13-3 (1)*. 2021. Accessed March 29, 2022. https://www.law.go.kr/lsInfoP.do?lsiSeq=228137&efYd=20210706&ancYnChk=0#J13:3
9. Ministry of Environment. *Regulation on the Types of Wastes and Generating Industries for Which Hazardous Characteristics Must be Checked*. Ministry of Environment Notification No. 2016-182, went into effect on 2016.9.9). 2016. Accessed March 9, 2022. https://www.law.go.kr/admRulLsInfoP.do?admRulSeq=2100000060890#AJAX
10. Ministry of Environment. *Properties of Waste Hazardous Characteristics and Corresponding Criteria*. Ministry of Environment Notification No. 2016-146. 2016. Accessed February 27, 2022. https://www.law.go.kr/admRulLsInfoP.do?admRulSeq=2100000054211
11. European Union. Commission Regulation (EU) 2017/776 of 4 May 2017 amending, for the purposes of its adaptation to technical and scientific progress, Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures (Text with EEA relevance). *Journal of the European Union*. Published May 5, 2017. Accessed March 4, 2022. https://eur-lex.europa.eu/legal-content/GA/TXT/?uri=CELEX:32017R0776
12. European Union. *Commission Notice on Technical Guidance on the Classification of Waste C/2018/1447*. European Union. Published April 9, 2018. Accessed March 28, 2022. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.C_.2018.124.01.0001.01.ENG
13. BC-VI/26. *Interim Guidelines on Hazardous Characteristic H12 – (Ecotoxic)*. Basel Convention, 2003. Accessed 28 March 2022. http://www.basel.int/Implementation/HazardCharacteristics/Decisions/tabid/3932/Default.aspx
14. United States Environmental Protection Agency. *Permit Limits-Whole Effluent Toxicity (WET)*. 2018. Accessed March 29, 2022. https://www.epa.gov/npdes/permit-limits-whole-effluent-toxicity-wet
15. United States Environmental Protection Agency. *Acute Toxicity WET Methods Freshwater and Marine Organisms*. 2017. Accessed March 28, 2022. https://www.epa.gov/cwa-methods/acute-toxicity-wet-methods
16. Ministry of Environment. *Annex 1 of Enforcement Regulation of the Wastes Control Act, Standard of Harmful Substance Classified as Hazardous Waste*. Ministry of Environment Notification No. 979. 2022. Accessed March 31, 2022. https://law.go.kr/LSW/lsBylInfoP.do?bylSeq=14426867&lsiSeq=241691&efYd=20220331
17. Antoniadis V, Shaheen SM, Levizou E, et al. A critical prospective analysis of the potential toxicity of trace element regulation limits in soils worldwide: are they protective concerning health risk assessment? A review. *Environ Int*. 2019;127:819-847.
18. Singh MK, Kumar S, Ratha D. Physiochemical and leaching characteristics of fly and bottom ash. *Energy Sources A Recovery Util Environ Eff*. 2016;38:2377-2382.
19. Risdanareni P, Puspitasari P, Januarti Jaya E. Chemical and physical characterization of fly ash as geopolymer material. *MATEC Web Conf*. 2017;97:01031.
20. Dahl O, Nurmesniemi H, Pöykiö R, Watkins G. Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. *Fuel Process Technol*. 2010;91:1634-1639.
21. Wang W. Factors affecting metal toxicity to (and accumulation by) aquatic organisms—overview. *Environ Int*. 1987;13:437-457.
22. El-Deeb Ghazy MM, Habashy MM, Mohammady EY. Effects of pH on survival, growth and reproduction rates of the crustacean, *Daphnia Magna*. *Aust J Basic Appl Sci*. 2011;5:1-10.
23. Pérez E, Hoang TC. Responses of *Daphnia magna* to chronic exposure of cadmium and nickel mixtures. *Chemosphere*. 2018;208:991-1001.
24. Nguyen VT, Huynh AT, Dao TS. Acute and chronic toxicity of mixtures of bisphenol A and trace metals (Cd and Pb) to micro-crustacean, *Daphnia magna*. *IOP Conf Ser Earth Environ Sci*. 2022;964:012012.
25. Cooper NL, Bidwell JR, Kumar A. Toxicity of copper, lead, and zinc mixtures to *Ceriodaphnia dubia* and *Daphnia carinata*. *Ecotoxicol Environ Saf*. 2009;72:1523-1528.
26. Ali H, Khan E, Ilahi I. Environmental Chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity, and bioaccumulation. *J Chem*. 2019;2019:1-14.
27. Korea Environment Corporation. *Whole Effluent Assessment/Toxicity*. Accessed March 28, 2022. https://www.keco.or.kr/kr/business/water/contentsid/2844/index.do
28. Power EA, Boumphrey RS. International trends in bioassay use for effluent management. *Ecotoxicology*. 2004;13:377-398.