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BEHAVIOR OF LANDFILLED STABILIZED FLY ASH TREATED BY DIFFERENT TREATMENT METHODS FOR THE PAST 27 YEARS

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ABSTRACT

Municipal solid waste incineration (MSWI) fly ash (FA) contains toxic substances and hence, direct landfilling of MSWI FA is prohibited in Japan Complying with Japan's stringent Waste Disposal and Public Cleansing Law, which demands adherence to landfill disposal and effluent standards, is crucial for ensuring environmental safety. To address the issue, various treatment methods including treatment by chemical, phosphoric acid, and melting and solidification can be used to stabilize the MSWI FA through the immobilization of heavy metals. However, the long-term stability of these treatment methods has not been thoroughly investigated. Therefore, the purpose of this study is to evaluate the long-term effectiveness of these three treatment methods for MSWI FA respectively, both independently and in conjunction with compost. This study involves the monitoring of changes in the concentration of heavy metals, including lead (Pb), cadmium (Cd), total-chromium (T-Cr), copper (Cu), and zinc (Zn), that have been leached over a period of 27 years. This study aims to conduct a detailed analysis of the impact of various treatment methods on the concentration levels of these individual heavy metals. Notably, the results suggest that independently, phosphoric acid treatment outperforms chelate treatment in the long run, but when combined with compost, both treatments exhibit enhanced efficacy, suggesting a promising approach for immobilizing heavy metals.

1. INTRODUCTION

Municipal solid waste incineration (MSWI) fly ash contains potentially hazardous substances which are known to have harmful effects on ecosystems and human health, and their accumulation in the environment can pose long-term risks (Mojtaba Ajorloo et al., 2022) (Yun Pan et al., 2013). These hazardous substances originate from the municipal solid waste (MSW) that is incinerated, or formed during the combustion process (David Laner et al., 2012). In 2002, the world generated approximately 0.68 billion tons of municipal solid waste (MSW) in a year (Hoornweg Daniel, 2012). In less than two decades, it increased more than threefold by 2020 at an estimated 2.24 billion tons, and the annual MSW generation is expected to increase by 73% to 3.88 billion tons in 2050 (BRIEF, 2022). As for Japan, the amount of municipal solid waste (MSW) generated has been gradually decreasing in 30 years according to data from the Ministry of the Environment of Japan. In 1991, Japan generated approximately 50.77 million tons of MSW (Ministry of the Environment, Government of Japan, 1995), whereas in 2020, the amount reduced to approximately 41.67 million tons (Ministry of the Environment, Government of Japan, 2022).

Although the statistics show a significant decrease of approximately 18% reduction in overall waste generated in the past three decades, Japan's high population density and mountainous terrains poses the issue of the scarcity of available landfill space to dispose the cumulated MSW (Kosuke Kawai, 2016). Hence, the Government of Japan enforced stricter regulations through the revision of the Waste Disposal and Public Cleansing Law in 1991 as an effort to achieve waste volume reduction (History and Current State of Waste Management in Japan, 2014). Incineration not only reduces MSW volume by approximately 85% to 90% and decreases the mass of original MSW by 60% to 90%, it also has the advantage of energy recovery (Yuying Zhang et al., 2021) (Xiang-Guo Li et al., 2012). As a result, incineration became the most common method used to manage MSW in Japan up until today (Hiratsuka-Sasaki A., 2020). In fact, with advance technology and environmentally friendly incineration equipment, Japan is one of the

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leading countries for waste incineration (Md Manik Mian et al., 2017).

However, MSWI essentially produces two-types of solid by-products, that is fly ash (FA) and bottom ash (BA) (Feng-He Wang et al., 2015) (Margarida J. Quina et al., 2010). In general, MSWI FA is more dangerous than MSWI BA because it contains relatively higher proportion of hazardous substances that can have negative environmental impacts on air, water, and soil quality if not properly managed before landfill disposal (Evangelina Atanes et al., 2019) (Yun Pan et al., 2013) (David Laner et al., 2012). Some of these toxic elements released includes organic pollutants, and high levels of leachable toxic heavy metals (THMs) such as lead (Pb), cadmium (Cd), and chromium (Cr) (Rahman Zeeshanur, 2019) (Wan Chen et al., 2017). These THMs from the MSWI FA pollutes natural resources through leachate accumulation from water-soluble chemicals mixing with the moisture present in the landfill, and hence, direct landfilling of MSWI FA is prohibited in Japan without effective immobilization of THMs (Hiroki Kitamura et al., 2016). The concentration of the THMs has to meet Japan's landfill disposal criteria and effluent standards before landfilling (Ministry of the Environment, Government of Japan, 2015) (Shimaoka Takayuki, 1996). Various treatment methods are used to stabilize the MSWI FA by immobilizing the THMs to largely reduce the substantial amount of hazardous compound in the MSWI FA. To address this issue, treatment methods including (1) cement solidification, (2) treatment by chemical, (3) acid and other solvent, and (4) melting and solidification can be used to stabilize the MSWI FA through immobilization of heavy metals (Zhikun Zhang et al., 2022) (Mojtaba Ajorloo et al., 2022) (Cao Yi-nan et al., 2021) (Zeyuan Liu et al., 2019) (Shimaoka Takayuki, 1996).

Cement solidification is the most common method for stabilizing MSWI FA in Japan due to its effectiveness in immobilizing hazardous contaminants and encapsulating them in the cement matrix (Pengfei Ren et al., 2022 'a'). However, the effectiveness of heavy metals immobilization is heavily influenced by the conditions of the treatment process as well (Charles H. K. Lam et al., 2010). In the long-run, the pH value in the cement matrix will be affected by carbonation during natural aging, and the high concentration of toxic heavy metals in FA may result in physical deterioration of the cement matrix, which increases the treatment cost, and also raises concerns on the long-term stability and durability of the cement-solidified MSWI FA (Bing Du et al., 2019).

Simultaneously, the long-term stability of alternative treatment methods (2), (3), and (4) have not been thoroughly studied. Therefore, this study was conducted for the past 27 years to comprehensively investigate the long-term stability of the three treatment methods respectively. The aim is to assess whether the treated and landfilled MSWI FA will persistently produce harmful levels of leachate over an extensive duration. This analysis creates the opportunity to evaluate the potential for discontinuing ongoing landfill monitoring after a specified period. The MSWI FA samples in this study are from the same source treated with different methods. After treatment, the samples are stored in large columns simulating the external environment that landfilled ashes are exposed to. The changes in concentration of heavy metals leached, particularly lead (Pb), cadmium (Cd), total-chromium (T-Cr), copper (Cu), and zinc (Zn), were monitored for the past 27 years.

2. MATERIALS AND METHODS

2.1 Ash samples and pre-treatment methods

The MSWI FA used in this study is from the same source, and treated with different methods, namely chelate treatment, phosphoric acid treatment, compost, combination of compost and chelate treatment, combination of compost and phosphoric acid treatment, and melting and solidification (Table 1). After treatment, the samples are stored in columns simulating a semi-aerobic landfill structure which is widely used in Japan (Figure 1) (K. Miyawaki et al., 2000). The top end of the column is exposed to natural rainfall, which seeps through the ashes, forming leachate and the leachate is collected at the bottom of the column. The BAFACG group has a 60:20:15:5 ratio corresponding to BA: FA: Garbage: Compost. BAFA(U) and SMS has a 3:1 ratio for BA:FA whereas PMS has a 4:1 of BA to FA ratio. The rest of the samples are purely FA and BA respectively.

TABLE 1: Fly ash with different treatment methods and its abbreviation.

Column No.	Sample Name	Abbreviation
1	Bottom Ash + Untreated Fly Ash + Crushed Garbage + Compost	BAFACG(U)
2	Bottom Ash + Chelate-treated Fly Ash + Crushed Garbage + Compost	BAFACG(C)
3	Bottom Ash + Phosphoric-acid-treated Fly Ash + Crushed Garbage + Compost	BAFACG(P)
4	Untreated Bottom Ash	BA(U)
5	Untreated Fly Ash	FA(U)
6	Untreated Bottom Ash + Fly Ash	BAFA(U)
7	Surface melting slag Fly Ash + Bottom Ash	SMS
8	Plasma melting slag Fly Ash + Bottom Ash	PMS
9	Chelate-treated Fly Ash	FA(C)
10	Phosphoric-acid-treated Fly Ash	FA(P)

Where (U) = untreated, (C) = chelate-treated, (P) = phosphoric-acid-treated

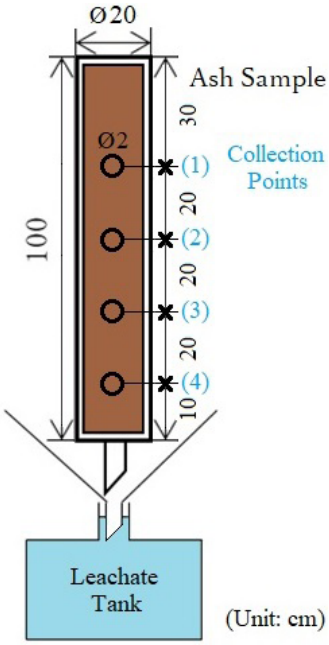

FIGURE 1: Column sketch.

2.2 Sample Collection Method

The leachate (hereinafter effluent) was collected from the leachate tank annually since 1995 for column experiment. As for ash collection, 2cm hole was drilled on 4 collection points, at the depth of 90cm, 70cm, 50cm, and 30cm as shown in Figure 1. 120g of ashes were collected from every point.

2.2.1 Sample Prepration

30g of ash samples were oven dried at 105°C for 24h to remove moisture for X-ray fluroscence (XRF) test, while another 30g were oven dried at 50°C for 24h for X-ray diffraction (XRD) test. 10g of the 105°C oven-dried ash samples were further heated at 600°C for 2h to calculate the Loss on Ignition (LOI). The 50°C dried ash samples were manually grounded using the mortar and pestle until powder form was achieved for XRD test. Thin section for polarization microscopy and scanning electron microscopy with energy dispersive X-ray (SEM-EDX) spectroscopy were made with selected ash sample pieces of approximately 3mm to 5mm in length, height, and width. The points to investigate were selected using polarized light microscopy.

To prepare for JLT-13 following Notification 13 of the Environment Agency, 500mL of super pure water were mixed with 50g ash sample to achieve a liquid to solid (L/S) ratio of 10, and shaken horizontally for 6h at 200 oscillations per minute. The samples were then filtered through a glass-fiber filter, followed by separating 50mL of the filtered sample for analyzing. For column experiment, 500mL of leachate samples were collected from all ten columns. Similarly, the leachate was filtered through a glass-fiber filter and 50mL were separated for analyzing.

For both the column experiment and leaching test, 5mL of 61% nitric acid (HNO_3) was added to the 50mL of filtered sample prepared in a conical flask, which was left to evaporate until 10mL of solution remains using the HPR-4030 hot plate that was preheated to 150°C. Another 5mL of 61% HNO_3 was subsequently added to the 10mL solution. Glass lids were placed onto every conical flask before evaporating the solution again until 5mL remains. The 5mL solution was diluted with 1% HNO_3 in a 50mL volumetric flask.

2.2.2 Analytical Methods

The chemical composition of MSWI FA were determined by using XRF spectrometer (Rigaku RIX3100). 4g of oven-dried ash samples were formed into pressed pellets by pulverization with a 4:1 ash sample to binder ratio. X-ray diffraction (XRD, MultiFlex, Rigaku) was applied for bulk mineral detection using Cu-K radiation within the 2-theta range of 2e75 and scanning step of 0.02 at the voltage of 44 kV and the beam current of 30 mA. Phase identification was carried out using Jade (v. 6.1) and PDXL (v. 2.1.2.0) software packages. Subsequently, the mineral compositions on the thin section were identified using SEM-EDX spectroscopy (Hitachi SU3500).

The concentration of heavy metals and light metals leached were determined by using Inductively Coupled Plasma Optical Emission Spectroscopy (720 ICP-OES). The prepared samples were tested against standard solutions of 0.005mg/L, 0.01mg/L, 0.02mg/L, 0.050mg/L, 0.100mg/L, 0.500mg/L, and 1.000mg/L.

3. RESULTS AND DISCUSSIONS

In this section, the targeted samples for discussion are the BAFACG group: BAFACG(U), BAFACG(C), BAFACG(P), and FA group: FA(U), FA(C), FA(P). Firstly, the bulk chemical and mineral composition analysis is provided, followed by detail analysis on the factors that resulted in the immobilization of heavy metals, with respect to the treatment method, according to the timeline of 27 years in total.

3.1 Bulk chemical composition analysis

XRF test was conducted to determine the constituents present in the ash samples. XRF is an elemental analysis technique that provides quantitative chemical information (Seifollah Nasrazadani, 2016). According to Table 2, the MSWI ash samples comprises mainly of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron (III) oxide (Fe_2O_3), and calcium oxide (CaO).

Interestingly, the FA group: FA(U), FA(C), and FA(P) have higher CaO weight percentage (wt%) than that of SiO_2. Inversely, samples consisting BA have higher SiO_2 content. These three trace constituents, which are also amphoteric heavy metals: Pb, Cu, and Zn displayed significant concentrations. Cd and Cr have a smaller concentration in comparison, but Cd and Cr are considered harmful heavy metals, hence, these five trace constituents are selected for discussion in this study.

3.2 Phase identification of minerals and weathering phenomenon of the MSWI fly ash

While the bulk chemistry data offer a reliable projection of the total elemental composition of the non-homogenous

TABLE 2: Bulk composition analysis of the ten samples (XRF).

Sample Name		BAFAC-G(U)	BAFAC-G(C)	BAFAC-G(P)	BA(U)	FA(U)	BAFA(U)	SMS	PMS	FA(C)	FA(P)
Major Constituent (mass%)	SiO_2 [%]	25.5	33.9	34.5	29.3	18.7	25.9	33.8	40.2	20.6	11.7
	Al_2O_3	16.2	16.4	16.3	18.6	8.8	17.4	17.7	19.4	10.1	6.5
	Fe_2O_3	7.6	7.7	7.8	17.4	2.1	15.1	11.4	3.6	2.3	1.7
	CaO	23.3	20.9	20.9	19.5	38.0	24.7	26.5	30.3	40.0	33.6
	Sub Total	72.5	78.9	79.6	84.8	67.7	83.1	89.4	93.6	73.0	53.5
Minor Constituent (mass%)	TiO_2 [%]	1.26	1.26	1.24	1.47	0.79	1.18	1.24	1.34	0.88	0.61
	MnO	0.11	0.10	0.12	0.21	0.07	0.17	0.17	0.17	0.07	0.06
	P_2O_5	2.59	2.86	3.74	1.97	0.72	1.49	2.66	0.16	0.80	25.1
	MgO	2.86	2.79	2.79	2.50	2.17	2.47	2.69	2.56	2.47	1.08
	Na2O	1.30	1.43	1.60	1.09	0.67	0.90	1.85	0.67	0.70	4.54
	K2O	0.52	0.56	0.58	0.37	0.02	0.27	0.48	0.11	0.05	0.23
	Cl	0.13	0.14	0.11	0.08	0.13	0.10	0.24	0.44	0.12	0.70
	S	0.05	0.05	0.05	0.10	1.49	0.14	0.04	0.39	1.13	0.47
	F	0.03	0.03	0.03	0.01	0.19	0.09	0.00	0.03	0.24	0.21
	Sub Total	8.84	9.22	10.26	7.80	6.25	6.81	9.37	5.87	6.45	32.95
Trace Constituent (ppm)	Zn [ppm]	5865	5034	5497	4511	16188	7444	4650	496	16776	5907
	Cu	2388	2536	1847	3507	822	2342	1341	207	831	650
	Pb	3865	4871	4364	1729	2414	2826	715	49	4130	1941
	Cr	243	228	231	782	304	601	1182	715	294	215
	Ni	103	106	97	311	83	188	162	26	81	77
	Ba	851	791	756	1235	339	1014	1100	1460	468	362
	Sb	0	0	0	106	0	0	0	0	0	1
	Sn	139	157	162	305	289	235	101	49	317	227
	Sr	359	316	324	292	59	251	392	502	93	134
	As	26	33	29	12	16	19	5	0	28	13
	V	3	3	3	4	2	3	4	3	2	2
	Cd	107	102	102	98	174	120	95	79	199	105
	Co	7	6	6	3	1	3	7	13	2	3
	Sub Total [%]	1.40	1.42	1.34	1.29	2.07	1.50	0.98	0.36	2.32	0.96
	LOI [%]	9.8	10.4	8.9	6.1	24.0	8.5	0.3	0.2	18.3	12.6
	Total [%]	82.75	89.58	91.15	93.93	75.97	91.47	99.75	99.85	81.73	87.45

MSWI ash samples, it does not provide information about the speciation and source of the elements (Saffarzadeh Amirhomayoun et al., 2011). Therefore, the collective utilization of rapid analytical technique (XRD), and microanalytical technique (optical microscopy and SEM-EDX spectroscopy), are essential for the recognition of crystalline phases and the characterization of the phase transformation phenomenon in the MSWI ash (Estevanus Kristian Huliselana et al., 2010).

Usually, fresh MSWI fly ash consist mainly of Ca-containing phases such as portlandite ($Ca(OH)_2$), calcium chloride hydroxide (CaClOH), and anhydrite ($CaSO_4$) (Pengfei Ren et al., 2022 'b'), along with chloride salts (halite (NaCl) and sylvite (KCl)) (Kaixing Zhao et al., 2020). Whereas minerals like lime (CaO) and $Ca(OH)_2$ can be found in the fresh bottom ash (Yunmei Wei et al., Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases, 2011 'b'). However, in the BAFACG group, quartz (SiO_2) and calcite ($CaCO_3$) are the major crystalline phases being recognized instead as shown in Figure 2a. The secondary minerals detected are $CaCO_3$ and hematite (Fe_2O_3), which is rather different in comparison to the minerals that are commonly found in fresh MSWI FA and BA. Secondary minerals are formed as a byproduct of weathering, and the formation occurs near the site where primary minerals are being attacked (William H. Schlesinger, 2020). As for the FA group in Figure 2b, ettringite and calcite are the major crystalline phases, while the detection of the principal secondary mineral gypsum ($CaSO_4{\cdot}H_2O$) suggests that changes occurred in the primary anhydrite ($CaSO_4$) as a result weathering, and the access of water molecule from the landfill column is responsible for the crystallization of secondary gypsum.

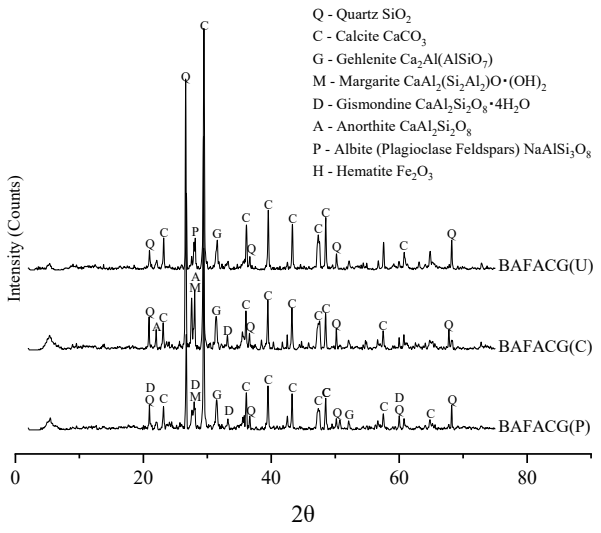

FIGURE 2: X-ray diffractogram of (a) BAFACG group ash sample, and (b) FA group ash sample.

3.2.1 Influence of weathering on heavy metals

The presence of CaO in MSWI FA results in a significantly high alkaline content, posing challenges to its potential for reuse. Nevertheless, the presence of carbon dioxide (CO_2) within the MSWI ash offers a solution by facilitating the transformation of Ca-containing phases such as CaO and $Ca(OH)_2$ from fresh MSWI FA into thermodynamically stable $CaCO_3$ (H. Mehdizadeh et al., 2021), thereby reducing the alkalinity of the ash. Carbonation is expressed by the following equations (Giampiero P. Sorrentino et al., 2023):

$$2CaClOH + CO_2 \rightarrow CaCO_3 + CaCl_2 + H_2O \quad (1)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (2)$$

Even though the results from XRD and SEM-EDX tests only shows the mineral phases and its chemical composition of the weathered MSWI FA in the current year (Year 27), the abundant formation of calcite ($CaCO_3$) minerals (Figure 3a and Table 3) and the absence of the aforementioned Ca-containing phases as shown in Figure 2 suggests that carbonation reaction occurred throughout the years of the MSWI ash weathering in the landfill column, thereby reducing the alkalinity of the MSWI ash.

The principal secondary mineral hematite (Fe_2O_3) is considered as a crystalline ferric mineral. This mineral was present in the SEM-EDX analysis for all samples in the BAFACG and FA group. Due to the large amount of data, the discussion will be represented by the results of BAFACG(U) sample. Table 3 shows the chemical composition of BAFACG(U) in the SEM-EDX analysis in Figure 3. Fe_2O_3 is particularly in abundance at Point B, C, and D in Figure 3b. At Point B, a small amount of Zn, a bivalent metal, was detected. The substitution of Fe with bivalent metals (hereinafter metallic inclusions) such as Pb, Cu, and Zn, which are bounded to crystalline ferric minerals, takes place in the course of glass alteration. When glass alteration occurs, dissolution of metallic inclusions results in the leaching of Pb, Cu, and Zn metal (Yunmei Wei et al., 2011 'a'). This phenomenon influences the leaching concentration of heavy metal.

3.3 Leaching characteristics of MSWI fly ash

Leaching test was conducted in three separate years to study the leaching characteristics of the five selected heavy metals. For BAFACG group, the results are from Year 0 (Y0), Year 5 (Y5), and Year 27 (Y27), while the timeline of FA group begins from Year 1 (Y1), followed by Y5 and Y27. With only results from 3 different years, it is difficult to determine an accurate change in behavior of the heavy metals. However, it is still important to ensure that the THMs (Pb, Cd, T-Cr) satisfies Japan's landfill disposal standards to prevent contamination in the environmental systems (Rahman Zeeshanur, 2019). Hence, this section assesses the heavy metals released and its compliance with landfill disposal standards.

From the results in Table 4 and Table 5, the high concentration of chloride salt in five years (Y5) in the study indicates high soluble chloride (Cl) content in FA, which is detrimental to the reuse of FA due to the potential risks

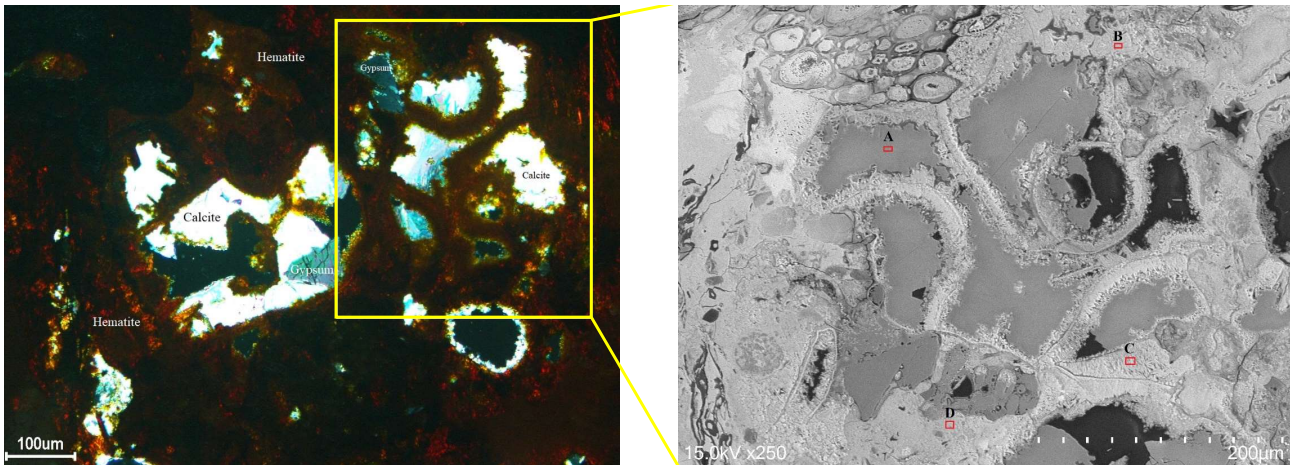

FIGURE 3: Photomicrograph of (a) presence of iron-rich constituent, calcite, and gypsum in BAFACG(U) under crossed-polarized light (xPL), and (b) a 90° anticlockwise BSE image of fig. 3a with four label points.

TABLE 3: Chemical composition of corresponding to the points in Figure 3b.

Point	A	B	C	D
Element	Wt%			
CK	10.77	5.44	8.12	4.74
OK	37.76	27.27	26.85	27.23
MgK	0.67	0.22	-	0.26
AlK	0.50	2.30	1.14	2.85
SiK	0.63	4.22	1.77	5.81
PK	-	0.29	0.13	0.37
SK	1.48	0.06	-	0.10
ClK	-	0.16	-	-
KK	0.17	0.13	-	0.24
CaK	41.84	2.62	1.89	3.83
FeK	6.18	57.00	60.09	54.56
ZnK	-	0.29	-	-

posed to the environment (Kaixing Zhao et al., 2020) (Xiongfei Chen et al., 2016) (Wei-Sheng Chen et al., 2012). This high chloride content also assists in the leaching of Pb, Cd, and Zn metals during dissolution, increasing the content of these harmful heavy metals at the landfill and in the environmental systems if not carefully treated and disposed (Mojtaba Ajorloo et al., 2022).

In Y1 and Y5, the Pb leached from FA(U) was above the landfill disposal standard, while the leached Pb, Cd, and T-Cr of the remaining samples already satisfied the landfill disposal standard since the beginning of the study. By Y27, the THMs (Pb, Cd, and T-Cr) leached from both BAFACG and FA group is well below Japan's landfill disposal criteria of 0.3 mg/L for Pb and Cd, and 1.5 mg/L for Cr^{6+} (Shimaoka Takayuki, 1996). While the data does satisfy the landfill disposal standard, it is important to note that solely relying on these criteria does not provide complete assurance that the treated FA is safe for landfill disposal.

3.4 Behavior of heavy metals in the effluent

A major concern related to the operations of landfills is the inevitable consequences of heavy metals releasing with leachate (C. Righi et al., 2022). Landfill leachate containing high levels of THMs affects the environmental system through water contamination if the MSWI ash is not given proper treatment to meet the Japanese effluent standards (Yunmei Wei et al., 2022 'c') (Hiratsuka-Sasaki A., 2020) (Ministry of the Environment, Government of Japan, 2015). However, even if the concentration of individual THMs is not very high, it does not mean that the total amount of heavy metals in the leachate is negligible (Athanasius P. Bayuseno, 2011).

The behavior of heavy metals in the effluent of thermal-treated FA has been very consistent throughout the

TABLE 4: Leached concentration of heavy and light metals in BAFACG group corresponding to timeline of the study.

Sample Name		BAFACG(U)			BAFACG(C)			BAFACG(P)		
Year		0	5	27	0	5	27	0	5	27
	pH	11.3	7.9	8.9	10.5	7.8	8.8	10.5	8.1	9.0
Leached Concentration (mg/L)	Pb	0.06	0.07	0.04	0.05	0.49	0.04	0.05	0.37	0.02
	Cd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
	Cr	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.01
	Zn	0.10	0.28	0.05	0.10	0.25	0.05	0.10	0.34	0.05
	Cu	0.53	0.64	0.03	0.10	0.18	0.02	0.40	0.17	0.02
	Ca	381	60.1	21.0	339	69.6	22.6	430	64.3	19.1
	Na	647	98.2	2.13	805	214	2.15	680	121	1.83
	Cl	35.5	2075	1.05	19.9	2320	0.62	17.3	2320	0.64

TABLE 5: Leached concentration of heavy and light metals in FA group corresponding to timeline of the study.

Sample Name		FA(U)			FA(C)			FA(P)		
Year		0	5	27	0	5	27	0	5	27
	pH	12.2	12.6	11.7	12.2	12.6	10.1	7.2	7.3	8.5
Leached Concentration (mg/L)	Pb	95.0	23.5	0.02	0.09	0.16	0.01	0.05	0.05	0.01
	Cd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	Cr	0.03	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.01
	Zn	9.80	1.11	0.04	0.02	0.58	0.05	0.02	6.03	0.03
	Cu	0.26	0.02	0.01	0.02	0.02	0.03	0.02	0.02	0.01
	Ca	9100	7300	12.6	8600	6250	7.02	6400	3205	20.8
	Na	-	-	0.39	-	-	1.07	-	-	3.56
	Cl	17000	14000	3.60	17000	11750	1.86	13000	6575	4.83

study. This treatment successfully encapsulates the heavy metals long-term through high temperature heating. Thus, the discussion for this treatment method is omitted for this paper. As for other treatment methods, significant changes can be observed from the concentration of heavy metals leached from the beginning of the study (Year 0) up until today (Year 27).

3.4.1 Immobilization mechanisms of chelate/acid treatment

pH value of the effluent plays a huge influence in the immobilization of heavy metals in MSWI FA. The ash in the FA group is soft and fine apart from FA(C), which coagulated from the treatment but crushes relatively easily. Figure 4 shows the effluent pH changes of FA group for the past 27 years.

In Figure 5, from Y1-Y5, the leaching of Pb decreased for all FA group. Chelate treatment proved effective on immobilizing Pb in FA as the Pb leached were significantly lower in comparison to FA(U) and FA(P). Phosphoric-acid treatment not only reduces the effect of the high dissoluble chloride content, but also reduces the high alkalinity of MSWI fly ash (Guo Xian Ma, 2013). The pH value of FA(P) falling into the acidic spectrum promotes the leachability of amphoteric metal Pb, reflected by the steep fall in the Pb concentration in Figure 5.

From Y6-Y15, leached Pb from the FA group fell below the Japanese effluent standard of 0.1 mg/L, with the exception of an outlier, FA(P) in Y14. The soluble Cl leached (Figure 6) from FA(P) effluent decreases in similar pattern as leached Pb, and the slight increase in soluble Cl leached in Y12-Y15 and Y22-Y25 resulted in the leached Pb fluctuation (Mojtaba Ajorloo et al., 2022). From Y16-Y27, both chelate and acid treatment displays effectiveness in immobilizing Pb by meeting the effluent criteria.

The pH value of the effluent also plays an important role in the immobilization of Cd (Mojtaba Ajorloo et al., 2022). The leached Cd from Y1-Y5 in Figure 7 corresponds to the effluent pH in Figure 4. Chelate treatment is the most effective in stabilizing Cd, in the span of two years. From Y6-Y27,

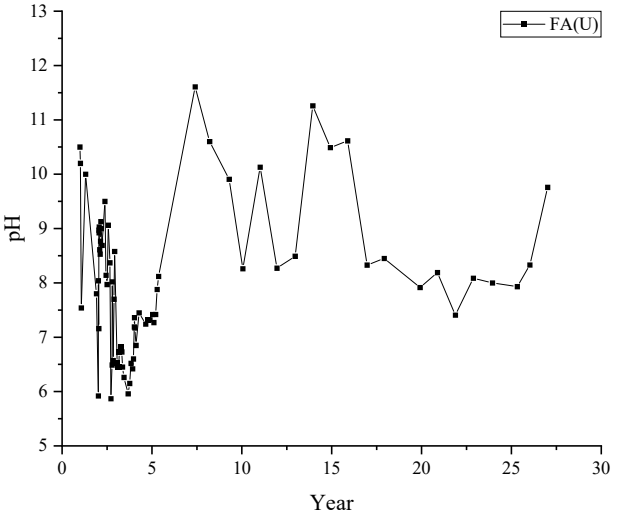

FIGURE 4: pH value of the effluent in the FA group: (a) FA(U), (b) FA(C), and (c) FA(P).

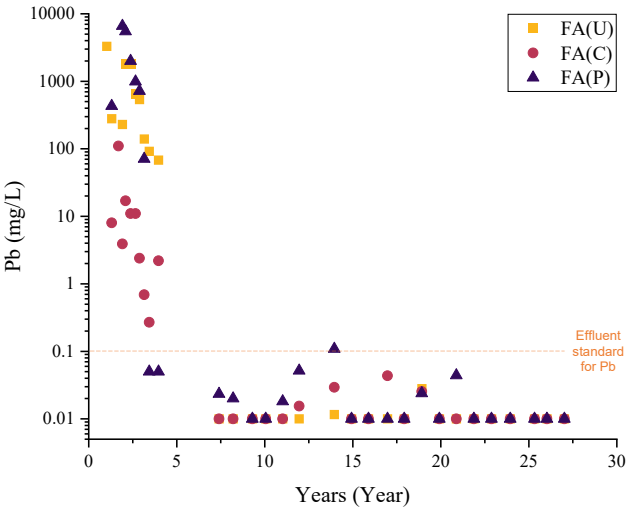

FIGURE 5: Leached Pb concentration (FA group).

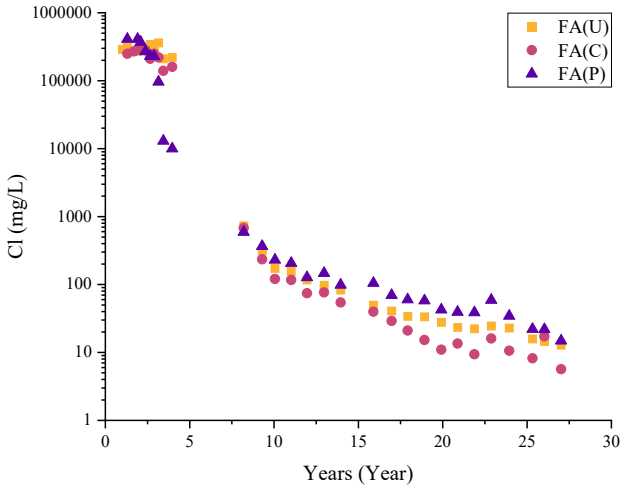

FIGURE 6: Leached concentration of chloride salt Cl (FA group).

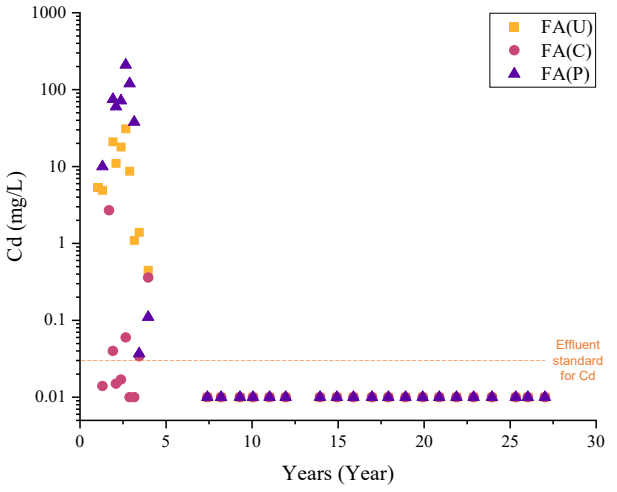

FIGURE 7: Leached Cd concentration (FA group).

leached Cd meets the effluent standard of 0.03 mg/L and is at the machine's detection limit. This pattern is expected to continue in the long-term.

In Figure 8, the immobilization of Zn from Y1-Y5 is of similar pattern as that of Pb and Cd. However, Zn is more sensitive to the changes in pH as compared to Pb and Cd. The slight fall in pH from Y18-Y25 (Figure 4) resulted in the fluctuation of leached Zn in Figure 8. Despite the leached Zn of FA group meeting the effluent standard of 2.0 mg/L since Y6, the possibility of it remaining below the criteria is uncertain in the long-run regardless of the treatment method in this case, especially if the fluctuation of effluent pH occurs between 7.0 and 8.0.

Chelate and acid treatment proved to be effective on the stabilization of T-Cr as the leached T-Cr meets the Japanese effluent standard of Cr^{6+} of 0.5 mg/L from the beginning of the study (Figure 9). From Y1-Y5, FA treated with phosphoric acid took immediate effect in the immobilization of T-Cr than chelate treatment. In Y14, there is a small spike in leached T-Cr that is similar to that in Pb. In this case, this increase is not of concern as the effluent standard is set for Cr^{6+}. Thus, it is safe to conclude that the immobilization of T-Cr with both chelate and acid is safe and effective in the long-run.

In contrast, these treatment methods are not as effective on Cu as shown in Figure 10. From Y1-Y5, the treatment methods promoted the leaching of Cu instead of immobilizing them. Acid treatment seems to be more effective in stabilizing Cu in the long-run in comparison to chelate treatment. From Y6-Y10, leached Cu of FA(C) did not satisfy the effluent criteria of 3.0 mg/L. Chelate treatment resulted in the coagulation of the ash, forming larger particles that easily crumbles upon small forces acting on it. The other two samples are very fine in comparison to FA(C). The particle size led to the fluctuation of leached Cu in FA(C) as Cu are mostly concentrated in larger particles (Davide Bernasconi et al., 2022).

Between chelate treatment and phosphoric acid treatment, chelate treatment is more stable and less fluactuative in the short-term. On the other hand, phosphoric acid treated FA promotes the leaching of amphoteric metals in the short-run, but shows effective immobilization of heavy metals within 3 years and is more promising in the long-run, especially Cd, T-Cr, Zn, and Cu. Overall, the leaching of heavy metals is heavy influenced by the effluent pH, followed by Cl content and ash particle size.

3.4.2 Immobilization mechanisms of chelate/acid treatment with compost

With the addition of compost alongside chelate or acid treatment, a rich CO_2 environment is created. Crushed garbage consisting of glass shards were also added which enhances the porosity of the ash. Due to these changes, the results varied drastically from using only one treatment method. The particle size and hardness of the BAFACG group ash mix is also much coarser in comparison to the soft and fine ash from FA group. Figure 11 shows the effluent pH changes of BAFACG group for the past 27 years.

From Y0-Y5, the Pb leached fluctuated above and below the Pb effluent standard of 0.1 mg/L (Figure 12).

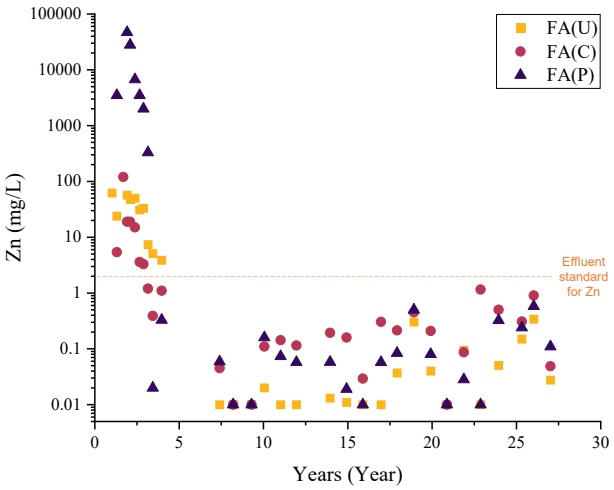

FIGURE 8: Leached Zn concentration (FA group).

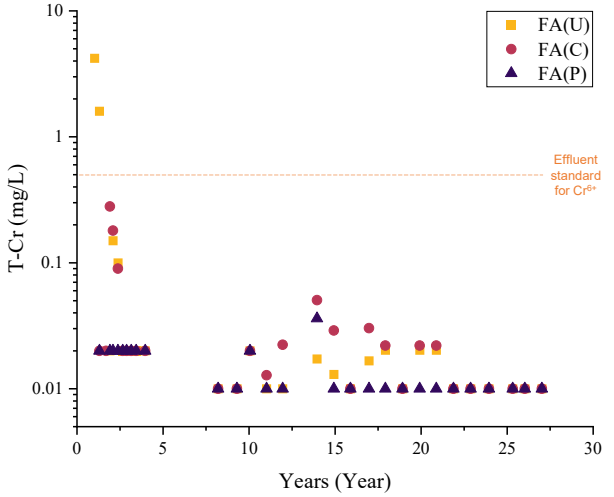

FIGURE 9: Leached T-Cr concentration (FA group).

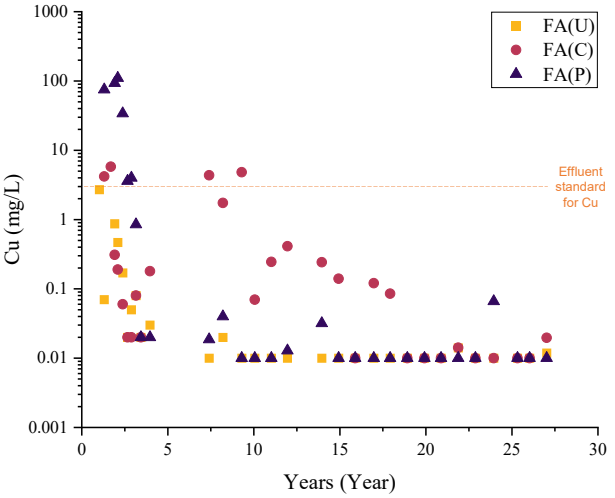

FIGURE 10: Leached Cu concentration (FA group).

treatment methods is equally as effective as using only chelate/acid treatment in the immobilization of Cd.

The drastic changes in Pb leached in the first 5 years is attributed to the heterogeneous ash composition and accelerated carbonation. From Y6-Y15, the leached Pb of BAFACG group satisfies the effluent criteria. The soluble Cl in this ash group is also significantly lower compared to the FA group (Figure 13), hence the lower concentration of leached Pb. The immobilization of heavy metals for FA treated with the combination of compost is highly affected by the accelerated carbonation from the breaking down of compost. From Y16-Y27, the organic matter in the compost eventually broke down, releasing some heavy metals, hence the small increment in leached Pb from BAFACG(U) in Figure 12.

Leached Cd, on the other hand, is generally concentrated above the effluent standard 0.03 mg/L from Y0-Y5 (Figure 14). Apart from accelerated carbonation, the effluent pH of BAFACG group falling below the neutral value of 7 from Y0-Y5 (Figure 11) also promoted the leaching of Cd to a certain extent. From Y4 onwards, the combination of two

In Figure 15, accelerated carbonation largely contributed to the low concentration leaching of Zn from Y0-Y5 in comparison with the leached Zn from the FA group. Although accelerated carbonation is the main factor in immobilizing the amphoteric metal Zn, the effluent pH also plays an important role in maintaining the leached Zn concentration below the effluent standard of 2.0 mg/L. From Y10-Y27, the leaching pattern of Zn mirrors the pH of the effluent, indicating an inverse correlation between Zn and pH.

Leached T-Cr was below the Cr^{6+} effluent criteria of 0.5 mg/L (Figure 16) within a year (Y0-Y1) from the commencement of this study. From Y8-Y27, both treatment methods proved effective in immobilizing T-Cr in the long-run, as shown in Figure 16.

In Figure 17, FA treated with combinations of two treatment methods satisfies the effluent standard of Cu almost immediately. The addition of a CO_2-rich environment fur-

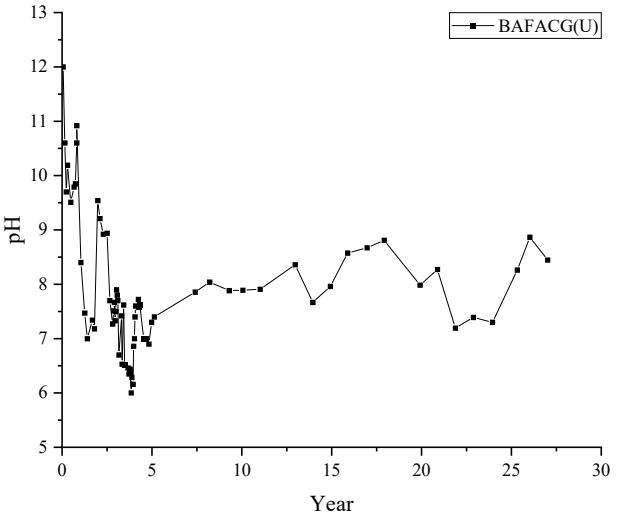

FIGURE 11: pH value of effluent in BAFACG group: (a) BAFACG(U), (b) BAFACG(C), and (c) BAFACG(P).

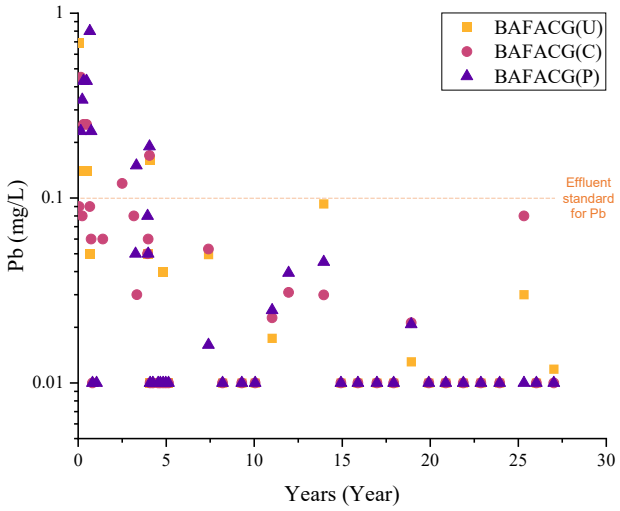

FIGURE 12: Leached Pb concentration (BAFACG group).

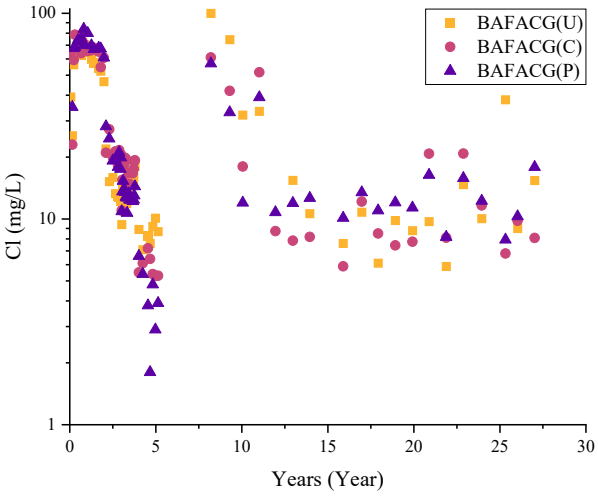

FIGURE 13: Leached concentration of chloride salt Cl (BAFACG group).

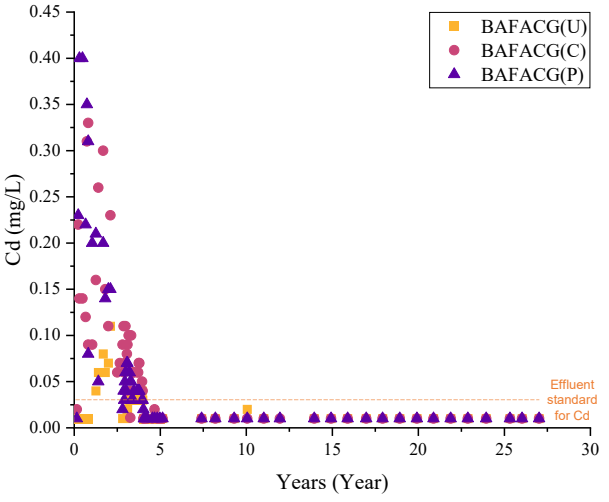

FIGURE 14: Leached Cd concentration (BAFACG group).

ther enhanced the immobilization of Cu. However, relying solely on compost on the stabilization of Cu does not seem as effective as combining the treatment methods in the beginning (Y0-Y3). From Y4-Y15, further reduction in Cu leached as the pH value of BAFACG group shifts towards the alkaline spectrum. As for the remaining 12 years, the leaching of Cu is independent of the pH of the effluent, and the compost has fully broken down by then. However, precipitation reactions with other elements present in the environment may occur, leading to the formation of insoluble compounds such as the copper hydroxides, carbonates, sulfides, or phosphates, which can limit its leaching. Furthermore, the weathering process over a long period of time results in formation of Al- and Fe-hydrates due to mineral alteration that can permanently bind elements such as Cu to provide definitive stability (Saffarzadeh Amirhomayoun et al., 2011).

The porosity and CO_2-rich environment (Figure 18b) contributed by the compost accelerated the carbonation process, which is effective in removing Cl and simultaneously leading to low concentrations of heavy metals in the effluent (Lei Wang et al., 2012). However, it is considered a short-term solution because the organic matter in the compost can eventually break down, releasing the heavy metals back into the environment. Therefore, combining compost with a long-term stabilization method such as chelate or acid treatment is recommended for effective and sustainable treatment of MSWI FA.

4. CONCLUSIONS

The current study was designed to understand the long-term behavior of heavy metals in MSWI FA and the factors influencing their immobilization over a period of 27 years. Comparing treatment methods, we observed that chelate treatment is more effective in the short run in immobilizing heavy metals, while phosphoric acid treatment yields superior long-term results. However, when combined with compost, both chelate and acid treatments exhibit enhanced

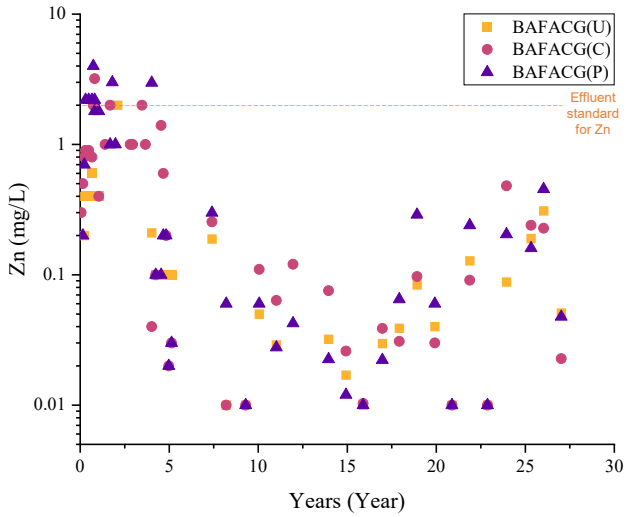

FIGURE 15: Leached Zn concentration (BAFACG group).

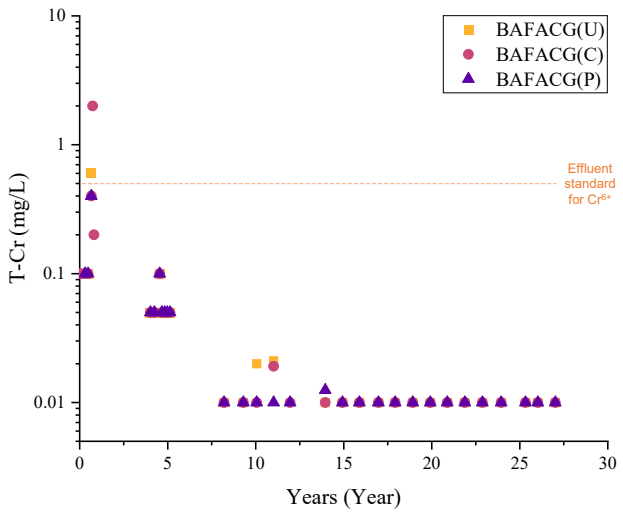

FIGURE 16: Leached T-Cr concentration (BAFACG group).

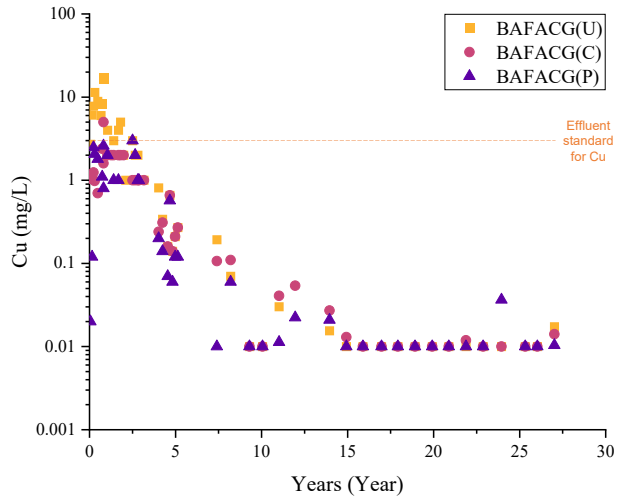

FIGURE 17: Leached Cu concentration (BAFACG group).

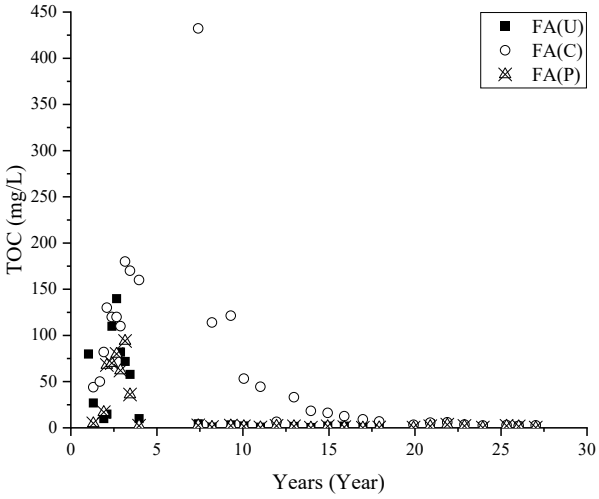

FIGURE 18: TOC concentration of (a) FA group, and (b) BAFACG group.

efficacy, suggesting a promising approach for immobilizing heavy metals. It is worth noting that compost treatment alone is not a feasible method for heavy metal immobilization. Furthermore, all heavy metals analyzed in this study comply with Japan's landfill disposal criteria and effluent standards of Japan, demonstrating the potential for the developed immobilization processes to meet regulatory requirements and reduce environmental impacts.

Several essential factors contributing to the immobilization of heavy metals were identified. These factors, namely carbonation, soluble Cl content, pH value, dissolution, weathering, and particle size have emerged as significant contributors in the immobilization process, in descending order of importance. An inverse relationship between pH and Zn was also observed, especially between the range 7.0 and 8.0, highlighting the role of pH variations in the leaching behavior of Zn. As pH levels fluctuate, it can alter the solubility and mobility of heavy metals, affecting their immobilization and subsequent leaching behavior.

In conclusion, our study provides valuable insights into the long-term behavior and immobilization of heavy metals in MSWI FA. Factors such as carbonation, Cl content, pH value, dissolution, weathering, and particle size have been identified as significant in the immobilization process. These findings contribute to our understanding of waste management strategies and offer a foundation for further research and the development of sustainable practices in handling heavy metal-containing waste materials. Further research is encouraged to deepen our understanding and develop innovative approaches for mitigating the environmental impact of heavy metals in waste materials.

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