

# Chemical Leaching of Metals from Landfill's Fine Fraction

E. Balkauskaitė, A. Bučinskas, R. Ivanauskas, M. Kriipsalu, G. Denafas

**Abstract**—Leaching of heavy metals (chromium, zinc, copper) from the fine fraction of the Torma landfill (Estonia) was investigated. The leaching kinetics studies have determined the dependence of some metal's concentration on the leaching time. Metals were leached with Aqua Regia, distilled water and EDTA (Ethylenediaminetetraacetic acid); process was most intensive 2 hours after the start of the experiment, except for copper with EDTA (0.5 h) and lead with EDTA (4 h). During leaching, steady concentrations of Fe, Mn, Cd and Pb were fully stabilized after 8 h; however concentrations of Cu and Ni were not stabilized after 10 h.

**Keywords**—Landfills, fine fraction, leached metals, leaching kinetics.

## I. INTRODUCTION

LANDFILLS are the places where the lifetime of products is ended. The Baltic Sea region has 75-100 thousand old landfills, which pose a threat to soil, water and air due to polluted leachate and greenhouse gas emissions [2]. On the other hand, landfills contain large quantities of recyclable and energy-efficient materials, so recovery of these materials can become a significant part of the circular economy. As a result, landfill mining can recover not only valuable materials and areas needed for other activities, but also save costs on covering and maintaining closed landfills after their operation, thus reducing the negative environmental impact of landfills [1]. Thousands of landfills, which are sources of environmental pollution, are becoming important objects for resource recovery and reduction of environmental impact [3].

Fine granulometric fraction and even colloidal materials make up the largest part of old landfills. Landfills fine fraction (LFF) with mud and colloidal matter contains significantly more valuable metals than the coarse fraction [3].

Leaching of metals from waste varies with time of year and temperature changes. Leachate pollutes the soil, surface water and groundwater [4]. Many factors influence the leaching of metals from landfill waste: physicochemical properties of soil, precipitation, temperature, microbiological environment, pH,

presence of complexing agents in the environment.

In this study, the influence of pH and complexing agents on the leaching of metals from LFF was determined. For the study by excavation, sampled fine fraction of the closed Torma landfill in Estonia was selected. The fine fraction (< 20 mm) is predominant with an average of 53% [2]. Plastics and textiles accounted for the largest percentage by weight of 27% in LFF. Preliminary results on elemental concentration determined by AAS and ICP-MS for Torma landfill are summarized in Table I [1]

TABLE I  
CONTENT OF MAJOR AND TRACE ELEMENTS IN FINE FRACTION OF TORMA LANDFILL

Metals	Averaged, mg/kg	SD, mg/kg	%
Al	10.684	6144	11.8
Na	705	578	0.8
Mg	8594	4115	9.5
K	1401	795	1.5
Ca	17.913	10.639	19.7
Fe	49.39	35.791	54.4
Cr	260	193	0.3
Mn	356	204	0.4
Co	7	3.8	<0.1
Ni	34	18.8	<0.1
Cu	321	1801	0.4
Zn	1046	572	1.2
Cd	0.5	0.8	<0.1
Pb	141	96	0.2

During the work, leached metals were identified by analytical methods and their leaching kinetics was investigated using media of different pH values and solutions of complexing agents.

## II. METHODIC

### A. LFF Decomposition with Aqua Regia

Decomposition of the LFF with Aqua Regia is used to determine the content of chemical elements. The samples are dissolved in Aqua Regia consisting of a mixture of  $\geq 65\%$  nitric acid  $\text{HNO}_3$  and 36.5% hydrochloric acid  $\text{HCl}$  (1: 3 by volume). The prepared acid's mixture is mixed with test samples in glasses in the liquid/solid ratio  $L/S = 10$  (l/kg). The prepared three samples are heated for 2 hours at  $120^\circ\text{C}$  with the regularly addition of Aqua Regia (due to evaporation and stirring).

The concentrations of metals (like Cu, Cd, Mn, Cr, Ni, Pb, Zn, Ag, and Fe) in the obtained solutions were measured in eluates by atomic absorption spectrometry (AAS).

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### B. Leaching by Different Media

The following media were used for leaching:

- distilled water;
- 2% solutions of complexing agents like EDTA, citric acid and tartaric acid;
- 2% solution of sodium bicarbonate  $\text{NHCO}_3$ ;
- solutions of various pH (0, 4, 11, 14).

$\text{HNO}_3$  was used to prepare the pH 0 and pH 4 solutions and sodium hydroxide - for pH 11 and 14.

The value of liquid to solid ratio L/S is 10 (l/kg). For each leaching the three samples of 3 g each was mixed with 30 ml of leaching media. The samples are shaken in a horizontal shaker (200 rpm). The experiment lasted for 24 h, and the obtained eluate was then filtered through a paper filter.

The concentrations of leached metals (like Cu, Cd, Mn, Cr, Ni, Pb, Zn, Ag, and Fe) were measured in eluates by atomic absorption spectrometer SHIMADZU AA-7000.

### C. Leaching Kinetics Investigation

The leaching kinetics investigations were performed using distilled water and 0.05 mol/l (1.5%) EDTA solution. Investigations were performed on three samples and one blank sample to avoid randomization and to eliminate large deviations and human factor.

The vials with the flooded samples are placed in a horizontal shaker (200 rpm). There are nine leaching times of 5, 15, 30 minutes and 1, 2, 4, 6, 8, 10 hours. During the leaching obtained eluate is centrifuged for 10 min at 200 rpm and filtered using paper filter.

The concentrations of leached metals (like Cu, Cd, Mn, Cr, Ni, Pb, Zn, Ag, and Fe) were measured in eluates by AAS.

### D. Analysis of Kinetic Processes

To evaluate the change of leaching of metals from LFF in time, leaching kinetics studies were performed. The leaching kinetics of the corresponding metal is described by the first-order reaction exponential equation (1):

$$C = C_1 * [1 - \exp(-k_1 * t)], \quad (1)$$

where  $C$  is the content of metal leached from LFF at time  $t$ , mg/kg;  $C_1$  - equilibrium leachable metal content from LFF, mg/kg;  $k_1$  - kinetic constant,  $\text{h}^{-1}$ ;  $t$  - leaching time, h.

The standard first-order exponential equation (1) may not be appropriate for description of the leaching kinetics for some metals. In this case, Fanguiero et al. al. [5] proposed an exponential equation (2) for the first-order reaction of two speeds, which considers two-stage (fast and slow) leaching mechanisms:

$$C = C_1 * [1 - \exp(-k_1 * t)] + C_2 * [1 - \exp(-k_2 * t)], \quad (2)$$

where  $C$  is the content of metal leached from LFF at time  $t$ , mg/kg;  $C_1$  - content of metal leached from the LFF at higher leaching rate, mg/kg;  $k_1$  - kinetic constant,  $\text{h}^{-1}$ ;  $C_2$  - content of metal leached from LFF at lower leaching rate, mg/kg;  $k_2$  is the kinetic constant,  $\text{h}^{-1}$ .

It is assumed that fast and slow leaching processes are independent of each other. A graphical representation of this formula is presented in Fig. 1. In this way, the total content of the metal in the waste is divided into three parts - the part  $C_1$  is rapidly leached, the part  $C_2$  is leached more slowly and the part  $C_3$  is insoluble.

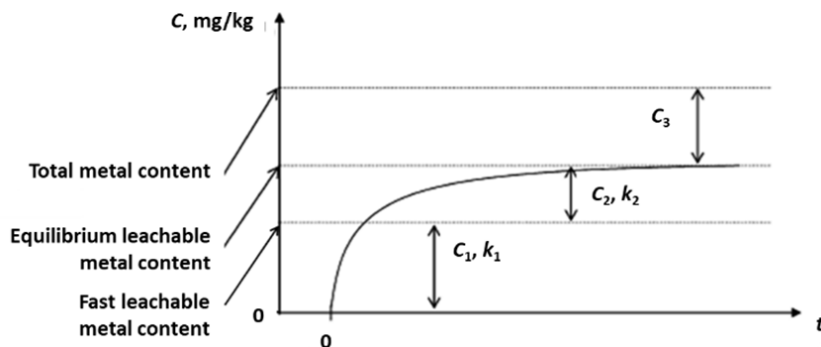


Fig. 1 Distribution of leachable metal content using a two-step reaction model

## III. RESULTS AND DISCUSSIONS

### A. Results of Leaching Investigations with Aqua Regia

Table II gives the results of leaching investigations with Aqua Regia, assuming that this reagent leaches the metals completely and that these values correspond to the total metal content of the fine fraction. The determined metals contents are compared with limit values in the soil according to Lithuanian Hygiene Norms HN 60: 2004 [6]. The limit values are exceeded by chromium Cr (1.6 times), zinc Zn (8.6 times) and copper Cu (3.4 times), the level of nickel (Ni) is close to the limit. These results confirm the need to evaluate the

properties of LFF under different environmental conditions using various leaching methods.

### B. Results of Leaching Investigations at Different pH Values

Leaching results at different pH values are presented in Table III. The highest leached amount of metals was for acidic medium at pH 0 (except for Ag at pH 14). Compared to the total metal content, the leached content of manganese at pH 0 is 56.22% of the total manganese content in fine fraction, 61.41% for zinc, 76.28% for copper, 69.90% for iron and 38.87% for nickel. For lead it is 50.26% and for silver 55.55% at pH 14.

TABLE II  
WITH AQUA REGIA LEACHED METALS CONTENT IN FINE FRACTION OF  
TORMA LANDFILL (ESTONIA)

Metals	Content, mg/kg	Limit values in the soil, mg/kg
Fe	1654.94	-
Cr	125.24	80
Mn	558.91	1500
Ni	63.46	75
Cu	251.87	75
Zn	2578.08	300
Cd	0.06	1.5
Pb	3.88	80
Ag	0.18	0.5

TABLE III  
METALS CONTENT LEACHED FROM FINE FRACTION AT DIFFERENT pH  
(TORMA LANDFILL, ESTONIA)

Metals	Leached content on the corresponding pH value, mg/kg					Total content, mg/kg
	pH 0	pH 4	pH 6	pH 11	pH 14	
Fe	1156.81	11.17	5.63	9.83	165.00	1654.94
Cr	0.00	0.00	0.00	0.00	0.00	125.24
Mn	314.22	0.00	0.00	0.00	0.00	558.91
Ni	24.67	0.00	0.00	0.00	0.00	63.46
Cu	192.13	0.51	0.43	0.39	63.04	251.87
Zn	1583.29	7.44	2.37	5.32	240.83	2578.08
Cd	0.01	0.00	0.00	0.00	0.00	0.06
Pb	1.95	0.71	0.69	0.74	0.89	3.88
Ag	0.06	0.06	0.06	0.06	0.10	0.18

The leaching rate of silver at different pH values was very similar, except at pH 14 the leaching rate was 1.7 times higher. Lead was also leached at different pH values, but 2.8 times more than it was leached at pH 0. Larger amounts of zinc, copper and iron were leached in highly acidic (pH 0) and highly alkaline (pH 14) media. The leaching amounts of these metals were very low at pH 4, pH 6 and pH 11. Zinc was leached 6.6 times more at pH 0 than at pH 14, copper 3 times more, and iron 7 times more. Nickel was leached only in very acidic or highly alkaline media. At pH 0 nickel was leached 2.7 times more than pH 14. Manganese was only leached at pH 0, cadmium also, and chromium was not leached under any pH conditions.

#### C. Results of Leaching Investigations with Complexing Agents

Using complexing agents, leaching investigations were conducted to evaluate the ability of the metals to form complexes and to predict the properties of LFF under the influence of natural dissolved organic matter. The influence of inorganic  $\text{NaHCO}_3$  on the leaching of metals has also been tested for a comprehensive evaluation. Leaching results with complexing agents' values are presented in Table IV.

Zinc, copper, nickel and lead were mostly leached with EDTA solution, significantly less with citric acid and even less with tartaric acid. Cadmium was only leached with EDTA solution. Compared to the total metal concentration, the zinc content leached with EDTA solution is 65.82% of the total zinc content, copper - 50.92%, nickel - 25.21%, lead - 82.22%, cadmium - 83.33%.

TABLE IV  
METALS CONTENT LEACHED FROM FINE FRACTION WITH DIFFERENT  
COMPLEXING AGENTS (TORMA LANDFILL, ESTONIA)

Metals	Leached content with the corresponding complexing agent, mg/kg				Total content, mg/kg
	EDTA, 2%	Citric acid, 2%	Tartaric acid, 2%	$\text{NaHCO}_3$ , 2%	
Fe	1161.71	1397.06	858.56	0.00	1654.94
Cr	0.00	12.84	0.40	0.00	125.24
Mn	152.93	294.13	208.01	0.00	558.91
Ni	16.00	8.75	7.00	0.00	63.46
Cu	128.25	25.69	14.97	11.99	251.87
Zn	1696.96	852.25	784.84	13.44	2578.08
Cd	0.05	0.00	0.00	0.00	0.06
Pb	3.19	0.98	0.94	0.80	3.88
Ag	0.06	0.06	0.06	0.06	0.18

Chromium, manganese and iron were best leached with citric acid solution. Their leached amounts with citric acid solution represent 10.25%, 52.63% and 84.42% of the total metal content. All the complexing agent solutions leached the same amount of silver - 33.33% of the total silver content.

Using the inorganic compound  $\text{NaHCO}_3$  for leaching investigation, the content of leachable metals is very low or the metals are not leached except iron. With  $\text{NaHCO}_3$  leached iron content is 7.38% of the total iron.

#### D. Leaching Kinetics Investigation Results

The leaching kinetics of the metals were investigated using distilled water and 1.5% EDTA solution due to the reason that such leaching conditions are close to natural conditions. The results of the studies described in the previous section show that only copper and iron are leached practically in distilled water (pH 6), therefore it has been limited to leaching investigations. For the same reason, the kinetics of chromium leaching in both media was not investigated. The leaching kinetics of silver could not be investigated due to its relatively low concentration in the fine fraction. Investigations on the kinetics of leaching of zinc in both media and of lead in distilled water were not possible.

The obtained results are the dependence of the concentration of metals leached from LFF on the leaching time. The kinetic curves are shown in Figs. 2-9. It can be seen that the leaching of metals with distilled water and EDTA solution was most intensive 2 hours after the start of the process, except for copper with EDTA (0.5 h) and lead with EDTA (4 h). The leaching rate is highest at the beginning of experiment as soon as the liquid and solid phase contact of the heterogeneous system occurs. Significant increase of leached metal concentration is visible after 5 min. from the start of experiment.

In terms of equilibration time of the leaching process, stable concentrations were most likely achieved in the iron, manganese, cobalt and lead cases within 8 hours of the study. Concentrations increased steadily over 10 hours and did not reach steady state for copper and nickel. The obtained data on the change of leaching of metals from LFF over time are used to derive kinetic equations describing the leaching processes. Using the determined kinetic constants it is possible to

calculate theoretically the leachable metal concentrations at any point in time. According to (1), the estimated coefficients are given in Table V.

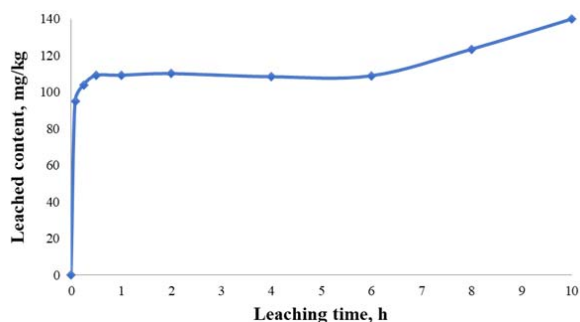


Fig. 2 Kinetic curve for copper (Cu) leaching with 1.5% EDTA

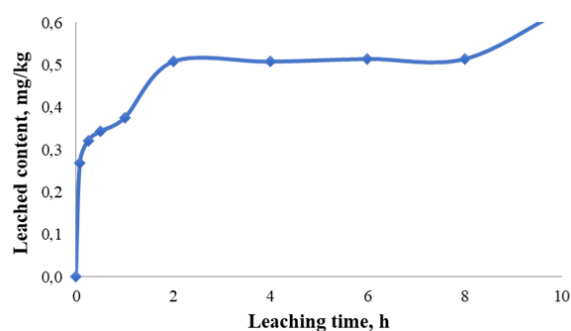


Fig. 3 Kinetic curve for copper (Cu) leaching with distilled water

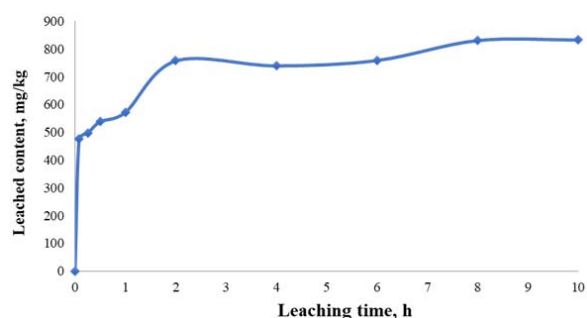


Fig. 4 Kinetic curve for iron (Fe) leaching with 1.5% EDTA

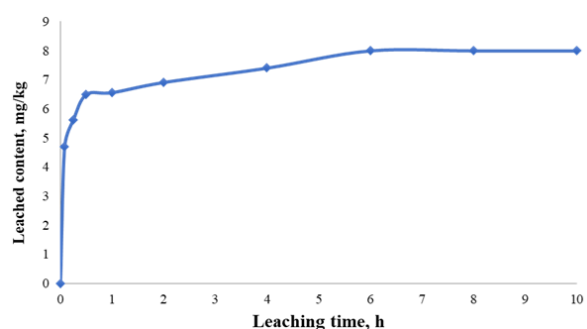


Fig. 5 Kinetic curve for iron (Fe) leaching with distilled water

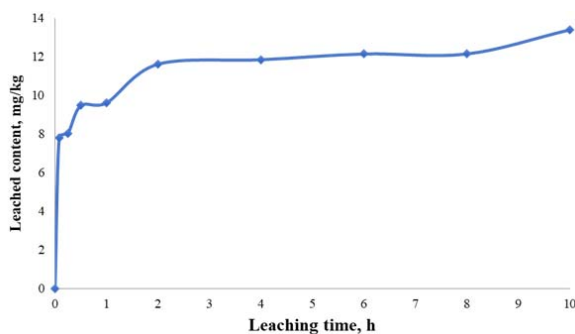


Fig. 6 Kinetic curve for nickel (Ni) leaching with 1.5% EDTA

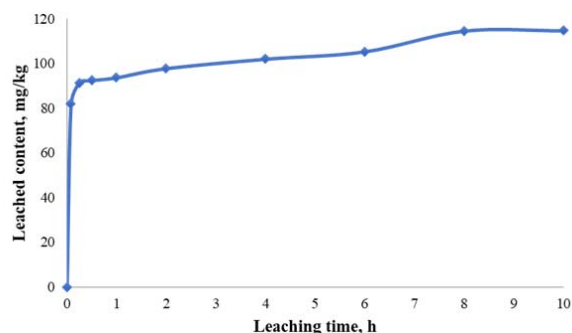


Fig. 7 Kinetic curve for manganese (Mn) leaching with 1.5% EDTA

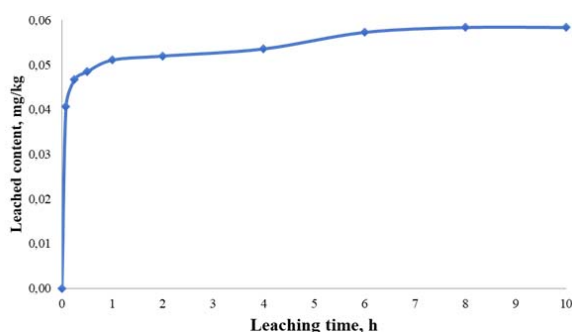


Fig. 8 Kinetic curve for cadmium (Cd) leaching with 1.5% EDTA

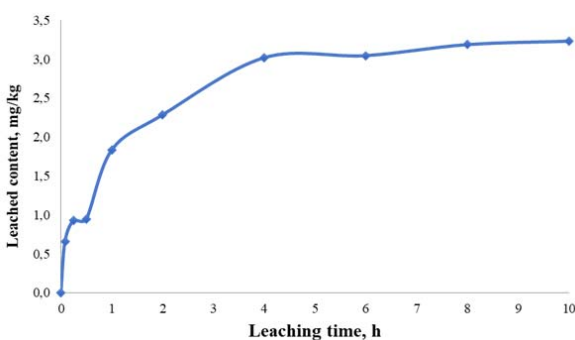


Fig. 9 Kinetic curve for lead (Pb) leaching with 1.5% EDTA

In the kinetic equation, the reaction kinetic constant ( $k_1$ ) represents the metal leaching rate. The higher the  $k_1$ , the faster the metal is leached. The rates for metal complexes with EDTA generation should decrease in the following order: iron,

lead, cadmium, copper, manganese, nickel.

TABLE V  
CALCULATED COEFFICIENTS OF KINETIC EQUATIONS FOR METAL LEACHING  
FROM LFF (TORMA, ESTONIA)

Metals	$C_1$ , mg/kg	$k_1$ , h <sup>-1</sup>	$R^2$
Leaching with distilled water			
Cu	0.63	1.55	0.981
Fe	8.00	1.06	0.999
Leaching with 1.5% EDTA			
Cu	140.00	19.02	0.979
Fe	833.68	26.47	0.996
Mn	114.80	9.25	0.996
Ni	13.40	2.89	0.995
Cd	0.06	21.41	0.999
Pb	3.23	25.11	0.994

#### IV. CONCLUSIONS

The research results of the project provided information on the composition and properties of the fine fraction of the Torma landfill (Estonia). According to the experimental results with Aqua Regia, the limit value for the substance in the soil is exceeded by chromium (1.6 times), zinc (8.6 times) and copper (3.4 times), nickel's level is close to the limit value. The presence of high levels of heavy metals in LFF well above the limit value in soil confirms the need to assess the environmental hazard and properties of LFF under different environmental conditions.

According to the results of the leaching of metals from the LFF at different pH 0-14 values, it can be stated that the minimum amount of metals was leached with distilled water at pH 6. The amount of leached metals increased as the solution medium acidified or alkalized. According to the results of experimental research it can be concluded that under natural conditions rainfall leaches very small amount of metals from LFF of the Torma landfill.

Taking into account that some metals make complex with EDTA, citric and tartaric acids, it can be concluded that different complexing agents do not have the same effect on different metals. The results show that metals have a strong ability to form complexes, suggesting that, under natural conditions, metals in the fine fraction of the landfill react with soil organic matter.

The leaching kinetics studies have shown that the concentration of some metals in the eluate is dependent on the leaching time. In the experiment with distilled water and EDTA solution, the metal leaching was most intensive 2 hours after the start of the experiment, except for copper with EDTA (0.5 h) and lead with EDTA (4 h). Steady-state concentrations were most likely achieved for iron, manganese, cobalt and lead within 8 hours of the experiment. Concentrations increased steadily over the 10 hours of experiment and did not reach steady state for copper and nickel. Coefficients of kinetic equations for leaching of metals, which can be used for estimation of heavy metal release into landfill leachate, have been calculated.

#### REFERENCES

- [1] M. Hogland et al. "Remarks on Four Novel Landfill Mining Case Studies in Estonia and Sweden". *Journal of Material Cycles and Waste Management*, 2018, vol. 20, no. 2. pp. 1355-1363.
- [2] Y. Jani et al. "Composition of Waste at an Early EU-Landfill of Torma in Estonia". *Iranian Journal of Energy and Environment*. 2017, vol. 8. pp. 112-117.
- [3] J. Burlakovs et al. "On the Way to 'zero Waste' Management: Recovery Potential of Elements, Including Rare Earth Elements, from Fine Fraction of Waste". *Journal of Cleaner Production*, 2018, vol. 186. pp. 81-90.
- [4] S. Fu and J. Lu "Temperature-Driven Variation in the Removal of Heavy Metals from Contaminated Tailings Leaching in Northern Norway". *Environmental Monitoring and Assessment*. 2019, 191:123
- [5] D. Fangueiro et. al. "Kinetic approach to heavy metal mobilization assessment in sediments: choose of kinetic equations and models to achieve maximum information", *Talanta*, 2005, vol. 66, no. 4, p. 844-857.
- [6] Lithuanian Hygiene Norm HN 60: 2015 Limit Values for Hazardous Chemicals in Soil (Lith.). Ministry of Health of the Republic of Lithuania. Vilnius, V-1441, 2016.

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