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Heavy Metals Leaching from Fluorescent Lamps Physicochemical Treatment Residuals

Inga Urniežaitė, Gintaras Denafas
Department of Environmental Engineering, Kaunas University of Technology

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Waste generated during the process of physicochemical treatment of fluorescent lamps contains relatively high quantities of heavy metals. Physicochemical treatment is employed with the aim to concentrate toxic substances present in the lamps. This study attempts to evaluate the leaching properties of treatment residuals. Waste of a similar composition has been not fully researched yet, thus the limited data are available on leaching of heavy metals from residues of similar processes. Concentrations of heavy metals leaching from the residuals into various complex-forming agents (ethylenediamine tetraacetic acid (EDTA), Citric acid, Tartar acid) have been analyzed. EDTA is selected for further kinetics experiments as a complex-forming agent known for its most effective leaching properties as stated in literature on this subject and in most cases practically observed.

Kinetic experiments have shown that almost all water-soluble heavy metals are mobilized from the samples within the period of approximately 20 hours, with time variation for different heavy metals. An increase in the leaching concentrations when using EDTA as a complex-forming agent has been observed. Extraction with EDTA has resulted in heavy metal concentrations ranging from 0.41 mg kg^{-1} of dry mass (DM) for Co to as much as 1576.00 mg kg^{-1} DM for Zn. Exposure of the samples to different temperatures has revealed the influence of the temperature as an important factor of experimental conditions. The concentration of leaching Hg has increased 3 times after heating the samples in the temperatures from 20^{o} to 120^{o}C.

Keywords: *mercury, fluorescent lamps, leaching kinetics, heavy metals, EDTA.*

1. Introduction

This study is unique since it is focused on residuals formed during physicochemical treatment of fluorescent lamps waste containing Hg and other heavy metals. The residuals are produced in a fluorescent lamps utilization device (Urniezaite et al. 2007). During the process Hg is concentrated in residuals without recycling it for further reuse. This type of waste utilization may be considered as one of the most feasible ways of final Hg stabilization and storage. The EU is encouraging the international efforts of phasing out Hg use and trade (The EU 2008). Efficient Hg conversion from metallic form to inorganic water-insoluble salts is considered as one among several alternatives. The European Commission plans to phase out the Hg export from the Member States by 2011. In this perspective technological developments in transforming liquid Hg into a solid compound should be considered before its disposal.

Demineralised water proposed as a leaching agent in many test procedures (DIN 38414 S4 1984; EN 12457 2002) is not reproducing natural conditions. Naturally emergent water (precipitation, landfill leachate) usually has much higher ionic strength because of dissolved substances present in it. Complex-forming agents are considered to be important substances in modelling natural conditions. Different complex-forming agents are present in natural leachants during the leaching from solid wastes. Particular inorganic ions and organic substances show their complex abilities (Janos et al. 2002). Therefore, leaching tests of different complex-forming agents help to realize heavy metals leaching abilities in various solutions.

Various researchers used a range of complex-forming agents. Schwedt et al. (2005) analyzed the influence of citric acid, wine acid and EDTA on heavy metal mobilization from ashes. Ohki et al.

(2004) used EDTA, citric acid, iminodiacetic acid and aspartic acid for heavy metals leaching from coal testing. Schwedt et al. (2005) having concluded citric acid forming a steady chelate complex with heavy metals ions to be the best complex-forming agent, many other researchers (Ohki et al. 2004, Sun et al. 2001, Vengris et al. 2003) indicated EDTA as the best complex-forming substance. Decision was made to test leachability of particular residuals with the following complex-forming agents: EDTA, citric acid and tartaric acid.

Heavy metal leaching from different kinds of waste and heavily polluted soils has been studied by various researchers. The total leaching concentration is usually determined, but it does not give information about mobility and availability of metals. Several studies have been done on the leaching kinetics. Janos et al. (2002) carried out research on metals leaching from fly ashes, stating that naturally occurring complexing agents increased mobility of most metals and the equilibrium state was attained in a shorter time. Fangueiro et al. (2005) and Kandpal et al. (2005) were also researching kinetics of heavy metals mobilization. Researchers tested experimental data applying them to the kinetic equations and concluded that kinetic extractions could be an efficient tool to study heavy metals mobility characteristics.

During this research leaching kinetics measurements of demineralised water and EDTA solution have been also performed. Kinetic measurements can be used for modelling and prediction of heavy metals leachability from waste. In addition, these results representing the time of reaching the concentration equilibrium can be used for verifying the agitation/contact time typically set for 24h in standard leaching methods. The time of reaching the equilibrium concentration can show whether the specified time is sufficient for obtaining valuable results or the agitation time of the method should be adjusted for similar waste testing.

2. Materials and Methods

2.1. Research Object

Solid residuals of the waste fluorescent lamps treatment process have been analyzed on purpose both to evaluate heavy metals leaching properties in complex-forming agents and to study leaching kinetics in various leaching agents.

The waste treatment technology is described by Urniezaite et al. (2007) and patented as a Lithuanian patent (LT patent 2002). The process is defined as a physicochemical treatment of solid wastes (BREF 2006). Waste fluorescent lamps are broken while being submerged into reactive liquid in a closed compartment. Oxidative liquid consists of an oxidizing agent – $KMnO_4$ and hydrochloric acid for pH adjustment. Residuals which remain after treatment consist of a mixture of luminophore powder and Hg conversion products.

2.2. Waste sampling

Samples of residuals from a technological process were collected by a fluorescent lamp treatment company. Residuals were sampled in equal portions from different parts of a storage container and mixed together to form an approximately 2 kg sample. The sample was divided to analytical sub-samples of various weights depending on a subsequent analysis. The analytical part of this project was accomplished in Clausthal Technical University, the Institute of Inorganic and Analytical Chemistry, Germany.

Moisture content in residuals was determined under the conditions of German standard DIN 38414-S2. Samples were conditioned at the temperature of 105^{O}C for 4 hours.

2.3. Leaching tests

Leaching capabilities of Hg and other heavy metals were examined using different complex-forming compounds: EDTA, citric acid, and tartaric acid.

A test procedure was similar to all complex-forming agents. Leachants were prepared from complex-forming agents as 2% solutions in demineralized water. The analyzed samples were treated with leachant at the Liquid to Solid (L/S) ratio L/S=10. The extraction process was performed by shaking the mixture in a horizontal shaker for 24h. After a certain time the solution was separated by filtrating it with Cellulose nitrate membrane filters of 0.45 µm. The solution was acidified with nitric acid and then analyzed for the presence of heavy metals.

2.4. Kinetics experiments

Leaching dynamics experiments were performed using demineralized water and EDTA solution (0.05 mol/l in demineralized water).

The analyzed samples were treated with leachant at the ratio of L/S=10. The extraction process was performed by shaking the mixture in a horizontal shaker for different periods of time (5, 15, 30 min and 1, 2, 4, 6, 8, 16, 24 h). After a certain time the solution was separated by filtration using membrane filters of 0.45 µm. The solution was acidified with nitric acid and further analyzed for the presence of heavy metals.

2.5. Heavy metals analysis

Hg concentration in the samples was determined by Cold Vapour Atomic Absorption Spectrometry (CVAAS), using Philips PU9200 Series Atomic Absorption Spectrometer with Philips PU9360 Continous Flow Vapour System. Acidified solution of Sodium Borohydride ($NaBH_4$) was used for Hg reduction to a metallic form. Quantitative analysis measurements of other heavy metals (Pb, Cd, Zn, etc.) were taken by Atomic Absorption Spectrometry (AAS) using Philips PU9200 Series Atomic Absorption Spectrometer.

3. Results and discussion

3.1. Leaching quantities

The analyzed residuals were tested for heavy metals leachability in solutions of the following complex-forming agents: EDTA, citric acid and tartaric acid. These substances were selected as well known chelating agents used in similar experiments by many researchers (Yuan et al. 2007; Schwab A.P. et al. 2008; Evangelou et al. 2007). Results of the performed analysis are presented in Fig. 1. The graph shows complex-forming agents efficiency in heavy metals mobilization from the analyzed waste residuals.

Leaching metals ability varies depending on the used complex-forming agent.. Classical complex-forming agent EDTA being able to form water soluble metal complexes shows the highest leaching ability for Hg and Pb. Hg leaching in the presence of EDTA was 15 times higher than that in the solutions of other complex-forming substances. Tartaric acid demonstrated very high complex-forming ability for Cd when compared to other substances used. Citric acid showed no particular ability to form water soluble complexes with the analyzed heavy metals. In accordance with the above presented results EDTA was selected for further leaching kinetics experiments.

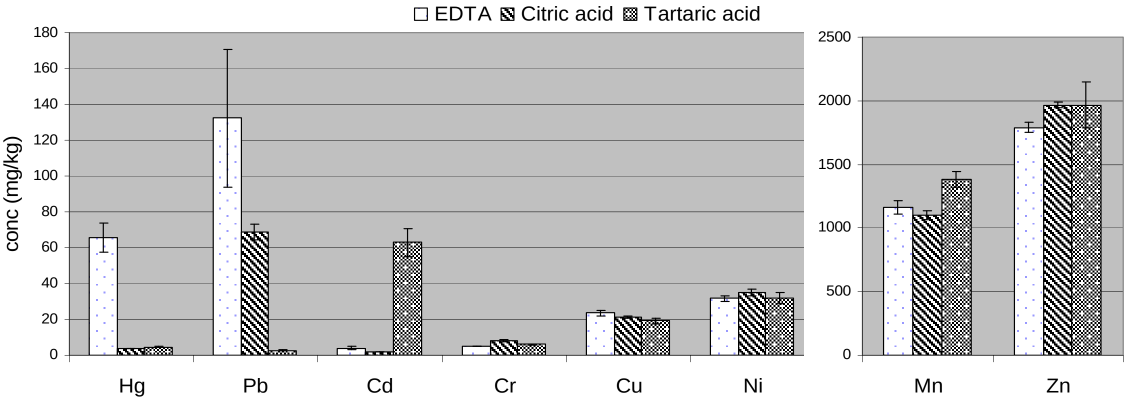

Fig.1 . Quantities of heavy metals leached in the presence of complex-forming agents

3.2. Leaching kinetics

Kinetics of selected heavy metals leaching was analyzed using demineralized water and EDTA demineralized water solution (0.05 mol l^{-1}). Results of experimental analysis are plotted in Fig. 2.

A single exponential equation (Eq.1) was used to describe leaching kinetics:

$$y = a_1 \cdot (1 - \exp(-k_1 \cdot x)) \qquad (1)$$

where:

a_1 - total equilibrium concentration of measured metal in mg/kg,

k_1 - complex-forming rate constant in $h^{-1.}$

For some metals leaching could not be described by a single kinetic equation. A double exponential equation (Eq. 2) was derived for them:

$$y = a_1 \cdot (1 - \exp(-k_1 \cdot x)) + a_2 * (1 - \exp(-k_2 * x)) \quad (2)$$

That equation explained two rate (fast and slow) reaction. Calculated coefficients are given in Table 1.

Heavy metals leaching in EDTA solution research has shown the greatest rate of leaching and reaching the equilibrium state for Pb. That is confirmed by highest reaction rate coefficient k_1. Fast complex-forming of Pb was also observed by the other researchers (Fangueiro et al. 2005, Labanowski et al. 2007). As to the other measured metals, their reaction rate declined in the following order – Cd, Zn, Hg, Mn, Cu, Cr. The leaching equilibrium of Pb, Cd, Zn, Hg, Mn was reached after 8 hours of the samples agitation in EDTA solution. On the contrary, Ni concentration did not reach equilibrium during the 24 h agitation period, therefore application of a kinetic equation to Ni leaching in EDTA solution results in no definitive derivation. In accordance with the obtained results it may be stated that leaching in complex-forming solutions highly depends on the heavy metals concentrations in samples, agent's concentration in the solution and agitation time.

Results of kinetic leaching in water experiments revealed that a water soluble part of Hg leached very fast and reached the equilibrium state after the first hours of the leaching process. Pb, Cu, Cr, Ni reached the reaction equilibrium during the standard leaching procedure period i.e. in 24h. The slowest leaching rate occurred to Cr and Cd, supposedly, because of their low solubility and, therefore low leaching concentrations.

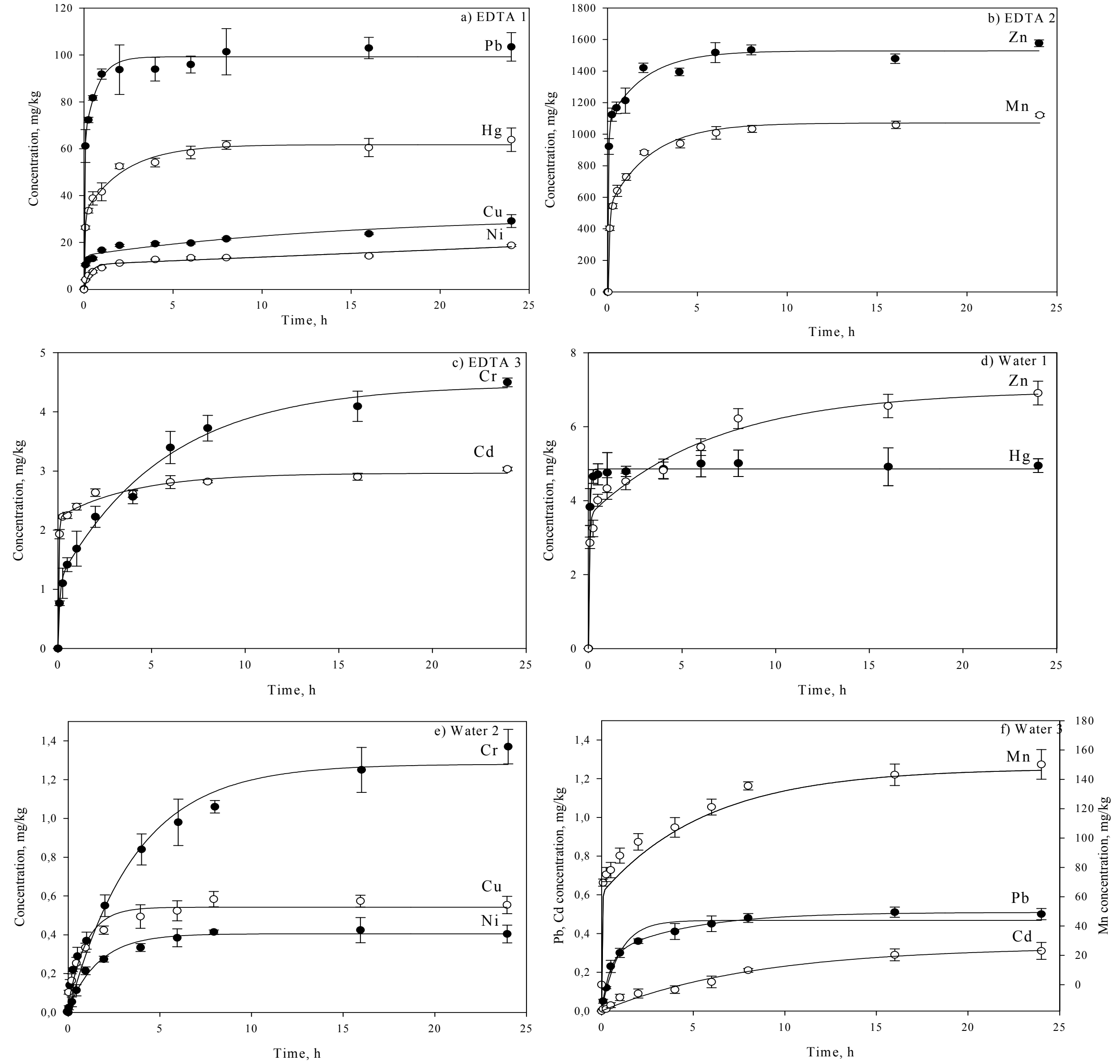

Fig. 2. *Quantities of heavy metals leached during kinetic experiments*

Table 1. *Coefficients of kinetic equations calculated from experimental data*

	a_1 (mg kg^{-1})	k_1 (h^{-1})	a_2 (mg/kg)	k_2 (h^{-1})	R^2
Leaching in demineralized water					
Hg	4.86	18.38			0,997
Mn	72.99	33,33	77,55	0,17	0,998
Zn	3.58	17,53	3,39	0,15	0,994
Pb	0.47	1,03			0,985
Cd	0.33	0,12			0,991
Cu	0.54	1,03			0,984
Ni	0.40	0,59			0,995
Cr	1.28	0,28			0,985
Leaching in EDTA solution					
Hg	31.99	18.42	29,75	0.44	0.996
Mn	532.51	14.82	538,88	0.43	0.997
Zn	1070.51	22.38	457,71	0.48	0.996
Pb	62.28	29.51	36,82	1.39	0.995
Cd	2.21	24.26	0,76	0.25	0.998
Cu	14.56	13.65	16,96	0.07	0.985
Ni	10.68	3.00	2249,34	0.0001	0.984
Cr	1.13	1088	3,33	0.17	0997

It should be emphasized that in almost all the cases kinetics of leaching in demineralized water was described by a common single exponential kinetic equation. Mn and Zn leaching in demineralized water kinetics was described by a two-rate reaction. The leaching of all heavy metals in EDTA solution was best described by a two-rate reaction model. It suggested that leaching in EDTA occurred due to a different and more complex leaching mechanism. The equilibrium concentrations were considerably higher and were reached faster compared to the most of the leaching cases in demineralised water.

3.3. Temperature dependence

Influence of the temperature as a factor of experimental conditions was tested. In order to assure that no metallic Hg was present in residuals after treating the samples at various temperatures, Hg concentration was measured while leaching by a standard leaching procedure (DIN 38414 S4 1984). The obtained results are presented by a graph in Fig. 3. The samples of residuals were heated for 24h at the temperature from 20° to 120°C stepping by 20°C. Since metallic Hg evaporates at the temperatures up to 40°C, a decrease in the leaching of Hg concentration was expected in that temperature range. In that case no decrease was observed. On the contrary, Hg concentration leaching from the analyzed samples increased.

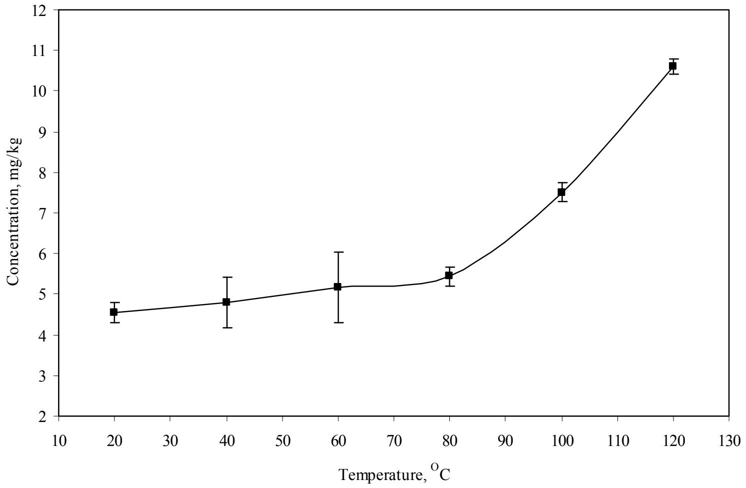

Fig. 3. Hg leaching dependence on the temperature

Hg showed different leachability properties after residuals were exposed to different temperatures. The leachable concentration increased 3 times after heating the samples at the temperatures from 20^{o} to 120^{o}C.

The most possible explanation of that phenomenon could be the process of complex substances destruction, resulting in formation of more water soluble Hg compounds. Fluorapatite and hydroxylapatite, forming from the fluorescent coating during the fluorescent lamps operation, were found to be the predominant minerals in these residuals (Urniezaite et al. 2007). These minerals are known to have high ion-exchangeability (Choi et al. 2008). A part of Hg is presumed to be oxidized and bound by these minerals during the fluorescent lamps operation period. Therefore, a possible explanation of its increasing release could be the destruction of these and other newly formed substances.

4. Conclusions

Leaching of heavy metals from highly contaminated residuals resulting from fluorescent lamps waste treatment is a very complex process. It depends on a lot of different conditions taking place during leaching. Even if it is one of the ways of final Hg disposal, after phasing out its use and export, the residuals must be well studied. Their leaching properties are changing in accordance with the conditions such as leachant pH value, dissolved substances, contact time, etc. In most of the cases the quantities of pollutants released to the environment are increasing.

During this research influence of complex-forming substances on heavy metals leaching has been tested. Among EDTA, citric acid and tartaric acid, analyzed as complex-forming agents, EDTA has shown the best complex-forming characteristics in overall heavy metals leaching concentrations. In the presence of EDTA heavy metals leaching was up to 15 times higher (Hg) than in the solutions of the other complex-forming substances.

The leaching kinetics experimental analysis has enabled the authors to estimate how fast leaching occurs and to apply kinetic equations to the undergoing processes. The main observations from this experimental work were that in almost all the cases agitation time of 24h is sufficient to reach the equilibrium state. The leaching in demineralized water proceeds slower than in EDTA solution, and it can be explained by a standard single kinetic equation. Leaching in EDTA is a more complex process, therefore it involves more complex equations.

The observed increase in leaching Hg amount, depending on the residuals drying temperature, is a subject for further research in the field of detailed residuals structure analysis, substances interactions in the residuals matrix, etc. Nevertheless, the results show that standard tests involving drying of residuals should be applied with certain caution.

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Prof. dr. habil. Gintaras Denafas – professor in Department of Environmental Engineering at Kaunas University of Technology.
Main research areas: air pollution control, environmental impact assesment, energy systems and environment, waste management and treament.
Address: Radvilėnų pl. 19,
LT-50254, Kaunas, Lithuania
Tel.: +370 37 300183
Fax: +370 37 300152
E-mail: Gintaras.Denafas@ktu.lt

MSc. Inga Urniežaitė – assistant in Department of Environmental Engineering, Kaunas University of Technology.
Main research areas: hazardous waste management, wastewater treatment.
Address: Radvilėnų pl. 19,
LT-50254 Kaunas, Lithuania
Tel.: +370 37 300182
Fax: +370 37 300152
E-mail: Inga.Urniezaite@ktu.lt

Sunkiųjų metalų išplovimo iš liuminescencinių lempų nukenksminimo liekanų tyrimas

Inga Urniežaitė, Gintaras Denafas
Inžinerinės ekologijos katedra, Kauno technologijos universitetas

(gauta 2009 m. liepos mėn.; atiduota spaudai 2009 m. rugsėjo mėn.)

Atliekose, susidarančiose fizikiniu-cheminiu būdu apdorojant nenaudojamas liuminescencines lempas, sukoncentruojami dideli sunkiųjų metalų kiekiai. Fizikinis-cheminis atliekų apdorojimo būdas naudojamas siekiant nukenksminti ir sukoncentruoti pavojingas medžiagas, esančias lempose. Šio tyrimo tikslas – įvertinti tiriamųjų atliekų savybes dėl aplinkos poveikio. Panašios prigimties ir sudėties atliekos iki šiol nebuvo plačiau tyrinėtos, taigi duomenų apie galimą pavojingų medžiagų išplovimą iš atliekų trūksta. Atliekų savybės buvo tiriamos atliekant išplovimo bandymus. Atliekant tyrimus analizuotas Hg ir kitų sunkiųjų metalų (Pb, Cd, Cr, Cu, Zn, Ni, Mn) išplovimas iš atliekų naudojant įvairias kompleksus sudarančias medžiagas (etilendiamintetraacto rūgštį (EDTA), citrinų rūgštį, vyno rūgštį). Literatūroje minima ir atliktų tyrimų metu parinkta EDTA kaip kompleksus su sunkiaisiais metalais sudarantis junginys, buvo naudojama tolesniems kinetiniams tyrimams atlikti.

Atliekant kinetinius eksperimentus nustatyta, kad tirpi sunkiųjų metalų dalis išplaunama iš bandinių per laiką neviršijantį 20 valandų. Atskirų sunkiųjų metalų išplovimo laikas skiriasi. Išplaunant EDTA, išplaunamos sunkiųjų metalų koncentracijos didėja, palyginti su išplovimo vandeniu rezultatais. Koncentracijos eliuate svyruoja nuo 0,41 mg kg^{-1} sausos masės (SM) Co iki 1576,00 mg kg^{-1} SM Zn. Atliekant išplovimo tyrimus su atliekomis, džiovintomis skirtingose temperatūrose, nustatytas ryšys tarp džiovinimo temperatūros ir atliekų išplovimo savybių: džiovinimo temperatūrai padidėjus nuo 20 ^{o}C iki 120 ^{o}C, išplaunamo Hg kiekis padidėja daugiau nei 2 kartus. Nustatytos sunkiųjų metalų išplovimo kinetinės išraiškos leidžia supaprastintai vertinti išplaunamų iš atliekų sunkiųjų metalų koncentracijas.