

EXTRACTION REMOVAL OF LEAD FROM SOIL

TEOFIL KOROLEWICZ, MARIAN TUREK, JERZY CIBA

Silesian Technical University, Institute of Chemistry, Inorganic Technology and Electrochemistry,
ul. B. Krzywoustego 6, 44-100 Gliwice

Keywords: contaminated soil, speciation, lead, sequential extraction.

EKSTRAKCYJNE USUWANIE OŁOWIU Z GLEBY

Oznaczono całkowitą zawartość ołowiu w glebie z terenu wytwórni akumulatorów oraz przeprowadzono analizę specyacyjną metodą sekwencyjnej ekstrakcji wg Rudda. Stwierdzono, że ołów występuje głównie w mało ruchliwej, ale potencjalnie dostępnej dla roślin, formie związanej organicznie oraz umiarkowanie ruchliwej formie węglanowej. Przeprowadzono ekstrakcję ołowiu z gleby przy użyciu soli sodowej kwasu etylenodiaminatetraoctowego oraz wodorotlenku sodu, a także próby jego elektrochemicznego wydzielenia z roztworów ługujących. Ekstrakcja roztworem $\text{Na}_2\text{-EDTA}$ umożliwia usunięcie 86% ołowiu z gleby, jednak roztwór po elektrochemicznym wydzieleniu Pb ma znacznie mniejszą zdolność ponownego ługowania. Ekstrakcja roztworem NaOH daje gorsze wyniki, umożliwia mianowicie usunięcie 70% ołowiu z gleby, ale roztwór po elektrochemicznym wydzieleniu Pb zachowuje większą zdolność ponownego ługowania.

Summary

The total content of lead in soil from the battery plant site was determined and a speciation analysis of this element was carried out using Rudd's method of sequential extraction. It was found out that lead is present in soil samples mostly in a low mobility organically bound form, which under certain conditions can, however, be absorbed by plants, and in a moderately mobile carbonate form. Lead was extracted from soil using sodium salt of ethylenediaminetetraacetic acid and sodium hydroxide solution and tests were also conducted to separate it from leaching solutions electrochemically. Extraction with $\text{Na}_2\text{-EDTA}$ solution makes it possible to remove 86% of lead from soil, but the solution shows much lower lead extraction power when used for renewed leaching after having been electrochemically freed of lead. Extraction with NaOH solution gives worse results, namely only 70% of lead can be removed from soil, but the solution after having been electrochemically freed of Pb shows higher Pb leaching power when used for renewed leaching than in the case of $\text{Na}_2\text{-EDTA}$ solution.

INTRODUCTION

Polluted soils, on account of the possibility of leaching the pollutants contained in it by rain water and transferring them into ground water, pose a serious threat to the natural environment. Among various techniques being used

for the restoration of soils to their original condition the most advantageous are those which ensure a complete removal of toxic substances. The soil cleaning methods that have been developed in recent years can be divided into two groups: those methods which do not require the excavation of polluted soil (*in situ*) and those which require its excavation (*ex situ*) and subjecting soil to reconditioning on site or after its delivering to a waste processing plant (off site) [1, 9].

Among the methods used for pollutant removal: biological, thermal and physico-chemical, only the latter make it possible to free soil both of organic and inorganic (heavy metals) pollutants. Heavy metals content is one of the major parameters characterising the soil quality, while both their concentration and the form of their occurrence, so-called speciation, are of importance. Knowledge of the quantitative fractions of the individual element forms enables us to assess the bioavailability of the elements in question and makes it also possible to suggest the ways of reducing toxic metal content in soil.

Mobility of chemical elements in soil, which constitutes a criterion of their bioavailability, can be evaluated by various methods [4, 13]. Most often sequential chemical extraction is used, consisting in successive treatment of a sample with chemical agent solutions of various leaching power for metals and their compounds. The methods developed by Rudd and Tessier [15, 18] are regarded as the standard. Water-soluble, exchangeable and adsorbed, and sometimes carbonate-bound metal fractions are generally thought to be the most mobile, i.e. easily soluble and readily absorbed by plants. Metal fractions, which are more strongly bound to solid phase (to iron and manganese oxides as well as to organic matter and also the sulphide fraction), also show some bioavailability potential but metals are released much more slowly from them. The least mobile is the "residue", a fraction which can be leached only by concentrated mineral acids.

The presence of lead in soil is the most dangerous for the environment. Due to their poor solubility, both lead and its compounds do not undergo a microbiological degradation and accumulate in soil thereby influencing the metabolic processes unfavourably [2, 12].

The sequential analysis of lead in soils, sediments and composts is discussed in several papers [7, 11]. Organic and inorganic acids, bases, complex compounds and surface active agents can be used for the extraction removal of heavy metals from soil, including lead and its compounds using the off-site method [9]. Comparative studies were conducted to evaluate the metal extraction capabilities of ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) [8]. The study focused on the removal efficiency of the two chelating agents when mixed with a contaminated soil from a former battery recycling facility that contained 211 000 mg/kg Pb. Comparing EDTA and NTA concentrations from 0.01 M to 0.08 M over a pH range of 4–12, the authors found that, given equal concentrations of reagents EDTA was generally a more effective extracting agent than NTA. Pb removal efficiency of EDTA ranged from about 35% at pH = 10.5 and a concentration of 0.02 M to approximately

95% at pH = 4 and a concentration of 0.08 M. Pb extraction using NTA ranged from about 11% at pH = 11.5 and a concentration of 0.01 M to roughly 63% at pH = 10 and a concentration of 0.06 M. Laboratory studies were conducted on both acids and chelating agents to evaluate their ability in extracting heavy metals from contaminated soils [12]. Several samples of soil contaminated with lead, cadmium and chromium were selected for use in this study. Lead concentrations in the various soils ranged from 4000–30 000 mg/kg. Pb removal efficiency of EDTA ranged from about 34% at concentration of 0.01 M to approximately 61% at concentration of 0.1 M. The remediation process involves mixing polluted soil with washing solution, separating the cleaned soil from the solution, regenerating the washing solution and utilising of the pollutant-containing precipitate [16]. Acid extraction of soils and metal removal from post-extraction solutions are described in [10, 20]. Copper, zinc and cadmium were, for example, removed in this way to reduce their concentration to levels conforming to the Dutch standards in a pilot plant [3]. The authors of this paper removed, among others, lead from composted municipal waste in a similar way obtaining a very low final metal content (52 mg/kg) [5]. Nitric and sulphuric acid solutions were used as the leaching agents. High consumption of acid resulting from the neutralisation of the basic components of compost or soil is a disadvantage of this method.

The process of the remediation of soil containing heavy metals, utilising a combination of extraction with organic acids and electrochemical cleaning of extractant to make it suitable for renewed leaching is described in [19]. Lead, antimony and cadmium were in this way removed from soil in the area around the battery producing plant. The starting content of lead in the soil was 110 g/kg. Acetic acid of 6 M concentration was used for the extraction. The acidity of the solution was adjusted by adding concentrated nitric acid until pH = 2. In spite of leaching the same portion of soil twice, only 65% of the starting lead content could be removed.

In the experiments made, the concentration of lead in the soil at the battery plant site was determined, the sequential extraction of lead from soil was performed to find out the forms of lead occurrence in it and tests were conducted to remove lead from soil by extraction and to electrochemically separate lead from the post-extraction solution.

EXPERIMENTAL

Equipment and reagents:

- atomic absorption spectrometer Perkin Elmer 3300, fuel: air-acetylene mixture, resonance line wavelength $\lambda = 283.3$ nm,
- shaking machine WU-4 with continuously variable rotation control,
- potassium nitrate(V), potassium fluoride, sodium pyrophosphate(V), EDTA (disodium salt), conc. nitric(V) acid, conc. chloric(VII) acid, ammonium nitrate(V), ammonium acetate, sodium hydroxide, ammonium carbonate, amino-

acetic acid, ammonium chloride, sodium phosphate(V) (all reagents: analytically pure grade),

- lead(II) standard solution, 1 g/dm³ (Merck).

A soil sample was dried until constant weight at 25°C, ground and then homogenised. In order to determine the total lead content in the soil the following procedure was adopted: to four weighed dry soil samples, 2.5000 g each, 10 cm³ of concentrated nitric(V) acid and 5 cm³ of concentrated chloric(VII) acid were added. The content was heated on a heating plate at 90–100°C for 1 hour and then evaporated to dryness. 15 cm³ of 4 M nitric(V) acid was added to the dry residue, which was heated at 90–100°C for 1 hour. The mixture was then filtered while quantitatively transferring the solution into 50 cm³ measuring flask and made up to the mark with redistilled water. Lead content was determined in the solutions obtained by atomic absorption spectrometry. The average lead content was found to be 32 320 mg/kg of soil.

SEQUENTIAL ANALYSIS

In order to determine the forms in which lead occurs in soil, the sequential extraction technique of Rudd [15] was used. Water, solutions of potassium nitrate(V), potassium fluoride, sodium disphosphate(V), sodium salt of ethylenediaminetetraacetic acid, nitric(V) acid and a mixture of nitric(V) and chloric(VII) acid were used as extractants.

The following procedure was adopted; a homogenised soil sample was mixed with a portion of extractant (with solid to liquid phase ratio = 1:10) and shaken periodically (for 15 minutes each hour) for a total of 72 hours. The samples were then centrifuged, the solid phases washed with water and treated with successive extractant type while determining lead contents in the extracts obtained by AAS method. The contents of the individual forms of lead in the soil examined as determined on four parallel samples are shown in Table 1.

Table 1. Content of various forms of lead occurrence in the soil determined by the sequential extraction method

Extraction conditions			Contents of the specific lead forms in the soil mg/kg
Form	Extractant	Concentration M	
soluble	H ₂ O	—	10
exchangeable	KNO ₃	1.0	490
adsorbed	KF	0.5	10
organically-bound	Na ₄ P ₂ O ₇	0.1	18 390
carbonate	EDTA	0.1	10 320
sulphide	HNO ₃	6.0	2330
insoluble	conc. HNO ₃ , conc. HClO ₄	—	770
Sum			32 320

LEAD REMOVAL EXTRACTION

The sequential analysis extraction results show that a major part of lead contained in soil can be leached using sodium salt of ethylenediaminetetraacetic acid. Literature data show that also other extractants can be used for leaching heavy metals from soil, sediments and composts [6, 17]. Therefore, experiments were made of leaching lead with such extractants as solutions of ammonium nitrate(V), ammonium acetate, ammonium carbonate, ammonium chloride, sodium hydroxide, aminoacetic acid, sodium phosphate(V), sodium disphosphate(V) and Na_2 -EDTA. The extraction was performed as follows: 5 g of soil was introduced to 50 cm³ of extractant and shaken periodically for 15 minutes each hour, for a period of 24 hours in total. Then the sample was centrifuged, the solution was additionally filtered and the lead content in it determined using AAS method. The results are shown in Table 2.

Table 2. Lead content in the solutions after extraction

Extractant		Lead content in the solution mg/kg*
Formula	Concentration	
NH_4NO_3	1 M	660
$\text{CH}_3\text{COONH}_4$	1 M	4200
$\text{NH}_2\text{CH}_2\text{COOH}$	1 M	12400
$(\text{NH}_4)_2\text{CO}_3$	1 M	320
NH_4Cl	1 M	1260
NaOH	2 M	22800
$\text{Na}_4\text{P}_2\text{O}_7$	0.1 M	24050
$\text{Na}_4\text{P}_2\text{O}_7 + \text{EDTA}$ (1:1)	0.1 M	27600
Na_3PO_4	0.1 M	200
EDTA	0.1 M	28100

* as converted to the original soil sample

The results obtained have shown that among the agents tested Na_2 -EDTA solution shows the highest extraction power. This agent was just used for the extraction removal of lead from soil.

In order to select proper leaching conditions when using Na_2 -EDTA solution, the influence of its concentration, the ratio of extractant volume to solid phase and phase contact time on the amount of lead leached were investigated. The results are given in Tables 3, 4, 5.

Table 3. The dependence of the amount of lead leached on EDTA concentration

EDTA concentration M	0.1	0.05	0.01	0.005	0.001
Amount of lead leached mg/kg	27600	25100	15800	7400	2000

Table 4. The dependence of the amount of lead leached on the EDTA solution volume to solid phase ratio

Extractant volume to solid phase ratio cm ³ /g	10	8	6	5	4	3	2
Amount of lead leached mg/kg	28 100	28 080	28 050	28 030	28 020	27 260	23 200

Table 5. The dependence of the amount of lead leached on the phase contact time

Time, h	1	2	4	6	24
Amount of lead leached, mg/kg	25 850	27 240	28 020	28 040	28 060

Based on the results given in Tables 3, 4 and 5, Na₂–EDTA solution concentration of 0.1 M, the EDTA solution volume to solid phase ratio of 4 and phase contact time of 4 h were used in further experiments.

No significant relationship between pH and the leaching results was found when additionally examining the influence of the solution acidity on the leaching results. Na₂–EDTA solution of pH = 4.4 (without correcting its pH) was used in further experiments.

Removal extraction of lead from soil was conducted under steady state conditions of the extraction process. 120 cm³ portions of 1 M Na₂–EDTA solution were mixed with soil samples, 30 g each. The content of the flask was mixed (100 rpm) for 4 hours, then the solid phase was separated by centrifuging and the solution was additionally filtered. The extract I (the solution after 1st leaching) was subjected to a preliminary analysis for lead content and then lead was separated by electrolysis. An electrolytic cell equipped with Ti/Pt anode with dimensions of 30 × 30 mm and two Pb cathodes of the same dimensions placed on the both anode sides at the distance of 1 cm from the anode surfaces was used for the separation of lead from the leaching solution.

The electrolysed solution was then once again analysed in order to determine lead content and then used again for leaching lead from a new soil portion. Lead was determined using the atomic absorption spectrometry in the extract II (the solution after the 2nd extraction).

It was found that 28 020 mg of Pb per one kilogram of soil is transferred to a solution on the first leaching. The electrolysis process conditions and the results of lead content determination in the solution after electrolysis and after the 2nd leaching are shown in Table 6.

From the data summarised in Table 6 it was found that the amount of lead being transferred to the solution on the 2nd leaching was only 14 000–15 200 mg/kg. This weakened leaching power of the solution regenerated by electrolysis was presumably due to decarboxylation of EDTA during electrolysis.

Table 6. Conditions and results of the electrolysis process after EDTA solution leaching of soil

Pos.	Current mA	Terminal voltage, V		Electro- lysis time h	pH of solution		Amount of lead after electrolysis mg/kg	Amount of lead after 2nd leaching mg/kg
		starting	final		after 1st leaching	after electrolysis		
1	2	3		4	5	6	7	8
1	300	5.3	5.0	1.5	4.7	5.9	24 250	—
2	600	6.0	5.7	1.5	4.7	7.4	2550	—
3	600	6.0	5.4	3	4.7	8.1	900	—
4	600	6.0	5.3	4	4.8	8.2	700	—
5	600	6.0	5.3	4	4.8	8.2	690	15 200
6	600	6.0	5.2	4	4.8	8.3	600	14 500
7	600	6.0	5.2	4	4.8	8.3	580	14 000

As it became evident that repeated use of Na_2 – EDTA solution for leaching lead from soil is not possible, a search for another leaching agent was necessary. Bearing in mind that lead and some of its compounds have amphoteric properties, experiments with leaching soil with sodium hydroxide solution were undertaken. Leaching was performed using 0.25 – 2.0 M NaOH solution under similar conditions as in the case of leaching with Na_2 – EDTA. Under these conditions (at pH above 13), lead ions are present as $[\text{Pb}(\text{OH})_4]^{2-}$. Lead was separated electrolytically from the leachate on Ti/Pt electrodes using 600 mA current. The electrolysis time was 1.5 h. The solution after electrolysis was again used for leaching another soil portion. The results are shown in Table 7.

Table 7. The results of soil leaching with NaOH solution and its electrolysis

Operation	Lead content in solution mg/kg	NaOH solution concentration M				
		0.25	0.5	1.0	1.5	2.0
Leaching I		7150	12 600	21 100	22 000	22 800
Electrolysis		200	1400	2100	2300	2600
Leaching II		5500	11 200	18 200	18 900	19 100

DISCUSSION AND CONCLUSIONS

Lead content in polluted soil was determined, sequential analysis and removal extraction of lead from soil using Na_2 – EDTA and NaOH solution were carried out. Electrochemical separation of lead from leachates was also investigated.

It was found that the sample of soil taken shows a high concentration of dangerous pollutant – lead; its content is 32 320 mg/kg. Based on the sequential analysis results it was found that lead occurs mostly in an organically bound

form of low mobility but potentially available for uptake by plants and in a moderately mobile carbonate form.

Among the extractants tested, $\text{Na}_2\text{-EDTA}$ has proven to be the best and was used for removal extraction of lead from soil. Under the selected leaching conditions (concentration 1 M, $\text{pH} = 4.4$, extractant to solid phase ratio = 4, time 4 h) 86% of lead can be removed by extraction. From $\text{Na}_2\text{-EDTA}$ solution after leaching lead was separated electrochemically. It was found, that it was possible to separate ca. 97% of Pb contained in soil when using the electrolysis process for $\text{Na}_2\text{-EDTA}$ solution regeneration, however, the solution regenerated in this way shows much lower lead leaching power than the primary $\text{Na}_2\text{-EDTA}$ solution used in the 1st leaching, which is presumably due to its decarboxylation. This means that regeneration by electrolysis and renewed use of the leaching solution regenerated in this way is in practice impossible. Therefore, the possibility of using NaOH solution as a leaching agent was examined. It was found that using 2 M NaOH solution enables 70% of the total content of lead in soil to be removed by leaching, so much less as in the case of $\text{Na}_2\text{-EDTA}$. Contrary to $\text{Na}_2\text{-EDTA}$ however, NaOH solution regenerated by electrochemical separation of lead shows a higher capacity for renewed leaching of lead and its compounds from soil. A drawback of leaching with sodium hydroxide solution is a risk of soil impoverishment.

In the literature cited, only several cases corresponds to a similarly high content of lead in polluted soil from the battery plant site [8, 12, 17]. Based on the results presented in the paper, and comparing them to those reported in the literature, it can be stated that it was possible to leach lead from the soil to a higher degree in spite of using less concentrated leaching agents.

REFERENCES

- [1] Adamski W.: *Nowoczesne technologie rekultywacji skażonych gleb*, Ochrona Środ., 1–2, 7–17 (1993).
- [2] Alloway J.B.: *Heavy Metal in Soils*, Blackie and Son Ltd, Glasgow 1990.
- [3] Anonymons (1988) Leidraad Bodensanering. Deel II. Ministerie van Volkhuising, Ruimtelijke Ordening en Milieubeheer (VROM),SDU, Den Haag. The Netherlands.
- [4] Baldi M., M.C. Negri, A.G. Campodaglio: *Chemical speciation of heavy metals in soils following land application of conditioned biological sludges raw pig manure*, Internat. Conf. Sorption Onto Surfaces, 377–392 (1986).
- [5] Ciba J., T. Korolewicz, M. Turek: *The occurrence of metals in composted municipal wastes and their removal*, Water, Air and Soil Pollution, 111, 1/4, 159–170 (1999).
- [6] Clayton P.M., K.G. Tiller: *CSIRO Div. of Soils*, Tech. Papers, 41, 1–17 (1971).
- [7] Das A.K., R. Chakraborty, M.L. Cervera, M. de la Guardia: *Metal speciation in solid matrices*, Talanta, 42, 1007–1030 (1995).
- [8] Elliot H.A., G.A. Brown: *Comparative evaluation of NTA and EDTA for extractive decontamination of Pb polluted soils*, Water, Air and Soil Pollution, 45, 361–369 (1989).
- [9] Furdyn G., Z. Kawala: *Odnowa zanieczyszczonych gruntów metodami in situ*, Ochrona Środ., 2, 27–34 (1996).
- [10] Hasse B., M. Render, J. Luhede: *Reinigung hochkontaminierter Boden mittels Waschverfahren*, Teil II: *Chrom(III)-kontaminationen*, Chem. Ing. Tech., 63, 392–393 (1991).

- [11] Lo J.M.C., X.Y. Yang: *Removal and redistribution of metals from contaminated soils by a sequential extraction method*, Waste Management, **18**, 1–7 (1998).
- [12] Neale C.N., R.M. Bricka, A.C. Chao: *Evaluating acids and chelating agents for removing heavy metals from contaminated soils*, Environ. Prog., **16**, 4, 274 (1997).
- [13] Olson B.H.: *Applied Environmental Geochemistry*, Thornon, Academic Press, 201–230 London 1983.
- [14] Piotrowska M.: *Wybrane zagadnienia związane z chemicznym zanieczyszczeniem gleb*, Ossolineum, Wrocław – Warszawa – Kraków 1989.
- [15] Rudd T., D.J. Lake, J. Mehrota, R.M. Sterritt, P.W.W. Kirk, J.A. Campbell, J.N. Lester: *Characterisation of metal forms in sewage sludge by chemical extraction and progressive acidification*, The Science of the Total Environment, **74**, 149–175 (1988).
- [16] Rulkens W.H., J.T.C. Grotenhuis, E.R. Soczo: *Remediation of contaminated soil: state of the art and desirable future developments*, [in:] F. Arendt, G.J. Annokkee, R. Bosman, J. Van den Brink (eds), *Contaminated Soil' 93*, Kluwer Academic Publisher, 1007–1018 (1993).
- [17] Sauerbeck D.R., P. Styperck: *Chemical Methods for Assessing Bioavailable Metals in Sludges and Soils*, R. Leschber, R.D. Davis, P. L'Hermite (eds), Elsevier, Amsterdam 1985, p. 49.
- [18] Tessier A., P.C. Campbell, M. Bisson: *Sequential extraction procedure for the speciation of particulate trace metals*, Anal. Chem., **51**, 844–851 (1979).
- [19] Thoming J., W. Calmano: *Remediation of heavy metal contaminated soils by acid leaching and electrolytic metal separation*, [in:] J. Van den Brink, R. Bosman, F. Arendt (eds), *Contaminated Soil' 95*, Kluwer Academic Publisher, 895–902 (1995).
- [20] Tuin B.J.W.: *Extraction of heavy metals from contaminated clay soils*, Dissertation, Technische Universiteit Eindhoven, Eindhoven 1989.

Received: March 19, 1999, accepted: June 23, 1999.