DOI: 10.22616/rrd.28.2022.036

TOWARDS 'BEYOND THE ZERO WASTE CONCEPT': INNOVATIVE SOLUTIONS FOR VALORIZATION OF FINE RESIDUAL WASTE FRACTION FROM LANDFILLS: RARE EARTH ELEMENTS POTENTIAL

***Juris Burlakovs[1], Ruta Ozola-Davidane[2], Zane Vincevica-Gaile[2], Magdalena Wdowin[1], Inga Grinfelde[3], Jovita Pilecka-Ulcugaceva[3], Ivar Zekker[4]**
[1]Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Poland
[2]University of Latvia, Latvia
[3]Latvia University of Life Sciences and Technologies, Latvia
[4]University of Tartu, Estonia
*Corresponding author's email: juris@geo-it.lv

Abstract
The growing population of the planet and the population's desire for ever-higher welfare standards have contributed to a linear economy-based consumer society model that is one of the main reasons for the increased volume of waste. Global sustainability, mitigation of climate change, and the reduction of pollution are strongly related to the waste management issue, and there is a need to switch from linear economy models to the circular economy. The maintaining solution for keeping and storing waste over the last century has been landfilling as its costs are the lowest. A sustainable approach such as landfill mining (LFM) can be applied to recover rare earth elements (REEs) and other valuable metals from waste that make fundamental assets in terms of economy and essential for developing industrial technologies. This study investigated concentrations of REEs and other metals in waste material. Samples from Ida-Virumaa (Estonia) landfilled waste fine fraction were taken to estimate the element concentration proceeded through sequential extraction. Additionally, the method of clay modification was developed that may serve as a sorbent to extract the REEs from the inert landfill fine fraction waste using hydroxyapatite modified clay. The amount of REEs might become of industrial interest if a feasible landfill mining approach for remediation of landfills and degraded industrial soils is applied together with innovative recovery methods, e.g., sorption by modified clays.
Key words: landfill mining, modified clay sorbents, resources recovery, waste valorization.

Introduction

We can assess seventeen Sustainable Development Goals (Nations, 2015) in case if six transformations of our economies are made (Sachs *et al*., 2019). The Europe Green Deal is based on six transformations, but the decarbonization and digitalization increase the demand for rare elements (REEs) and intensify risks of environmental pollution and hazardous waste disposal problem. The only solution is to transform from a linear economy to a circular economy, where waste is transformed into a resource.

Maintenance and storage of the waste is a key goal for the circular economy, and the purpose for that is the lowest possible cost with maximum environmental benefit. A kind of sustainable approach called landfill mining (LFM), means digging out and processing untreated old dump deposited materials (Krook, Svensson, & Eklund, 2012). Environmental concerns are respective to contaminated areas, often old dumpsites included (Kabata-Pendias, 2000). Mixed half-degraded and degraded inert material often create pollution problems with contamination leaching out to the environment. The problem is also the stability and bioavailability of potential contaminants as a threat to the environment (Burlakovs *et al*., 2013; Saaremäe *et al*., 2013). Waste could contain toxic chemical elements deeming it hazardous (Burlakovs *et al*., 2013). Dumpsites and landfills are extensive resources – it is as stock for the future that we can mine as a resource. Valuable materials might appear nevertheless of chemical extraction difficulties with nowadays technology – the rare earth elements resources (Burlakovs *et al*., 2020).

Technology advances at the highest level move on the electronic device market. More powerful, more efficient, and faster devices are released each year. As a result, thousands of tons of electronic devices are discarded annually as consumers upgrade to newer versions. These components are becoming one of the fastest-growing waste segments globally (Ruan & Xu, 2016). Fluctuating 'supercycles' of commodity markets are sharply affecting minerals and – especially, rare earth resource prices. Demand is high; supply is low. It is the market game. LFM might be one of the extra solutions when rising prices play a greater role in raising the value of previously unconsidered resources for use (Burlakovs *et al*., 2013).

Overall, the largest opportunity is mining from historical dumps macroelements such as Zn, Al, Fe, P, Ni, Cu, and others; on the other hand, in this way, we diminish the dissipation of unwanted concentrations to the environment (Burlakovs *et al*., 2015; Vincēviča-Gaile, 2014).

There are many sorption materials (raw as well as modified) that are used for the removal of REEs from aqueous solutions, e.g., carbonized polydopamine nano carbon shells (Xiaoqi *et al*., 2016), granular hybrid (Zhu, Zheng, & Wang, 2015), modified clays

Figure 1. Clay modification with hydroxyapatite and possible usage in REEs recovery.

(Gładysz-Płaska, Majdan, & Grabias, 2014), and many others (Krauklis *et al*., 2017; Ozola *et al*., 2019; Ozola, Klavins, & Burlakovs, 2018). After the removal of REEs from aqueous solutions, clay sorbents can also be used to recover these valuable elements (Iannicelli-Zubiani *et al*., 2017) (Figure 1).

The work aimed to explore the concentration of various elements in the samples derived from a landfill site situated in Ida-Virumaa (Estonia), taken from fine fraction of waste, as well as try to develop an innovative type of sorbent that can be used to recover lost REEs through the process of sorption.

Materials and Methods

Materials, sampling, and preparation

The waste sampling was done in the Ida-Virumaa landfill site (Estonia), and preparation was done according to the methodology described in previous works (Burlakovs *et al*., 2016; Hogland *et al*., 2018).

To develop a clay sorbent montmorillonite (Mt), the material with the trade name Montmorillonite K10 was used. According to the product specification, montmorillonite is a faint grey powder with pH 2.5-3.5, with a specific weight 300-370 kg m^{-3} and surface area 220-270 m^2 g^{-1}. The cation exchange capacity (CEC) of the Mt clay is 0.50±0.03 mmol g^{-1} (determined by the methylene blue test). Lanthanum (III), neodymium (III), and cerium (III) as model REEs were chosen for sorption experiments. Analytical grade chemicals and deionized water was used in experiments (10-15 MΩ cm^{-1}) purified in a standard way.

Sequential extraction

To obtain the results and analyze the bioavailability and mobility of metals, fine fraction was performed by sequential extraction. These areas have future potential recovery materials (Burlakovs *et al*., 2013).

The extraction procedure was worked out in various steps, water-soluble fraction was determined as the first one. A sample of 3 g was taken in 100 mL glass beaker; 40 °C water was added, and the beaker was shaken mechanically. It was filtered by 0.45 µm membrane filter, and acidified in a tube with 0.2 mL of HNO_3 (1:1) solution, then left at +4 °C.

Sequentially, acid-soluble fraction was determined through the use of 40 mL of 0.11 M CH_3COOH; afterward, extraction of 16 hours was performed. Filtering followed again with acidification.

The last step was a reducible fraction where 0.5 M NH_2OH×HCl was added. The same procedures with shaking and acidification were done as in the previous two steps.

Sorbent development and sorption experiments

Mt clay modification with synthetic hydroxyapatite (Hap, $Ca_{10}(PO_4)_6(OH)_2$) was prepared by the precipitation method under continuous mechanical stirring as described in previous research (Ozola-Davidane *et al*., 2017). 20 g of clay sample was mixed with 100 mL 0.5 M $CaCl_2$. Then 5 mL of 2 M KH_2PO_4 was slowly added to get 1.667 equimolar proportions of Ca and P. pH for reactions was adjusted with 0.5 M NH_4OH to maintain the range of pH 9 and 9.5. The reaction temperature was kept at 50 °C. After that, the synthesis mixture was left overnight, then decanted and washed with deionized water until a neutral environment was achieved. Drying was done 24 h at 40 °C. As a result, the composite material has increased sorption sites for positively charged elements, such as model rare earth elements, lanthanum (III), neodymium (III), and cerium (III).

La(III), Ce(III), and Nd(III) from aqueous solutions removal were determined. Sorption-isotherm research included 0.1 g prepared material (Mt-Hap) that was placed in a 100 mL glass vessel and added with 100 mL of La(III), Ce(III), or Nd(III)with concentrations of 5 mg L^{-1} to 1000 mg L^{-1}. Agitation of 24 h followed by centrifugation at 3000 rpm for 12 min was done, and the supernatants were analyzed using an iCAP7000 coupled plasma-optical emission spectroscopy. The quantity of the model REEs sorbed was calculated as in the formula:

$$q_e = \frac{C_i - C_e}{m * v} \quad (1)$$

where q_e is the amount of La(III), Ce(III), or Nd(III) adsorbed on the sorbent (mg g^{-1}), C_i and C_e are initial and equilibrium liquid-phase concentrations of La(III), Ce(III) or Nd(III) (mg L^{-1}), respectively, v is the volume of solution (mL), and m is mass of sorbent used (g).

Results and Discussion

Results from element fractionation analysis by sequential extraction and total content in Ida-Virumaa landfill have shown a wide range of elements in the inert fine fraction. The highest average concentrations were detected for macro elements as Ca (>55%), Fe (>20%), Al (>12%), and Mg (>5%), followed by microelements. Seemingly one of the reasons for Ca, Fe, Al, and Mg come from the addition of construction and demolition waste in municipal masses as well as from the dissipation of other inert municipal waste after the organic fractions are gone. REEs have also been detected in ranges from 1-40 ppm, which is not a high amount compared to average Clark numbers in geochemistry; however, with improved technologies of separation in the future, the latter's recovery additionally to macroelements might be of the particular interest.

Results of this study presented that the municipal landfill in Ida-Virumaa has slight potential for recovery of metals, and certain REEs might also be of interest. The second part of the study involved modification of the raw clay with hydroxyapatite in order to test theoretical opportunities to recover the REEs from the landfill leachate or other aquatic media linked to industrial wastewaters.

The initial concentration of La(III), Ce(III), and Nd(III) in the range of 5 mg L^{-1} to 1000 mg L^{-1} influenced the sorption of chosen model REEs on the raw and modified Mt clay with hydroxyapatite. Raising La(III), Ce(III), and Nd(III) concentration also increased the sorption capacity of modified clay (Figure 2). It happens due to less occupied sites, i.e., when concentrations are lower, these sites are free. However, sorption capacity of La(III), Ce(III), and Nd(III) by the selected sorbent (Srivastava & Sillanpää, 2017) increases.

The sorption capacity increased more than two times after Mt modification with hydroxyapatite; these ranged from the highest of 284 mg g^{-1} to 252 mg g^{-1} and 255 mg g^{-1} for La(III), Ce(III), and Nd(III), respectively. Ranges of respective concentrations were 1000 mg L^{-1}, 600 mg $L^{-1,}$ and 600 mg L^{-1}.

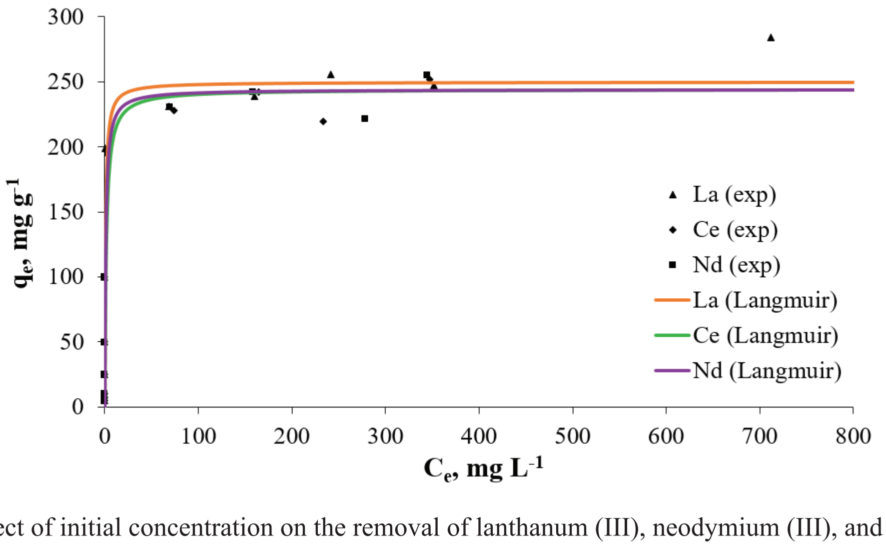

Figure 2. Effect of initial concentration on the removal of lanthanum (III), neodymium (III), and cerium (III) by modified montmorillonite with hydroxyapatite (experimental conditions: Ci = 5–1000 mg L^{-1}, pH = 6, contact time = 24 h, T = 24 °C).

The LFM approach in former dumpsites might play an essential role in the recycling of so-called lost material – it can be called ‘hunting the valuables’. The excavated waste provides a theoretical collection of considerably large amounts of rare earth, macro- and microelements. Studies are a part of the complete picture from a circular economy perspective, which in this paper is given as the sketch. On the other hand, new technologies, such as innovative sorbents, should be developed and elaborated to make this action feasible from an economic perspective.

REEs are at significantly lower concentrations than in geological prospects; however, it might be of distinct interest in the future due to scarce supplies and improvement in technology and prices. An innovative approach needed, and further research of sorbents and sorbates for that reason should be performed. Some of the elements regarding preliminary results might be called ‘reserves’, as we are forced to remediate the land by the law anyway if the concern is about contamination. The most important is to fulfill the SDGs and implement innovation for the recovery of rare earth and other elements, and if it might be done by specific sorption measures. There is additional value if low pollutant concentrations might be cached out of leachate mixtures.

Conclusions

Hereby the study has approved the paradigm of valuables’ recovery possible from lost material in dumps and wastewater discharges. The amount of REEs might become of industrial interest if a feasible LFM approach for the reconstruction of past landfills and degraded industrial soils is applied together with innovative recovery methods, e.g., sorption by modified clays. The circular economy perspective is taking a brave course to the resurrection of the last material from the industrial cycle whereas saving the environment from the degradation through reconstruction of ecosystem services and even landscapes. The zero waste and the beyond the zero waste concept must be developed and improved, resulting in higher material standards, but it is not likely that the style of life and attitude of society will change significantly during the foreseeable future.

Acknowledgements

The work was supported by the PASIFIC program GeoReco project funding from the European Union’s Horizon2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No 847639 and from the Ministry of Education and Science.

References

Burlakovs, J., Kriipsalu, M., Arina, D., Kaczala, F., Shmarin, S., Denafas, G., & Hogland, W. (2013). Former dump sites and the landfill mining perspectives in Baltic countries and Sweden: the status. In *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM* (Vol. 1, pp. 485–492). DOI: 10.5593/SGEM2013/BA1.V1/S03.035.

Burlakovs, J., Vincevica-Gaile, Z., Krievans, M., Jani, Y., Horttanainen, M., Pehme, K.-M., … Klavins, M. (2020). Platinum group elements in geosphere and anthroposphere: Interplay among the global reserves, urban ores, markets and circular economy. *Minerals*, *10*(6), 1–19. DOI: 10.3390/min10060558.

Burlakovs, J., Kaczala, F., Vincevica-Gaile, Z., Rudovica, V., Orupõld, K., Stapkevica, M., … Hogland, W. (2016). Mobility of Metals and Valorization of Sorted Fine Fraction of Waste After Landfill Excavation. *Waste and Biomass Valorization*, *7*(3), 593–602. DOI: 10.1007/s12649-016-9478-4.

Burlakovs, J., Kaczala, F., Orupõld, K., Bhatnagar, A., Vincevica-Gaile, Z., Rudovica, V., … Klavins, M. (2015). Field-portable X-ray fluorescence spectrometry as rapid measurement tool for landfill mining operations: comparison of field data vs. laboratory analysis. *International Journal of Environmental Analytical Chemistry*, *95*(7), 609–617. DOI: 10.1080/03067319.2015.1036865.

Gładysz-Płaska, A., Majdan, M., & Grabias, E. (2014). Adsorption of La, Eu and Lu on raw and modified red clay. *Journal of Radioanalytical and Nuclear Chemistry*, *301*(1), 33–40. DOI: 10.1007/s10967-014-3111-4.

Hogland, M., Āriņa, D., Kriipsalu, M., Jani, Y., Kaczala, F., de Sá Salomão, A.L., … Hogland, W. (2018). Remarks on four novel landfill mining case studies in Estonia and Sweden. *Journal of Material Cycles and Waste Management*, *20*(2), 1355–1363. DOI: 10.1007/s10163-017-0683-4.

Iannicelli-Zubiani, E.M., Cristiani, C., Dotelli, G., Stampino, P.G., Pelosato, R., & Finocchio, E. (2017). Effect of pH in the synthesis of organo-clays for rare earths removal. *Environmental Engineering and Management Journal*, *16*(8), 1719–1728. DOI: 10.30638/eemj.2017.187.

Kabata-Pendias, A. (2000). *Trace Elements in Soils and Plants*. CRC Press. DOI: 10.1201/9781420039900.

Krauklis, A., Ozola, R., Burlakovs, J., Rugele, K., Kirillov, K., Trubaca-Boginska, A., … Klavins, M. (2017). FeOOH and Mn8O10Cl3 modified zeolites for As(V) removal in aqueous medium. *Journal of Chemical Technology & Biotechnology*, *92*(8), 1948–1960. DOI: 10.1002/jctb.5283.

Krook, J., Svensson, N., & Eklund, M. (2012). Landfill mining: A critical review of two decades of research. *Waste Management*, *32*(3), 513–520. DOI: 10.1016/j.wasman.2011.10.015.

Nations, U. (2015). No Title. *Transforming Our World: The 2030 Agenda for Sustainable Development*.

Ozola-Davidane, R., Krauklis, A., Burlakovs, J., Vincevica-Gaile, Z., Rudovica, V., Trubača-Boginska, A., … Klavins, M. (2017). Illite clay modified with hydroxyapatite – innovative perspectives for soil remediation from lead(II). *Int. J. Agri and Env Res.*, *3*, 177–189.

Ozola, R., Klavins, M., & Burlakovs, J. (2018). Clays, intercalated with organic substances for environmental technologies. In *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM* (Vol. 18, pp. 197–202). DOI: 10.5593/sgem2018/5.2/S20.026.

Ozola, R., Krauklis, A., Burlakovs, J., Klavins, M., Vincevica-Gaile, Z., & Hogland, W. (2019). Surfactant-Modified Clay Sorbents for the Removal of p-nitrophenol. *Clays and Clay Minerals*, *67*(2), 132–142. DOI: 10.1007/s42860-019-00015-2.

Ruan, J., & Xu, Z. (2016). Constructing environment-friendly return road of metals from e-waste: Combination of physical separation technologies. *Renewable and Sustainable Energy Reviews*, *54*, 745–760. DOI: 10.1016/j.rser.2015.10.114.

Saaremäe, E., Liira, M., Poolakese, M., & Tamm, T. (2013). Removing phosphorus with Ca-Fe oxide granules – a possible wetlands filter material. *Hydrology Research*, *45*(3), 368–378. DOI: 10.2166/nh.2013.101.

Sachs, J.D., Schmidt-Traub, G., Mazzucato, M., Messner, D., Nakicenovic, N., & Rockström, J. (2019). Six Transformations to achieve the Sustainable Development Goals. *Nature Sustainability*, *2*(9), 805–814. DOI: 10.1038/s41893-019-0352-9.

Srivastava, V., & Sillanpää, M. (2017). Synthesis of malachite@clay nanocomposite for rapid scavenging of cationic and anionic dyes from synthetic wastewater. *Journal of Environmental Sciences*, *51*, 97–110. DOI: 10.1016/j.jes.2016.08.011.

Vincēviča-Gaile, Z. (2014). *Impact of Environmental Conditions on Micro- and Macroelement Content in Selected Food from Latvia*. University of Latvia.

Xiaoqi, S., Huimin, L., Mahurin, S. M., Rui, L., Xisen, H., & Sheng, D. (2016). Adsorption of rare earth ions using carbonized polydopamine nano carbon shells. *Journal of Rare Earths*, *34*(1), 77–82. DOI: 10.1016/S1002-0721(14)60582-2.

Zhu, Y., Zheng, Y., & Wang, A. (2015). Preparation of granular hydrogel composite by the redox couple for efficient and fast adsorption of La(III) and Ce(III). *Journal of Environmental Chemical Engineering*, *3*(2), 1416–1425. DOI: 10.1016/j.jece.2014.11.028.