

# Removal of Cadmium, Zinc, Lead and Copper by Sorption on Leaching Residue from Nickel Production

Miroslava Václavíková<sup>1</sup> and George P. Gallios<sup>2</sup>

## Odstránenie Cd, Zn, Pb a Cu sorpciou na vylúhovanom zvyšku z produkcie Ni

A leaching residue from the nickel production (LRNi), was used to study the removal of selected bivalent cations (Cd, Pb, Cu and Zn) from model aqueous solutions. Batch-type experiments have been performed in solutions with initial concentrations of heavy metals in the range of 20-400 mg.L<sup>-1</sup> and the adsorbent dosage 2 g.L<sup>-1</sup>. All adsorption experiments were carried out at ambient temperature (22±1°C) in orbital shaker. The experimental data were modeled with Langmuir and Freundlich isotherms. The relatively high uptake indicated that LRNi can adsorb considerable amounts of cadmium and zinc (maximum uptake capacity for cadmium: 25 mg/g at pH 7.2 and ca. 40 mg/g for zinc at pH 7). A significant uptake was also observed for copper and lead at pH 5.8 and 6 respectively, which was attributed to the precipitation of the respective insoluble hydroxides.

**Key words:** leaching residue from nickel production, by-products, wastewater, heavy metals, sorption.

## Introduction

Heavy metals have a sufficient distribution and abundance and they are in some way environmentally or biologically significant as toxic substances (Lester 1987). These include metals such as lead (Pb), chromium (Cr), nickel (Ni), copper (Cu), cadmium (Cd), and zinc (Zn). These toxic metals are released into natural waters by industrial and domestic wastewater discharges (Paterson 1987). The necessity to reduce the amount of heavy metal ions in wastewater streams from hydrometallurgical and other industries, and subsequent possible re-use of these metal ions, has led to an increasing interest in selective sorbents. The mobility and bio-availability of aqueous metal cations in soils and sediments is often controlled by sorption onto iron oxides. A molecular understanding how the metals sorb onto mineral surfaces is needed before we can reliably model equilibria from sorption isotherm measurements. Sorption of ions onto mineral surfaces may occur via outer-sphere complexes, inner-sphere complexes, surface precipitates or via ion exchange (Peacock 2000). A considerable research work has been done in the search of inexpensive adsorbents especially obtained from various industrial waste materials/by-products. In this research we assess the potential of a leaching residue from the Ni production as a sorbent for the removal of toxic metal ions such as cadmium, lead, copper and zinc.

## Experimental

All chemicals used were of analytical grade, obtained from Merck, Germany. Deionized water was used throughout the experiments. Model contaminant aqueous solutions were prepared by dissolving Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, and Zn(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in 0.01M NaNO<sub>3</sub>. The pH of the solutions was adjusted with a suitable concentration of NaOH or HNO<sub>3</sub>.

The leaching residue was obtained from the nickel production Sered, Slovakia and fully characterized by the chemical analysis, neutron activation analysis and the powder X-ray diffraction (Philips X'Pert Pro X-ray diffractometer, CuK<sub>α</sub> radiation). The specific surface area of the material was determined by the low temperature nitrogen adsorption using a Gemini 2360 equipment, whereas a Helos and Rodos apparatus (Sympatec GmbH, Germany) with the wet dispersion base Rodos 11 SROV was utilized for the grain size analysis. The magnetic properties of the material were investigated as well.

The adsorptions of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> were performed in the orbital shaker at the temperature 22±0.1°C. The initial total metal ion concentration range was 20-400 mg.L<sup>-1</sup>, and the sorbent concentration was 2 g.L<sup>-1</sup>. The quantity of heavy metal ions in solutions has been determined both before the introduction of sorbent and after the reaction with the metals in solution. All experiments were carried out at a constant ionic strength (0.01M NaNO<sub>3</sub>) for 24 hours. The metal uptake was determined by Atomic Absorption Spectroscopy; the sorption isotherms were fitted using the Langmuir- and Freundlich- type equation.

<sup>1</sup> Ing. Miroslava Václavíková, PhD., Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, SK-043 53 Kosice, Slovak Republic, [vaclavik@saske.sk](mailto:vaclavik@saske.sk)

<sup>2</sup> Dr. George P. Gallios, Lab. Gen. & Inorg. Chemical Technology, School of Chemistry, Aristotle University, GR-540 06 Thessaloniki, Greece, [gallios@chem.auth.gr](mailto:gallios@chem.auth.gr)

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As the metals precipitate at different pH values, the thermodynamic equilibrium diagram of each cation were constructed with the use of the computer code Mineql Plus (Mineql +, 1998) for a total concentration of 100 mg.L<sup>-1</sup> of metal and constant ionic strength (0.01 M NaNO<sub>3</sub>). A suitable pH, where the metals were dissolved fully, was chosen for the adsorption studies.

### Results and discussion

The chemical composition of the sorbent used is given in Table 1. The XRD pattern is shown in Fig. 1. and the mineral composition of LRNi is given in Table 2. The specific surface area of the sorbent, determined by the BET method, was found to be 26.6 m<sup>2</sup>.g<sup>-1</sup>, whereas 90 % of its particles had a size smaller than 20 μm. The grain size distribution is presented in Fig. 2.

Tab. 1. Chemical composition of LRNi.

Compound	Fe <sub>Total</sub>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sub>met</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Cr <sub>2</sub> O <sub>3</sub>	NiO
Content [%]	45.89	17.60	26.97	1.32	15.02	4.08	3.54	2.29	2.10	0.17

Tab. 2. Mineral composition of LRNi.

Phase	magnetite	quartz	wüstite	calcite	ferrochrompicotite
Content [%]	54.09	13.15	8.02	6.32	5.51

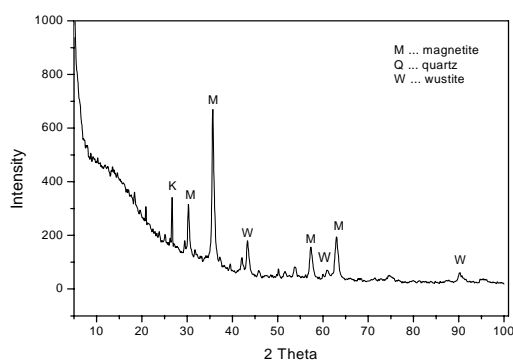


Fig. 1. X-Ray diffraction pattern of LRNi.

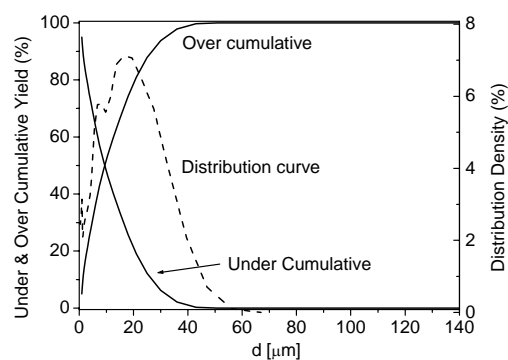


Fig. 2. Grain size distribution of LRNi.

It is well known that heavy metal ions hydrolyse in water solutions and precipitate as insoluble hydroxides at appropriate pH values. If someone is interested to investigate the sorption of metal cations on a sorbent it has to make sure that the metal ion remains in a soluble form. Otherwise, it is very difficult to determine what amount is removed by sorption and what is abstracted from the solution due to precipitation. Thermodynamic calculations with MINEQL+ (for a total metal concentration of 100 mg.L<sup>-1</sup> and 0.01 M NaNO<sub>3</sub>) have shown that cadmium remains in solution mainly as Cd<sup>2+</sup> up to a pH value of about 8.4, where it starts precipitating as insoluble Cd(OH)<sub>2(s)</sub>. At pH 9.1 more then 90 % of cadmium precipitates. Lead remains soluble up to pH value of about 5.7 where it starts to precipitate as insoluble Pb(OH)<sub>2(s)</sub>. At pH 6.3 more then 90 % of lead is precipitated.

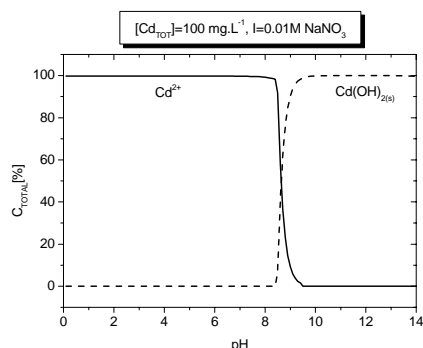


Fig. 3. Thermodynamic equilibrium diagram of Cd.

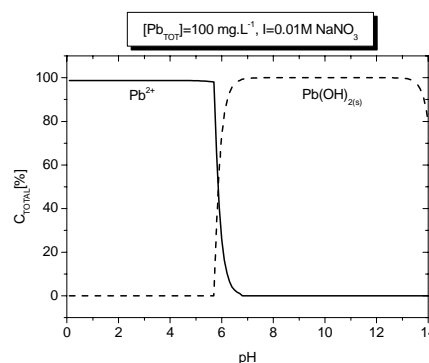


Fig. 4. Thermodynamic equilibrium diagram of Pb.

Similarly, it was observed that copper hydrolyzes in water up to pH value of about 5.4 where it is starts to precipitate as insoluble Cu(OH)<sub>2</sub>. According to calculations, Zn remains soluble up to the pH value

of about 7.3, where it starts to precipitate and at pH 7.8 more than 90 % of zinc is precipitated as insoluble ZnO. The thermodynamic equilibrium diagrams of Cd, Pb, Zn and Cu in the water system are given in Fig. 3-6.

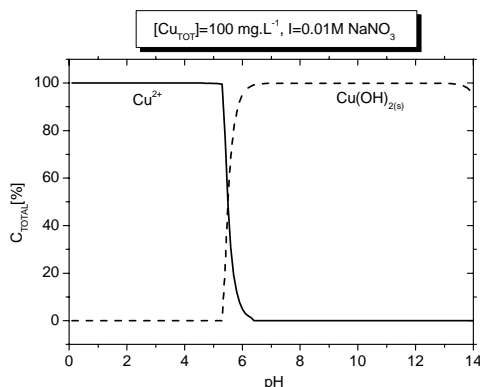


Fig. 5. Thermodynamic equilibrium diagram of Cu.

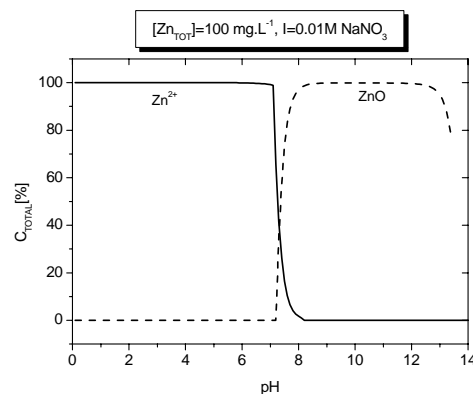


Fig. 6. Thermodynamic equilibrium diagram of Zn.

The results for Cd and Zn removal from aqueous solutions and the adsorption isotherms are given in Fig. 7.

The sorption isotherms and experimental data were modelled by the Freundlich-type equation. The Freundlich adsorption parameters ( $K$ ,  $b$ ,  $R^2$ ) were calculated from the model and the data are given in table 3. It is obvious that LRNi has a higher affinity to zinc (c. a 40 mg Zn/g of sorbent) than to cadmium (c a. 25 mg Cd/g of sorbent). The coefficient of determination  $R^2$ , which was calculated to be 0.98 and 0.97 respectively, confirmed that sorption isotherms are satisfactorily reproduced by the Freundlich model.

Tab. 3. Freundlich adsorption parameters.

Element	Freundlich parameters		
	K	b	R <sup>2</sup>
Cd <sup>2+</sup>	2,93	0,38	0,98
Zn <sup>2+</sup>	14,72	0,19	0,97

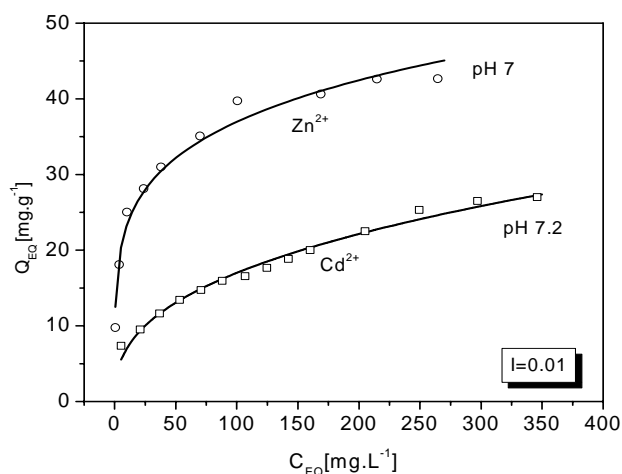


Fig. 7. Cadmium and zinc uptake by LRNi – Freundlich isotherms comparison.

As the thermodynamic calculations have shown that Pb remains soluble up to pH 5.8 and Cu up to pH 5.4, it is obvious that the lead and copper removal, from the solution at pH 6 and 5.8 respectively is most probably due to precipitation and not to sorption. Therefore, the results in Fig. 8 are expressed as efficiency  $E$  (%) and not as uptake  $Q$  (mg/g). It is pointed out though, that the presence of solid has an effect on  $\text{Cu}^{+2}$  and  $\text{Pb}^{+2}$  removal. The solid phase is more easily separated due to the precipitation of the metals on the surface of the sorbent. When the metals are precipitated from solution without a sorbent, a colloidal phase with very small particles is produced which is difficult to be separated from the liquid.

The removal efficiency for small initial metal concentrations is very good (90 % for 20 mg.L<sup>-1</sup> Cu<sup>+2</sup> and almost 100 % for up to 60 mg.L<sup>-1</sup> Pb<sup>+2</sup>). However, with an increasing initial concentration of Pb<sup>+2</sup> and Cu<sup>+2</sup> in solutions, their removal efficiency decreases. This is due to the fact that the solid to metal ratio decreases with the increase of the initial metal concentration. There is a fixed number of sorption sites on the solid which are occupied fully with the higher metal concentrations and the solid is not able to remove

more metal from the solution. This can be solved with an increase in the solid concentration. Taking into account that the sorbent used is already a solid waste (readily available and very cheap), the results are considered very satisfactory.

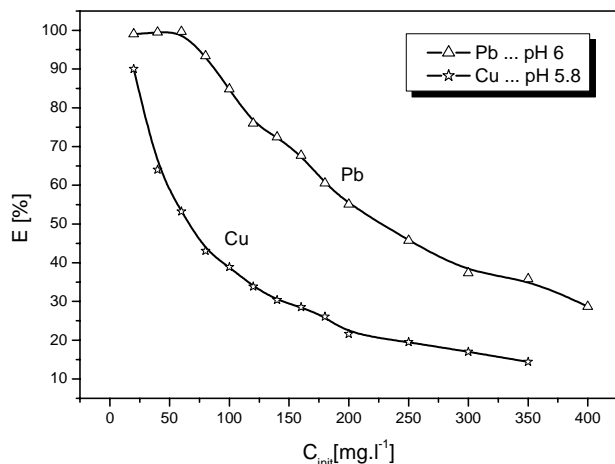


Fig. 8. Pb and Cu removal by ALR as a function of initial concentration.

### Conclusion

The leaching residue from the nickel production industry was found to be an efficient sorbent for the removal of cadmium, lead, copper and zinc from aqueous solutions. The maximum sorption capacity of Cd in the presence of 0.01M NaNO<sub>3</sub> at pH 7.2 was found to be 25 mg/g or 0.22 mmol Cd/g. The LRNi showed a higher affinity to Zn<sup>+2</sup> with a capacity of about 40 mg/g or 0.61 mmol/g for pH 7 in the presence of 0.01M NaNO<sub>3</sub>. The data were satisfactorily fitted by a Freundlich equation (R<sup>2</sup> =0.98 and 0.97 respectively).

The removal of Cu(II) and Pb(II) cations from the aqueous solution by the investigated LRNi was mainly due to precipitation effects.

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