



Pb²⁺ and Ni²⁺ Adsorption on Limestone and Dolomite Tailings

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Summary

The present paper investigates the Ni²⁺ and Pb²⁺ adsorption on limestone and dolomite, with the further goal of utilisation of their tailings in landfills as substrates capable of retaining heavy metals. The experiments have been carried out for fractions of different particle size: -4+1mm, -1mm+315µm, -315+90µm, -90µm. For the sorption studies separate solutions containing 5, 100, 500 mg/L of Ni²⁺ and Pb²⁺, have been used. The metal concentrations have been selected so as to simulate wastewater deriving from electroplating, metal-finishing, paint and plastic manufacturing activities. The pH of the solutions has been adjusted to 5 so as to avoid hydrolysis and precipitation of metal ions. The adsorption of metal ions on limestone and dolomite takes place mainly via a physical adsorption mechanism, absorption/solid-state diffusion and surface precipitation/co-precipitation between the Mg and Ca ions within the mineral and metal ions in aqueous solutions. In particular, Ni²⁺ adsorption increases by decreasing the solution concentration, varying on both minerals from 78 to 100% at 5ppm, from 24 to 89% at 100ppm, and from 17 to 45% on limestone and from 9 to 94% on dolomite at 500ppm. In contrast, Pb²⁺ adsorption increases by increasing the solution concentration, varying on limestone from 58 to 78% and on dolomite from 84 to 100% at 5ppm, and exceeding 99% on both minerals at 100 and 500ppm. The particle size has not proved such important as to make the grinding of the minerals necessary. Leaching tests according to EN12457-2, in order to investigate the strength of metal adsorption on the minerals, have shown very low leaching of both examined metal ions, retained on both examined minerals, varying from 0.1 to 5%.

Keywords: nickel, lead, adsorption, limestone, dolomite

Introduction

The chemical behaviour of carbonate natural materials in aqueous media containing dissolved heavy metals is a subject of current research in earth, chemical and environmental sciences. Carbonate minerals and rocks strongly interact with metal ions, removing them from aqueous solutions by adsorption, absorption/solid-state diffusion, and surface precipitation/co-precipitation. The sorption processes normally occur simultaneously with dissolution of the solid surface at the mineral-water interface.

The surface precipitation/co-precipitation is associated with heterogeneous nucleation/crystal growth processes, leading to the formation of metal carbonate and hydroxycarbonate phases which are overgrown or deposited on the surface of the crystals. The potential formation of solid solutions, i.e., (Me,Ca)CO₃, during surface growth processes is also an important issue (Godelitsas et al., 2007).

The accumulation of heavy metal in water supplies such as Pb²⁺ and Ni²⁺ is a result of increasing population and industrialization (plating, mining, battery manufacturing etc.). Research has forced on locally available low-cost adsorbents, such as natural materials, rock minerals, industrial, mining or demolition waste. Several techniques are associated with the elimination of toxic metals from aqueous environment, but adsorption process has been widely used in environmental chemistry, because of its low cost and simplicity in pollutant removal at low concentrations. The benefits of adsorption as a treatment process have led to the development of low cost raw materials of high ad-

sorption capacity, such as natural materials, rock minerals, agricultural or industrial waste materials (Irani et al., 2011).

Because of Ni and Pb toxicity, data describing their behaviour and fate are required for valid assessment of risk and designing of effective remediation strategies. The only study of Ni adsorption on calcite was published by Zachara et al. (1991), who used a single exchange constant for Ni, as well as for Cd, Mn and Co, to describe sorption over a wide range of pH and Ca activity and surface concentration, suggesting that Ni, as well as Zn and Co, forms surface complexes that remain hydrated until the cations are incorporated into the bulk structure by recrystallization (Lakshtanov and Stipp, 2007).

It is generally considered that the dissolution rates of the common divalent metal carbonates at 5 ≤ pH ≤ 8 increase in the order Ni < Mg < Co < Fe < Mn < Zn < Cd < Sr ≤ Ca ≈ Ba ≈ Pb and that cerussite, though adequately insoluble (log K_{sp}CER=-13.23), weathers easily to hydrocerussite, which appears to be more stable in nature. From the thermodynamical point of view, the system Pb²⁺ - Ca²⁺ - CO₃ - H₂O is particularly complex (Godelitsas et al., 2003).

The present paper aims at the utilization of waste materials, resulting as tailings from the excavation of limestone and dolomite, as substrate in landfills capable of retaining heavy metals and preventing their penetration in subsoil. The particle size of the minerals has been selected as the main parameter of the experiments so as to investigate if any grinding of the minerals is required.

Materials and methods

Samples of dolomite and limestone, supplied respectively from the regions of Attiki-Boeotia and from Milaki at South Evia in Greece, have been examined. They have been separated by mechanical screening into four (4) fractions of different particle size: ($-4+1\text{mm}$), ($-1\text{mm}+315\mu\text{m}$), ($-315+90\mu\text{m}$) and ($-90\mu\text{m}$). Their chemical composition has been determined by X-Ray Fluorescence (XRF, ARL ADVANT XP) and Thermogravimetric Analysis (Mettler TGA/STDA 851°C) and their mineralogical composition by X-ray diffraction (XRD, Siemens 500 D-500 Diffractometer), and the results for the initial minerals are shown respectively in Table 1 and Figure 1.

For the determination of heavy metal sorption capacity aqueous solutions of 5, 100, 500 mg/L of Pb^{2+} as well as Ni^{2+} was prepared. The pH has been adjusted to 5 by adding HNO_3 or NaOH , in order to avoid hydrolysis and precipitation of metal ions beyond pH 6. Furthermore, dolomite has proved more effective in acid conditions (Pehlivan et al., 2009; Kocaoba, 2007). In particular 5g of each fraction

of both samples has been added to 30mL of solution under stirring at 450rpm for 20min, 1h and 2h. After mixing the pH has been measured, the solid material has been collected by filtration, dried, weighted and its microstructure has been investigated by Energy-Dispersive X-ray Spectrometry (EDS-SEM, JSM-6300 JEOL), whereas any remaining Pb^{2+} and Ni^{2+} in the filtrate has been determined by Flame Atomic Adsorption Spectroscopy (FAAS, Perkin Elmer 3300).

Leaching studies have also been carried out according to EN 12457-2, in order to investigate the retention of the examined metals on the samples.

Results and discussion

Since the goal of the present study is the utilisation of waste materials, that is limestone and dolomite tailings, any further cost for their effective utilisation is undesirable. To this direction, the effectiveness of fractions of different particle size in metal adsorption has been investigated, so as to examine whether the minerals need grinding for their

Tab. 1 Physicochemical characteristics of limestone and dolomite

Tab. 1 Charakterystyka fizykochemiczna wapienia i dolomitu

element	limestone	dolomite
CaO (%)	55.4	31.9
MgO (%)	0.30	20.3
SiO ₂ (%)	0.23	0.27
Al ₂ O ₃ (%)	0.22	0.11
Cl (ppm)	-	53
Cu (ppm)	-	10
Fe ₂ O ₃ (%)	0.12	0.17
K (ppm)	280	77
P (ppm)	340	50
S (ppm)	180	65
Sr (ppm)	700	170
Lol (%)	42.5	47.5
pH	9.1	10.3

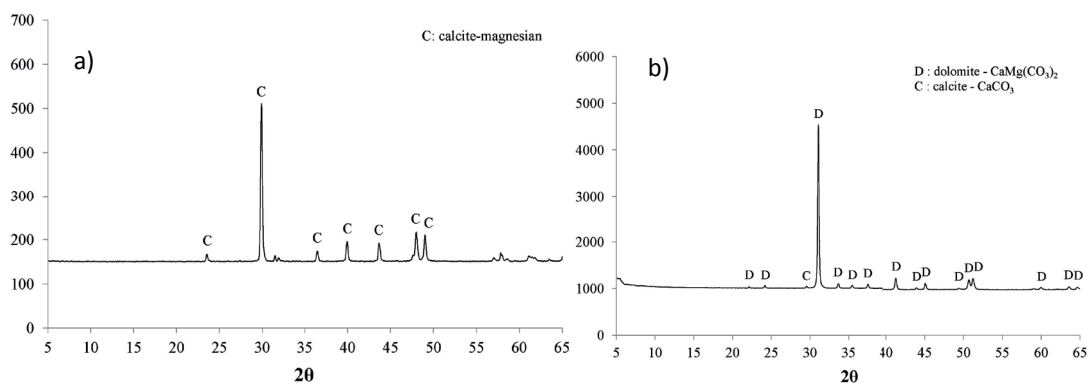


Fig. 1 Mineralogical composition of limestone (a) and dolomite (b)

Rys. 1 Skład mineralogiczny wapienia (a) i dolomitu (b)

effective use as substrates in landfills.

In Figure 2 the Ni²⁺ adsorption on all fractions of both limestone and dolomite is shown. As it is obvious, the Ni²⁺ adsorption is higher from solutions of lower concentration. In particular at 5ppm Ni²⁺ adsorption on both limestone and dolomite varies from 78 to 100% independent of the particle size.

In contrast, at 100ppm Ni²⁺ adsorption on both lime-

stone and dolomite varies from 24 to 89%, with the fractions of particle size between -1mm+315µm performing better. At 500ppm Ni²⁺ adsorption on limestone varies from 17 to 45% and on dolomite from 9 to 94%, with no significant differences between the fractions of different particle size, except in case of the fraction -90µm of dolomite that performs better in 60min. The relationship between distribution coefficients for the divalent cations and solubility

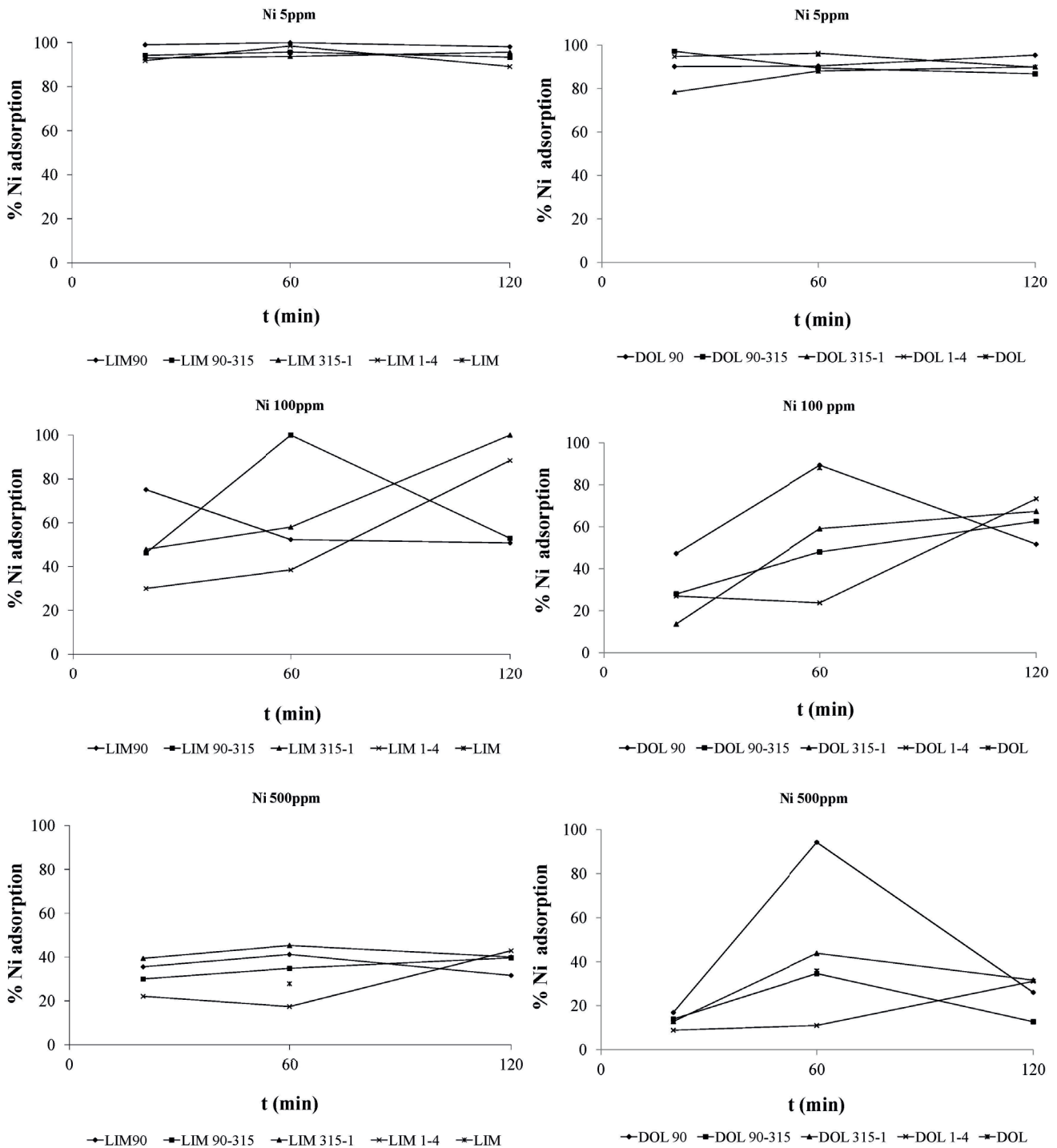


Fig. 2 Ni²⁺ adsorption on fractions of different particle size (-90µm, -315+90µm, -1mm+315µm and -4+1mm, all the fractions) of limestone (a) and dolomite (b)

Rys. 2 Adsorpcja Ni²⁺ we frakcjach o różnej wielkości cząstkach (-90µm, -315+90µm, -1mm+315µm and -4+1mm, wszystkie frakcje) wapienia (a) i dolomitu (b)

products predicts a limited occurrence of Ni²⁺ substitution into calcite (Rimstidt et al., 1998) and the relationship can be explained by the atom's electron configuration.

In Figure 3 the Pb²⁺ adsorption on all fractions of both limestone and dolomite is shown. No significant differences in Pb²⁺ adsorption on the fractions of different particle size are observed. At 5ppm Pb²⁺ adsorption on limestone varies from 58 to 78% and on dolomite from 84 to 100%. At 100 and 500ppm, Pb²⁺ adsorption on both minerals ex-

ceeds 99%. The dissolution of the carbonate phase causes a rapid increment of pH in the solid-water interface and a decrease in [CO₂]_{aq}. As a consequence, hydrocerussite can crystallize (Godelitsas et al., 2003).

Concerning the results of leaching studies, the leaching of both retained heavy metals, Ni and Pb, on both examined materials, limestone and dolomite, is very low. In particular, higher leaching is observed in metal solutions of 5ppm: Ni leaching reaches up to 4% in case of limestone and 5%

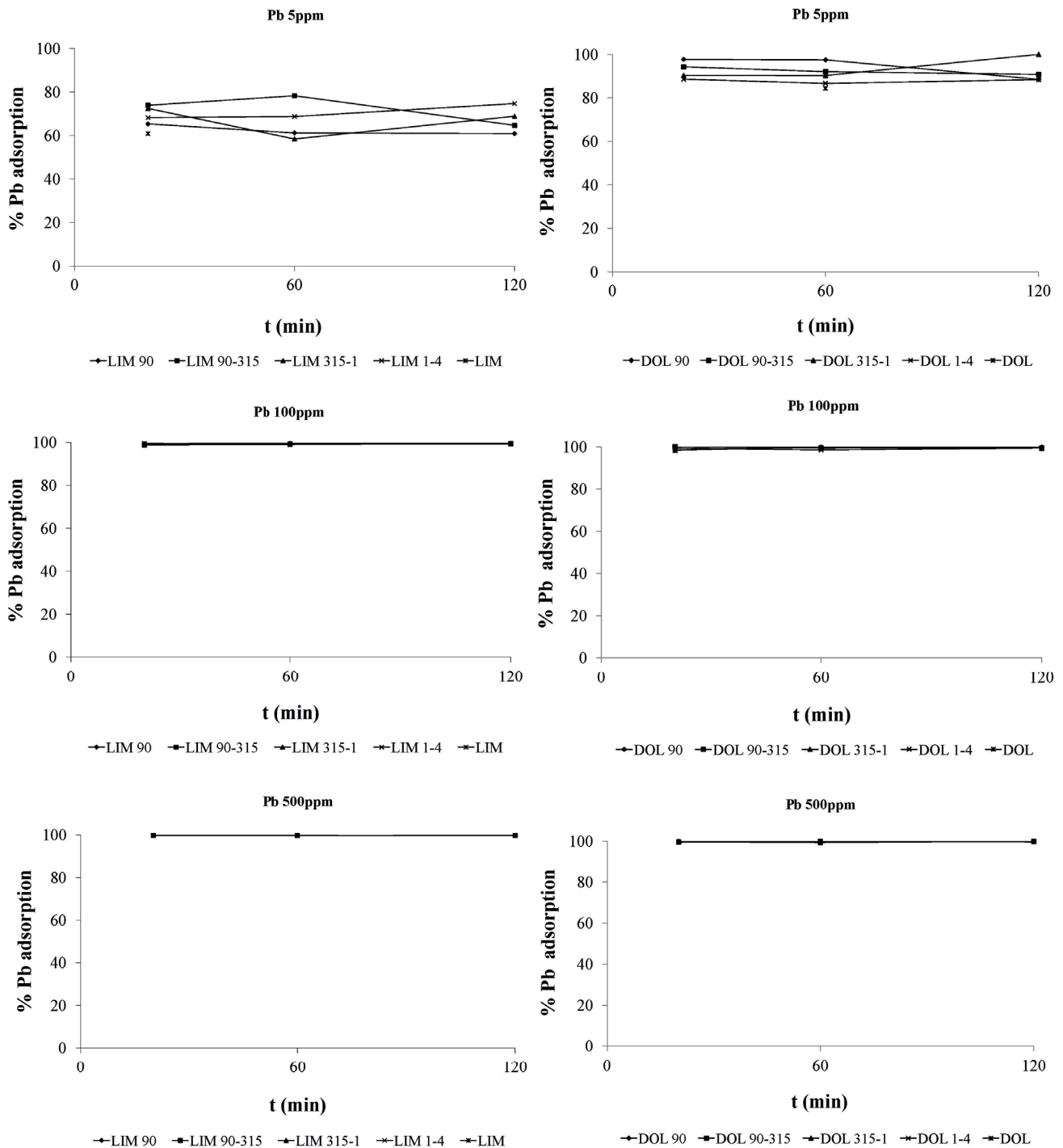


Fig. 3 Pb²⁺ adsorption on different granulometric fractions (–90µm, –315+90µm, –1mm+315µm and –4+1mm, all the fractions) of limestone (a) and dolomite (b)

Rys. 3 Adsorpcja Pb²⁺ różnych frakcji ziarnistych (–90µm, –315+90µm, –1mm+315µm and –4+1mm, wszystkie frakcje) wapienia (a) i dolomitu (b)

in case of dolomite, whereas Pb leaching reaches up to 3% in case of limestone and 2-16% in case of dolomite.

In metal solutions of 100ppm the leaching is lower: Ni leaching reaches up to 0.5% in case of limestone and 1% in case of dolomite, whereas Pb leaching reaches up to 0.5% in case of both limestone and dolomite. Even lower is leaching in metal solutions of 500ppm: Ni leaching reaches up to 0.2% in case of limestone and 2% in case of dolomite, whereas Pb leaching reaches up to 0.1% in case of limestone and 0.2% in case of dolomite.

Conclusions

Utilisation of mineral tailings, such as limestone and dolomite, has been seriously considered due to the material low cost involved and its availability for further exploitation. Low energy demand necessitates the minimum possible pretreatment process but at the same time the highest

efficiency of such materials, for their further application. The increased metal concentration in wastewaters already constitutes a reason of concern, in terms of safe disposal, focused on toxicity and overall metal-containing wastewater treatment, which have been largely confronted due to strict legislative requirements.

The study of both minerals in several particle sizes aimed at investigating the possibility of using them as substrates in landfills or lagoons with known mobilisation of heavy and toxic metals. Results verified that they can remove effectively Ni and Pb ions from aquatic environment. The concentration, as well as the pH of metal solutions, seems to be determinative for metal retention, whereas the particle size has not proved as decisive a factor as to necessitate the minerals' grinding before their application as landfill substrates, a process that is undesirable due to its high cost.

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Adsorpcja Pb^{2+} AND Ni^{2+} na wapieniach i dolomitach

Prezentowany artykuł bada adsorpcję Pb^{2+} AND Ni^{2+} na wapieniach i dolomitach, mając na celu utylizację ich odpadów na wysypiskach jako substratów mogących zatrzymywać metale ciężkie. Eksperymenty przeprowadzone zostały dla frakcji o różnych rozmiarach cząstek: $-4+1mm$, $-1mm+315\mu m$, $-315+90\mu m$, $-90\mu m$. W celu przeprowadzenia badań sorpcji użyto oddzielnych roztworów zawierających 5, 100, 500 mg/L of Ni^{2+} i Pb^{2+} . Stężenie metali zostało wybrane tak, aby symulować ścieki uzyskane z elektrolitycznego pokrywania metalem, wykańczania metali, czynności związanych z wytwarzaniem farb i plastików. pH roztworów zostało wyregulowane do wartości 5, aby uniknąć hydrolizy i wytrącania się jonów metali. Adsorpcja jonów metali na wapieniu i dolomicie ma miejsce głównie poprzez mechanizm adsorpcji fizycznej, absorpcji/dyfuzji w stanie stałym i wytrącania powierzchniowego/współstrącenia między jonami Mg i Ca w minerale i jonów metali z roztworów wodnych. W szczególności adsorpcja Ni^{2+} wzrasta wraz ze zmniejszeniem stężenia roztworu, zmieniając się na oby minerałach od 78 do 100% przy 5ppm, od 24 do 89% przy 100ppm, i od 17 do 45% na wapieniu, i od 9 do 94% na dolomicie przy 500ppm. W przeciwieństwie adsorpcja Pb^{2+} zwiększa się wraz ze zwiększającym się stężeniem roztworu, wahając się w przypadku wapienia od 58% do 78% i w przypadku dolomitu od 84% do 100% przy 5ppm, i przekraczając 99% w przypadku obu minerałów przy 100 i 500 ppm.

Nie wykazano aby rozmiar cząstki był na tyle ważny aby mielenie minerału było konieczne. Testy ługowania zgodne z normą EN12457-2, wykonane w celu zbadania siły adsorpcji metalu na powierzchni minerału, wykazały bardzo niskie ługowanie w przypadku obu badanych jonów metali, zatrzymanych na obu badanych minerałach, wahające się od 0,1 do 5%.

Słowa kluczowe: nikiel, ołów, adsorpcja, wapień, dolomit