

Purification of natural zeolite-clinoptilolite for medical application-Extraction of lead

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Abstract: A series of experiments of the leaching of lead and other cations from three samples of natural zeolite-clinoptilolite, (Sample 1–deposit Zlatokop, Vranjska Banja, Serbia and Montenegro; Sample 2–deposit Bala Mare, Romania; Sample 3–Igrös near Brus, Serbia and Montenegro) using EDTA was conducted. The results of the experiments showed that the extraction efficiencies from the examined samples were different. If a sufficiently large amount of EDTA was applied, most of the lead was extracted only from Sample 1–deposit Zlatokop. Similar effects were obtained for the leaching of iron. The differences in the extraction efficiencies may be due to the difference of the of lead and iron species present in the zeolite crystals. The effects of EDTA concentration and solid/liquid ratio on the extraction of lead, iron and aluminum were studied.

Keywords: zeolite, leaching, lead, EDTA.

INTRODUCTION

The increasing use of the natural zeolite (clinoptilolite) and clays (montmorillonite, kaolinite) for healing purposes and their use in pharmaceutical formulations necessitates new aspects of quality control to be taken into consideration. Scientific information concerning their safety is hard to obtain, because of the limited toxicological data available. Natural zeolite and clay minerals are geo-materials, the compositions of which include many trace elements.

Natural zeolites are used in many industrial applications, such as for the purification of water, soil improvement, animal production, food supplements and additives, radioprotection, *etc.* However, it is less known that in recent years these exciting materials are increasingly being used in biomedical applications. Since many biomedical processes are closely related to ion exchange, adsorption and catalysis, it is evident that natural zeolites can make a significant break-through in the pharmaceutical industry and in medicine in the near future.^{1,2} The reasons for this are as follows: (a) zeolites have known biological properties along with long-term chemical and biological stability, (b) they reversibly bind small molecules, (c) they

posses size and shape selectivities, (d) they offer the possibility of metalloenzyme mimics, (e) they have immunomodulatory activity.³

The various biomedical effects and application of zeolite are given in Fig. 1² (with the permission of the authors).

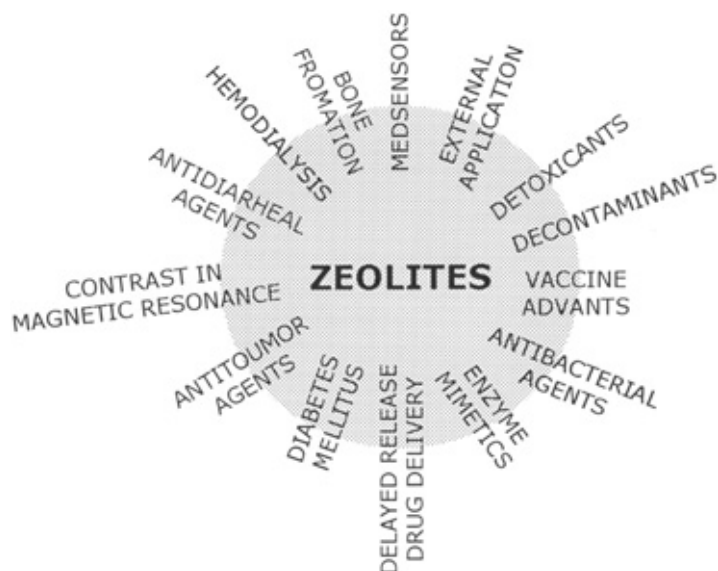


Fig. 1. Biomedical applications of zeolites.²

In vitro and *in vivo* investigations,⁴⁻⁶ the use of the natural zeolite-clinoptilolite for treatment of cancer-bearing mice and dogs led to improvements in the overall health status, prolongation of the life span and a decrease of the tumor size in some cases. An immunostimulatory effect of natural clinoptilolite has been detected,⁷⁻⁹ and it is possible that this is the mechanism of its antimetastatic ability.¹⁰

Clay minerals are used for therapeutical purposes, with beneficial effects on health, in pharmaceutical formulations and spa and aesthetic medicine. In pharmaceutical formulations, clays are as orally administered active principles.¹¹ In spa and aesthetic medicine, clays play a very active role during cation exchange reactions,¹² controlling the mobility of major and trace elements. From an inorganic point of view, the documented mobility of elements in spa treatments in medicine, was the first step.

Of the many aspects which have been investigated, the content and mobility of toxic metals are the least considered. This occurred because their occurrence in clay and zeolite minerals was ignored. Organisms absorb chemical elements from natural minerals, a fact documented by Mascolo *et al.*,¹³ who evaluated this behavior during digestion of selected toxic chemical elements. By analyzing the content of toxic elements in the urine of orally clay-treated rats, they showed that absorption of elements occurs after clay ingestion. The authors concluded that toxic elements have hazardous effects on the blood, organs and/or the whole body. In a sub-

sequent study,¹⁴ the same authors gave a future elucidation on the distribution process of hazardous elements (Hg, Pb, As, Sb, Tl, Cd). Rats fed with clays had unincreased concentrations of the elements in their organs, in the following order: kidney>liver>heart>brain. Thus, the distribution of the elements was not homogeneous throughout the body.

Even if it is not possible to extrapolate these data in terms of toxicity for human health, the use of natural minerals (zeolite and clay) must be under control, due to their side effects.^{15,16} Using clays might cause serious health problems. Moreover, there is an urgent need for systematic control of the quality of geo-materials.¹⁴

Understanding their bioavailability is the key to an assessment of the potential toxicity of metallic elements and their compounds. Bioavailability depends on biological parameters and on the physicochemical properties of metallic elements, their ions, and their compounds.¹⁷

Lead is one of the many toxic metals, usually present in clay and zeolite minerals. The mobility of lead in organism and its toxicity for human health are well known. The toxicity of this element is further complicated by red/ox $\text{Pb}^{4+}/\text{Pb}^{2+}$ reaction.¹⁷

The concentration of lead in uncontaminated soil is between 10 and 200 ppm.¹⁸ The presence of toxic metals in natural zeolites and clays minerals differ depending on the deposit. Usually, the content of lead in natural clinoptilolite is below 30 ppm. For medical use, the concentration of lead must be reduced to a minimum level (a few ppm).

During the past years, the rapid development of various treatment technologies for the removal of lead (purification of lead-contaminated soils, waters and industrial wastewaters) using EDTA as a chelating agent has been untessed.^{18–20} When lead-contaminated soil is washed with EDTA solution, the supernatant contains Pb–EDTA and various other metal–EDTA complexes (generally Al–, Ca–, Fe–, Mg, Mn–, Zn–EDTA complexes). The concentrations of the extracted metal in the supernatant depends on the stability constants, pH of the solution, the concentration of metals and EDTA.²¹

Based on the conditional stability constants of the Pb–EDTA complexes, EDTA complexes with lead in preference to the other cations at $4 < \text{pH} < 10$, except for Cu^{2+} in all the pH region, and Fe^{3+} at pH values below 6.5.

The aim of this research was to investigate the extraction efficiency of lead, present as impurities in natural clinoptilolite, using EDTA as the chelating agent. Several natural zeolite-clinoptilolite samples, under variables such as liquid/solid ratio, particle size and concentration of EDTA, were investigated.

EXPERIMENTAL

The samples of natural zeolite-clinoptilolite from different deposit were used for this research. The samples (*Sample 1–deposit* Zlatokop, Vranjska Banja, Serbia and Montenegro, *Sample 2–deposit* Bala Mare Romania, *Sample 3–deposit* Igros near Brus, Serbia and Montenegro), were pre-

pared below 0.2 mm in size. Sample 1 was prepared in three size fractions: below 200 microns (Sample 1-a), $-0.4+0.2$ mm (Sample 1-b) and $-0.8+0.4$ mm (Sample 1-c). A full characterization of Samples 1 and Sample 3, was published elsewhere,²²⁻²⁴ The concentration of metals before and after leaching in EDTA, were determined by the AAS method using a Perkin-Elmer M-703 instrument.

Extraction procedure

Extraction experiments were conducted to assess the effects of the origin of the samples (*i*), the solid/liquid ratio (*ii*) and the concentration of EDTA (*iii*). A typical extractions procedure consisted of stirring a certain amount (10–50 g) of prepared sample in 100 ml of EDTA (known concentration), on a magnetic stirrer for 2 h at 60 °C. The sample was then centrifuged for 10 min at 10,000 r.p.m. (Heraeus Biofuge type 17), and the pH of the supernatant and the concentration of cations were measured. Separate experiments were conducted to measure the effect of particle size (sample 1) on the leaching of lead.

The effect of the solid/liquid ratio (1:10 and 1:20) on the efficiency of lead extraction (Sample 1-a) was assessed by using different EDTA concentration: 0.1 M, 0.05 M, 0.02 M and 0.01 M. The extraction of lead from Sample 1-a into 0.05 M EDTA, was also examined using different solid/liquid ratios: 1:10; 2:10; 3:10; 4:10 and 5:10.

The pH in all experiments was between 4.0 and 4.2.

X-Ray powder diffraction analysis of the raw Sample 1 and after EDTA treatment (0.1 M EDTA, 10 % suspension), were performed using a Philips PW-1710 diffractometer with monochromatic Cu-K α radiation, to determine whether the EDTA treatment resulted in any change in the crystalline structure of the zeolite.

RESULTS AND DISCUSSION

Selected physical-chemical properties, chemical composition and major cation concentrations in the three examined samples are presented in Table I.

TABLE I. Chemical composition, major cation concentrations, pH (5 % suspension) and cation exchange capacity-CEC (total) of the zeolite samples

| Parameters | Sample 1 | Sample 2 | Sample 3 |
|-----------------------------------|----------|----------|----------|
| SiO ₂ /% | 66.01 | 68.56 | 69.95 |
| Al ₂ O ₃ /% | 12.40 | 12.77 | 12.76 |
| Fe ₂ O ₃ /% | 1.84 | 2.78 | 1.25 |
| CaO/% | 3.45 | 3.22 | 2.80 |
| MgO/% | 0.80 | 1.11 | 0.29 |
| Na ₂ O/% | 0.91 | 0.78 | 0.45 |
| K ₂ O/% | 0.82 | 1.12 | 3.13 |
| L. I./% | 13.45 | 9.55 | 9.17 |
| Microelements/ppm | | | |
| Pb | 29 | 35 | 38 |
| Mn | 305 | 282 | 240 |
| Zn | 35 | 62 | 30 |
| Cu | 32 | 8 | 6 |
| CEC/(meq/100 g) | 142 | 147 | 150 |
| pH (5 % suspen.) | 7.55 | 7.78 | 7.60 |

Comparing the samples, it is obvious that all three zeolites (from different deposits), have similar cation exchange capacity: CEC(142–150 meq/100 g) and pH (5% suspension in water). However, the contents of microelements, iron, magnesium and potassium are different in the different samples.

The efficiencies of lead extraction, as well as the leaching of aluminium, iron manganese, zinc and copper, for the three samples used in these experiments (under the same experimental conditions) are given in Table II. The leached metal ions in the supernatant were determined after treatment of the zeolite samples with EDTA (10% suspension in 0.1 M EDTA).

EDTA was chosen because it forms strong bonds with metals,²¹ as reflected by their high equilibrium formation constants ($\log k$ Pb²⁺EDTA–17.9, Zn²⁺EDTA–17.5, Cu²⁺EDTA–18.8, Mn²⁺EDTA–14.5 and Fe³⁺EDTA–25.1). The conditional stability constant of the metal–EDTA complexes²¹ as a function of pH, for pH 4 may be assumed to follow the sequence: Fe³⁺>Cu²⁺>Pb²⁺>Zn²⁺>Al³⁺>Mn²⁺. The stability sequence at pH 6 is similar. The extraction of metal ions from the examined samples do not follow the sequence of the conditional stability constants, as shown in Table II.

TABLE II. Extraction of cations from natural clinoptilolite (10% suspension of zeolite in 0.1 M EDTA)

| Leached cations/ppm | Sample 1 | | Sample 2 | | Sample 3 | |
|---------------------|----------|--------|----------|--------|----------|--------|
| Pb | 25 | (29)* | 10 | (35)* | 10 | (38)* |
| Al | 900 | | 1300 | | 1000 | |
| Fe | 10600 | | 880 | | 330 | |
| Mn | 265 | (305)* | 242 | (282)* | 220 | (240)* |
| Zn | 22 | (35)* | 26 | (62)* | 21 | (30)* |
| Cu | 15 | (32)* | 7 | (8)* | 2 | (6)* |

*Data before extraction, ppm

The effectiveness of lead leaching from the examined samples is different. The best results were obtained for Sample 1: more than 86 % of the total lead present was extracted. Less lead was leached from the other two samples, the effectiveness was about 25 %.

The main factor for the leaching of Fe is the form in which it exists. More than 80 % of the total content of iron in Sample 1 was leached. Under the same conditions, less than 50 % and less than 40 % had been leached from Sample 2 and 3, respectively, after the same time. More than 80 % of the manganese was leached from all the samples, between 40 % and 70 % of the Zn and between 30 % and 80 % of the Cu.

The leaching of aluminium is also different and probably depends on the crystalline structure of the zeolite, and/or on the presence of amorphous phases.

The obtained data confirm that both parameters (the form in which the cation exists and the conditional stability constants of the metal–EDTA) complexes have

an influence on the leaching, of the metal ions present in the zeolite. Which parameter is dominant, depends on the origin of the deposit (Ch. Kim *et al.*).¹⁸ The results of the leaching of cations from Sample 1 show that the conditional stability constants of the metal–EDTA complexes is the dominate factor, while in Samples 2 and 3, both parameters have an influence.

The influences of the liquid/solid ratio (*ii*) and the concentration of EDTA (*iii*) on the extraction of lead were determined for all three samples, using 10 % and 20 % solid and 0.1 M and 0.05 M EDTA. The results are given in Table III.

As can be seen from Table III, the extraction of lead decreases with increasing concentration of solid and decreasing concentration of EDTA. This can be clearly seen for Sample 1. The extraction efficiencies for Pb under the conditions 10 % solid and 0.1 M EDTA was 86 % Pb, while 76 % was extracted with 20 % solid and 0.05 M EDTA. Under the conditions of 20 % solid and 0.1 M EDTA and of 10 % solid and 0.05 M EDTA, the same extraction efficiencies were obtained. In these cases, the stoichiometric ratio EDTA–Pb are identical.

TABLE III. The influence of the concentration of solid and EDTA on the extraction of Pb

| Sample | Solid/% | Conc. EDTA mol/dm ³ | Pb/ppm | | Pb leached/% |
|----------|---------|-----------------------------------|-----------------|----------------|--------------|
| | | | Before leaching | After leaching | |
| Sample 1 | 10 | 0.1 | 29 | 4 | 86 |
| | 20 | 0.1 | 29 | 6 | 80 |
| | 10 | 0.05 | 29 | 6 | 80 |
| | 20 | 0.05 | 29 | 7 | 76 |
| Sample 2 | 10 | 0.1 | 35 | 25 | 29 |
| | 20 | 0.1 | 35 | 25 | 29 |
| | 10 | 0.05 | 35 | 26 | 26 |
| | 20 | 0.05 | 35 | 26 | 26 |
| Sample 3 | 10 | 0.1 | 38 | 28 | 26 |
| | 20 | 0.1 | 38 | 28 | 26 |
| | 10 | 0.05 | 38 | 29 | 23 |
| | 20 | 0.05 | 38 | 30 | 21 |

These data (Table III) demonstrate that the efficiency of lead extraction was different for each sample. Lead extraction was not only a function of the stoichiometric ratio of the applied EDTA concentration to the total lead concentration in the zeolite sample. The efficiencies of lead extraction from the examined zeolite samples (at the same stoichiometric ratio EDTA–Pb) differ due the presence of different lead species in the samples. A similar explanation can also be applied for the extraction of iron.

The effects of particle size on the extraction of Pb, Al and Fe, using 0.1 M EDTA and 10 % solids, were examined using Sample 1. The results are presented in Table IV.

For effective extraction of lead, the particle size should be below 200 microns (Table IV). The obtained results show that the leaching of all three examined cations (Pb, Al, Fe) decreases with increasing particle size.

TABLE IV. Effects of particle size on the extraction of Pb, Al, and Fe (Sample 1)

| Leached cation | Sample 1-a (-0.2+0 mm) | Sample 1-b (-0.4+0.2 mm) | Sample 1-c (-0.8+0.4 mm) |
|----------------|---------------------------|-----------------------------|-----------------------------|
| Pb | 25 ppm | 13 ppm | 5 ppm |
| Al | 900 ppm | 420 ppm | 105 ppm |
| Fe | 1.06 % | 275 ppm | 98 ppm |

The results of lead, aluminium and iron extraction, from Sample 1-a using: 0.1 M, 0.05 M, 0.02 M and 0.01 M EDTA are given in Table V (10 % solids).

TABLE V. Pb, Al and Fe extracted using different EDTA concentrations (Sample 1-a)

| EDTA/(mol/dm ³) | Leached Pb/ppm | Leached Al/ppm | Leached Fe/% |
|-----------------------------|----------------|----------------|--------------|
| 0.10 | 25 | 900 | 1.06 |
| 0.05 | 23 | 900 | 1.02 |
| 0.02 | 9 | 570 | 0.34 |
| 0.01 | 1 | 450 | 0.26 |

The results given in Table V show that the extraction efficiencies of lead, aluminium and iron (for Sample 1), using 0.10 M and 0.05 M EDTA are similar; more than 80 % of the total lead present was leached. Simultaneously, EDTA dissolved the same amount Al (900 ppm) and Fe (more than 1 %). Initial (total) concentration of Fe in Sample 1 was 1.28 % Fe, meaning that about 80% of the iron present was dissolved in EDTA (0.05 and 0.1 M).

The extraction of lead, aluminium and iron from Sample 1-a, using 0.05 M EDTA, with solid/liquid mass ratios of 1:10; 2:10; 3:10; 4:10 and 5:10 were also examined. The results are presented in Table VI.

TABLE VI. The effect of the solid/liquid mass ratio on the extraction of Pb, Al and Fe (Sample 1-a)

| Solid:liquid ratio | Leached Pb/ppm | Leached Al/ppm | Leached Fe/% |
|--------------------|----------------|----------------|--------------|
| 1:10 | 23 | 900 | 1.02 |
| 2:10 | 22 | 900 | 1.01 |
| 3:10 | 15 | 550 | 1.00 |
| 4:10 | 4 | 375 | 0.71 |
| 5:10 | 2.5 | 330 | 0.51 |

The obtained results (Table VI) show that the extractions of an three examined cations, lead, aluminium and iron at solid/liquid ratios of 1:10 and 2:10 (on a mass basis) were similar. With increasing solid/liquid ratio, the extraction of lead and aluminium decreases more than the extraction of iron. At pH 4.2, the conditional

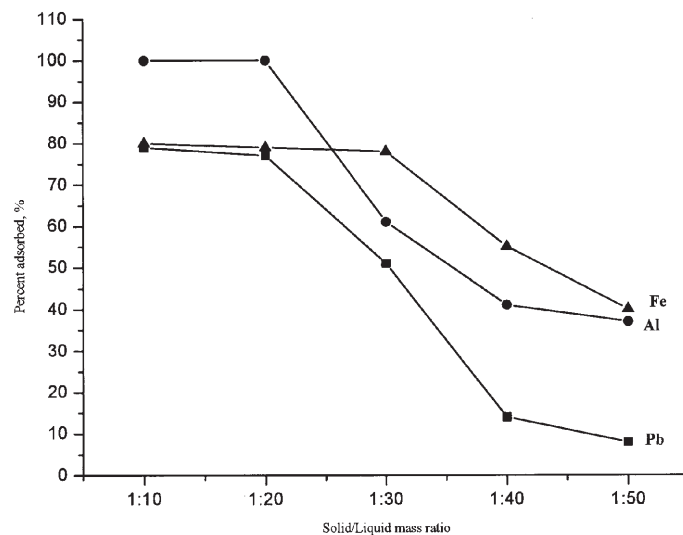


Fig. 2. Impact of the solid/liquid ratio on the extraction of Pb, Al and Fe in 0.05 M EDTA (two hours, 60 °C, continual mixing, pH 4.2)

stability constant of Fe–EDTA is higher than those of Pb–EDTA and Al–EDTA. At a solid/liquid ratio 5:10, about 10 % of the total lead and about 40 % of the total iron present are leached out.

The extraction efficiency (%) of lead, aluminium and iron, at different solid/liquid ratios, but keeping the quantity of EDTA (0.05 M), the pH 4.2, the extraction time 2 h at 60 °C, constant presented in Fig. 2. Under these conditions a maximum of 900 ppm of Al was dissolved. This value was taken as 100 %.

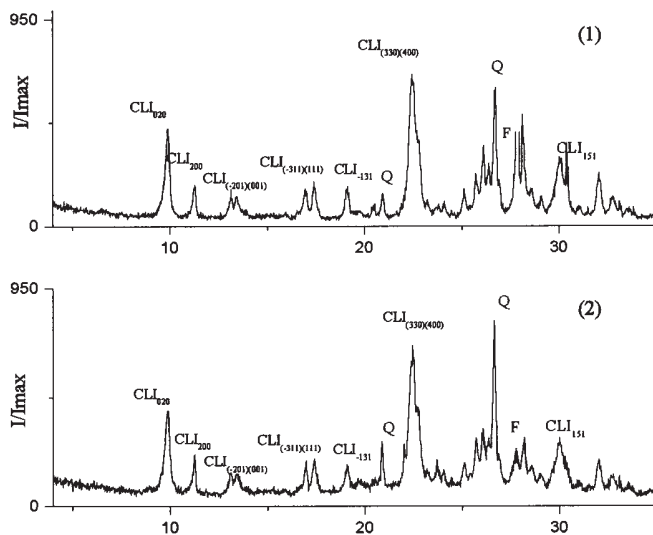


Fig. 3. XRD Sample 1: (1)–starting sample; (2)–sample after treatment with 0.1 M EDTA (10 % suspension, two hours, 60 °C, continual mixing, pH 4.2)

Figure 2 shows that the extractions with solid/liquid ratios of 1:10 and 2:10 were similar for all three examined cations. With increasing concentration of solid, the extraction efficiencies decrease (as per the conditional stability constants), first for lead and aluminium and then for iron.

The pH in all experiments was between 4.0 and 4.2. The (log) conditional stability constants – EDTA complexes under this condition were Fe–EDTA–15; Pb–10; Al–7.5.²¹ For Sample 1, all the obtained data show that the extraction efficiency of the examined cations (Pb, Al, Fe), were mainly a function of the conditional stability constants and the stoichiometric ratio of the applied EDTA to the total cation concentration.

XRD-analysis of Sample 1 before and after treatment with a 10 % suspension in 0.1 M EDTA showed no difference in the crystalline structure of the examined zeolite, Fig. 3.

CONCLUSION

Based on the experimental results, it has been shown that both the available form in which the cation exists and the conditional stability constants metal–EDTA have an influence on the EDTA extraction of the metal ions present in zeolite. Which parameter is dominant depends on the origin of the deposit. The examination of three samples of natural zeolite-clinoptilolite from different deposit, (Sample 1–deposit Zlatokop, Vranjska Banja, Serbia and Montenegro, Sample 2 – deposit Bala Mare, Romania, Sample 3 – Igros near Brus, Serbia and Montenegro) showed that the conditional stability constants metal–EDTA is the dominant factor for the leaching of cations from Sample 1, while for Samples 2 and 3, both parameters have an influence.

The results of the extraction with solid/liquid ratios 1:5 and 1:10 were similar when EDTA \geq 0.05 M was used. If a sufficiently large amount of EDTA was applied, most of lead was extracted only from Sample 1. With increasing concentration of solid, the extraction efficiencies decreased, first for lead and aluminium and then for iron. For Sample 1, the extraction efficiency of the examined cations were mainly a function of the conditional stability constants and the stoichiometric ratio of the applied EDTA to the total cation concentrations. The differences in the extraction efficiencies from the three examined samples may be due to differences in the type of lead and iron present in the zeolite crystals.

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ИЗВОД

ПРЕЧИШЋАВАЊЕ ПРИРОДНОГ ЗЕОЛИТА-КЛИНОПТИЛОЛИТА ЗА
УПОТРЕБУ У МЕДИЦИНИ – ЕКСТРАКЦИЈА ОЛОВА

МАГДАЛЕНА ТОМАШЕВИЋ-ЇАНОВИЋ

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Природни зеолит-клиноптилолит све више налази примену у решавању проблема везаних за здравље људи. Пошто се ради о природној сировини која садржи разне примесе, међу којима се често срећу и токсични метали, неопходна је строга контрола квалитета. Олово припада првој групи токсичних метала које је углавном увек присутно у неметалним сировинама, у мањем или већем проценту. У раду су дати резултати екстракције олова из три лежишта клиноптилолита, применом EDTA. Добијени резултати показују да се олово лужи са EDTA, више или мање ефикасно, зависно од лежишта. На ефикасност лужења олова, поред концентрације EDTA и односа чврсто/течно, евидентан је утицај облика у коме је олово присутно у зеолиту.

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