

LEACHING OF LEAD FROM CLINOPTILOLITE AT ACIDIC CONDITIONS

Y. PETRAKAKIS
E. MYLONA
D. GEORGANTAS
H. GRIGOROPOULOU*

*Laboratory of Chemical Process Engineering
Section of Process Analysis and Plant Design
School of Chemical Engineering
National Technical University of Athens
Zografus Campus, GR-15780, Athens, Greece*

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*to whom all correspondence should be addressed:

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e-mail: lenag@chemeng.ntua.gr

ABSTRACT

The leachability of Pb^{2+} from natural greek clinoptilolite was investigated according to the standard procedures TCLP/EPA/RCRA (1311), EPA Methods 1310, 1320 and DIN 38414-S4. Through SEM/EDAX analysis it was shown that lead was uniformly loaded onto the particles subjected to acid treatment. Sorption was fast during the first few hours and equilibrium was practically attained after 24 h. pH was the dominant factor affecting leaching and for values 3 and higher less than 1% of the metal was leached out while at pH=1 up to 20% of the lead initially present on the solid was leached out. At 1.5 and 2, lead was re-adsorbed after initial leaching. % leaching after 24h was found to increase with increasing initial load (17 to 44% for 15 to 100 $mgPb^{2+}/g_{clin}$). Agitation rate (50-180 rpm) and particle size (1.4-2 mm and 5-6 mm) did not affect leaching. Higher temperature (25-40 °C) resulted in increased leaching rates. Despite the limited number of data, leaching seems to follow third-order kinetics. Finally, exposure to acid conditions increased markedly the specific surface (from 35.1 to 79.4 $m^2 g^{-1}$) and lowered the average pore diameter (from 80.8 to 42.9 Å) of the clinoptilolite particles.

KEYWORDS: clinoptilolite, lead, leaching, acid treatment.

1. INTRODUCTION

Heavy metals are well-known and wide-spread pollutants of surface waters, due to their use in various industrial processes and ultimate discharge to the environmental systems of air, water and land. Their severe toxicity imposes treatment of wastewaters, before safe disposal. Heavy metal removal from wastewater is usually practiced through physicochemical processes. Ion exchange is actually one of the most widely used methods for low metal concentrations. Natural and synthetic materials are used in such processes, either in batch mode or in flow-through systems, depending on the specific case. Synthetic materials have many advantages, namely a pre-designable selectivity in cases of the simultaneous presence of many ions. They are however high-cost materials and therefore regeneration is usually applied. On the other hand, natural materials such as zeolites and clays are abundant, in exploitable deposits, and low-cost. They have however varying structures, and therefore their properties and metal removal effectiveness cannot be estimated without pilot tests. Zeolites are eventually being modified prior to application, in an attempt to produce a solid with more exchangeable sites. This pretreatment might be cost-effective since they can be used during several metal removal cycles, with intermediary regeneration.

Clinoptilolite is a natural zeolite widely used in environmental applications, namely for the removal of NH_3 , Pb^{2+} , Hg^{2+} , Cd^{2+} , Zn^{2+} etc from aqueous solutions (Tsitsishvili *et al.*, 1992). The adsorption/ion exchange of these substances on clinoptilolite has been extensively studied, regarding kinetics, equilibrium and selectivity (Inglezakis *et al.*, 2002). Selectivity order has been obtained in complex mixtures and in several operation schemes and the following orders are proposed for Na-clinoptilolite, which shows best ion exchange potential:

$Pb^{2+} > Ag^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Na^+$, $Pb^{2+} > NH_4^+ > Ba^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$ (Kesraoui *et al.*, 1994; Blanchard *et al.*, 1984).

On the other hand, used clinoptilolite, loaded with heavy metals, is usually being disposed, being a low-cost material for which regeneration is not cost-effective. Used clinoptilolite is eventually incorporated into cement together with nuclear wastes (Atkins *et al.*, 1995), into sewage sludge compost (Zorpas *et al.*, 2002) or land-deposited. The stability of such metal-loaded zeolites is then of environmental importance, since eventual heavy metal leaching into surface or groundwater may constitute an environmental hazard.

Clinoptilolite is known to attract metals, which are not expected to leach out at neutral and alkaline conditions. The only possibility for leaching is during contact with acid solutions, as for example acid rain or acid leachates from industrial and municipal landfills. Acidity is known to influence heavy metal removal since H^+ can be considered as competitive cations in ion exchange processes (Inglezakis *et al.*, 2003). Zeolites may also absorb H^+ in salt solutions of almost neutral acidity (Charistos *et al.*, 1997). Standard procedures have been developed to evaluate potential metal leaching from solids. The most widely used is the Toxicity Characteristic Leaching Test (TCLP 1311) from EPA/RCRA. Other tests available are EPA Methods 1310, 1320 and DIN 38414-S4. The tests are based on the contact of the solid to be evaluated with acids (acetic, nitric/sulfuric) or with deionized water for 18-24 hours, eventually with repeated contact cycles, at 20-40°C, at pH between 2,88 and 5 (U.S.E.P.A. 1986; 1992; 2004; DIN 3841-4, 1984).

In the present study the leachability of lead (Pb^{2+}) from natural clinoptilolite, batch-loaded with lead, was investigated according to the above stated standard procedures. In a next step, the influence of pH, initial load of lead in clinoptilolite, agitation rate, temperature and particle size on kinetics of lead leaching was studied. In order to check uniformity of lead dispersion in the loaded particles, scanning electron microscopy with simultaneous chemical analysis (SEM-EDAX) was used. Finally, the influence of acid treatment during the loading-leaching cycle on specific surface and average pore diameter of clinoptilolite was checked by nitrogen porosimetry (B.E.T).

2. MATERIALS AND METHODS

2.1. Experimental procedure

2.1.1. Loading process

Lead loading of clinoptilolite of various particle sizes was performed in a batch reactor. 10-50 g of solid were added to 5 L of lead solution at 500-5000 ppm Pb^{2+} , stirred at 600 rpm at ambient temperature for 3-7 hours. pH was adjusted to 4 in order to avoid Pb precipitation. Then the mixture was left to equilibrate for 24 h – 8 days. Clinoptilolite was separated by filtration and the remaining Pb^{2+} was measured in the supernatant.

2.1.2. Leaching tests

For the leaching tests, clinoptilolite samples loaded with lead as above were brought into contact with deionized water or acid solutions (HNO_3 , HCl, HNO_3/H_2SO_4 and CH_3COOH) and kept at 30°C at a thermostated bath under agitation (80 rpm). Ratio of solution to solid was 16 ml g^{-1} . If necessary, solution pH was monitored at the desired value. During the test, solution samples were taken and Pb^{2+} was measured in order to study kinetics. After 24 h, clinoptilolite was separated by filtration and the remaining Pb^{2+} was measured to check equilibrium. For the EPA 1320 method, the solution/solid ratio was 20/1 and the whole procedure was repeated 5 times. In the second group of experiments, clinoptilolite samples, of various particle size, loaded with lead, were brought into contact with nitric acid at various pH values, and kept at 25-40°C under 140 rpm (unless stated otherwise) for time intervals between 10 min and 24 h (unless stated otherwise). Clinoptilolite was separated from the supernatant by filtration and the Pb^{2+} present in solution was measured.

2.1.3. Materials and analytical procedures

The mineral used was collected from a deposit in the northern part of Greece (Skaloma, Thrace). It was ground and then sieved to different fractions of which 1.4-2 and 5-6 mm were used in the study. The samples were thoroughly washed with deionised water prior the ion

exchange experiments in order to remove the surface dust. The chemical composition of the material was determined by SEM/EDS (scanning electron microscopy) measurements, using the model JSM-6100 of Jeol Scanning Microscope. Furthermore, X-ray diffraction measurements using XRD diffractometer (D500 of Siemens) and N₂ porosimetry measurements (BET) using QUANTA CHROME NOVA 2000 series model were performed. Lead was measured in the supernatant with Atomic Absorption Spectrometry (Perkin Elmer model 350B spectrophotometer equipped with a Photron Pb Hollow Cathode lamp).

Lead nitrate of analytical grade (SERVA) and HNO₃, HCl, H₂SO₄ and CH₃COOH (Merck) were used.

3. RESULTS AND DISCUSSION

3.1. Clinoptilolite characteristics

The chemical analysis of the completely dehydrated clinoptilolite samples is reported in Table 1 below (Elaiopoulos *et al.*, 2005).

Table 1. Chemical composition of natural clinoptilolite

Oxide	% w/w
SiO ₂	75,0
Al ₂ O ₃	12,6
K ₂ O	2,9
CaO	2,6
Fe ₂ O ₃	0,9
Na ₂ O	0,7
MgO	0,6
Other	4,6
Si/Al ratio	5,1

In Figure 1 the XRD diagram of the sample is reported.

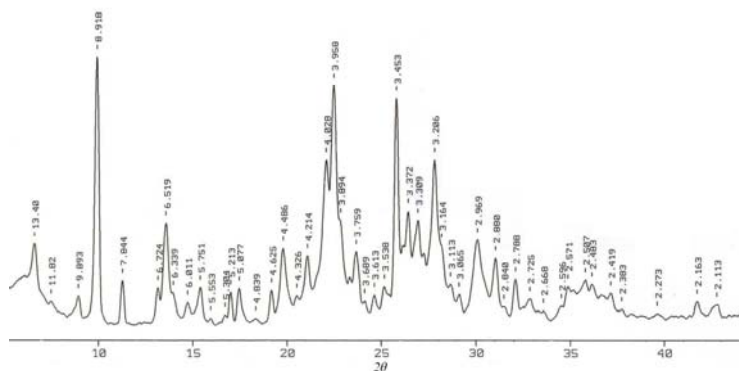


Figure 1. XRD diagram of natural clinoptilolite

It can be deduced that the main mineral component belongs to the clinoptilolite/heulandite group ($d=8.918$ Å, $d=3.950$ Å) mixed with mordenite ($d=3.453$ Å, $d=3.206$ Å). The presence of cristobalite ($d=4.028$ Å), moskovite ($d=9.893$ Å), smectite and feldspar was also assessed.

3.2. Lead sorption on clinoptilolite

The critical parameter for metal loading was proved to be the ratio $\text{mgPb}^{2+}/\text{g}_{\text{clinoptilolite}}$ in the contact solution. Sorption was fast during the first few hours and equilibrium was practically attained after 24 h. The loaded samples had $12\text{-}103 \text{ mgPb}^{2+}/\text{g}_{\text{clinoptilolite}}$. SEM/EDAX analysis was used on a particle cross-section and representative images are given below in Figures 2a and b.

It can be clearly seen that metal loading on the surface of the solid follows the progressive-conversion model (Levenspiel, 1998) and the samples used further for leaching experiments can be considered as uniformly loaded.

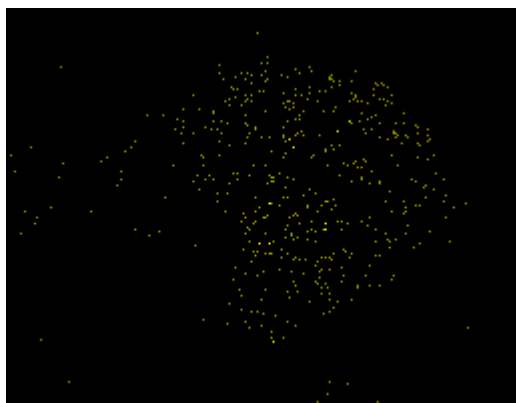


Figure 2a. Lead “spots” after 4 h impregnation time

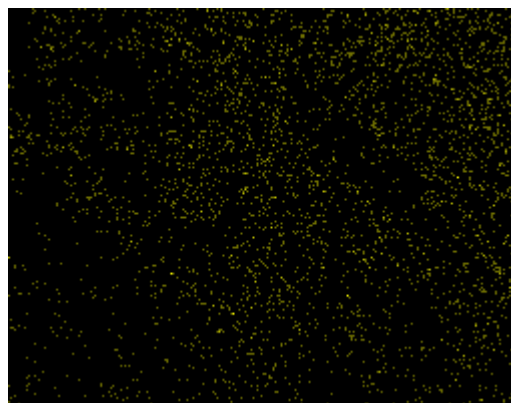


Figure 2b. Lead “spots” after 4 days impregnation time

3.3. Standard leachability tests.

The samples used contained typically $30 \text{ mgPb}^{2+}/\text{g}_{\text{clinoptilolite}}$. In Table 2 the test conditions are reported together with the experimental results, while in Figure 2 typical leaching evolution vs. time is presented.

% leaching was calculated according the equation

$$\% \text{ leaching} = \frac{\text{mgPb}^{2+} \text{ lost by clinoptilolite}}{\text{mgPb}^{2+} \text{ initially loaded on clinoptilolite}}$$

Table 2. Experimental conditions and results for the standard leachability tests.

pH	acid	test	% leaching
1.0	HNO ₃		22.6
1.5	HNO ₃		5.1
2.0	HNO ₃		3.5
3.0	HNO ₃		0.84
4.0	HNO ₃		0.045
1.0	HCl		18.7
3.0	HNO ₃ /H ₂ SO ₄	EPA 1320	1.07
3.0	CH ₃ COOH	EPA 1311	1.65
4.0	CH ₃ COOH	EPA 1311	0.424
5.0	CH ₃ COOH	EPA 1310, 1311	0.053

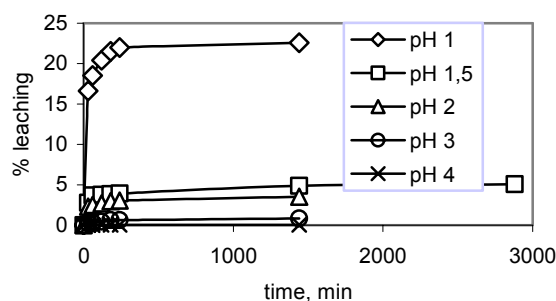


Figure 2. Time evolution for lead desorption from 1.4-2 mm particles

Lead solubilization experiments were also performed with water (tap or deionized) at 30°C for 24 h (DIN 38414-4), and in all cases less than 0.02% of the metal initially loaded was

detected in the solution. According to the experimental data, it can be deduced that lead practically is not leached from clinoptilolite, except for strong acid solutions (pH=1).

3.4. pH effect on leaching

The influence of solution pH on lead leaching from clinoptilolite was further investigated at 40°C and the results are reported in Figure 3.

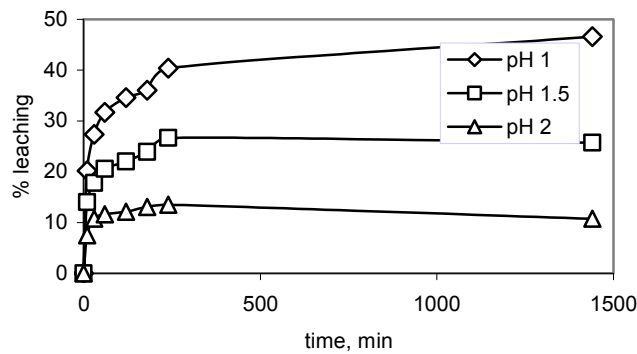


Figure 3. pH effect on desorption at 140 rpm, 1.4-2 mm particles, 28 mg Pb²⁺/g_{clin}

It can be seen that after a short-time-ion-exchange between H⁺ and Pb²⁺ ions, equilibrium is shifted towards Pb²⁺ re-uptake and the effect is more pronounced for higher pH values. This could probably be due to the known strong preference of clinoptilolite for lead, but further investigation is needed.

3.5. Initial metal load on leaching

Higher initial lead loading results in lower % leaching, of the same order of magnitude, as can be seen in Figure 4.

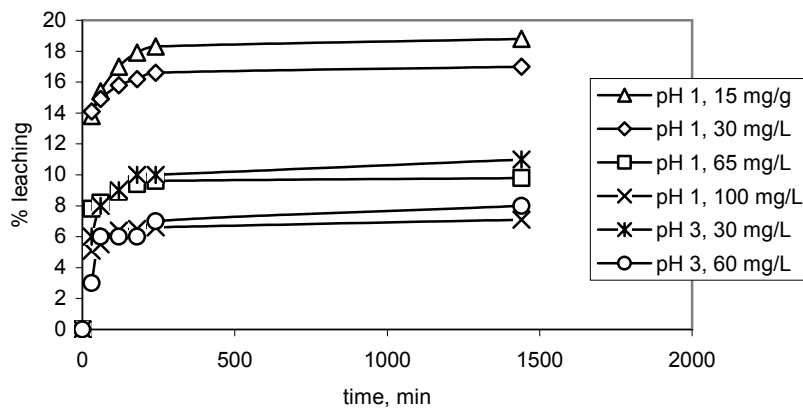


Figure 4. Initial load effect at 140 rpm, 1.4-2 mm particles, pH 1-3

3.6. Temperature effect on leaching

In Figure 5 experimental results are reported for different temperatures at various pH values. As it can be seen, temperature initially increases the rate of lead leaching, as theoretically expected. After some time however, as already stated, at "high" pH values lead is re-adsorbed, resulting in lower leaching values and this effect is more pronounced for increasing pH values.

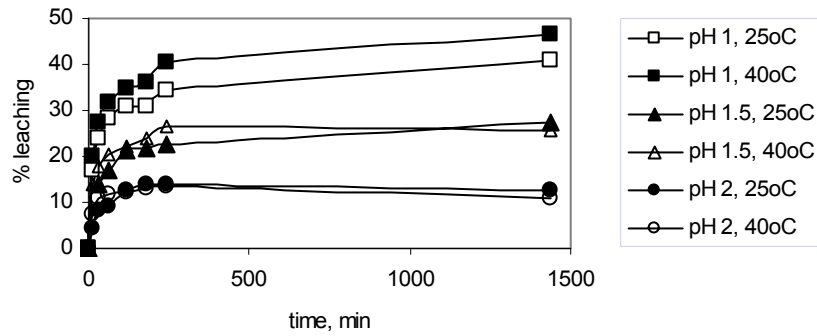


Figure 5. Temperature effect at 140 rpm, 1.4-2 mm particles

3.7. Particle size and agitation rate effect on leaching

After sieving, clinoptilolite fractions of 1.4-2 mm and 5-6 mm, loaded with the same amount of lead were compared for leaching and the results are presented in Figure 6. It can be seen that, within experimental error, no effect can be depicted on both kinetics and equilibrium.

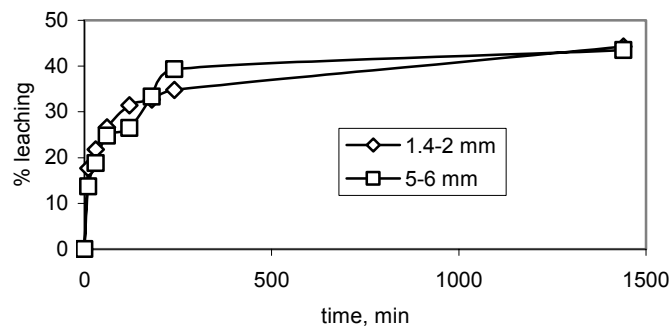


Figure 6. Particle size effect at 140 rpm, 30 mg Pb²⁺/g_{clin}

Agitation rate was varied from 50 to 180 rpm and, within experimental error, no effect could be depicted.

3.8. Kinetics of lead leaching

Kinetics was investigated using the rate model $\frac{dq}{dt} = k \cdot (q - q_{\infty})^n$, where q clinoptilolite load (meqPb²⁺/g_{clin}), q_{∞} load at infinite time (equilibrium), k rate constant and n reaction order. Few experimental data could be checked, because either equilibrium was not attained and in these cases reaction order was heavily dependent on the choice of q_{∞} , or re-sorption was evidenced and the model is clearly not applicable. There is limited evidence however that leaching follows third-order kinetics.

3.9. Acid treatment effect on clinoptilolite characteristics

The influence of acid treatment on the specific area and the average pore distribution of the solid particles were investigated and the results are reported in Table 3.

Table 3. Acid treatment effect on solid characteristics

Treatment time, h	Temperature, °C	pH	Specific surface, m ² g ⁻¹	Average pore diameter, Å
Raw material			35.1	80.8
1	40	1.5	71.1	48.4
3	25	1	75.7	41.0
24	25	1	79.4	42.9

It can be noted that acid treatment affects markedly the solid structure, resulting in an increase of specific surface and a decrease of average pore diameter, creating thus additional micropores in the solid.

4. CONCLUSIONS

From the experimental findings the following conclusions can be drawn:

- pH is the dominant factor for lead leaching from clinoptilolite
- Lead may in certain circumstances be reabsorbed on the solid particles
- Initial lead load increases %leaching
- Higher temperature results to increased leaching rates
- Acid treatment increases specific surface and lowers average pore diameter.

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