



Effects of the buffering capacity of the soil on the mobilization of heavy metals. Equilibrium and kinetics



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HIGHLIGHTS

- Aqueous Pb concentration can be obtained from the pH value and equilibrium models.
- For the same amount of acid, the pH is lower when the acid addition rate increases.
- The aqueous Pb/Ca and Pb/Mg ratios increase with the acid addition rate.
- Kinetic limitations affect Pb release, even when the first highlight is also true.
- The BCR results can be predicted with the equilibrium models, with new insights.

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ABSTRACT

Understanding the possible pH-buffering processes is of maximum importance for risk assessment and remediation feasibility studies of heavy-metal contaminated soils. This paper presents the results about the effect of the buffering capacity of a polluted soil, rich in carbonates, on the pH and on the leaching evolution of its main contaminant (lead) when a weak acid (acetic acid) or a strong one (nitric acid) are slowly added.

In both cases, the behavior of lead dissolution could be predicted using available (scientifically verified freeware) models assuming equilibrium between the solid and the aqueous phase. However, the experimental results indicate that the dissolution of calcium and magnesium carbonates is kinetically controlled. These kinetic limitations affect the overall behavior, and should be considered to understand also the response of the metals under local equilibrium.

The well-known BCR sequential extraction procedure was used before- and after-treatment, to fractionate the lead concentration in the soil according to its mobility. The BCR results were also in agreement with the predictions of the equilibrium model. This agreement allows new insights about the information that could be derived from the BCR fractionation analysis.

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1. Introduction

Risk assessment and feasibility studies of the techniques used for the remediation of heavy metal polluted soils should consider the possible variations of the pH value of the aqueous phase present in the soil as one of the most important variables. For instance, we can consider the acid-enhanced electrokinetic remediation (EKR), since one of the key aspects for the performance of this technique is the pH-buffering capacity of the soil, which slows or prevents the movement of the acid front and

therefore the mobilization of metals (Acar and Alshawabkeh, 1993; Alshawabkeh, 2009). Lab experiments, together with mathematical models, are used to understand and predict the behavior of the remediation techniques at the field-scale.

Local equilibrium among the chemical species present in the aqueous phase is usually assumed in most mathematical models used for the simulation of electrokinetic decontamination. In many other cases also local equilibrium is assumed between the chemical species present in the aqueous phase and the solid matrix (precipitation, ion exchange, adsorption, etc.) (Wilson et al., 1995; Vereda-Alonso et al., 2004; Garcia-Gutierrez et al., 2007; Ribeiro et al., 2007; Paz-Garcia et al., 2012a, 2012b). Obviously, it is important that this assumption is in agreement with the experimental

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results, and this should be checked out. In this paper we have explored this issue and found that even when the main contaminant behavior is in agreement with the local equilibrium assumption, some other species mobilization could behave under kinetic limitations. If this is so, the overall system is affected by these limitations, including the behavior of the main contaminant.

Among the lab experiments performed for risk assessment and feasibility studies, the Tessier et al. (1979) and BCR (Rauret et al., 2000) sequential extraction procedures (SEPs) are among the most used (Nystrom et al., 2003; Garcia-Gutierrez et al., 2007; Wang and Mulligan, 2008). It is known that the presence of carbonates and other pH-buffering compounds is relevant for this fractionation. These SEPs are used to obtain the changes in the mobility of the toxic metals after the contamination ageing (Liang et al., 2014a) or after a remediation process (Kirkelund et al., 2010; García-Rubio et al., 2011; Subirés-Muñoz et al., 2011; Liang et al., 2014b). In some cases, the BCR fractionation before- and after-remediation reveals an increase of the weak-acid soluble fraction, which is the most mobile one of BCR. This would indicate a poor performance in the risk abatement even when important removal ratios are achieved. This paper also compares the BCR experimental results for a real contaminated soil with those obtained from local equilibrium mathematical models, for a better understanding of the BCR results.

2. Experimental methods

2.1. Soil characterization

The detailed characterization of the soil samples, that were collected downstream from slag heaps located in the mining district of Linares (Spain), is given elsewhere (Villen-Guzman et al., 2014). Table 1 summarizes the main properties.

As can be seen, this soil has low organic matter content, is slightly alkaline with important carbonate content, and presents a medium–low cation exchange capacity (CEC), similar to a kaolinite. The hydraulic conductivity value is very low, in agreement with the particle size distribution results. The results for the total metal concentration are consistent with those obtained for the mining district of Linares (Martinez Lopez et al., 2008) and it can be concluded that lead is the main contaminant, with a presence clearly above the reference levels. The X-ray diffraction with Rietveld refinement, allows the quantification of 51% of the soil sample as amorphous, but, for instance cerussite (1.7 ± 0.6)% and calcite (2.0 ± 1.0)% are detected under crystalline forms, as was shown with more detail in Villen-Guzman et al. (2014). Nevertheless, from the values given in Table 1 it looks reasonable to expect most of the Pb, Ca and Mg to be present as carbonates.

2.2. Metal fractionation

The metal fractionation was performed according to the BCR method (Rauret et al., 2000). In brief, the BCR procedure uses three

sequential extractions, to obtain different fractions of each metal present in the soil: The sample is first placed in a vial and treated with acetic acid for 24 h with end over end agitation. Then the vial is centrifuged and the aqueous phase is carefully separated; the metals extracted are the exchangeable and the acid-extractable metals, that we will denominate here the weak acid soluble (WAS) fraction. The remaining solid phase is then treated with a solution of hydroxylamine hydrochloride, in a similar fashion, to solubilize the metals associated to the reducible (RED) fraction. In the third sequential step, the residue of the second step is treated with hydrogen peroxide, to obtain the oxidizable (OXI) fraction. Usually a fourth step is performed in which the residue of step three is digested with aqua regia, to obtain the residual (RES) fraction. This fourth step allows the comparison of the results obtained in each step with the total content of each metal in the soil that can be obtained by the digestion of the original soil. The metal concentration of each supernatant is determined by AAS.

2.3. Batch extraction experiments

The experimental system basically consists of a 2 L reaction vessel (with flat flange and a mechanical stirrer) that contains the initial water/soil mixture. The reactor is closed with a glass lid with flat flange and 5 ground-glass necks. The experiments are performed at lab temperature, which is maintained at $(24 \pm 1)^\circ\text{C}$.

The pH value is continuously registered by means of Hamilton pH electrode that is connected to a pH-control system, provided by Vacoquing. In this case, instead of the control of the pH value, this system is used to control the rate of acid addition.

Two PVC tubes are used: The first one protects the pH electrode from the impact of solid particles, and second one is used for sampling. These tubes also act as baffles that improve mixing, and are fitted to the ground-glass necks of the reactor lid by foam adaptors. The foam adaptors close the reactor system in a way that minimizes the exchange of gas with the surrounding atmosphere while allows a slow release of the headspace gas, once CO_2 or any other gas begins to evolve and develops a little gauge pressure.

At the beginning of an experiment, a mass of 400 g (dry basis) of soil is introduced in the reactor. Then, the reactor is closed and the system described above is assembled. The zero time of the assay starts with the addition of 1.2 L of distilled water to the reactor and turning on of the stirring system. Since that time, the pH control system feeds the acid solution at the selected value of addition rate while the evolution of the pH values is registered. Thus, the system provides a titration curve of the water–soil mixture for a given acid addition rate (pH versus moles of acid added).

At the selected experimental times a 10 mL sample was withdrawn by means of a plastic syringe. The samples are then centrifuged and the supernatant stored at a temperature below 5°C until analysis. The aqueous concentrations of Pb, Ca and Mg were determined by AAS. About 20 samples were withdrawn by the end of the assay. On the other hand, the maximum volume of acid solution added throughout each assay was between 80 and 120 mL. Therefore, the volume change is considered negligible.

At the end of each experiment, the metal concentrations and BCR fractionation are determined in the soil according to the same analytical procedures described in the soil characterization section.

Table 1
Soil properties.

Particle size distribution (%)	Sand	22 ± 2	Total concentration	
	Silt	43.96 ± 0.05	d.b (mg kg ⁻¹)	
	Clay	34 ± 2		
Specific gravity of dry soil (g cm ⁻³)		2.23	Pb	45200 ± 700
Porosity (%)		51.0 ± 1.9	Mn	2300 ± 200
Hydraulic Conductivity (m s ⁻¹)		10 ⁻¹¹ to 10 ⁻¹²	Cu	530 ± 16
Organic matter d.b. (%)		1.86 ± 0.18	Ca	34000 ± 2000
pH (distilled water) (1/1 w/w)		9.28 ± 0.01	Mg	6000 ± 400
CEC (cmol kg ⁻¹)		16.4 ± 1.0	Fe	37000 ± 2000
Humidity (%)		<2	CO ₃ ²⁻	85000 ± 1900

3. Results and discussion

3.1. Batch extraction experiments

The titration curve results for the three rates of acid addition assayed are presented in Fig. 1a, where the pH of the water–soil

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