Electrokinetic treatment in the recovery of valuable metals from waste repositories: Metal speciation and transient behaviour of metals during EK

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Abstract

This paper reports a preliminary experimental programme on the application of electrokinetic processing to two different waste materials: a mine tailings deposit and a metallurgical dust. The speciation of Pb in particular is studied as it is of particular prevalence in these materials. Based on a selective sequential extraction method the different forms of chemical speciation of the metal are identified: Pb was mainly enriched in the exchangeable fractions and in the residual fraction for the mine tailings, while for the metallurgical dust it was mainly enriched on the carbonatic phase and in the residual fraction. Both materials show similar trends with respect to the Pb concentration movement between the 2 most mobile fractions. The increase in exchangeable fraction would suggest that availability of the lead is slightly enhanced by the application of an electric field. Change in pH is identified as being a critical factor.

Introduction

The application of an electric field to remediate contaminated land, known as electrokinetics, has been used since the early 90's in countries such as the United States (Acar, Yalcin B, et al., 1995) and the Netherlands (Lageman, 1993), for the treatment of low-permeability soils containing inorganic (e.g. heavy metals) or organic (e.g. light hydrocarbons) chemical species.

A low voltage between two electrodes set in the ground induces an electric field in the soil. The acidic environment established by the electrolysis of water at the anode enhances the dissolution or desorbing of contaminants adsorbed and/or complexed on soil particles which then migrate toward the cathode by electromigration and

electroosmosis. Subsequently pH has been identified as one of the key factors controlling the mobility of metals during electrokinetics processes (Cauwenberghe, 1997, Acar, Yalcin B, et al. 1993). Moreover, the success of an electrokinetic treatment depends on the initial concentration of the chemical species and their chemical speciation, which can be determined by sequential extraction analysis (Reddy et al., 2001).

In the last ten years a few studies have been undertaken exploring the application of electrokinetic techniques on different types of material such as fly ashes, sludges and mine tailings (Guiqun Peng, 2011, Pedersen et al., 2003, Zhu et al., 2015). The studies conducted on the speciation of the metals in mine tailings and fly ashes have shown Cd, Cu, Pb, Zn, Cr, are mainly concentrated in the least exchangeable forms, and are especially present in the organic, sulphide and residual fractions (Kim and Kim, 2001).

In the aforementioned studies, the technology has been applied with the main aim to remediate the waste, whereas in this study the deposition of waste in geological repositories is not only seen as a potential source of contamination, but represents a potential source of valuable resources. Consequently, the aim is to explore the impact of the electric field on the transport, availability and extractability of such resources. In particular, the work seeks to develop an understanding of the changes to the distribution of valuable metals between the easily accessible (exchangeable or adsorbed) and the less accessible (oxidisable, reducible and residual) fractions. Whilst it is expected that the former may be transported and extracted more easily, the effect on the latter, where much of the resource may be located, is unknown.

This paper reports a preliminary experimental programme on the application of electrokinetic processing to two different waste materials: a mine tailings deposit and a metallurgical dust. The speciation of lead in particular is studied it is of particular prevalence in these materials. Based on a modified Tessier selective sequential extraction scheme (SSE) (Tessier et al., 1979, modified by Mester et al., 1998), the different forms of chemical speciation of the metals are identified: exchangeable and carbonate phase, easily reducible phase (oxides), oxidisable phase (sulphides), and residual part. The initial findings of this study demonstrate the effects of the electric field on the forms of metals present in waste materials and set the baseline to model the solid-metal interactions as a function of pH.

Materials and Methods

Waste materials

Two different types of wastes and industrial residues have been identified as candidates for this first run of experiments: a mine waste and an industrial residue. The mine waste is a mine tailing (MT) that comes from Frongoch, a former Pb-Zn mine in the Ystwyth catchment of mid-Wales. The material was collected on site in February

2015 and stored in sealed containers at 4°C to maintain its original moisture content. The industrial residue is an Electric Arc Furnace Dust (EAFD). The metallurgical dust is a by-product of the process of melting steel scrap metal in an electric arc furnace, the dust is collected from the air control system, filtered and then stored in large bags waiting to be reprocessed in other plants or disposed. The characterization of these two materials is summarized in Table 1.

Table 1: Materials characterization.

Property	MT	EADF
Particle size distribution	3% fine sand(>63μm), 91% silt (>2μm), 6% clay (<2μm)	9% fine sand (>63μm), 85% silt (>2μm), 6% clay (<2μm)
Mineralogical composition (XRD)	Quartz (SiO_2), Nimite, Sphalerite, Muscovite, Galena	Zincite (ZnO)/Franklinite ($ZnFe_2O_4$)
Specific gravity (g/cm^3)	2.911	D= 4.555
Moisture content (%)	43.35	5.30
Saturation* (S_R, %) *volume-mass	95.03	5.27
pH	5.8	10
Total Pb content at t0 (mg/kg)	53151.42	20222.49

Electrokinetic experiments

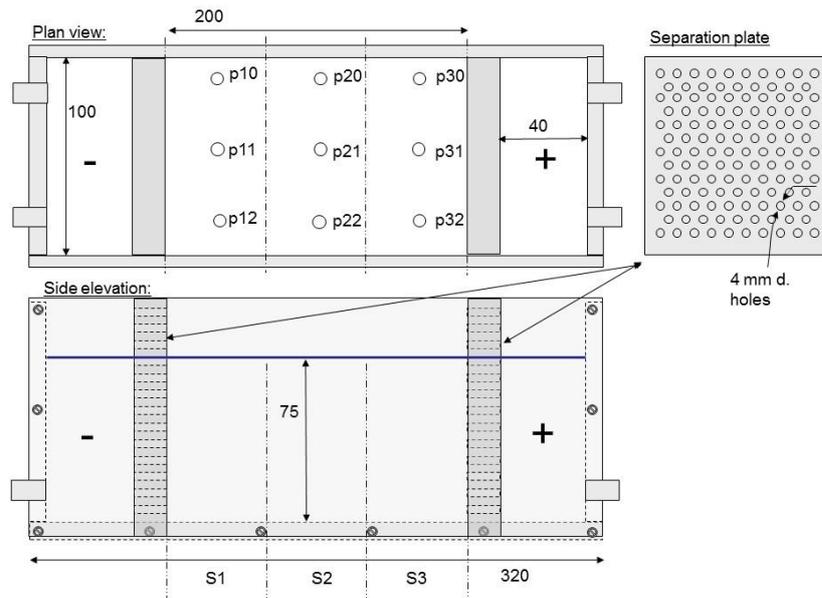Experiments were carried out in specially constructed acrylic containers, as shown in Figure 1.

Figure 1: Schematic diagram of electrokinetic cell. Dimensions in mm.

The central, 200 mm long, chamber holds the waste material, separated from electrode chambers at either end by a 10 mm thick perforated acrylic plate lined with coarse-grained filter paper. Both wastes were placed to a depth of 75 mm, corresponding to a weight of 2.75 kg of MT and 1.2 kg of EAFD, at the moisture contents quoted in Table 1. These initial experiments were performed on saturated materials. The electrode chambers were initially filled with deionized water as an electrolyte and left under a constant head for one week to ensure full saturation. Two sets of compressed graphite plate electrodes, 100 mm high 95 mm wide and 10 mm thick, were installed in the electrode chambers.

Power was supplied by a bench-top power supply (max 30 V) and current was monitored by a digital ammeter.

During testing, the pH was measured in the electrode chambers twice a day for the first week and once a day for the second week. The measurements were carried out by switching off momentarily the power supply and immersing the probe into the solution present in the electrode chamber.

A core borer of 6 mm diameter, pushed down through the whole depth of the specimen, was used to take three samples from each specimen after 0 (t0), 7 (t1) and 14 (t2) days, with the following order of position: close to the cathode, centrally, and close to the anode, as indicated on Figure 1 (the first number refers to position (e.g. p12 is close to the cathode), whilst the second refers to the time (e.g. p12 is taken at 14 days).

Selective sequential extraction (SSE) method

In order to be able to compare metal speciation among the different materials, it has been chosen to apply the same SSE scheme. The Tessier's method (Tessier et al., 1979), modified as described by Mester (Mester et al., 1998), and Forstner (FÖRSTNER, 1985), was employed. This splits Tessier's oxyhydroxides extraction into two steps: a milder reduction for manganese oxyhydroxides and amorphous iron oxyhydroxides, followed by a strong reduction of the well crystallized iron oxyhydroxides. This method is fully described by Mester et al. (1998), and is used by Dold (2003) to assess the metal speciation in mine tailing, it resembles the same scheme used by Hansen et al. (2001) with combustion fly ashes, and in MSW by Esakku et al. (2005). The scheme is presented in Table 2.

All the extractions were carried out after drying the three samples taken from each material in an oven at 105 ℃ for 2-3 hours and weighing. The extractions were performed by shaking in a mechanical shaker at room temperature. The solids were continually in suspension during the extraction.

All the extractions were carried out in 50 ml polypropylene centrifuge tubes. The extract was separated from the solid residue by centrifugation at 3000 rpm. The residue was washed by adding 10 ml of deionized water, shaking for 15 min and centrifuging. The supernatant was discarded, taking care not to discharge any of the solid residue which underwent the following step. The adjustment of pH of the extracting solution was done by adding nitric acid (2 M). The time and conditions of each extraction step are reported in Table 2.

Table 2: SSE scheme. *r.t. = room temperature. **OAc=acetate

Step	Fraction	Normal target phases	Chemical Used	Duration, temperature
1	Exchangeable, water soluble	Soluble species, CE sites.	10 ml, 1 mol l^{-1} ammonium acetate, at pH=7	2 h, r.t*.
2	Carbonatic phase	Precipitated as Carbonates	10 ml, 1 mol l^{-1} sodium acetate, at pH=5	5 h, r.t*.
3	Easily reducible	Manganese oxyhydroxides	50 ml, 0.1 mol l^{-1} hydroxylammonium chloride at pH 2	12 h, r.t*.
4	Moderately reducible	Crystallized Iron oxyhydroxides	50 ml, 0.2 mol l^{-1} ammonium oxalate, at pH=2	24 h, r.t*.

5	Oxidisable	Organic matter and sulphide	10 ml, 30% H_2O_2; once first reaction is over, 25 ml 1.0 mol l^{-1} ammonium acetate, at pH 2	1h manual shake + 3 h at 85°C in sand-bath for the extraction with H_2O_2, 16 h at r.t* with NH_4OAc**
6	Residual		HNO_3 + 2 ml HF + 2ml H_2O_2 digestion	

The extracts of the SSE from the initial time point were analysed with ICP-OES, whilst metal content in the extracts obtained from the SSE at time points 1 and 2 were analysed using x-ray fluorescence (XRF; X-5000 Olympus XRF analyser calibrated for liquid samples). The XRF analysis gives an immediate and fast response for the chemical composition, resulting in an extremely useful tool while running the experiment. The samples have been consequently tested via ICP-OES analysis with similar results obtained and it is these more reliable results that are presented here.

Results and discussion

Electrical performance and pH change

Initially in the MT experiment, the solution in both electrode chambers had a pH of 4. During the following 7 hours a rapid increase in pH (to pH 9) was observed in the cathode chamber, and a concomitant decrease (to pH 2) was observed in the anode chamber. Thereafter the pH changed more slowly and by the end of testing had increased to 10.7 in the cathode chamber and decreased to 1.8 in the anode chamber. Also over time a layer of orange precipitate was observed to form at the bottom of the cathode chamber. The rise of pH at the cathode end could cause precipitation of metals not only in the electrolyte solution but also within the solid sample matrix. In order to avoid this a pH control system could be implementing flushing the cathode with an acid solution (Rojo et al., 2006). At first in this experiment pH control was attempted, adding dilute hydrochloric acid (HCl 1M) to lower the pH. However after an initial drop to 6 the pH quickly returned to 9 in just 3-4 hours and so pH control was discontinued.

With EAFD the initial electrolyte pH was 11.5. PH then gradually increased in the cathode compartment (to pH 14.2) and dramatically decreased in the anode compartment, dropping to 2.5 in the first 12 hours and then 1.6 after two weeks. As with MT a pH control system was attempted, but even using a higher concentration of HCl in the cathode solution did not significantly affect the pH of the latter.

In MT waste the current dropped from 5 mA initially to 1.1 mA with a constant voltage of 31.4 volts. With EAFD, the material appeared to have a much higher conductivity and it was possible to set a constant current of 16 mA (requiring an increase in applied potential from around 5 to 15 Volts).

With an increasing presence of precipitates in the cathode compartment and in the holes of the separator plate in the MT experiment, a daily operation to clean the clogging holes with a very small rod was carried out during the last 7 days. After every cleaning operation a rise in current was noticed.

Sequential extraction

The variation in concentration of Pb within the MT and the EAFD is investigated in terms of its speciation before, during and after the electrokinetic treatment, as shown in Figures 2-3. The total Pb content at t0 is presented in Table 1 while in figures 2-3 the Pb distribution relative to the initial measurements made at day 0 is presented.

The initial characterization of metal speciation at t0 in MT, shows the presence of Pb for more than 50% in the easily extractable fractions (f1+f2) and from 20% to 35% in the residual fraction. This represents a favourable condition for the application of an effective EK treatment with a positive removal efficiency. Regarding the distribution of Pb in EAFD, the results of the SSE show a more complex and distributed situation, where the dominant fraction is represented by f2, acetic acid extractable fraction with approximately 30 to 40%, followed by the residual, between 20% and 30% and the remaining fractions (f1, f3 and f5) equally distributed around 10-15%. As a result, EK should have its highest impact on the f2, given the development of an acidic environment.

These preliminary results do not show significant variation over the relatively short period of the experiment in terms of overall removal efficiency, but they highlight an internal spatial re-distribution and a partial re-distribution between fractions.

Regarding MT, even though the recovered Pb concentrations in the electrolyte solution were very low relative to the total amounts present, an overall small decrease (5%) in Pb concentration in time can be observed in Figure 2.The trend is reflected by a decrease in Pb content over time in the carbonatic phase which was observed to correspond to an increase in the lead content of the exchangeable phase. The graph suggests the removal of Pb from the cathode end during the first week followed by a slightly reverse behaviour in week 2. The results from the second week suggest that Pb is moved by electromigration towards the cathode, but the intermediate data is more difficult to explain. It may be that competing mechanisms such as reversed electroosmotic flow and re-precipitation in high pH environment could play a role, but the likely natural variability in Pb distribution may be significant. This would suggest that availability of Pb is slightly enhanced by the application of the electric field mainly

due to the formation of a very acidic environment at the anode end (pH of the electrolyte = 2) that enhanced the dissolution and migration of the metal, although further work is needed to confirm this.

Regarding the EAFD, an overall increase in Pb concentration in time (18%) is found which could be the consequence of high spatial heterogeneity of the material composition, however the internal trends can still be investigated. Comparing the values at t1 to the ones at t0, an apparent decrease of Pb from the exchangeable fraction can be noticed and addressed as "first flush" of the easily removable fraction. However, there is a noticeable difference in behaviour from the material close to the cathode and that present in the central and anode sections. In the two sections closer to the anode, in the 2 most mobile fractions we can see a trend during the second week that shows a gradual decrease in time of concentration of Pb in the carbonatic phase with a contemporary increase in the exchangeable form. This was not observed in the material close to the cathode. Again, there are suggestions of transfer of lead between fractions enhanced by the decrease of pH of the electrolyte solution, but these need further confirmation.
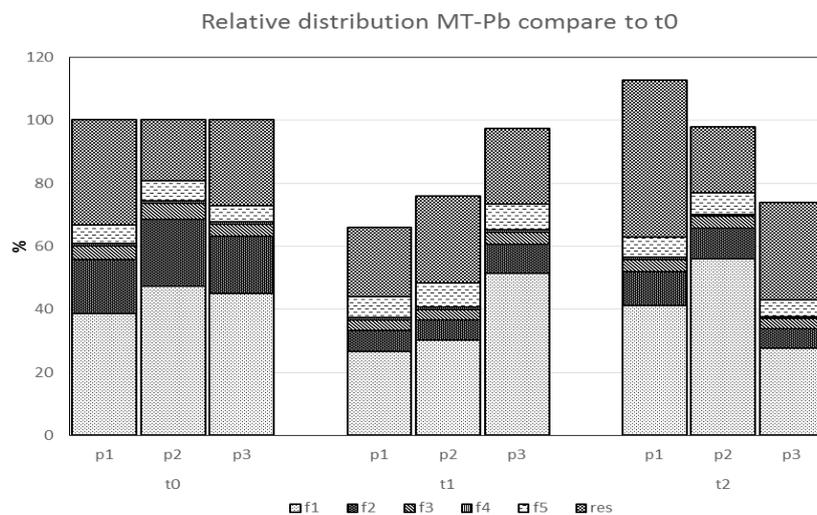

Figure 2: Variation and distribution of Pb concentration in the MT amongst 5 different fractions versus time in the 3 different positions (p1, p2, p3) relative to the concentrations in t0.
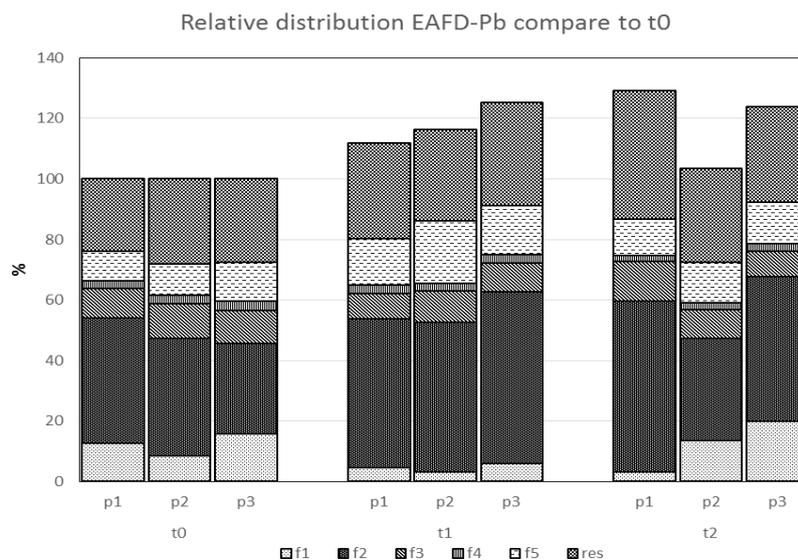
Figure 3: Variation and distribution of Pb concentration in the MT amongst 5 different fractions versus time in the 3 different positions (p1, p2, p3) relative to the concentrations in t0.

Conclusions

From these preliminary results of the electrokinetic experiment applied on the two different types of waste material (mine tailings and metallurgical dust), it is possible to make the following conclusions:

- The MT and the EAFD used in this study contained high concentrations of Pb in various chemical forms. In order to precisely estimate its forms and the actual concentrations of the metal present, the modified Tessier SSE method was used. Regarding the MT Pb was mainly enriched in the exchangeable fractions and the residual fraction. For EAFD, Pb was more distributed, but mainly enriched on the carbonatic phase and in the residual fraction.

- The applied electric field did not lead to significant movement of Pb over this short timescale, with low removal and mobilization of the Pb fractions, but there are indications of changes in Pb speciation although these will need further confirmation. In spite of the large difference in nature and composition, both materials show similar trends with respect to the Pb concentration movement between the 2 most mobile fractions (f1, f2). The apparent mobilization from carbonatic to exchangeable form and consequent transport towards the cathode would suggest that availability of the lead is slightly enhanced by the application of the electric field. Observation of the pH decrease in the electrolyte solution suggests this as the main factor.

References

1. CAUWENBERGHE, L. V. 1997. Electrokinetics.

2. DOLD, B. 2003. Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste. Journal of Geochemical Exploration, 80, 55-68.

3. ESAKKU, S., SELVAM, A., JOSEPH, K. & PALANIVELU, K. 2005. Assessment of heavy metal species in decomposed municipal solid waste. Chemical Speciation & Bioavailability, 17, 95-102.

4. FÖRSTNER, W. S. A. U. 1985. Metals in the Hydrocycle. Berlin, Heidelberg, New York, Tokyo: Springer Verlag, 349 S., 149 Abb., DM 98.—. Acta hydrochimica et hydrobiologica, 13, 267-267.

5. GUIQUN PENG, G. T., JUNZHI LIU, QIBEI BAO, LING ZANG 2011. Removal of heavy metals from sewage sludge with a combination of bioleaching and electrokinetic remediation technology. Desalination.

6. HANSEN, H. K., PEDERSEN, A. J., OTTOSEN, L. M. & VILLUMSEN, A. 2001. Speciation and mobility of cadmium in straw and wood combustion fly ash. Chemosphere, 45, 123-128.

7. KIM, S.-O. & KIM, K.-W. 2001. Monitoring of electrokinetic removal of heavy metals in tailing- soils using sequential extraction analysis. Journal of Hazardous Materials, 85, 195-211. LAGEMAN, R. 1993. Electroreclamation. Applications in the Netherlands. Environmental Science & Technology, 27, 2648-2650.

8. MESTER, Z., CREMISINI, C., GHIARA, E. & MORABITO, R. 1998. Comparison of two sequential extraction procedures for metal fractionation in sediment samples. Analytica Chimica Acta, 359, 133-142.

9. PEDERSEN, A. J., OTTOSEN, L. M. & VILLUMSEN, A. 2003. Electrodialytic removal of heavy metals from different fly ashes: Influence of heavy metal speciation in the ashes. Journal of Hazardous Materials, 100, 65-78.

10. REDDY, K. R., XU, C. Y. & CHINTHAMREDDY, S. 2001. Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis. Journal of Hazardous Materials, 84, 279-296.

11. ROJO, A., HANSEN, H. K., OTTOSEN, L. M., ROJO, A., HANSEN, H. K. & OTTOSEN, L. M. 2006. Electrodialytic remediation of copper mine tailings: Comparing different operational conditions. Minerals Engineering, 19, 500-504.

12. TESSIER, A., CAMPBELL, P. G. C. & BISSON, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, 51, 844-851.

13. ACAR, Y. B., GALE, R. J., ALSHAWABKEH, A. N., MARKS, R. E., PUPPALA, S., BRICKA, M., & PARKER, R. (1995). Electrokinetic remediation: basics and technology status. Journal of Hazardous Materials, 40(2), 117-137.

14. ACAR, Yalcin B.; ALSHAWABKEH, Akram N. Principles of electrokinetic remediation. Environmental science & technology, 1993, 27.13: 2638-2647.

15. ZHU, N.-M., CHEN, M., GUO, X.-J., HU, G.-Q. & YU, D. 2015. Electrokinetic removal of Cu and Zn in anaerobic digestate: Interrelation between metal speciation and electrokinetic treatments. Journal of Hazardous Materials, 286, 118-126.