



# Towards sustainable remediation of contaminated soil by using diasporic bauxite: Laboratory experiments on soil from the sulfide mining village of Stratoni, Greece



Ariadne Argyraki<sup>a,\*</sup>, Zoe Boutsis<sup>a</sup>, Vassilis Zotiadis<sup>b</sup>

<sup>a</sup> Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistimiopolis Zographou, 15784 Athens, Greece

<sup>b</sup> Edafomichaniki S.A., Em. Papadaki 19, 141 21, N., Iraklion, Athens, Greece

## ARTICLE INFO

### Article history:

Received 24 July 2016

Revised 12 March 2017

Accepted 13 March 2017

Available online 18 March 2017

### Keywords:

Metal(oid) stabilization

In-situ soil treatment

Red diasporic bauxite

Thermal activation

## ABSTRACT

Various mineral-based amendments can be used in raw or modified form for inducing immobilization of inorganic contaminants in soil with different modes of molecular-scale sequestration. In this study, diasporic bauxite in raw form as well as after heat treatment at different temperatures (105 °C, 350 °C and 450° C) was tested for its effectiveness in reducing the mobility of potentially harmful elements (PHEs) in contaminated soil. A pot experiment was set up where raw and calcined bauxite was mixed at different proportions with contaminated soil from the sulfide ore mining village of Stratoni, north Greece. Total concentrations in soil have averages of 1000 mg/kg Pb, 712 mg/kg Zn, 6 mg/kg Cd, 2900 mg/kg Mn and 296 mg/kg As. The effectiveness of bauxite amendment was evaluated by comparing leachable PHE concentrations of treated and untreated soil after a four week period of repeated cycles of wetting and mixing. Both raw and calcined bauxite in a mixing proportion of 7% reduced leachable concentrations of the elements in comparison to the original soil. Samples that were mixed with activated bauxite (105 °C, 350 °C) and raw bauxite showed similar results. The corresponding reduction of water leachable fraction of PHEs was determined as high as 75% for Zn, 66% for Mn, 55% for Cd, 51% for Pb, and 41% for As. Extractable concentrations by the Toxicity Characteristic Leaching Procedure (TCLP) remained relatively low for Pb (60% reduction), Zn (30% reduction) and As (28% reduction). The maximum efficiency was observed by using treated bauxite at the temperature of 450 °C with negligible water leachable concentrations after treatment. This difference in retention efficiency of elements between the heat treated bauxite samples is attributed to phase transitions that occur in Al-oxyhydroxides and Fe-oxides/oxyhydroxides of bauxite when heated at higher temperatures.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Sustainable remediation of contaminated land, in contrast to traditional practices such as excavation and removal of impacted soil, requires the adoption of more efficient strategies that conserve resources and protect air, water, and soil quality through reduced emissions and other waste burdens (Hodson, 2010). The immobilization of inorganic - non degradable contaminants in soil has been suggested as a sustainable remediation method aiming in breaking the pathway between the source and the receptor in the widely used 'source- pathway-receptor' risk assessment approach. Within this framework, various mineral-based amendments can be used in raw or modified form for inducing immobilization of inorganic contaminants in-situ, with different modes of

molecular-scale sequestration within the soil matrix (e.g., Garau et al., 2007; van Herwijnen et al., 2007; O'Day and Vlassopoulos, 2010; Zotiadis et al., 2012; Almaroai et al., 2014). However, questions concerning the sustainability of soil treatment can only be addressed by long-term studies which are generally scarce, e.g. Mench et al. (2006).

Among the different natural materials that have been proposed as effective stabilization agents for metal(oids) in soil, oxides and their precursors have been extensively studied. Komárek et al. (2013) have critically reviewed literature data on mechanisms involved in the immobilization process by using iron, manganese and aluminum oxides as well as the influence of such amendments on plants and microbial population. Their conclusions underline that there is considerable elemental specificity with respect to the immobilization efficiency depending not only on the type of amendment, but also on the physicochemical characteristics of the soil. Also, they have identified research data gaps on the long term stability of the newly formed oxides in the treated soils and raised concerns

\* Corresponding author.

E-mail address: [argyraki@geol.uoa.gr](mailto:argyraki@geol.uoa.gr) (A. Argyraki).

on potential unwanted concentration increases of trace elements contained in some stabilizing amendments such as red mud and steel shot.

Bauxite, the primary Al ore, consists of a mixture of minerals including gibbsite ( $\text{Al}(\text{OH})_3$ ), boehmite ( $\gamma\text{-AlO}(\text{OH})$ ) and diaspore ( $\alpha\text{-AlO}(\text{OH})$ ), mixed with goethite ( $\text{FeO}(\text{OH})$ ) and haematite ( $\text{Fe}_2\text{O}_3$ ), the clay mineral kaolinite and small amounts of anatase ( $\text{TiO}_2$ ) and ilmenite ( $\text{FeTiO}_3$ ). It is the principal raw material in the production of alumina with a series of additional industrial uses that have been developed over the years. Studies on the potential use of bauxite for environmental applications are focused to water treatment and decontamination. Specifically, the use of bauxite has been proposed for the effective removal of anionic species such as phosphates (Altundoan and Tmen, 2002), fluoride (Sajidu et al., 2012; Lavecchia et al., 2012), Cr(VI) (Erdem et al., 2004; Baral et al., 2007) and As (Fares et al., 2009) from contaminated water and aqueous solutions. Calcined bauxite has been proven to be effective in the removal of both As(V) (Mohapatra et al., 2008) and As(III) (Bhakat et al., 2007) from water.

Concerning the treatment of contaminated soil, some studies have demonstrated the effective use of red mud, the industrial residue produced in large quantities during the extraction of alumina from bauxite, for metal immobilization (Lombi et al., 2002; Gray et al., 2006). Specifically, by employing laboratory or field scale experiments it has been shown that red mud results in a redistribution of heavy metals from soluble and exchangeable pools to the Fe, Al and Mn oxide fractions. Once heavy metals are specifically sorbed onto these oxide surfaces, potentially they may become irreversibly fixed as a result of several mechanisms, including migration of metal into micropores on the surface of the oxides, solid state diffusion of ions into the crystal lattice of the oxides, or perhaps occlusion of metals (Gray et al., 2006 and references therein). Red mud specific chemisorption and metal diffusion into the lattice of Fe and Al oxides combined with the effective raise in soil pH after amendment has been suggested as probable mechanisms responsible for the fixation of metals (Lombi et al., 2002). The effectiveness of synthetic  $\text{Al}(\text{OH})_3$  and  $\text{FeOOH}$  for decreasing the water-extractable fraction of As in contaminated soil from mining activities has also been demonstrated in lab-scale experiments (García-Sánchez et al., 2002). However, to the best of our knowledge, bauxite ore has never been tested as a mineral based amendment for immobilization of metal(oid)s in contaminated soil despite its favorable mineralogical-geochemical characteristics and relatively low cost.

The aim of this study is to assess the ability of red bauxite to reduce mobility and availability of a range of metal(oid)s in soil contaminated by sulfide mining and processing. In order to better understand the mechanism responsible for metal fixation bauxite was used in raw form as well as after thermal activation over a range of temperatures. We report on the changes in the mobility of Pb, Zn, Cd, As and Mn as affected by different mixing proportions of thermally activated bauxite and by mixing with bauxite calcined at different temperatures.

## 2. Materials and methods

### 2.1. Bauxite amendment and contaminated soil

The adsorbent material chosen for the present study was Greek diasporic bauxite. S&B Industrial Minerals S.A. (currently IMERYS S.A.) kindly provided the samples originating from baghouse dust collectors of the bauxite facilities at Itea, central Greece. In such facilities the major sources of dust emissions are the dryers and emissions are controlled with fabric filters; baghouse dust removal efficiencies of 99% are achievable. Dedusting of the fabric filters produces relatively fine grained bauxite material which is sorted in two fractions: a fine grained (<50  $\mu\text{m}$ ) and a coarser grained (50  $\mu\text{m}$ –1 mm). Preliminary testing of both grain sizes for the treatment of contaminated soil verified that the fine grained material was more effective for PHEs fixation and was subsequently used for the experiments of the present study without any further grinding. For heat activation, 100 g of bauxite samples

(<50  $\mu\text{m}$ ) placed in porcelain dish were heated in a muffle furnace at 105, 350, 450 and 800 °C for 4 h. After the heating period, the samples were cooled in a desiccator, and preserved in closed vessels containing silica gel during the experiments.

Contaminated soil was collected near the residential area of Stratoni mining village, at Chalkidiki, north Greece. A detailed discussion on the soil contamination and potential health concerns in this particular area is presented elsewhere (Argyraki, 2014). It is sufficient to say here that the area is the only example of active mining and processing of Pb-Zn sulfide ore in Greece. Mining operations and ore processing to produce sphalerite and galena concentrates at the Stratoni flotation plant over the last 60 years have resulted to surface soil contamination with Pb, Zn, Cd and As. A composite soil sample of 30 kg was collected from the 0–20 cm depth by mixing 5 sub-samples collected over an area of 2500 m<sup>2</sup>, air dried and sieved to <2 mm. The soil was thoroughly homogenized by manual mixing and was used to fill 1-kg polypropylene pots.

### 2.2. Soil treatment and analytical procedures

Six treatments were prepared by mixing calcined (350 °C) bauxite at different proportions (0%-control, 1%, 2%, 4%, 5% and 7%). Three additional treatments were prepared by mixing raw and heat treated (105 and 450 °C) bauxite at a proportion of 7%. All treatments were mixed thoroughly and watered with deionized water. Homogenization of treated soil was repeated on a weekly basis over a one-month period (4 weeks), in parallel with soil rewetting to maintain near-saturation soil conditions. Soil pH was monitored weekly by taking potentiometric measurements after mixing soil with distilled water at a ratio of 1 : 2.5. A final set of samples was collected at the end of the 4-week period to study the final geochemical characteristics of the treated soil against the control. Three subsamples (100 g) of each soil treatment sample were shaken by rotation in polyethylene bottles with 1000 ml of distilled water for a period of 24 h according to the standard leaching test EN 12457-2 (2002). The solids were separated by vacuum filtration through a 0.45  $\mu\text{m}$  cellulose filter. Concentrations of Pb, Zn, Cd, As and Mn in the collected solutions were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). An additional set of treated soil samples was subjected to the Toxicity Characteristic Leaching Procedure (TCLP) (USEPA, 1992) in order to examine the effect of induced acidity on the treated soil. Concentrations of the same elements as above were measured by ICP-MS. In addition to the pot experiment, 50 g of raw and calcined bauxite (350 °C) underwent four wetting cycles during the same 4-weeks time period in order to investigate any mineralogical and structural changes due to re-hydration.

The total elemental content of bauxite was determined by X ray fluorescence (XRF) while the mean concentrations in contaminated soil were measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) after total dissolution of five replicates of the collected composite field sample by using a mixture of strong acids. Mineralogical analysis of all materials used has been performed by powder X-ray diffraction (P-XRD) using a Siemens D-500 diffractometer with  $\text{Cu-K}\alpha$  radiation, and scans from 5° to 65° 2 $\theta$  with a scan rate of

**Table 1**  
Chemical and mineralogical composition of raw bauxite. (LOI: loss of ignition at 1000 °C).

Chemical composition		Mineralogical composition	
Parameter	w/w (%)	Mineral phase	w/w (%)
$\text{Al}_2\text{O}_3$	47.56	Boehmite/diaspore	21.1
$\text{Fe}_2\text{O}_3$	17.85	Diaspore	36.8
$\text{SiO}_2$	9.28	Kaolinite	14.7
CaO	4.44	Goethite	17.8
$\text{TiO}_2$	3.17	Hematite	3.4
S	0.45	Anatase/rutile	2.7
Mn	400 (mg/kg)	Calcite	5.4
Zn	89 (mg/kg)		
LOI	15.50		

**Table 2**  
Some physical and physicochemical properties of raw and heat activated bauxite.

Parameter	Raw	105 °C	350 °C	450 °C
pH	8.0			
CEC (meq/100 g)	27	27.8	NA	44.1
SSA (m <sup>2</sup> /g)	21	21	33.3	34

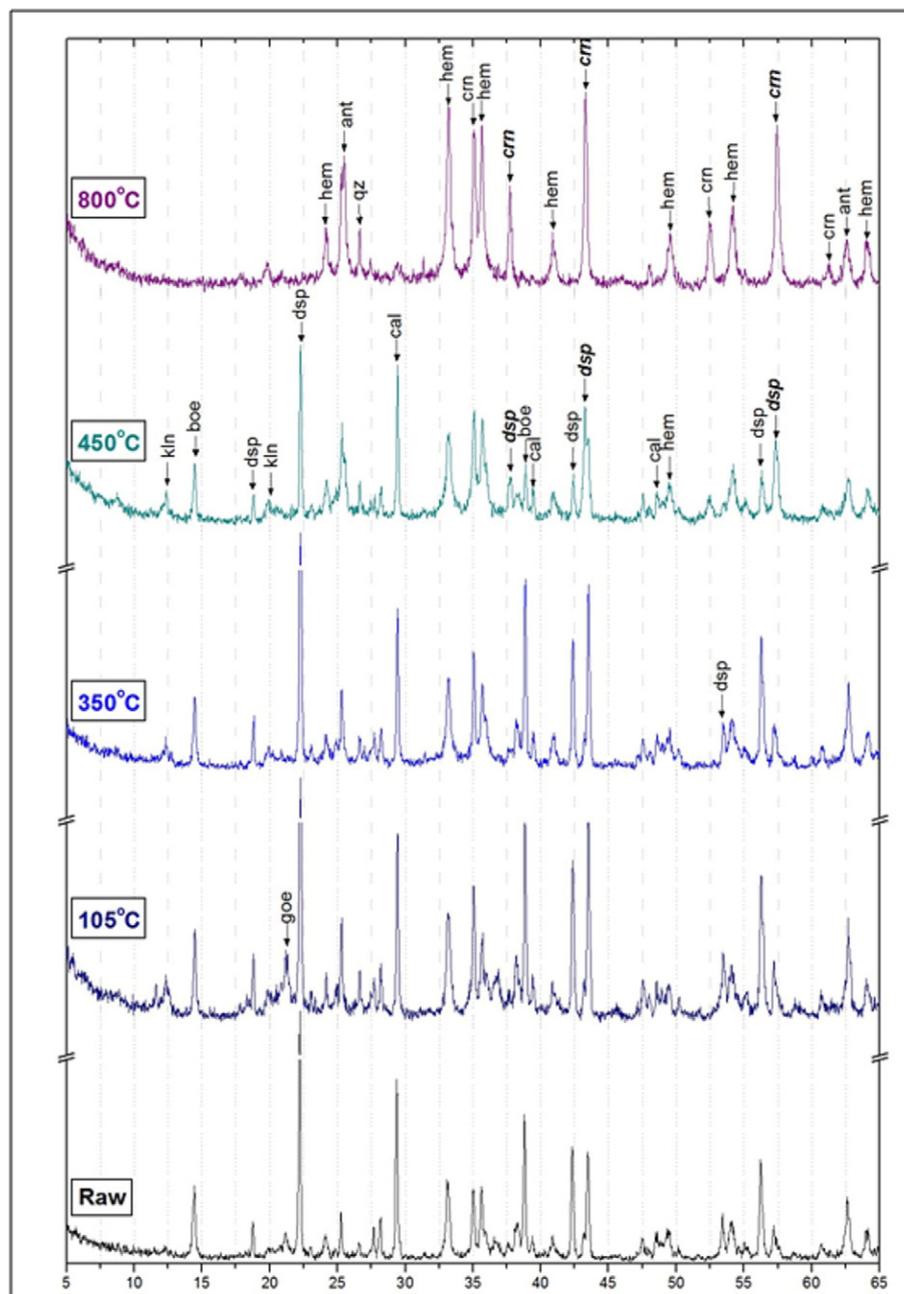
2°/min; step interval = 0.02; voltage 40 = kV; current = 30 mA. Scanning electron microscopy (SEM) and energy dispersive spectra (EDS) analysis were carried out on resin-impregnated/carbon-coated samples of bauxite and soil, using a Jeol JSM 5600 SEM instrument, equipped with an Oxford ISIS 300 micro-analytical device. Examination in the backscattered electron (BSE) mode permitted the localisation of areas where metal(oid)s were concentrated. The micro-morphology of bauxite material was examined by SEM on free- surface gold coated grains. The mineralogical study was performed at the Laboratory of Economic Geology and Geochemistry, National and Kapodistrian University of Athens. Additional bauxite characterization data were provided by

S&B Industrial Minerals S.A. These included thermal analysis (TG-DTA) diagrams for the temperature range 100–700°C, with step 5 °C/min in inert N<sub>2</sub> atmosphere, cation exchange capacity (CEC) data by using the Ag-Th method and specific surface area (SSA) measurements by using the B.E.T. method with N<sub>2</sub> as the absorbate. Physical properties of bauxite samples were determined by geotechnical laboratory tests (ASTM C136-06, ASTM D422-02, ASTM D4318-05).

### 3. Results and discussion

#### 3.1. Bauxite and contaminated soil characterization

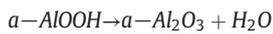
The chemical and mineralogical composition of raw bauxite is presented in Table 1 while some physical and physicochemical properties of raw and heat activated bauxite are provided in Table 2. According to Unified Soil Classification System the bauxite sample is classified as non plastic, sandy silt ( $\mu$ ). The raw bauxite sample is rich in Fe which is sequestered mainly in goethite and hematite (Table 1 and Fig. 1). P-



**Fig. 1.** XRD patterns of raw and heat activated bauxite. kln: Kaolinite, boe: Boehmite, dsp: Diaspore, hem: Hematite, qz: Quartz, ant: Anatase, crn: Corundum, cal: Calcite, goe: Goethite.

XRD data indicate that significant mineralogical changes take place at temperatures over 350 °C. Specifically, heating at 350 °C transformed goethite to hematite while the peaks of boemite and diaspore are visible up to the temperature of 450 °C. Literature data suggest that dehydroxylation of boehmite starts at 250 °C and is complete by 450 °C while the thermal decomposition of diaspore is complex (Kloprogge et al., 2002). At temperatures of 450 °C and higher, our P-XRD data indicate that dehydroxylation of Al phases leads to the formation of corundum. At 800 °C only oxide phases remain in the sample including hematite, anatase, corundum and quartz, while the peaks of kaolinite, calcite, boemite and diaspore are eliminated. It has to be noted that changes in mineralogy of the calcined bauxite sample at 350 °C were not reversible after the 4 wetting cycles, i.e. the formed hematite did not seem to gain back the lost hydroxyl units by rewetting.

Findings of P-XRD agree reasonably well with the TG-DTA patterns of raw bauxite (Fig. 2a) where two major endotherm peaks are observed. The first peak at a temperature of 260 °C corresponds to a mass loss of 2.27% and is attributed to the dehydroxylation of goethite. The second dehydroxylation maximum is observed around 438 °C. The bauxite sample loses about 4.84% of its mass up to the temperature of 486.8 °C. In the DTA graph a peak is observed at 477.2 °C and a second endotherm is observed at 499.2 °C corresponding to a 3% mass loss. In agreement with the XRD patterns dehydroxylation of diaspore may account for the observed endotherms according to the reaction:



An additional endotherm at a temperature of 686.5 °C appears in the end of the graph, possibly corresponding to the destruction of calcite and the release of CO<sub>2</sub> causing a mass loss of about 2.84%. However, since calcite transforms to CaO within a wide range of temperatures (550–900 °C) (Wu and Liu, 2012) this hypothesis can not be further

examined in the present study as the thermogravimetric analysis reached a maximum temperature of 700 °C.

No significant differences are observed between the TG-DTA patterns of raw bauxite described above and the bauxite sample previously heated at 105 °C (Fig. 2b). Thermogravimetric data of bauxite samples calcined at 350 and 450 °C present different patterns with respect to mass loss as well as temperatures of endotherm peaks (Fig. 2c–d). Specifically, the endotherm corresponding to goethite dehydroxylation is missing from both diagrams, verifying the transformation of this mineral to hematite during heat treatment as identified by XRD. A further difference between the two bauxite samples calcined in higher temperatures is apparent with respect to diaspore dehydroxylation. Although the total mass loss is the same for the two samples, dehydroxylation of diaspore starts at lower temperature (393.9 °C) and is completed at a temperature of about 564 °C for the bauxite sample previously heated to 450 °C. This is indicative of diaspore destruction within the temperature range 350–450 °C. Kloprogge et al. (2002) by combining DTA and infrared emission spectroscopy showed that the thermal decomposition of diaspore is complex and more than one mechanism of dehydroxylation is involved. According to their study it is possible that part of diaspore is converted to an amorphous alumina phase during heat treatment.

SEM microphotographs of bauxite samples are presented in Fig. 3. The pisoid texture of iron rich grains is evident in backscatter electron images (Fig. 3c–d) while microstructural differences between the heat activated samples are observed on the free-surface grain samples (Fig. 3e–h). It is well known that materials containing hydrated mineral phases can be activated by heating, which increases the porosity due to structural modifications (Mohapatra et al., 2008; Wu and Liu, 2012). With the influence of heating at 105 °C, bauxite loses the majority of its physically absorbed water. So Fig. 3f presents large particles and a high porosity, compared to a low density of raw bauxite (Fig. 3g). When calcined at 350 and 450 °C, with the decomposition of

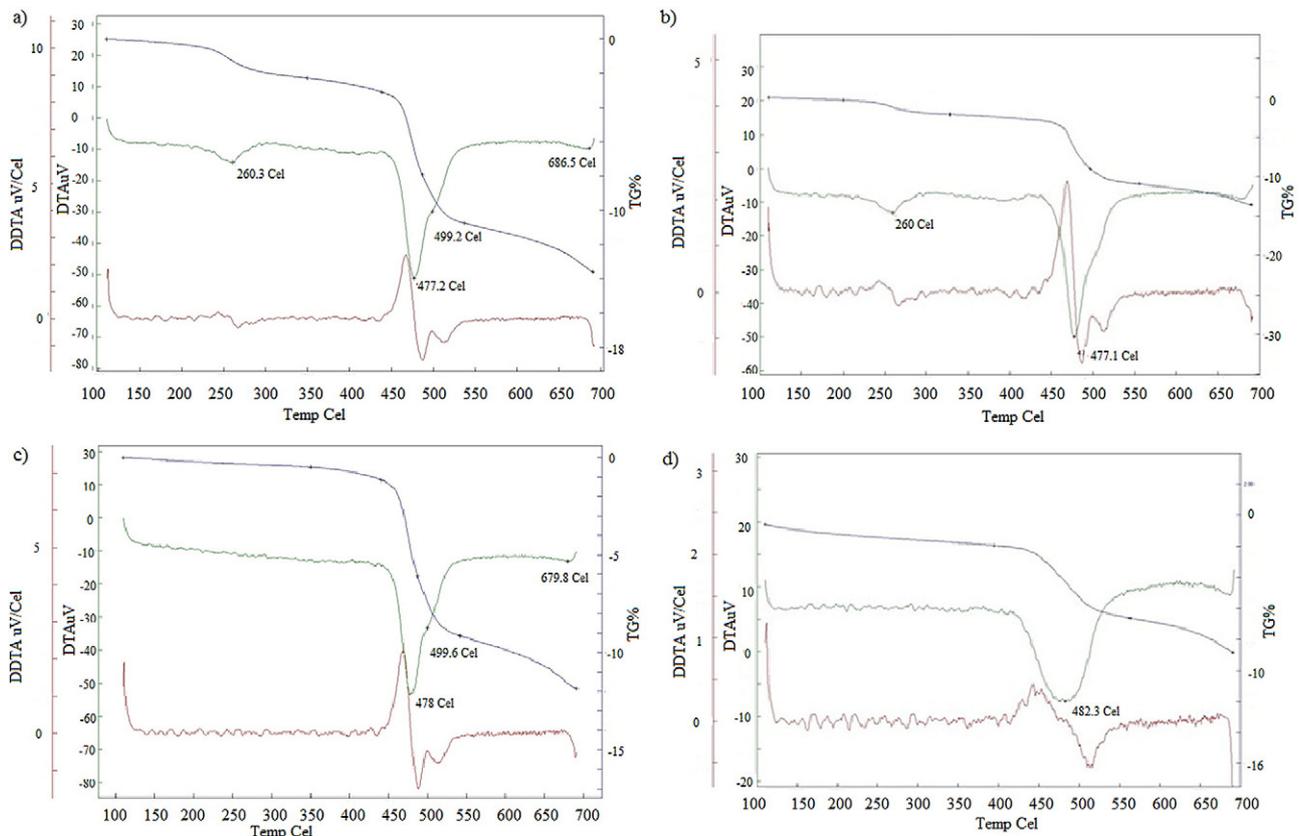
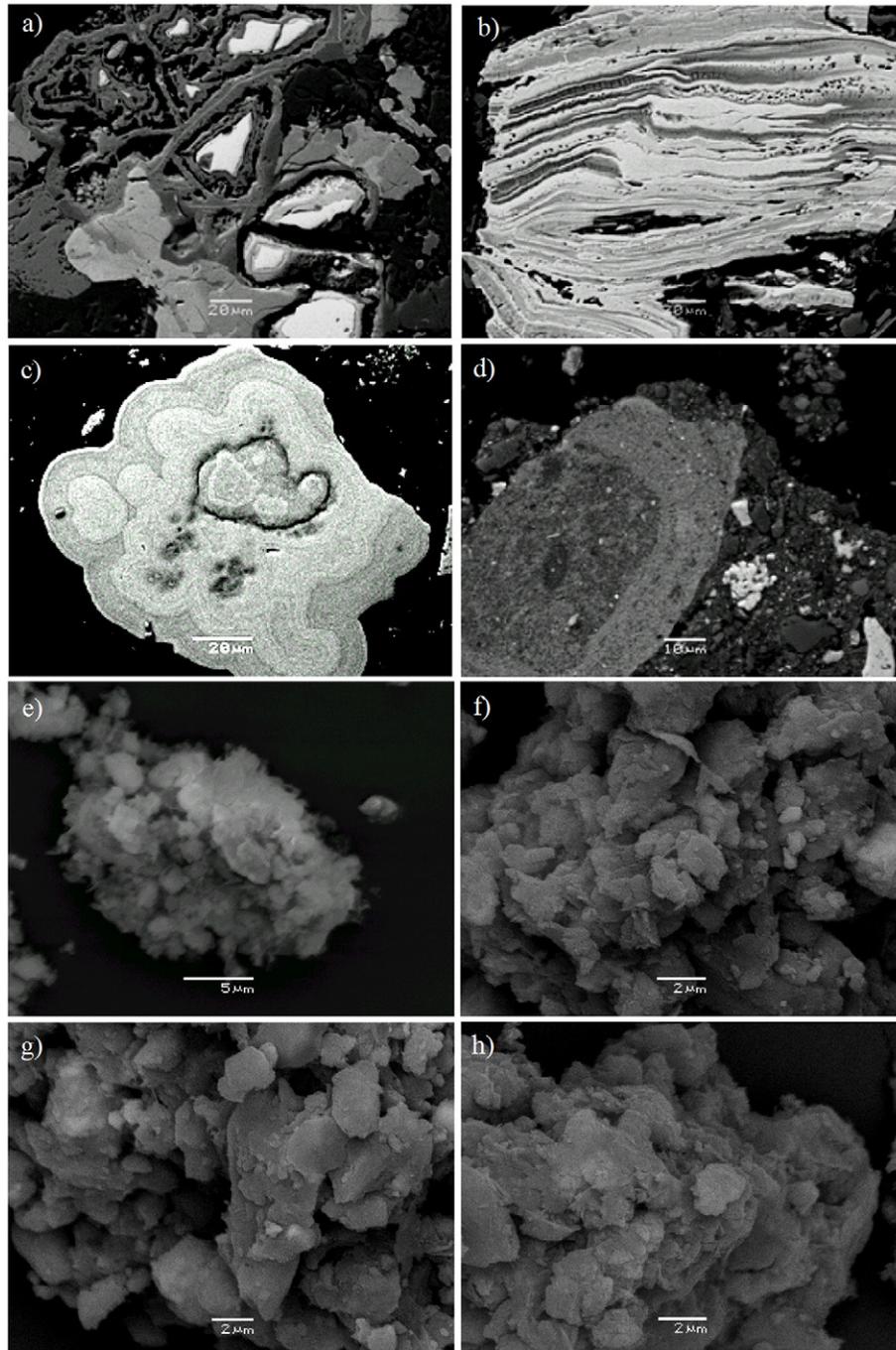


Fig. 2. TG-DTA diagrams of raw (a), and heat activated bauxite at 105 °C (b), 350 °C (c) and 450 °C (d).

Fe and Al phases, bauxite has lost almost all the chemically bound water and larger particles and higher porosity is observed. An increase in SSA with heat treatment (Table 2) was also evident in the present study. Ruan and Gilkes (1995) investigated the dehydroxylation of aluminous goethite and observed changes in unit cell dimensions, crystal size and surface area. Since bauxite is a complex, multi-mineral material Al-substitution in goethite can not be excluded. This would result in increases in de-hydroxylation temperature and excessive, non-stoichiometric OH. Some of this excess OH is inherited by hematite formed by the dehydroxylation of goethite. According to the same authors the “a” dimension of goethite and the “c” dimension of hematite are enlarged causing structural defects associated with an increase in pores which contributes to the increase in specific surface area during the thermal

transformation of goethite to hematite. Based on the above evidence, the heat activated bauxite sample at 350 °C has been selected for testing the effect of dosing during the laboratory experiment of metal(oid) stabilization in soil.

The treated soil sample had a sandy-silty texture with 64% sand, 34% silt and 2% clay by mass on average and relatively acidic pH of 4.8. Identified minerals with XRD analysis in soil comprise mainly (95%) common soil inorganic phases, such as quartz, feldspar, mica and clay minerals. The absence of calcite is noted, reflecting the predominance of silicate rocks in the area. The most abundant trace element bearing phase in soil found by SEM-EDS was Fe and Mn oxides and oxyhydroxides (Fig. 3a–b). Sulfide grains corresponding to the primary mineralization of the wider area were also identified including galena,



**Fig. 3.** Microphotographs of SEM-BSE mode of contaminated soil (a–b) and raw bauxite grains (c–d). SEM-SE mode images of raw and heat activated bauxite (e–h) showing changes in the micromorphology of grains.

sphalerite, arsenopyrite and pyrite (Fig. 3a). Total concentrations in soil have averages of 1000 mg/kg Pb, 712 mg/kg Zn, 6 mg/kg Cd, 2900 mg/kg Mn and 296 mg/kg As.

### 3.2. Water leachable metal(oid) concentrations after treatment

Changes in soil pH during the treatment period with calcined bauxite at 350 °C are presented in Fig. 4. A general increase is observed for all treatments within the first two weeks of the experiment after which soil pH values are stabilized. The increase corresponds to the increasing bauxite mixing proportion and reaches a maximum of 7.5 for the 7% bauxite treatment. It is also dependent of the wetting cycles as an increase of about one unit is observed in the control sample, possibly due to retention of H<sup>+</sup> by soil grain surfaces. The pH increase can modify the labile trace element pool in soil (Mench et al., 2006) and provide a favorable environment for precipitation of several heavy metals including Pb and Zn. The final pH measured in the filtered leachates after the application of the EN protocol ranged from 6 (control sample) to 8 (7% bauxite treatment).

Water leachable concentrations measured at the end of the experiment of applying the 350 °C activated bauxite in different proportions are presented in Fig. 5. Data of Pb and Zn show a general decreasing trend with increasing percentage of bauxite while Cd, Mn and As do not seem to respond differently to the change of bauxite dosing. In general, leachable concentrations are low and vary widely between different elements from <10 for Cd to over 5000 µg/kg for Mn. When assessed against the limit values for granular waste acceptable at landfills set by the EU Directive 3003/33/EC (Council of the European Union, 2003), a regulation based on the applied EN leaching protocol of the present study, the untreated soil meets the criteria of inert waste with the exception of Pb (Table 3). The 7%-heat activated (350 °C) bauxite treatment reduces the concentration of this element by about 50% and marginally changes the categorization of the material to inert waste.

The comparison between water leachable concentrations achieved by raw and heat-activated bauxite at different temperatures at a dosing of 7% is illustrated in Fig. 6. A significant decrease in comparison to the control sample is apparent for all treatments and all elements. However, although no significant differences are observed between the raw and heat activated bauxite up to the temperature of 350 °C, calcination at 450 °C seems to be extremely effective in reducing the mobility of all elements as evidenced by negligible water leachable concentrations after treatment (Fig. 6 and Table 3).

This difference is probably related to the mineralogical as well as structural changes induced by calcination in higher temperatures. The changes correspond to the dehydroxylation of both Fe and Al bauxite phases as discussed in Section 3.1. Dehydroxylation of diaspor which is the major Al phase in our samples shows different TG-DTA patterns for the 350 °C and the 450 °C heat activated samples. This is indicative of a gradual transformation of diaspor to corundum which involves the formation of an intermediate  $\alpha'$ -Al<sub>2</sub>O<sub>3</sub> phase containing 15–20% tetrahedral coordinated aluminum at around 400 °C, a process described by Carim et al. (1997) based on experimental data. The formation of such intermediate phase, results in the increase of surface area and promotes mineral surface reactions involving metal ions from the soil solution that may form inner or outer sphere complexes. Additional intermediate Fe-phases may form during the dehydroxylation of goethite to hematite such as protohematite (250–400 °C) and hydrohematite (>430–800 °C) (Yusiharni and Gilkes, 2012) contributing to metal(oid) retention. However, further research will be needed to get a better explanation of the higher efficiency of the process being achieved when bauxite previously calcined at 450 °C is being used. Further experiments should focus on the function of the amorphous or quasi-amorphous Al and Fe oxides being obtained by dehydroxylation of both bauxite Al and Fe hydroxides and kaolinite.

### 3.3. Extraction of metal(oid) by acidification

The effect of lowering the pH, by adding acid through the TCLP protocol, on the extraction of metals was investigated for soil treated by the 350 °C activated bauxite; the results are illustrated in Fig. 5. The acidification of the system led to a partial remobilization of most elements in soil. However, acidification had different effects for different elements. The change in solubility of Cd in response to changes in pH, was similar for the untreated and treated soil. In contrast, the extractability of Pb, Zn and As from the heat activated bauxite treatment was reduced, in comparison with untreated soil showing a general decreasing trend with increasing bauxite dosing. The opposite trend is observed for Mn where TCLP leachable concentrations in most treated samples exceeded that of the control. After acidification Zn, Cd and Mn showed at least one order of magnitude higher concentrations in the leachate compared to those estimated by the EN protocol. In contrast, the effect of acidification was not so strong for Pb and As.

The above observations provide evidence on the sequestration mechanisms of the various elements in bauxite treated soil. Indeed, Pb concentrations were systematically lower in the acidic environment for treated soil, indicating the sequestration of this element within the lattice of Fe and Al oxides and oxy-hydroxides (Lombi et al., 2002). Retention of arsenate anions by inner-sphere complexation on Fe and Al oxide and oxyhydroxide surfaces is also more effective in pH < 7 (Mohapatra et al., 2008). In contrast to Pb, Zn and Cd need higher pH values for effective retention, thus showing higher acid extractabilities. Assuming that the fraction of elements associated with carbonate phases is more easily extracted as a consequence of acidification, the higher Mn concentrations in the TCLP leachate in treated soil indicate its association with calcite in the initial bauxite sample.

Overall, the obtained results indicate that several fixation mechanisms are responsible for elemental retention by heat treated bauxite. Specific chemisorption and diffusion of Pb and As in the lattice of Fe oxides is a probable mechanism responsible for the fixation of these elements as previously suggested for the case of red mud by Lombi et al. (2002). Furthermore, for the elements showing lower acid-extractability compared with the control the fixation mechanism could be due to pH increase but also to ion exchange and precipitation or coprecipitation of metals with Al and Fe oxides. The pH increase played a dominant role in decreasing metal mobility in polluted soil for all studied elements. Still further research will be needed looking at the understanding of how pH firmly conditions the mobilization/immobilization degree of PHEs in soil.

## 4. Conclusions

The effectiveness of red diasporic bauxite as a stabilizing agent of Pb, Zn, Cd and As in contaminated soil from a sulfide mining area of

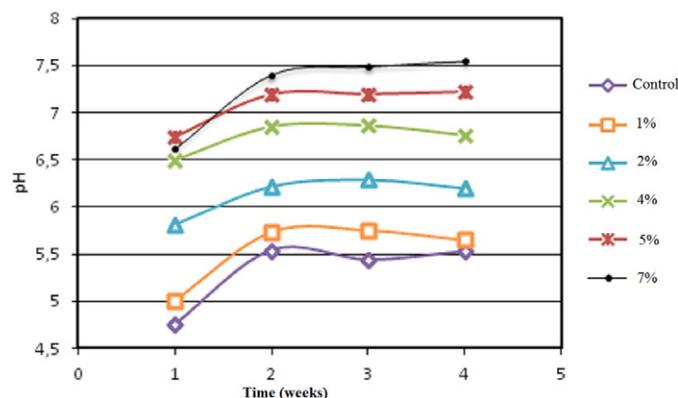


Fig. 4. Change of soil pH for mixing proportions of 0% to 7% calcined (350 °C) bauxite during the 4 week experimental period.

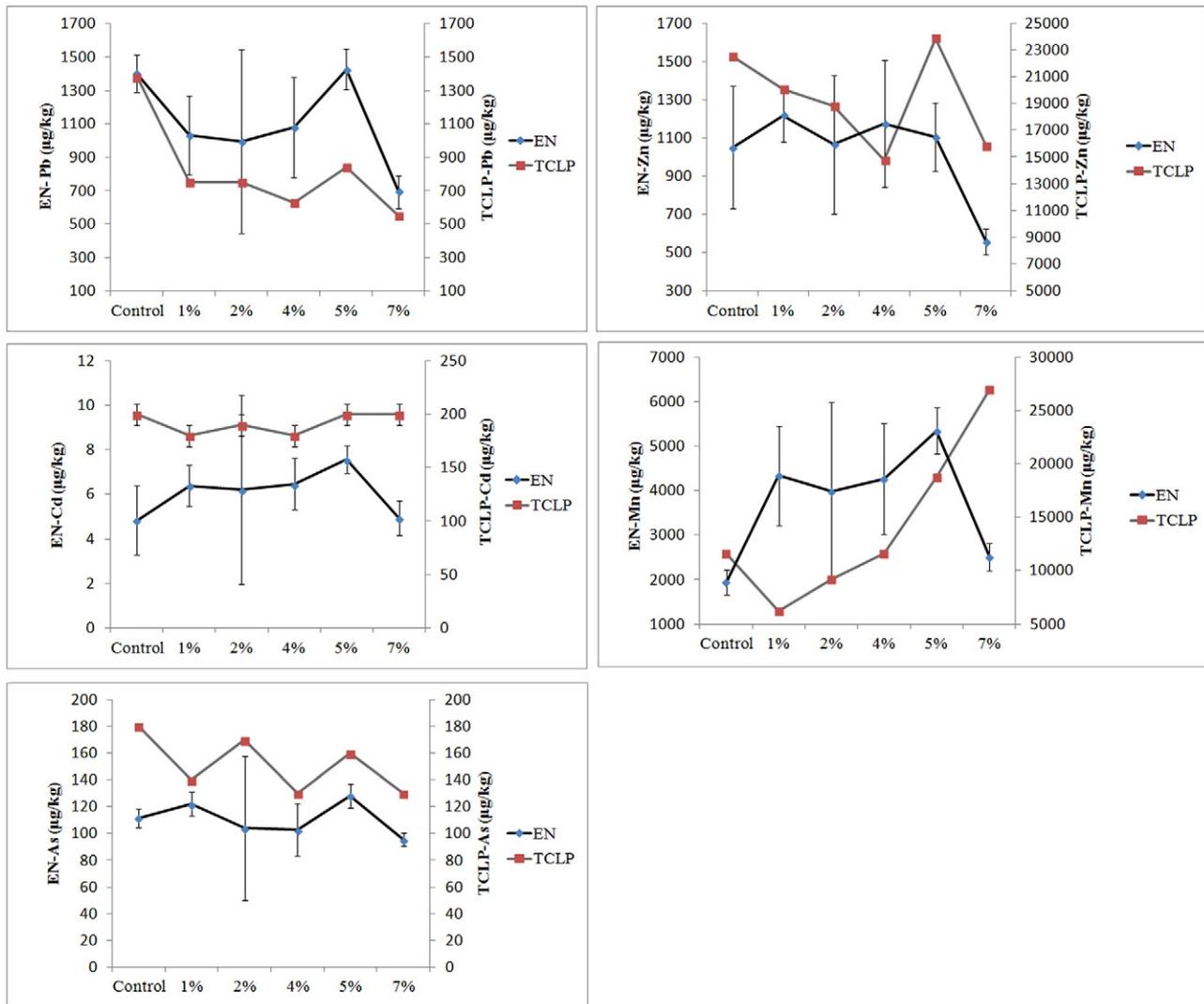


Fig. 5. Water extractable and TCLP leachate elemental concentrations in soil with increased mixing proportions of calcined (350 °C) bauxite.

northern Greece has been demonstrated in laboratory scale experiments. The utilization of fine grained (<50 µm) material produced during the dedusting of fabric filters at the bauxite ore production facility without any further treatment provides the opportunity for an innovative use of the raw material without any further production cost.

A mixing proportion of 7% raw bauxite with contaminated soil performed equally well as the heat activated bauxite at 105 and 350 °C with corresponding reduction of water leachable fraction of PHEs as high as 75% for Zn, 66% for Mn, 55% for Cd, 51% for Pb, and 41% for As. The maximum efficiency was observed by using bauxite calcined at 450 °C with negligible water leachable metal(oid) concentrations after treatment.

Mineralogical changes in bauxite during heat treatment within the range of 350–450 °C associated to dehydroxilation of both Fe and Al-rich phases lead to structural changes of the minerals resulting in higher SSA and greater efficiency for PHEs retention. The results obtained indicate that the pH increase played a dominant role in decreasing metal(oid) mobility in contaminated soil when bauxite was used. However, data from the acidification experiments showed that the fixation mechanism in bauxite-treated soil could also be due to specific chemisorption and metal diffusion into the lattice of Fe and Al oxides, such as in the instance of Pb and As, and subsequent lower risk of metal remobilization if soil pH were to decrease. Further research will be needed in order to enable the firm identification of the mechanism processes

Table 3

Water leachable concentrations of As, Cd, Pb and Zn in untreated (Control) and treated soil by 7% bauxite amendments, assessed against leaching limit values (mg/kg dry substance) set by EU Directive 3003/33/EC for granular waste acceptable at landfills for inert, non-hazardous and hazardous waste.

Element	Soil treatments					Limit values		
	Control	Raw	105 °C	350 °C	450 °C	Inert waste	Non-hazardous waste	Hazardous waste
As	0.203	0.095	0.089	0.090	0.043	0.5	2	25
Cd	0.011	0.004	0.005	0.005	0.003	0.04	1	5
Pb	1.382	0.572	0.424	0.700	0.067	0.5	10	50
Zn	2.117	0.652	0.558	0.600	0.126	4	50	200

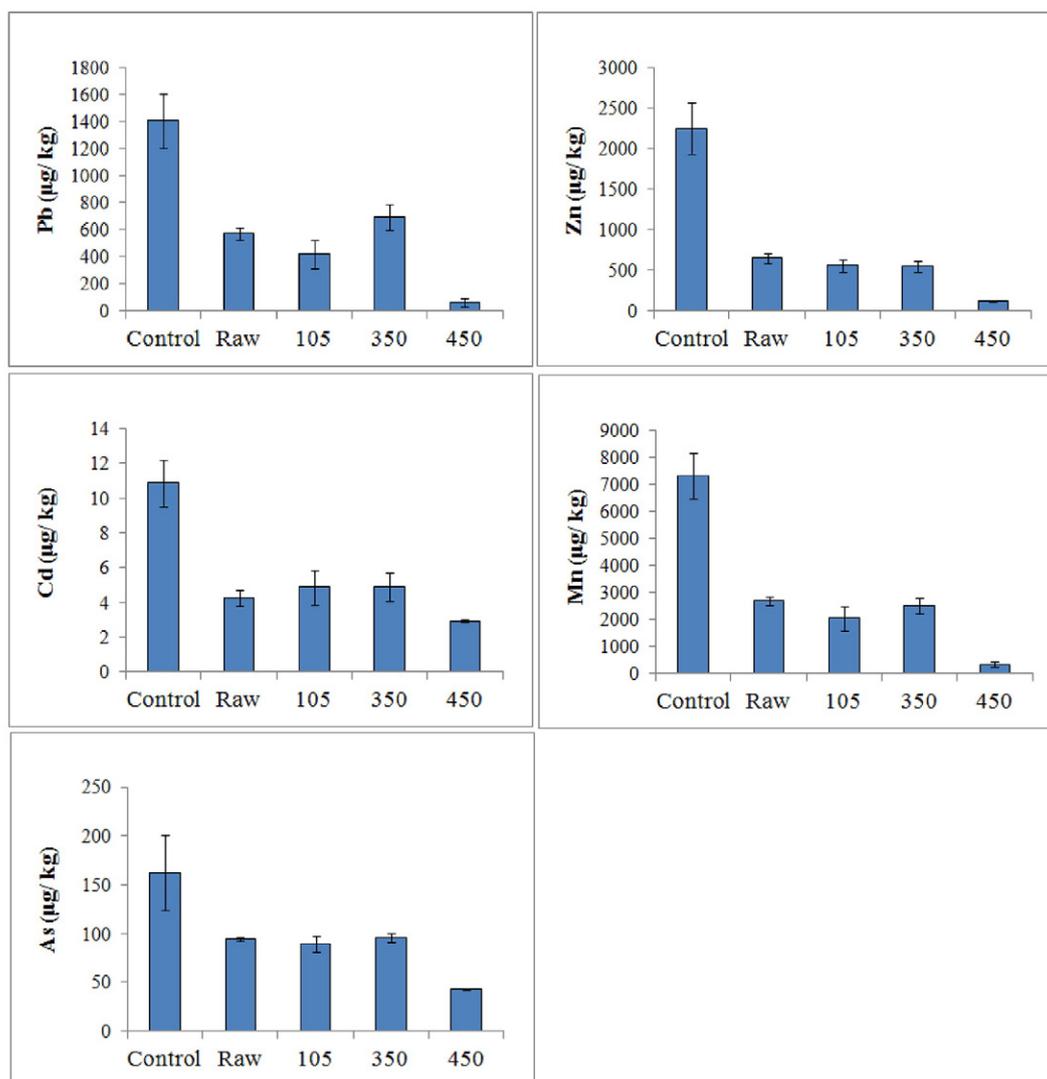


Fig. 6. Performance of raw and thermally activated bauxite amendments at a mixing proportion of 7%, in reducing water leachable metal(oid) concentrations in soil.

involved on the immobilization degree of the hazardous chemical elements existing in the investigated soil after being remediated with diaspore bearing bauxite, either in raw state or after activation through calcination.

Future work will focus on the up-scaling of the experiments in pilot field-scale areas of contaminated soil as well as the assessment of the long term stability of metal(oids) in soil after treatment. Also, further studies involving the application of bauxite amendments for treating different types of contaminated soil would contribute to the empirical knowledge of treatment performance and clarify to what extent the proposed remediation technique has to be assessed on a site specific basis.

#### Acknowledgments

This research was partially funded by Edafomichaniki S.A. (NKUA-SARG project no. 11993). The authors would like to thank Ms. Elena Ypsilanti, Ms. Rania Margariti and Ms. Antonia Ekonomakou of S&B Industrial Minerals S.A. for their invaluable help with laboratory measurements for bauxite characterization and the fruitful discussions during the project development phase.

#### References

- Almaroai, Y.A., Vithanage, M., Rajapaksha, A.U., Lee, S.S., Dou, X.M., Lee, Y.H., ... Ok, A.S., 2014. Natural and synthesised iron-rich amendments for As and Pb immobilisation in agricultural soil. *Chem. Ecol.* 30 (3):267–279. <http://dx.doi.org/10.1080/02757540.2013.861826>.
- Altundoan, H.S., Tmen, F., 2002. Removal of phosphates from aqueous solutions by using bauxite. I: effect of pH on the adsorption of various phosphates. *J. Chem. Technol. Biotechnol.* 77 (1):77–85. <http://dx.doi.org/10.1002/jctb.525>.
- Argyaki, A., 2014. Garden soil and house dust as exposure media for lead uptake in the mining village of Stratoni, Greece. *Environ. Geochem. Health* 36 (4), 677–692.
- Baral, S.S., Das, S.N., Rath, P., Chaudhury, G.R., 2007. Chromium(VI) removal by calcined bauxite. *Biochem. Eng. J.* 34 (1):69–75. <http://dx.doi.org/10.1016/j.bej.2006.11.019>.
- Bhakat, P.B., Gupta, A.K., Ayoob, S., 2007. Feasibility analysis of As(III) removal in a continuous flow fixed bed system by modified calcined bauxite (MCB). *J. Hazard. Mater.* 139 (2):286–292. <http://dx.doi.org/10.1016/j.jhazmat.2006.06.037>.
- Carim, A.H., Rohrer, G.S., Dando, N.R., Tzeng, S.Y., Rohrer, C.L., Perrotta, A.J., 1997. Conversion of diaspore to corundum: a new alpha-alumina transformation sequence. *J. Am. Ceram. Soc.* 80:2677–2680. <http://dx.doi.org/10.1111/j.1151-2916.1997.tb03171.x>.
- Council of the European Union, 2003. 2003/33/EC - Council decision establishing criteria and procedures for the acceptance of waste at landfills pursuant to article 16 of and annex II to directive 1999/31/EC. *Off. J. Eur. Communities* 27–49.
- EN 12457-2, 2002. Characterization of Waste, Compliance Test for Leaching of Granular Wastes Materials and Sludges, Part 2: One Stage Batch Test at a Liquid to Solid Ratio of 10 l kg<sup>-1</sup> for Materials with Particle Size Below 4 mm (without or with Size Reduction). European C.
- Erdem, M., Altundogan, H.S., Tumen, F., 2004. Removal of hexavalent chromium by using heat-activated bauxite. *Miner. Eng.* 17 (9–10):1045–1052. <http://dx.doi.org/10.1016/j.mineng.2004.04.013>.

- Fares, Yahay Alshaebi, Yaacob, Wan Zuhairi Wan, S., A.R., A., E., 2009. Arsenic adsorption on bauxite mineral using batch equilibrium test. *Am. J. Appl. Sci.* 6 (10), 1826–1830.
- Garau, G., Castaldi, P., Santona, L., Deiana, P., Melis, P., 2007. Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic microbial populations and enzyme activities in a contaminated soil. *Geoderma* 142 (1):47–57. <http://dx.doi.org/10.1016/j.geoderma.2007.07.011>.
- García-Sánchez, A., Alvarez-Ayuso, E., Rodríguez-Martín, F., 2002. Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soils. *Clay Miner.* 37 (1):187–194. <http://dx.doi.org/10.1180/0009855023710027>.
- Gray, C.W., Dunham, S.J., Dennis, P.G., Zhao, F.J., McGrath, S.P., 2006. Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud. *Environ. Pollut.* 142:530–539. <http://dx.doi.org/10.1016/j.envpol.2005.10.017>.
- van Herwijnen, R., Hutchings, T.R., Al-Tabbaa, A., Moffat, A.J., Johns, M.L., Ouki, S.K., 2007. Remediation of metal contaminated soil with mineral-amended composts. *Environ. Pollut.* 150 (3):347–354. <http://dx.doi.org/10.1016/j.envpol.2007.01.023>.
- Hodson, M.E., 2010. The need for sustainable soil remediation. *Elements* 6 (6):363–368. <http://dx.doi.org/10.2113/gselements.6.6.363>.
- Klopprogge, J.T., Ruan, H.D., Frost, R.L., 2002. Thermal decomposition of bauxite minerals: infrared emission spectroscopy of gibbsite, boehmite and diasporite. *J. Mater. Sci.* 37 (6):1121–1129. <http://dx.doi.org/10.1023/A:1014303119055>.
- Komárek, M., Vaněk, A., Ettler, V., 2013. Chemical stabilization of metals and arsenic in contaminated soils using oxides - a review. *Environ. Pollut.* 172:9–22. <http://dx.doi.org/10.1016/j.envpol.2012.07.045>.
- Lavecchia, R., Medici, F., Piga, L., Rinaldi, G., Zuerro, A., 2012. Fluoride removal from water by adsorption on a high alumina content bauxite. *Chem. Eng. Trans.* 26:225–230. <http://dx.doi.org/10.3303/CET1226038>.
- Lombi, E., Zhao, F.-J., Zhang, G., Sun, B., Fitz, W., Zhang, H., McGrath, S.P., 2002. In situ fixation of metals in soils using bauxite residue: chemical assessment. *Environ. Pollut.* 118 (3):435–443. [http://dx.doi.org/10.1016/S0269-7491\(01\)00294-9](http://dx.doi.org/10.1016/S0269-7491(01)00294-9).
- Mench, M., Vangronsveld, J., Beckx, C., Ruttens, A., 2006. Progress in assisted natural remediation of an arsenic contaminated agricultural soil. *Environ. Pollut.* 144 (1): 51–61. <http://dx.doi.org/10.1016/j.envpol.2006.01.011>.
- Mohapatra, D., Mishra, D., Park, K.H., 2008. A laboratory scale study on arsenic(V) removal from aqueous medium using calcined bauxite ore. *J. Environ. Sci.* 20 (6):683–689. [http://dx.doi.org/10.1016/S1001-0742\(08\)62113-0](http://dx.doi.org/10.1016/S1001-0742(08)62113-0).
- O'Day, P.A., Vlassopoulos, D., 2010. Mineral-based amendments for remediation. *Elements* 6 (6):375–381. <http://dx.doi.org/10.2113/gselements.6.6.375>.
- Ruan, H.D., Gilkes, R.J., 1995. Dehydroxylation of aluminous goethite: unit cell dimensions, crystal size and surface area. *Clay Clay Miner.* 43 (2):196–211. <http://dx.doi.org/10.1346/CCMN.1995.0430207>.
- Sajidu, S., Kayira, C., Masamba, W., Mwatseteza, J., 2012. Defluoridation of groundwater using raw bauxite: rural domestic defluoridation technology. *Environ. Nat. Resour. Res.* 2 (3):1–9. <http://dx.doi.org/10.5539/enr.v2n3p1>.
- USEPA, 1992. Method 1311 toxicity characteristic leaching procedure. SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. <http://dx.doi.org/10.1017/CBO9781107415324.004>.
- Wu, C.S., Liu, D.Y., 2012. Mineral phase and physical properties of red mud calcined at different temperatures. *J. Nanomater.* 2012 (3). <http://dx.doi.org/10.1155/2012/628592>.
- Yusiharni, E., Gilkes, R., 2012. Rehydration of heated gibbsite, kaolinite and goethite: an assessment of properties and environmental significance. *Appl. Clay Sci.* 64:61–74. <http://dx.doi.org/10.1016/j.clay.2011.12.005>.
- Zotiadis, V., Argyraki, A., Theologou, E., 2012. Pilot scale application of attapulgitic clay for stabilization of toxic elements in contaminated soil. *J. Geotech. Geoenviron.* 138: 633–637 MAY. [10.1061/\(ASCE\)GT](http://dx.doi.org/10.1061/(ASCE)GT).