

# Effect of grain size and heavy metals on As immobilization by marble particles

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**Abstract** The effect of grain size and the interaction of heavy metals on As sorption by marble waste with different particle sizes was investigated. Acidic solutions containing only arsenic and a mixture of arsenic, lead, zinc, and cadmium were put in contact with the marble waste. The amount of metal(loid)s that were immobilized was calculated using the difference between the concentration in the acidic solution and in the liquid phase of the suspensions. Approximately  $420 \mu\text{g As m}^{-2}$  was sorbed onto the marble grains, both nonspecifically and specifically, where  $\geq 80$  % of the total arsenic in the acidic solution remained soluble, which suggests that this amendment is not effective to immobilize arsenic. However, in mixed contamination, relatively stable Pb-Ca arsenates were formed on the surface of the marble particles, and the soluble arsenic was reduced by 95 %, which indicates that marble particles can effectively immobilize arsenic and lead when both appear together.

**Keywords** Waste · Marble · Specific surface area · Metal(loid)s · Sorption · Precipitation

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## Introduction

Soil and groundwater pollution by arsenic (As) is a serious environmental problem in many countries around the world (Mandal and Suzuki 2002). Stabilization of As through assisted natural remediation is a potentially reliable, cost-effective technique for the reclamation of As-polluted soils. It is widely accepted that metal oxides, particularly iron oxides, are among the most important constituents that control As mobility through sorption and co-precipitation processes (Kim et al. 2003; Bradl 2004; Drahotka and Filippi 2009), which thereby minimize the risk of environmental contamination and reduce leaching and uptake by soil organisms, crops, and humans (Hartley et al. 2004; Kumpiene et al. 2008; Hartley and Lepp 2008; Komárek et al. 2013).

The effectiveness of alkaline materials (AMs) to reduce As mobility is much more controversial. Lime and limestone, which are two of the most widely AMs used to remediate contaminated soils, primarily act by increasing both the pH values and the concentration of  $\text{Ca}^{2+}$  ions in soil solutions. In general, it is accepted that the increase in pH to values above neutrality promotes As mobility, which increases its concentration in the soil solution (Jones et al. 1997; Mench et al. 2003); however, the effect of  $\text{Ca}^{2+}$  ions has generated greater controversy. For example, Wenzel et al. (2001) concluded that  $\text{Ca}^{2+}$  ions had no significant effect on As binding, even in calcareous soils; however, other researchers have observed that lime reduces As mobility and leaching, which is most likely in response to the formation of As-Ca complexes (Bothe and Brown 1999; Hartley et al. 2004; Porter et al. 2004). Moon et al. (2004) indicated that As immobilization increases as the Ca/As molar ratio increases. However, Magalhães (2002) suggested that the As concentration in aqueous solutions in equilibrium with As-Ca complexes is too high to consider the formation of these complexes to be a feasible remediation measure.

In the case of limestone,  $\text{CaCO}_3$  might also adsorb As onto its surface. Romero et al. (2004) revealed that arsenate removal by carbonate-rich aquifer materials was attributable partly to adsorption onto calcite. Pokrovsky and Scott (2002) considered two types of sorption sites on a  $\text{CaCO}_3$  surface,  $>\text{Ca}^+$  and  $>\text{CO}_3^-$  sites, where arsenate was sorbed onto the  $>\text{Ca}^+$  sites. In arsenate-adsorption experiments, using similar pre-equilibrated calcite suspensions, Alexandratos et al. (2007) showed that corner-sharing coordination occurs between  $\text{AsO}_4$  tetrahedra and surface  $\text{CaO}_6$  octahedra, which forms an inner-sphere complex; this result suggests that calcite should be an effective sorbent for As(V). Additionally, Sørensen et al. (2008) indicated that the sorption of arsenate onto calcite can be modeled successfully by considering strong and weak sites where the sorption of two arsenate species ( $\text{H}_2\text{AsO}_4^-$  and  $\text{CaHAsO}_4^0$ ) occurs. Fernández-Caliani and Barba-Brioso (2010) found a strong decrease in EDTA-extractable As in mine soils amended with marble slurry waste. González et al. (2012) suggested that  $\text{CaCO}_3$  plays an active role in reducing the As concentration in pore water from metal-As-polluted soils. However, there are many aspects of this process that have been poorly studied or not at all.

Moreover, marble quarrying around the world produces large quantities of wastes, which should be reused. In this paper, marble particles with different grain sizes were placed in contact with two acidic solutions: (a) with a high concentration of As and (b) with high concentrations of As, zinc (Zn), cadmium (Cd), and lead (Pb). The objective was to assess the effect of grain size and the interaction of heavy metals on As sorption by marble particles in an effort to add value to marble waste through a better understanding of its properties.

## Materials and methods

### Preparation of the suspensions

Marble waste was ground and sieved at the following grain sizes: very coarse (2–1 mm), coarse (1–0.5 mm), medium-coarse (0.5–0.25 mm), medium-fine (0.25–0.10 mm), fine (0.1–0.05 mm), and very fine (0.05–0.01 mm). The  $\text{CaCO}_3$  equivalent content was estimated manometrically (Williams 1949). The specific surface area (SS) of each fraction was determined using a six-point  $\text{N}_2$ -BT method (ASAP 2020—Physisorption Analyzer). In order to study the effectiveness of  $\text{CaCO}_3$  under conditions of severe pollution, as in the case of acid drainage from sulfide mining characterized by extreme acidity (pH about 1) and very high concentrations of pollutants (mainly Zn, As, Pb, and Cd), two acidic

standard solutions in nitric acid were prepared from stock solutions ( $1000 \text{ mg L}^{-1}$ , reagent-grade, Merck): solution AS1 (Eh  $\sim 700 \text{ mV}$ ) that contained  $100 \text{ mg L}^{-1}$  of As(V) and solution AS2 (Eh  $\sim 700 \text{ mV}$ ) that contained  $100 \text{ mg L}^{-1}$  of As(V),  $100 \text{ mg L}^{-1}$  of Zn,  $90 \text{ mg L}^{-1}$  of Cd, and  $100 \text{ mg L}^{-1}$  of Pb (II). The pH of each solution was measured, and the concentration of As, Pb, Zn, and Cd was measured using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer NexION 300D spectrometer).

The ICP-MS operating conditions included three replicates in each measurement. All standards were prepared from ICP single element standard solutions (Merck, Darmstadt, Germany) after dilution with 10 %  $\text{HNO}_3$ . For calibration, two sets of multi-element standards containing all the analytes of interest at five different levels of concentration were prepared using rhodium as the internal standard. Procedural blanks for estimating the detection limits ( $3\sigma$ ;  $n=6$ ) were  $<0.21 \text{ ppb}$  for As,  $<2.68 \text{ ppb}$  for Zn,  $<0.02 \text{ ppb}$  for Cd, and  $<0.23 \text{ ppb}$  for Pb. The analytical precision was better than  $\pm 5 \%$  in all cases.

The concentration of the pollutants in the AS1 and AS2 solutions measured by ICP-MS (three replicates) ranged between 103 and 106 % for As, between 106 and 109 % for Zn, between 93 and 98 % for Cd, and between 97 and 103 % for Pb from that of the standard solutions. These results support the accuracy of pollutant concentrations measured by ICP-MS, so that the concentration of metal(loid)s in the AS1 and AS2 solutions was estimated from the mean value of the three replicates.

Two grams of each grain size was placed in contact with  $25 \text{ cm}^3$  of each acidic solution (three replicates) for a total of 36 suspensions. The suspensions with acidic solution AS1 were labeled E1, and the suspensions with acidic solution AS2 were labeled E2. The suspensions were shaken periodically, and after 3 days (when the equilibrium between the surface of the marble and the solution was reached, Sørensen et al. 2008), each suspension was filtered through cellulose filters ( $0.45\text{-}\mu\text{m}$  pore size) to separate the solid phase from the liquid phase.

### Liquid-phase analysis

The Eh; pH; alkalinity; and total concentration of As, Pb, Zn, and Cd in the liquid phases of the suspensions were measured immediately after filtering. The alkalinity was measured by the titration method (Golterman 1970), and the concentrations of As, Pb, Zn, and Cd were measured by ICP-MS. The amounts of immobilized metal(loid)s were calculated by the difference between the concentrations in the acidic solution and in the liquid phase of the suspensions (both measured by ICP-MS).

Solid-phase analysis

After reaction with the acidic solutions, both isolated marble grains, as included at vacuum in polyester resin and subsequently polished, were studied by scanning electron microscopy (SEM) using a Carl Zeiss DSM 950 instrument with a back-scattered electron (BSE) detector and a Tracor Northern 523 X-ray energy-dispersive spectrometer (EDS) with an Oxford Link ISIS microanalysis system. The first two steps of the As sequential extraction that was proposed by Wenzel et al. (2001) were performed for each solid phase, which are the following: step 1, extraction with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to estimate nonspecifically sorbed As and step 2, extraction with NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> to estimate specifically sorbed As. The concentration of As in the extracts was measured by ICP-MS and control samples were used to check the matrix effect of each extraction. Two standard solutions containing 50 mg As L<sup>-1</sup> were prepared from the same stock solution used above (1000 mg As L<sup>-1</sup>): one using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (0.05 M) and another using NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (0.05 M) as diluents. The concentration of As in both solutions was measured by ICP-MS (three replicates) and the results were between ±4 % from that of the standard solution.

Statistical methods

The data distributions in the different treatments were established by calculating the mean values and the standard deviations. The differences between the individual means were compared using Tukey's test (*p*<0.05). Correlation analysis, which used the diameter and specific surface area of the grains, the total amount of the immobilized As, and the total amount of

the As extracted, was performed. The SPSS (PASW Statistics 20) software package was used for all statistical analyses.

Results and discussion

Specific surface area of the marble grains and characteristic of the acidic solutions

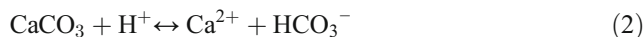
The CaCO<sub>3</sub> equivalent content of the marble wastes was 982±2 g kg<sup>-1</sup>. The SS of the marble grains ranged between 0.0425 and 0.6080 m<sup>2</sup> g<sup>-1</sup> and was found to be significantly related to the mean diameter of the grains (*D*) by a power regression:

$$SS (m^2 g^{-1}) = 0.045 D (mm)^{-0.687} \quad r^2 = 0.972 \quad p < 0.001 \quad (1)$$

The pH of AS1 was 1.3 with an As concentration of 105 mg L<sup>-1</sup>, whereas the pH of AS2 was 1.0 with metal(loid)s concentrations of 105 mg As L<sup>-1</sup>, 100 mg Pb L<sup>-1</sup>, 108 mg Zn L<sup>-1</sup>, and 86 mg Cd L<sup>-1</sup>.

E1 suspensions (marble-As interaction)

In all suspensions, Eh was around 400 mV. The H<sup>+</sup> of the acidic solution caused the weathering of CaCO<sub>3</sub>, which can be described by the following reaction:



Thus, H<sup>+</sup> becomes partially neutralized, and the pH in the liquid phase of the suspensions increases compared with AS1; the alkalinity (HCO<sub>3</sub><sup>-</sup>) was measured in the liquid phase (Table 1). Because the H<sup>+</sup> reacted with the marble grain

**Table 1** Mean values and standard deviation of the pH, alkalinity and metal(loid)s concentration in the liquid phase of the extracts

Extracts	Grain size (mm)	pH	Alkalinity (meq L <sup>-1</sup> )		As (mg L <sup>-1</sup> )	Pb	Zn	Cd
			CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>				
E1	2–1	5.9±0.1	nd	0.368±0.003	105±0.1			
	1–0.5	7.8±0.1	nd	0.413±0.003	104±0.1			
	0.5–0.25	8.1±0.1	nd	0.449±0.003	103±0.2			
	0.25–0.10	8.3±0.1	nd	0.402±0.002	100±0.2			
	0.10–0.05	8.3±0.1	nd	0.382±0.003	97±0.2			
	<0.05	8.2±0.1	nd	0.329±0.003	85±1.3			
E2	2–1	5.1±0.1	nd	0.397±0.005	77±1	3.3±0.3	88±4	73±1
	1–0.5	5.1±0.1	nd	0.351±0.002	72±1	2.9±0.1	90±2	72±1
	0.5–0.25	5.5±0.1	nd	0.347±0.002	66±2	0.60±0.03	90±3	69±1
	0.25–0.10	6.2±0.1	nd	0.319±0.002	43±6	0.09±0.01	72±3	54±2
	0.10–0.05	7.1±0.1	nd	0.302±0.003	26±5	0.02±0.002	48±2	39±2
	<0.05	7.7±0.1	nd	0.288±0.005	6±3	0.01±0.001	48±2	32±3

nd not detected

surface, the increase in pH and alkalinity should be higher when the grain size decrease; however, in the E1 suspensions, where the mean grain size was less than 0.25 mm, the alkalinity tended to decrease compared with that at a mean grain size greater than 0.25 mm.

The As concentration in the liquid phase of the suspensions decreased compared with that of the AS1 solution (Table 1), whereas the As that precipitated (AsPE1) was significantly related to the SS ( $\text{m}^2 \text{g}^{-1}$ ) of the grains by a linear regression (3), which indicates that the amount of immobilized As was approximately  $420 \mu\text{g m}^{-2}$ .

$$\text{AsPE1} (\mu\text{g g}^{-1}) = -0.78 + 420.76 \text{ SS} (\text{m}^2 \text{g}^{-1}) \quad (3)$$

$$r^2 = 0.984 \quad p < 0.001$$

The sequential extraction (Fig. 1a) showed that As(V) was sorbed by marble grains both nonspecifically (easily exchangeable and outer-sphere complexes, extracted with  $(\text{NH}_4)_2\text{SO}_4$ ) and specifically (inner-sphere complexes, extracted with  $\text{NH}_4\text{H}_2\text{PO}_4$ ). As(V) tetrahedral ( $\text{AsO}_4$ ) forms inner-sphere complexes via corner-sharing with the Ca octahedral ( $\text{CaO}_6$ ) at the surface of  $\text{CaCO}_3$  (Alexandratos et al. 2007), whereas the surface complexation model of Pokrovsky and Scott (2002) indicated that the density of surface sites ( $>\text{Ca}^{2+}$ ) on which arsenate would be able to form inner-sphere complexes is  $8.22 \mu\text{M m}^{-2}$ . In our experiment, the amount of arsenate ( $\text{AsO}_4$ ) extracted with  $\text{NH}_4\text{H}_2\text{PO}_4$  (presumably forming inner-sphere complexes) increased with the surface area of the marble grains (Fig. 2a), though tended to stabilize at approximately  $8 \mu\text{M m}^{-2}$  when the  $\text{SS} \geq 0.1252 \text{ m}^2 \text{g}^{-1}$ , which suggests a saturation of available sites to form inner-sphere complexes. In this case, the progressive reduction of arsenate extracted with  $\text{NH}_4\text{H}_2\text{PO}_4$  when the SS decreased to below

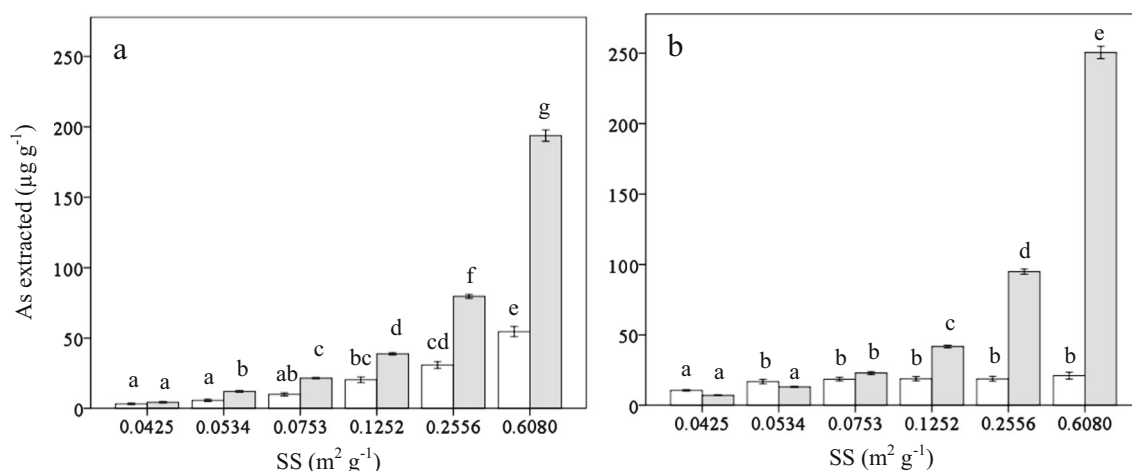
$0.1252 \text{ m}^2 \text{g}^{-1}$  may have been due to a decrease in the number of available sites, which implies that the density of the available sites to form inner-sphere complexes tended to diminish gradually when the marble grain size was larger than 0.25 mm.

Competition between arsenate and bicarbonate ions by sorption sites would justify the lower alkalinity in the liquid phase of the suspensions by decreasing the grain size and increasing the sorption sites (Sø et al. 2008). Specifically and nonspecifically sorbed As increased progressively by greater grain SS. The amount of specifically sorbed As was significantly higher ( $68 \pm 7\%$  of the total As extracted) than that of the nonspecifically sorbed As, and greater differences were observed as the grain size decreased (Fig. 1a). In addition, the total amount of As extracted with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  (AsXE1) was significantly and linearly related to the amount of AsPE1, and the slope of the fitted line was extremely close to 1.

$$\text{AsPE1} (\mu\text{g g}^{-1}) = 0.499 + 1.011 \text{ AsXE1} (\mu\text{g g}^{-1}) \quad (4)$$

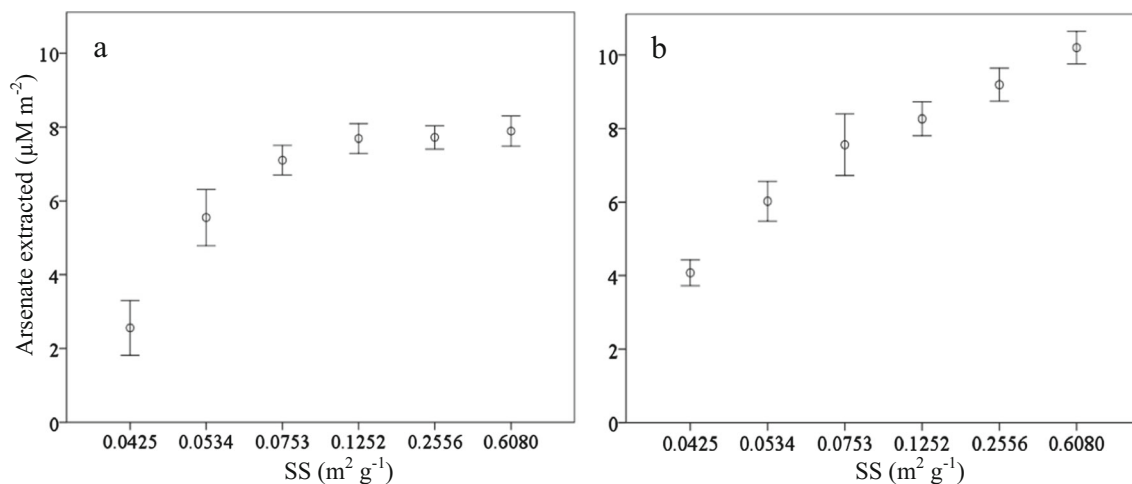
$$r^2 = 0.997 \quad p < 0.001$$

These results, together with the fact that the SEM study showed no formation of crystals on the surface of the marble grains, indicate that all the precipitated As was sorbed onto the surface of the marble grains, which formed inner-sphere complexes (major fraction) and outer-sphere complexes (minor fraction). This result accounts for the fact that the effectiveness of the marble to immobilize As is augmented as the SS of the grains increases. Moreover, in comparison with AS1, the decrease in the As concentration in the liquid phase of the E1 suspensions was relatively low (Table 1) and ranged between 0.6% (suspensions with the largest grain size, 2–1 mm) and 19.4% (suspensions with a smaller grain size, 0.05–



**Fig. 1** Mean values and standard deviation (error bars) of As extracted with  $(\text{NH}_4)_2\text{SO}_4$  (open bars) and  $\text{NH}_4\text{H}_2\text{PO}_4$  (gray bars) from the solid phases of the E1 (a) and E2 (b) suspensions versus specific surface area

(SS) of the grains. Mean values followed by the same letter do not differ significantly (Tukey's test:  $p < 0.05$ )



**Fig. 2** Mean values and standard deviation (*error bars*) of the arsenate extracted with NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> in the E1 suspensions (**a**) and E2 suspensions (**b**) versus specific surface area (SS)

0.01 mm), which indicates that the concentration of soluble As was excessively high in the liquid phase in all suspensions and that the CaCO<sub>3</sub> should not be considered an effective amendment to immobilize As (Magalhães 2002), especially in severe pollutions conditions.

E2 suspensions (marble-As-Pb-Zn-Cd interactions)

Similarly to what occurred in the E1 suspensions, in the E2 suspensions, the H<sup>+</sup> ions of the acidic solution caused the weathering of CaCO<sub>3</sub> and increased the pH of the liquid phase, and the alkalinity tended to decrease with diminishing grain sizes (Table 1). The As concentration in the liquid phase of the suspensions also decreased, although much more sharply than in the E1 suspensions, and the amount of As that precipitated (AsPE2) was significantly related to the SS of the marble grains by a logarithmic regression:

$$\text{AsPE2 } (\mu\text{g g}^{-1}) = 1434 + 347 \text{Ln SS } (\text{m}^2\text{g}^{-1}) \quad (5)$$

$$r^2 = 0.975 \quad p < 0.001$$

The sequential extraction (Fig. 1b) showed that As was also sorbed by marble grains in the E2 suspensions, both specifically and nonspecifically, and the competition between arsenate and bicarbonate for sorption sites would explain the lower alkalinity in the liquid phase of the suspensions by the smaller grain size (Table 1). However, only specifically sorbed As progressively increased with the SS of the grains, reaching higher values than those in the E1 suspensions, particularly when SS ≥ 0.1252 m<sup>2</sup> g<sup>-1</sup>, whereas nonspecifically sorbed As tended to remain constant with increasing SS. In any case, the total amount of As extracted with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> from the solid phase of the E2

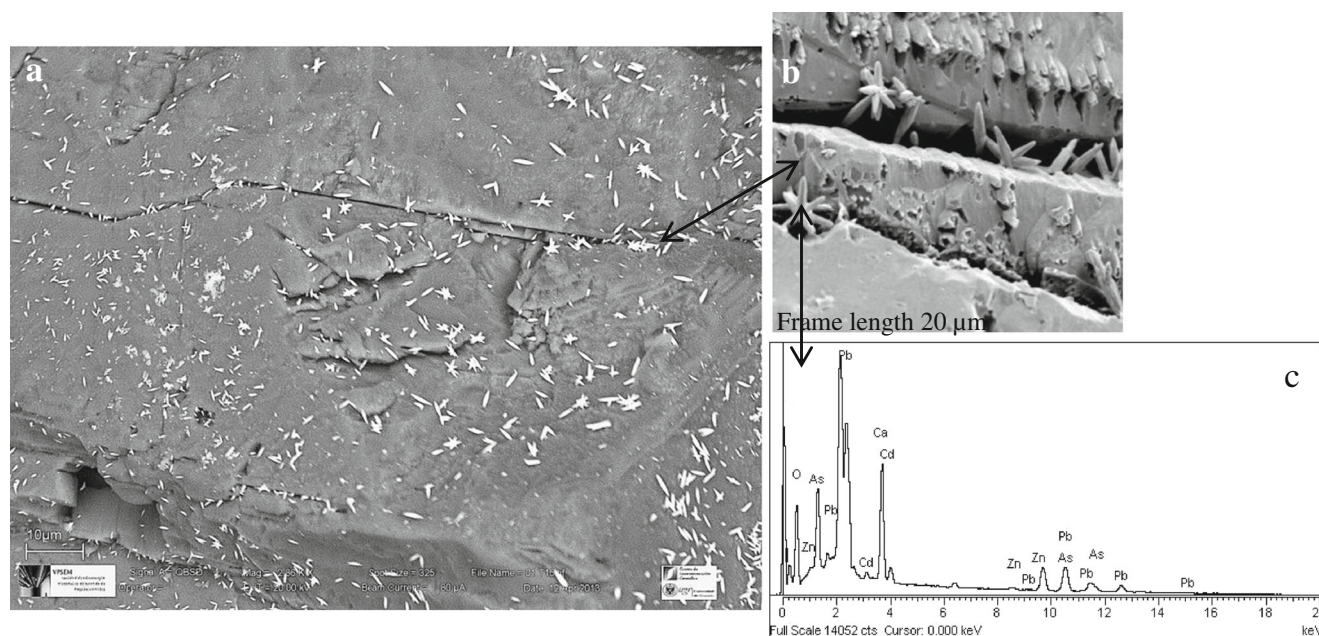
suspensions (AsXE2) was significantly and linearly related to AsXE1, and the slope of the fitted line is close to 1:

$$\text{AsXE2 } (\mu\text{g g}^{-1}) = 6.06 + 1.049 \text{AsXE1 } (\mu\text{g g}^{-1}) \quad (6)$$

$$r^2 = 0.995 \quad p < 0.001$$

These results indicate that the amount of As sorbed onto the surface of the marble grains was quantitatively and qualitatively similar in both types of suspensions. Nevertheless, the total amount of immobilized As in the E2 suspensions was quantitatively much greater than in the E1 suspensions (see Table 1 and compare Eq. 3 vs. Eq. 5), which suggests that in the E2 suspensions, a mechanism other than sorption onto the surface must act to immobilize As. SEM images of the marble grains from E2 suspensions showed elongated crystals, which occasionally formed rosettes on the marble grains (Fig. 3a, b), and the analysis of these crystals by SEM-EDS (Fig. 3c) revealed that they were formed by oxygen (O), As, Pb, Ca, and small amounts of Zn and Cd. In the polished samples, the semiquantitative analysis of the atomic percentage of these crystals indicated that the O/As atomic ratio was approximately 4, the Pb/Ca atomic ratio ranged between 1.2 and 2.0, and the Σ Pb+Ca+Zn+Cd/As atomic ratio ranged between 1.6 and 2.1, which suggests that it could be Pb-Ca arsenate with inclusions of small quantities of Zn and Cd. The formation of these crystals of Pb-Ca arsenates, presumably less soluble than Ca arsenate, must have been responsible for the sharp decline in the As concentration in the liquid phase of the E2 suspensions compared with AS2 (Table 1). This decline was greater when the grain size decreased and ranged between 25 % (suspensions with a coarser grain size, 2–1 mm) and 95 % (suspensions with a finer grain size, 0.05–0.01 mm). Thus, the As that precipitate as Pb-Ca arsenate (AsP<sub>Pb-Ca</sub>), estimated by the difference between AsPE2 and AsXE2, was





**Fig. 3** Backscattered electron scanning micrograph of elongated crystals, both isolated as forming rosettes on marble grains (a). Detail of these crystals (b). Spectrum of the crystal analysis by SEM-EDS (c)

also significantly related to the SS ( $\text{m}^2 \text{g}^{-1}$ ) by a logarithmic regression (7); this relation, together with the crystals on marble shown by SEM, suggests that the formation of Pb-Ca arsenates was encouraged by some chemical or physicochemical parameter of the grain surface, such as Ca concentration, pH or both, which would presumably boost by increasing SS.

$$\text{AsPb-Ca} (\mu\text{g g}^{-1}) = 1158 + 258 \text{Ln SS} (\text{m}^2 \text{g}^{-1}) \quad (7)$$

$$r^2 = 0.923 \quad p < 0.001$$

The amounts of arsenate extracted with  $\text{NH}_4\text{H}_2\text{PO}_4$  from the solid fractions of the E2 suspensions clearly differed with respect to the amounts extracted from the solid fractions of the E1 suspensions (Fig. 2). Thus, the amounts extracted from E2 suspensions were higher and continually increased with increasing SS of the marble grains, exceeding the saturation value of  $8.2 \mu\text{M m}^{-2}$  (Pokrovsky and Scott 2002) when the SS of the marble grains was  $\geq 0.1252 \text{ m}^2 \text{g}^{-1}$ . This comparative analysis suggests that the  $\text{NH}_4\text{H}_2\text{PO}_4$  could remove part of the As that precipitated as Pb-Ca arsenate. In any case, the amount removed was less than 5 % of the total As that precipitated as Pb-Ca arsenate, which suggests that the inclusion of Pb in the crystal structure resulted in relatively stable arsenate. Magalhães and Silva (2003) indicated that several Pb arsenates are very stable even at low concentrations of Pb and As(V) in solution. Therefore, the marble particles with the very fine grain size (0.05–0.01 mm) did effectively immobilize As and Pb when both elements were present in the

solution, as almost all the Pb was immobilized in the E2 suspensions that contained particles with finer grain sizes (Table 1).

In the case of Zn and Cd, the amount precipitated was significantly related ( $p < 0.001$ ) only with the pH of the solution through the following linear regressions:

$$\text{ZnPE2} (\mu\text{g g}^{-1}) = -948 + 226 \text{pH} \quad r^2 = 0.919 \quad (8)$$

$$\text{CdPE2} (\mu\text{g g}^{-1}) = -877 + 204 \text{pH} \quad r^2 = 0.970 \quad (9)$$

Therefore, these metals should mainly precipitate as hydroxides whose formation is boosted by increasing the pH of the solution (Lindsay 2001).

According to the above, fine particle of marble waste could be effective to prevent the dispersion of arsenic through runoff from mining waste. However, immobilization capacity is limited to  $250 \text{ mg As kg}^{-1}$  (Eq. 3), so it may not be effective in mining areas where runoff water have high As concentration or in wet areas where acid mine drainage are produced in a short time interval. In any case, given that the acid mine drainage can be very different depending on the type of mining, it would be necessary to do field studies to evaluate each mining district in particular. When the acid mine drainage containing high concentrations of As and Pb, the effectiveness of the fine particles of marble to immobilize As would increase considerably up to  $1250 \text{ mg As kg}^{-1}$  (Eq. 5), about five times more than without soluble Pb; while soluble Pb would also precipitate almost entirely. These results open a new line of research aimed at studying the possibility of using

controlled amounts of certain pollutants in the remediation of pollution, e.g., could fine marble particles and soluble Pb be used to recover groundwater with high As concentration? Further research would be necessary to give an adequate response to these issues.

**Conclusions**

Arsenic was sorbed onto marble grains both specifically (forming inner-sphere complexes) and nonspecifically (exchangeable and forming outer-sphere complexes). The sorbed amount was approximately  $420 \mu\text{g As m}^{-2}$ , with the inner-sphere complexes being the major fraction ( $61 \pm 7\%$  of the total As sorbed). The As that precipitated did not exceed 20 % of the total As in the solution, and therefore, marble particles should not be considered an effective amendment to immobilize As. However, when the contamination involved arsenic and other heavy metals (particularly Pb), in addition to sorbed As, Pb-Ca arsenate crystals formed on the surface of the marble grains. The formation of these crystals increased with a greater SS of the marble grains to the extent that in the suspensions with greater SS ( $0.608 \text{ m}^2 \text{ g}^{-1}$ ), the As concentration in the liquid phase decreased by 95 % relative to the total dissolved As, whereas the amount of Pb was reduced by almost 100 %. Arsenic that precipitated as Pb-Ca arsenates was not extracted with  $(\text{NH}_4)_2\text{SO}_4$  or with  $\text{NH}_4\text{H}_2\text{PO}_4$ , which suggests that they are relatively stable compounds and, therefore, effective in immobilizing As and Pb in contaminated water and soil.

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