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Scientific paper

Arsenic Release from Pyrite Ashes: Kinetic Studies

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Abstract

Arsenic mobility in pyrite ashes was studied because of the possible effects on water systems. The batch extraction method was used to assess kinetics and extent of As release induced by contact of the material either with rainwater or groundwater. Self-established pH-Eh range of pyrite ashes/water mixtures brought both As(III) and As(V) to be present in the water phase, as neutral arsenite H_3AsO_3 and anionic arsenate $HAsO_4^{2-}$, respectively. Tests in reagent water showed both rate and extent of arsenite release higher than arsenate; total As concentration ([As] = 12 μg/L) at equilibrium little exceeded its EU Maximum Concentration Level (MCL) for surface and groundwater ([As] = 10 μg/L). Tests in groundwater, instead, showed a much higher release rate and extent for arsenate than for arsenite and the chemistry of groundwater mainly influenced arsenate mobility; total As almost instantly exceeded its MCL and it was markedly higher ([As] = 31 μg/L) at equilibrium. Overall, the study has shown the environmental implications of As mobility in the pyrite ashes, also casting light on some limits of the environmental representativeness of leaching tests in reagent water.

Keywords: Pyrite ashes, arsenic, arsenite, arsenate, mobility, kinetics

1. Introduction

Arsenic is naturally present within igneous and sedimentary rocks and it represents the 20th most abundant element in the earth's crust.[1] Arsenic possesses toxic and carcinogenic properties[2] and weathering of the rock surfaces or other processes occurring in nature may cause the element to exist at dangerous levels in the water systems. Contamination of drinking water represents a serious problem in parts of the world like, e.g., in the Indian subcontinent[3,4] and the increasing concern about arsenic exposition has induced the USA and the EU to set the drinking water MCL (Maximum Contaminant Level) for arsenic to 10 μg/L. Daily consumption of 0.01 mg/kg body weight of arsenic, less than 0.2% of the fatal dose, can lead to problems with the skin, circulatory and nervous systems, higher doses still can result in fatality.[2] Dissolved arsenic in water essentially exists as arsenite and arsenate[4] and in consideration of the basic tenet that toxicity of trivalent arsenic is greater than pentavalent arsenic[5] their occurrence and the conditions able to influence their relative abundance in the water systems becomes of crucial interest. Together with natural processes, some anthropogenic sources of arsenic due to, e.g., agricultural use of arsenical herbicides and pesticides or related to industrial processes (and their relevant waste/by-products),[4] can be considered within the main causes of arsenic contamination of both soil and water. Among the industrial waste/residues which can release arsenic into the environment, the arsenic-containing roasted sulfide residues (the so called "pyrite ashes") as by-product of pyrite combustion for the production of sulfuric acid are included; their uncontrolled disposal may therefore represent a matter of concern for human health and environmental quality, being a potential arsenic contamination source for the local water systems. Specific site conditions can, in fact, influence arsenic release from the material: alterations of one or more physico-chemical parameters of the hosting media may induce the transfer of the contaminant from the solid to the water phase and the activation of possible contamination pathways towards adjacent environmental targets. Although several studies about arsenic contamination of water are available,[2] research on arsenic mobility within the pyrite ashes and the conditions able to promote its release in the water phase has only very little literature yet. Studies on the mobility of the arsenic forms in the pyrite ashes become therefore essential to minimize the impact of the material on the environment and for the definition of suitable protection and/or remediation strategies. As stability and mobility of arsenic associated with the solid phase depend upon its oxidation state and as the chemical form of the element is largely influenced by the characteristics of the environment in which it exist,[1] the objective of this research was therefore the study of arsenic mobility within a representative sample of pyrite ashes collected from an uncontrolled impoundment, through investigations on kinetic release processes of arsenite and arsenate in solid/aqueous systems. As in previous studies iron oxides and oxy-hydroxides – which represent the most abundant and diffused phase in the pyrite ashes -[6] have been recognized to be place of arsenic adsorption and desorption reactions and to be able to control its mobility,[7] the bulk characterization with investigations on the chemical and mineralogical composition of the pyrite ashes was preliminarily carried out. The studies on arsenic release processes were conducted on solid/aqueous systems prepared from aliquots of a powdered pyrite ashes sample mixed with reagent water or with groundwater collected at the site, initially determining the self-established pH and Eh values of the mixtures in consideration that these parameters play a key role in arsenic mobility as they control its fate and transport through their effects on As(V) and As(III) speciation, redox reactions of arsenic species and other redox pairs, precipitation and dissolution of minerals and metal (hydr)oxides, and the surface charges of the solid phases.[8] The kinetic tests were carried out in respect to the relative contribution of arsenite and arsenate to the total arsenic in the aqueous phase, the two most environmentally relevant inorganic forms of arsenic in water systems,[9] which affect the mobility of the element and are differently sensitive to the physico-chemical setting of the solid/liquid systems.[10] The kinetics and extent of arsenite and arsenate release from the mineral surfaces in desorption processes can be diversely influenced by solution pH and by the competition for sorption sites with anions (especially phosphate and sulfate) and control the input of the two species to the water phase,[11] therefore further complicating the fate and transport predictions of arsenic in natural systems. As arsenite and arsenate adsorb on many metal (hydr)oxides and clay minerals through formation of inner-sphere and/or outer-sphere surface complexes,[12] the research also aimed at identifying the prevalent involved mechanisms of their exchange between the pyrite ashes and the aqueous phase and at assessing their role in the phenomenological expression of arsenic mobility within the pyrite ashes.

2. Experimental

Field works in this study have been performed in the period 2008–2012. Representative samples of the pyrite ashes impoundment and of the local groundwater system were collected in-situ to carry out the present study.

2. 1. Sampling and Sample Preparation

2. 1. 1. Pyrite Ashes

Previous investigations[13] revealed an evident non homogeneous distribution of the pyrite ashes within the site and probable mixture with soil components. In order to obtain a representative sample of the impoundment three bulk samples were collected, then sifted in-situ by means of 20 mm opening sieve and manually homogenized. Each homogenized sample was placed in dark glass bottles provided with cap and PTFE under-cap and transported to laboratory in a cold box. All tools used for sampling were made of stainless steel. The three samples were stored in cold room at t<3 °C until used. A composite pyrite ashes sample was successively formed in laboratory by manually mixing and homogenizing a weighted equal amount of the three samples. Due to the heterogeneity of the larger sized particles assessed in preliminary tests, in order to ensure representative material the composite sample was then subjected to 2 mm sieving for the separation and collection of the $\Phi<2$ mm fraction, which was successively ground by means of a tungsten carbide mortar. A powdered composite pyrite ashes sample was finally prepared and used in all tests and experiments carried out within this study.

2. 1. 2. Groundwater

Sampling of groundwater was carried out at the monitoring wells present at the site. After well purging, representative samples of the groundwater system were collected by means of an stainless steel immersion pump (Grundfoss MP1 model) provided with PTFE tubing and placed in 1 L dark glass bottle for cations, anions and physico-chemical parameters determinations; for elemental determinations the samples were filtered in-situ using Millipore® cellulose nitrate membrane of nominal pore size 0.45 μm and placed in a conditioned 15 mL PTFE test tube. A composite groundwater sample for the kinetic tests was also formed in-situ by mixing in a 10 L HDPE tank an equal amount of sample collected at each relevant monitoring well. All samples were transported to the laboratory in portable refrigerators and stored in cold room at t < 3 °C until analyzed or used.

2. 3. Kinetic Studies

2. 3. 1. Arsenic Release Kinetics

Arsenic release kinetics were studied using the batch extraction method. For assessing the variation of arsenic concentration in the water phase with reaction time, a series of 1:10 (w_S/w_L) solid/liquid ratio mixtures was prepared by mixing 3 g aliquots of air-dried pyrite ashes sample with 30 g of MilliQ® reagent water (MQ test) or with 30 g of groundwater sample (GW test) collected at the site (exactly weighted to four decimals) in 40 mL capacity HDPE vials, quickly sealed after mixture preparation. The mixtures of the series were homogenized by shaking in orbital agitator (IKA Labortechnik, Staufen – Germany) set at 400 rpm where the vials were placed horizontally in order to achieve appropriate homogenization. At selected time intervals spanning the entire kinetic run until equilibrium or near-equilibrium state, the mixtures were subjected to solid/liquid separation in centrifuge (Hettich GmbH, Tuttingen – Germany) at 3600 rpm for 5 min and to a two-step filtration of the water phase using Millipore® cellulose nitrate membranes of nominal pore size 0.45 μm and 0.22 μm respectively. The pH and Eh values of each solution was measured by potentiometric method using a WTW multi-parametric instrument (WTW model Multi 350i, accuracy ±0.01 pH, ±0.1 mV) immediately after filtration in order to minimize possible ambient CO_2 absorption. Solutions were analyzed via Hydride Generation Inductively Coupled Plasma – Mass Spectrometry (HG-ICP-MS) immediately after filtration for total arsenic (As), As(III) and As(V) quantification. The experiments were carried out at an average room temperature of 20±1 °C. The adherence of arsenic release kinetic data to pseudo-first order, pseud-second order, Elovich, power function and parabolic diffusion equations was tested graphically for both reagent water and groundwater kinetic tests.

2. 4. Analyses

2. 4. 1. Pyrite Ashes Characterization

Mineralogical X-Ray Diffraction (XRD) analysis of the pyrite ashes composite sample was carried out at the Department of the Earth Science of the University of Trieste (IT) using a XR Siemens diffractometer (STOE D500 goniometer) equipped with a Cu radiation source, a graphite monochromator and a scintillator detector. Quantitative scan was run at 40 kV and 20 mA, from 2 to 70 2-Theta degree units, with a step interval of 0.05 2-Theta degree units and 1 s per step counting time. Elemental Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analyses were carried out at the Hydrotech Srl laboratory, AREA Science Park – Trieste (IT), on an air-dried aliquots of the composite pyrite ashes sample using an Agilent 7500 series ICP-MS, according to the methods US-EPA 3051A[14] and US-EPA 6020A.[15] A 0.5 g aliquot of the sample was digested in aqua regia (HNO_3/HCl = 1:3) in microwave oven (CEM Mars Xpress) at temperature t = 175 °C for a total time of 10 min with a temperature ramp from 20 °C to 175 °C in 5.5 min, and analyzed for elemental determination. Analyses were carried out using analytical-reagent grade chemicals unless otherwise stated. The dry matter value (d.m.) was measured by oven heating of a separated aliquot at t = 105 °C until constant weight.

2. 4. 2. Groundwater Characterization

Analyses were carried out using analytical-reagent grade chemicals unless otherwise stated. Physico-chemical parameters (i.e. pH, Eh, Cond., Temp.) of groundwater were measured at Hydrotech Srl laboratory by means of a WTW Multi 340i multi-parameter instrument (WTW GmbH, Weilheim, Germany), while elemental analyses were carried out via ICP-MS according to the methods US-EPA 6020A,[15] ISO 17294-1,[16] ISO 17294-2.[17] Analyses of anions and cations were carried out at R&C Lab, Altavilla Vicentina, VI (Italy) via ion-chromatography using a Dionex ICS-1600 ion-chromatographer (Thermo Fisher Scientific, Inc., Sunnyvale, CA, USA) according to the method US-EPA 300.1[18] and via spectrophotometry using a Perkin Elmer Lambda 40 UV/Vis spectrophotometer (Perkin Elmer Corp. Norwalk, CT, USA) according to the method APAT CNR-IRSA 29/2003.[19]

2. 4. 3. Arsenic Determination in the Kinetic Test Solutions

Total inorganic arsenic as well as As(III) and As(V) in the kinetic test solutions were determined at Hydrotech Srl laboratory via Hydride Generation ICP-MS technique (HG-ICP-MS) using an Agilent 7500 series ICP-MS (Agilent Techn., Santa Clara, CA, U.S.A.) coupled with an in-line automated hydride generation device (Hydride Generation – Integrated Sample Introduction System, HG-ISIS) provided by the same manufacturer. Analyses were carried out using analytical-reagent grade chemicals unless otherwise stated. After filtration (ref. Par. 2.3.1.), each test solution was split into three aliquots: the first aliquot was used to determine the As(III) concentration after its conversion to arsine using a stabilized reductant solution at 0.2% (w/v) sodium tetrahydridoborate ($NaBH_4$) and 0.05% (w/v) sodium hydroxide (NaOH); the second aliquot of the sample was used to determine the total arsenic [As] = [As(III)] + [As(V)] concentration after quantitative conversion of As(V) to As(III), achieved after 60 min reaction time by means of a reductant solution at 5% (w/v) potassium iodide (KI) and 5% (w/v) ascorbic acid ($C_6H_8O_6$); the third aliquot was used to calculate As(V) recovery yield by means of the addition of a spike solution at 10.0 μg/L As(V). Concentration of As(V) in the test solution was calculated by difference between the total As and the As(III) concentration measured in their respective aliquots. The recovery yield was considered acceptable for values >90%. All concentration values were always set equal to the mean value of at least three measurements, automatically calculated through the control software of the ICP-MS. Calibration plots were constructed using four As(III) and As(V) solutions at 0.0 (calibration blank), 0.5, 10.0, 20.0 μg/L, prepared respectively from stock solutions of $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$. The limit of detection for As 0.012 μg/L. Uncertainty of the measures was determined through a series of inter-laboratory comparison tests on standard solutions containing 10.0 μg/L As(III) and 10.0 μg/L As(V) ([As] = 20.0 μg/L), which provided a value of 0.2 μg/L and 0.5 μg/L for As(III) and As(V), respectively.

3. Results and Discussion

3. 1. Pyrite Ashes Characterization

3. 1. 1. Mineralogical Analysis

The main mineral phases of the pyrite ashes sample were identified from the XRD diffraction spectrum using the database and datasets of the Institute of Experimental Mineralogy.[20] The major mineral composition (% w/w), calculated by the normalized to 100 ratios of the relative main peak intensity of each identified mineral, showed the following distribution: hematite (47%), quartz (26%) and dolomite (21%); a minor contribution (6%) of elemental iron (Fe^0) was also measured. The significant contribution of typical soil minerals to the expected main fraction of iron oxides in the pyrite ashes therefore suggests probable mixture of the material with soil during its disposal.

3. 1. 2. Elemental Analysis

The ICP-MS analysis of the pyrite ashes sample gave the following main elemental composition (mg/kg d.m.): [Al] = 4828; [As] = 272; [Ba] = 1649; [Ca] = 15652; [Cd] = 7.5; [Co] = 43.2; $[Cr]_{tot}$ = 11.4; [Cu] = 2798; [Fe] = 401242; [K] = 735; [Mg] = 7317; [Mn] = 246; [Mo] = 22.0; [Na] = 26.9; [Ni] = 192; [Pb] = 3282; [Sb] = 44.8; [Sn] = 238; [V] = 11.1; [Zn] = 3992. The measured dry matter value (d.m.) was 98.3%. The high concentration of alkaline-earth elements like Ca and Mg in the sample seems to confirm the presence of soil portions within the pyrite ashes impoundment.

3. 2. Groundwater Characterization

The composite groundwater sample analyses gave the following main physico-chemical parameters values: pH =8.4; Eh = –88.4 mV; Cond.: = 412.5 µS/cm. The determined main anionic composition (mg/L) was: $[F^-]$ = 0.2; $[Cl^-]$<3.5; $[Br^-]$<0.1; $[CO_3^{2-}]$<0.1; $[HCO_3^-]$ = 284.8; $[NO_3^-]$<0.1; $[PO_4^{3-}]$ = 0.3; $[SO_4^{2-}]$ = 77.6; $[S^{2-}]$<0.1. Alkaline and alkaline-earth metals concentrations (mg/L) were: [Na] = 18.8; [K] = 1.6; [Ca] = 72.5; [Mg] = 25.2. Elemental analysis gave the following results (µg/L): [Al] = 1.1; [As] = 0.6; [B] = 27.2; [Ba] = 172.0; [Be] = 0.4; [Cd]<1.0; [Co] = 5.6; [Cr] = 104.3; [Cu] = 0.4; [Fe] = 118.0; [Hg]<0.1; [Mn] = 57.1; [Ni] = 19.5; [Pb]<0.1; [Sb]<0.1; [Se] = 1.1; [Tl]<0.1; [V] = 35.6; [Zn]<0.1.

Aliquots of the groundwater composite sample have been utilized to conduct the kinetic comparative tests (GW test) described below.

3. 3. Kinetic Studies

3. 3. 1. Arsenic Release Kinetics – MQ Test

The tests showed self-established pH and redox potential (Eh) values of the mixtures ranging from approx. 8.0 to approx. 8.4 and from approx. –93 to approx. –69 mV, respectively; according to arsenic Eh-pH thermodynamic stability diagrams, it can be therefore assumed that both As(III) and As(V) are present in the water phase of the mixtures as arsenite and arsenate in their neutral acidic H_3AsO_3 and anionic $HAsO_4^{2-}$ form, respectively. Total As, As(III) and As(V) concentration in the water phase of the MQ tests was measured at different reaction times; the obtained As, As(III) and As(V) concentration vs. reaction time (t) plot is shown in Figure 1. (dotted curves).

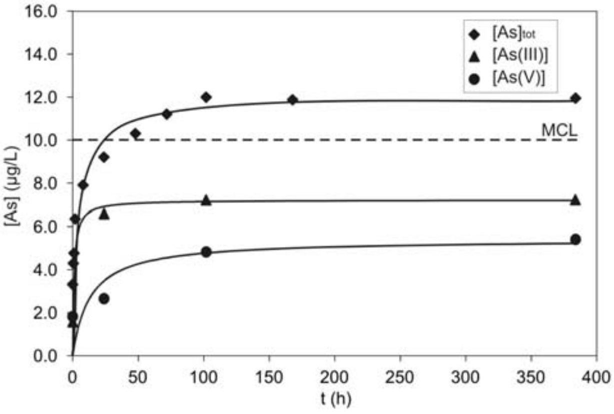

Figure 1. Kinetics of total As, As(III) and As(V) within the MQ test. Pseudo-second order kinetic model fits of experimental data are also shown

The results of the kinetic run showed a total arsenic concentration value in the liquid phase exceeding the MCL for surface water (10 µg/L) at already 48 h reaction time. Nevertheless, powdering to which the bulk pyrite ashes have been necessarily subjected for the preparation of the compositionally representative sample and the extensive shaking of the mixture inevitably used to conduct the kinetic tests might have significantly amplified the mobility of arsenic. Similar observations were, e.g., well pointed out by Ogwada and Sparks[21] in their analysis of the effects of the experimental conditions (i.e. degree of agitation) on specific surface area and rate of potassium absorption on soil. The arsenic release exceeding the MCL value in the kinetic test might not therefore actually occur so rapidly at the site scale where milder interaction mechanisms between the pyrite ashes impoundment and the environment are expected. As it can be observed from the kinetic plot, the speed of arsenic release appeared very fast at the earliest reaction times (up to approx. 2 h) with a following smooth downward bend towards the equilibrium concentration value, reached at ca. 102 h (curve plateau). It can also be seen that an amount approx. 50% of total arsenic was released within 2 h reaction time. Such a segmentation of the kinetic curve appears consistent with possible multiple release mechanisms occurring at different phases of the overall release process, the slower probably connected to transport phenomena within the micropores and defects of the solid phase or/and to more energetic chemical bonds of the element with the solid surface of pyrite ashes minerals. Various author[7,22–25] observed the same behaviour for As(III) and As(V) in their studies on adsorption/desorption kinetics of the element on different minerals. In particular, Arai et al.[24] observed the same initially rapid phase and following slower approach to equilibrium in their study on As(V) desorption on hematite while Fuller et al.[22] suggested that the rate-limiting step for As(V) desorption on iron oxides was controlled by its slow diffusion within the aggregates of the crystalline mineral. Gismera et al.[26] in their study on arsenic release kinetics in river sediment minerals suggested the occurrence of both less and more energetic bond sites for arsenic to explain the observed different release rates within the kinetic curve. As it can be also observed, within these tests the contribution of As(III) to the total As concentration in the liquid phase was greater than that of As(V) at any reaction time, with a more pronounced difference between the two arsenic oxidation states contribution in the initial phase of the release process. Such an observation brings to a preliminary consideration about the different mobility of the two species in the pyrite ashes/water systems in such experimental conditions, where As(III) seems to reach its equilibrium concentration markedly sooner than As(V) (at 24 h reaction time conc. As(III)≈100% while conc. As(V)≈54.2% of their corresponding concentration in the liquid phase at 102 h). In order to study the kinetics of total As, As(III) and As(V) release in the water phase, the adherence of time-dependent experimental data from the release runs to some frequently used kinetic models[27] was tested graphically. Linear fitting of the release kinetic data to pseudo-first order, pseudo-second order, Elovich, power function and parabolic diffusion equations (see Table 1.) was carried out over the whole dataset of the kinetic run.

Coefficients of correlation (r^2) obtained for the fit of time dependence of total arsenic (As), As(III) and As(V) release to the kinetic models are shown in Table 2.

As it can be seen, in respect to correlation coefficient r^2 the best fitting for total arsenic (As), As(III) and As(V) was obtained using the pseudo-second order equation. The slope $1/q_{eq}$ and the intercept A of the linear fit of pseudo-second order equation with experimental data in the form (t/q_t) vs. (t) give, respectively, the reciprocal ($\mu g^{-1} \cdot L$) of the equilibrium concentration and the reciprocal ($\mu g^{-1} \cdot L \cdot h$) of initial release rate in the process. The apparent constant rate (K_{2r}) ($\mu g^{-1} \cdot L \cdot h^{-1}$) of the process can also be calculated, being $K_{2r} = 1/(A \cdot q_{eq}^2)$. In Table 3. the apparent coefficients of the pseudo-second order kine-

Table 1. Equation models for the fit of arsenic release kinetic data

Kinetic model	Integral form of equation	Parameters	Linearized plot
Pseudo-first order	$\ln(q_{eq} - q_t) = A + K_1 \cdot t$	q_t is the amount of As release at time t.	$\ln[q_{eq}/(q_{eq} - q_t)]$ vs. t
Pseudo-second order	$t/q_t = A + t/q_{eq}$		t/q_t vs. t
Elovich	$q_t = A + K \cdot \ln(t)$	q_{eq} is the amount of As release at equilibrium.	q_t vs. $\ln(t)$
Power function	$\ln(q_t) = \ln(A) + K \cdot \ln(t)$		$\ln(q_t)$ vs. $\ln(t)$
Parabolic diffusion	$1 - (q_t/q_{eq}) = A - K \cdot t^{1/2}$	K_1, K and A are constants.	q_t vs. $t^{1/2}$

Table 2. Coefficients of correlation (r^2) obtained for the fit of time dependence of As, As(III) and As(V) release to the kinetic models

Arsenic release kinetics – MQ test	**Kinetic model r^2**				
Kinetic model	**Pseudo I-order**	**Pseudo II-order**	**Elovich**	**Power function**	**Parabolic diffusion**
As	0.9713	0.9995	0.9690	0.9509	0.9675
As(III)	0.9820	1.0000	0.9690	0.9933	0.9331
As(V)	0.9715	0.9962	0.7926	0.9928	0.8671

Table 3. – Pseudo-second order equation coefficients for As, As(III) and As(V) release kinetics;

Equation		**As release kinetics – MQ test**			
$q_t = t / [A + (t/q_{eq})]$		**unit**	**As**	**As(III)**	**As(V)**
Coefficients	A	($\mu g^{-1} \cdot L \cdot h$)	0.27	0.15	2.49
	q_{eq}	($\mu g \cdot L^{-1}$)	12.0 (11.9*)	7.2 (7.2*)	5.6 (5.4*)
	r_{0r}	($\mu g \cdot L^{-1} \cdot h^{-1}$)	3.7	6.7	0.4
	K_{2r}	($\mu g^{-1} \cdot L \cdot h^{-1}$)	0.03	0.13	0.01

* experimental value

tic model obtained from the fitting of total As, As(III) and As(V) release experimental data are presented. In Figure 1. the pseudo-second order kinetic model fits for As, As(III) and As(V) release are superimposed to the relevant experimental data.

According to the results obtained by the linear fitting of the kinetic data shown in Table 3. above, it can be seen that the calculated initial speed of As(III) release [r_{0r} = 6.7 ($\mu g \cdot L^{-1} \cdot h^{-1}$)] is considerably higher than that of As(V) [r_{0r} = 0.4 ($\mu g \cdot L^{-1} \cdot h^{-1}$)], as previously observed simply considering the experimental data plot. Similar observation can be made in respect to the calculated and experimental equilibrium concentrations, which appear in good agreement for total As, As(III) and As(V). Such results of the fit, together with the high correlation coefficients, bring to consider the pseudo-second order kinetic equation a good model for total arsenic, As(III) and As(V) release within the carried out tests. In Figure 3., the pseudo-second order equation linear fit plots for As(III) and As(V) release are shown. As it can be seen from the figure, the linear fit of As(III) and As(V) release data to pseudo-second order equation appears well representative of the relevant different release rates as resulted from the kinetic runs: the decreasing concentration gap between the two species at increasing reaction times can in fact be observed (being the y-axis value proportional to the reciprocal of As(III) or As(V) concentration in the liquid phase). According to the results of the kinetic study, it seems reasonable to expect a mobility of arsenite greater than that of arsenate within the pyrite ashes impoundment should the in-situ conditions approach, in a simplified conceptual model, the experimental pattern of the lab. tests. Under the reasonable hypothesis that the physico-chemical characteristics of the reagent water used in the test well approximate those generally shown by rainwater it could seem, at a first glance, that natural leaching processes to which pyrite ashes can be subjected bring to downstream water flows with total arsenic concentrations exceeding the relevant MCL for surface water at already 48 h ca. contact time between the impoundment and rainwater, with the major contribution given by the most toxic arsenic form. Nevertheless, the necessary powdering of the material for the preparation of a representative sample of pyrite ashes and the robust shaking for carrying out the kinetic tests have, most probably, significantly amplified both the rate and the extent of arsenic release from the material in respect to actual solid-liquid interaction mechanisms that might occur at the site scale. Some stability in respect to rainfall leaching can be therefore expected for both arsenite and arsenate within the pyrite ashes. According to such observations it appears reasonable to predict for the pyrite ashes impoundment less arsenic input in the water phase for downstream transport towards adjacent environmental targets and consequent minor environmental impact (e.g. an arsenic concentration in the water phase not exceeding the MCL) than that simply estimated through the sole analysis of arsenic mobility within the MQ kinetic tests.

3. 3. 2. Arsenic Release Kinetics – GW Test

Total As, As(III) and As(V) concentration in the water phase of the GW tests was measured at different reaction times together with the respective pH and Eh values. The tests showed self-established pH and redox potential (Eh) values of the mixtures ranging from approx. 8.2 to approx. 8.5 and from approx. –92 to approx. –76 mV, respectively; according to arsenic Eh-pH thermodynamic stability diagrams, it can be therefore assumed that both As(III) and As(V) are present in the water phase of the mixtures as arsenite and arsenate in their neutral acidic H_3AsO_3 and anionic $HAsO_4^{2-}$ form, respectively, as occurred in the MQ kinetic tests.

The obtained As, As(III) and As(V) concentration in the liquid phase vs. reaction time (t) plot is shown in Figure 2. (dotted curves). In the same figure, the pseudo-second order kinetic model fits obtained for As, As(III) and As(V) release are superimposed to the relevant experimental data.

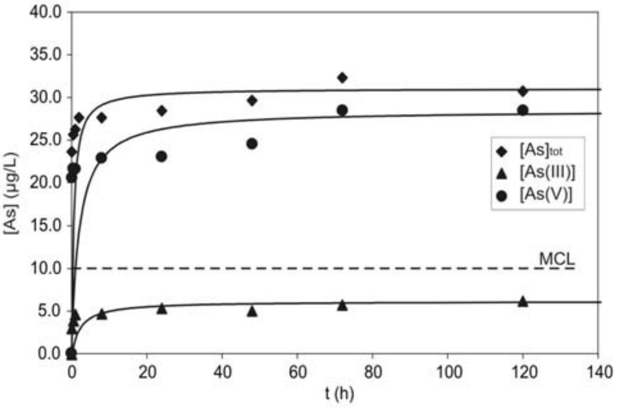

Figure 2. Kinetics of total As, As(III) and As(V) within the GW test. Pseudo-second order kinetic model fits of experimental data are also shown

Within the tests, total arsenic concentration value in the liquid phase exceeded the MCL for groundwater (10 μg/L) at already 0.1 h (6 min) reaction time, when an amount >70% ca. of total arsenic was released with the main contribution given by As(V), which remained significantly higher than that provided by As(III) all along the kinetic run up to equilibrium. As it can also be seen from the kinetic plot of Figure 2., the speed of release was significantly fast for both As(III) and As(V) at the earliest reaction times (up to approx. 1 h) with a following rapid downward bend towards the equilibrium concentration value, reached at ca. 120 h. The adherence of time-dependent experimental data from the release runs to the same kinetic models used within the test carried out with reagent water (MQ test) was tested graphically. Coefficients of correlation (r^2) obtained for the linear fit of time dependence of total arsenic, As(III) and As(V) release to the used kinetic models are shown in Table 4.

In respect to correlation coefficient r^2 the best fitting for total arsenic (As), As(III) and As(V) was obtained using the pseudo-second order equation, as previously occurred within the MQ kinetic test. In Table 5., the apparent coefficients of the pseudo-second order kinetic model obtained from the fitting of As, As(III) and As(V) release experimental data are presented.

In Table 6., the apparent coefficients of the pseudo-second order kinetic model obtained from the fitting of As(III) and As(V) release experimental data in the MQ and GW kinetic tests are compared.

Significant differences can be observed between this test and that carried out with reagent water, in terms of both kinetic behaviour of the two arsenic oxidation states and equilibrium, or near to equilibrium, arsenic concentration in the liquid phase. In this regard, a distinctly faster release of As(V) at the very first beginning of the kinetic run appears to occur in the mixtures prepared with groundwater in respect to that assessed in the kinetic tests carried out with reagent water (at 0.1 h reaction time, conc. $As(V)_{GW} \approx 82.2\%$ vs. $As(V)_{MQ} \approx 33.3\%$ of the corresponding equilibrium concentration in the liquid phase), with a significantly higher contribution of As(V) than As(III) to total arsenic concentration at any time of the run. Such a latter observed behaviour appears even more noteworthy considering that in the test carried out with reagent water, instead, As(III) was the form mainly contributing to the total arsenic in solution at any time just after the initial moments of the kinetic run. According to that seen above, the specific physico-chemical characteristics of the groundwater therefore markedly influenced the mobility of arsenic in the pyrite ashes. A further key observation has to be made about the fact that the release of As(V) only appears to be significantly influenced by the groundwater since As(III) concentrations in the liquid phase of this test are all very proximate to those observed in the tests with reagent water at reaction times (t>1 h ca.) approaching the equilibrium in the kinetic run. The use of groundwater in the kinetic test, therefore, appears to bring to a general increase in the extent and rate of As(V) release from the pyrite ashes with a notably minor influence on As(III) release in both kinetic and thermodynamic terms. In Figure 3. the pseudo-second order linearized plots for As(III) and As(V) release kinetics in the GW test are shown.

Table 4. Coefficients of correlation (r^2) obtained for the linear fit of time dependence of total As, As(III) and As(V) release to the kinetic models

Arsenic release kinetics – GW test	**Kinetic model r^2**				
Kinetic model	**Pseudo I-order**	**Pseudo II-order**	**Elovich**	**Power function**	**Parabolic diffusion**
As	0.5138	0.9987	0.9027	0.9362	0.9173
As(III)	0.6558	0.9931	0.9092	0.9598	0.9008
As(V)	0.7009	0.9951	0.7408	0.9377	0.7751

Table 5. Pseudo-second order equation coefficients for total As, As(III) and As(V) release kinetics;

Equation		**As release kinetics – GW test**			
$q_t = t / [A + (t/q_{eq})]$		**unit**	**As**	**As(III)**	**As(V)**
Coefficients	A	(µg^{-1}·L·h)	0.02	0.37	0.07
	q_{eq}	(µg·L^{-1})	31.1 (30.7*)	6.1 (6.2*)	28.5 (24.5*)
	r_{0r}	(µg·L^{-1}·h^{-1})	57.5	2.7	14.0
	K_{2r}	(µg^{-1}·L·h^{-1})	0.06	0.07	0.02

* experimental value

Table 6. Comparative table of pseudo-second order equation coefficients for As(III) and As(V) release kinetics within the MQ and GW tests;

Equation			**Coefficients**			
$q_t = t / [A + (t/q_{eq})]$			**A (µg^{-1}·L·h)**	**q_{eq} (µg·L^{-1})**	**r_{0r} (µg·L^{-1}·h^{-1})**	**K_{2r} (µg^{-1}·L·h^{-1})**
As release kinetic test	MQ	As(III)	0.15	7.2	6.7	0.13
		As(V)	2.49	5.6	0.4	0.01
	GW	As(III)	0.37	6.1	2.7	0.07
		As(V)	0.07	28.5	14.0	0.02

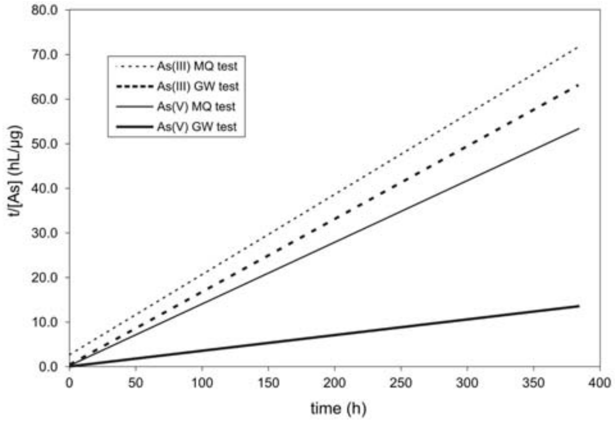

Figure 3. Pseudo-second order kinetic equation linear plots for As(III) and As(V) release. MQ and GW tests

As it can be seen from the pseudo-second order linearized release plot for the kinetic test carried out in groundwater (GW test) presented in Figure 3., the separation between the two As(III) and As(V) linear fits well represents the different behaviour of the two arsenic forms shown in the experimental kinetic curve, with a significantly higher contribution of As(V) in respect to As(III) to the total arsenic in solution at any time of the run and an higher gap between their relevant concentrations at the initial phase of the release process. Such a behaviour, as previously observed, is markedly different to that shown in the kinetic test carried out with reagent water (MQ test), where arsenite was the form mainly contributing to total arsenic at any time of the run. As it can be observed comparing the pseudo-second order linear fit plots of the two kinetic experiments, while groundwater characteristics show only a minor effect on As(III) release (being the two relevant MQ and GW plots very close to each other) they appear to considerably amplify the mobility of As(V), which shows a significantly higher rate and extent of the release process in the GW test in respect to those observed in the MQ test. The same considerations can be made by analysing the values of initial rate (r_{0r}) and equilibrium concentration (q_{eq}) obtained for As(III) and As(V) by the linear fitting of the experimental data of the two tests (i.e. MQ and GW) with the pseudo-second order kinetic equation, shown in the comparative Table 6. Although it appears arbitrary to give a precise and sound mechanistic justification of the observed phenomena because of the intricate compositional characteristics of both pyrite ashes and groundwater, some reasonable hypotheses could be made. In respect to thermodynamic aspects, a first element emerges observing the significantly higher amount of As(V) released at equilibrium in the test carried out with groundwater (GW test) in respect to that released in the tests carried out with reagent water (MQ test). Such a behaviour could be an effect of the, although a little, higher pH mean value of the liquid phase occurred at equilibrium or near-equilibrium state in the GW test than that in the MQ test (i.e. $pH_{GW} \approx 8.4$ vs. $pH_{MQ} \approx 8.2$), which might have promoted an increase of both the negative charge on the surface of the minerals of which the pyrite ashes are composed and the negatively charged arsenate species (i.e. $HAsO_4^{2-}$) present in the test solution, with a consequent combined result of increased arsenate concentration in the liquid phase of the GW test, having minor or no effect on the neutral arsenite species (i.e. H_3AsO_3). Studies[23–25,28] on arsenic adsoption/desorption in minerals and heterogeneous systems, e.g., have demonstrated that electrostatic factors play a key role in such processes. So, although concurrence of other phenomena besides desorption (e.g. dissolution of neogenic amphoteric arsenic precipitates like ferric arsenate, which is not thermodynamically stable in neutral to high pH region[1]) cannot be excluded within the overall release process from pyrite ashes, the assessed effect of increased rate and extent of As(V) release induced by the increased pH value in the GW kinetic test could bring to ascribe to desorption, among the other possible processes, the key role. Further cause of the amplified As(V) mobility assessed in the GW test could be the competition of the occurring anions detected in the groundwater sample utilized in the test (e.g. phosphate, PO_4^{3-} and bicarbonate, HCO_3^-) with arsenate for the adsorption sites on the metal oxide surfaces of which pyrite ashes are composed. Several studies[8,29–32] have, in fact, demonstrated that an increase of strongly adsorbing anions like, e.g., PO_4^{3-} and HCO_3^- can remobilize the arsenic sequestered on iron, aluminium and manganese (hydr)oxides and clay minerals through competitive adsorption. Changes in ionic strength of the aqueous phase can also affect the electrostatic forces near the solid surface and induce the release of weakly adsorbed anions (i.e. outer-sphere complexes) from the minerals.[12] Should, in this test, the mobilized arsenate (or part of it) originate from outer-sphere complexes rather than from inner-sphere complexes formed with the minerals present in the pyrite ashes, the observed higher release of arsenate in the GW test in respect to the MQ test could also be attributed, hence, to the largely higher ion content of groundwater in respect of reagent water. The combination of all the above considered factors might probably explain the observed enhancement of As(V) release in the GW kinetic test. Although an amplification of arsenic release phenomena might have occurred because of the specific experimental conditions of the GW kinetic tests in respect to probably milder interaction mechanisms which might occur between the pyrite ashes impoundment and the groundwater system at the site scale – as previously discussed with relation to release kinetic tests carried out in reagent water (MQ test) – in consideration of the markedly high MCL exceedances assessed in the GW kinetic test, it appears reasonable to predict arsenic concentration in groundwater exceeding the relevant MCL since the first moments of a possible direct contact of the pyrite ashes impoundment with the underlying aquifers.

In consideration of the complex composition of the pyrite ashes and the possible participation and interplay of the different constituents of the material within the whole release process, a rigorous mechanistic justification of such an observed arsenite and arsenate kinetic behaviour based on the sole kinetic data cannot be given and it would appear arbitrary to ascribe it to precise and specific physico-chemical mechanisms being not supported by sound spectral evidences and previous comprehensive studies on such an intricate matrix. Nevertheless, in terms of possible mechanistic aspects, the kinetic behavior shown by arsenite and arsenate in the tests might be explained by ascribing to As(V) a non-specific adsorption (i.e. outer-sphere complexation) ruled by rapid electrostatic attraction of arsenate with the solid surface at low equilibrium concentrations, with the occupancy of energetically equivalent sites and the coverage of a monolayer on the minerals' surface. Support to such a hypothesis may be provided by the results of the arsenic release kinetic tests conducted using the groundwater sample (GW test), in which the formation of outer-sphere complexes of arsenate with the solid surface appears consistent with the higher release rate observed for As(V) also because of the ionic strength of the solution. A combination of weak electrostatically (outer-sphere complexation) and more energetically (i.e. inner-sphere complexation) bonded arsenate on the pyrite ashes minerals would also appear consistent with the results of the release kinetic test carried out using reagent water (MQ test), in which arsenite was the form showing the higher release rate. Having, in fact, the material been exposed to weathering for decades it might be possible that large part of the weakly bonded and more mobile arsenate had been sequestered from the solid surface by the interaction with water phases at the site while the more strongly bonded arsenate only remained available for release within the test. Being neutral arsenite not able to participate in weak electrostatic bonds with the solid surface, a less energetic than arsenate inner-sphere complexation with the pyrite ashes mineral surfaces should be in this case assumed for arsenite because of its observed higher mobility.

4. Conclusions

The results of this study provided previously unavailable information about the kinetic behavior of arsenic in pyrite ashes within experiments approaching the scenario of leaching processes induced by rainfall or direct contact with groundwater systems at the site scale. The kinetic experiments, conducted according to the batch extraction method, evidenced the presence of As(III) and As(V) oxidation states in the form of neutral arsenite and anionic arsenate in both the water phases of mixtures prepared with reagent water and groundwater. The tests carried out using reagent water showed both a rate and extent of arsenite release higher than arsenate, with total arsenic concentration ([As] = 12 μg/L) at equilibrium or near-equilibrium conditions only little exceeding the arsenic MCL ([As] = 10 μg/L) for surface waters and probably not topping the MCL in the downstream flows of pyrite ashes deposit at the milder than experimental conditions established at the site scale. A reverse behavior was, instead, observed within the kinetic experiments using a groundwater sample collected at the site, where a significantly higher release rate and extent for arsenate than for arsenite occurred, the physico-chemical characteristics of groundwater mainly conditioning arsenate mobility in the system. Within these test, total arsenic in the water phase exceeded the relevant MCL for groundwater ([As] = 10 μg/L) since the first moments of the kinetic run and, at equilibrium or near-equilibrium, was markedly higher ([As] = 31 μg/L) than such a value. Although milder than experimental interactions could be in general expected at the site scale, the assessed extent of arsenic release in the water phase cannot exclude possible exceedances for total arsenic in the aquifer in event of direct contact of the pyrite ashes impoundment with the groundwater system. In all kinetic tests the best fitting for arsenite as well as arsenate release data was obtained using a pseudo-second order kinetic model with good correlation coefficients. The shape of all experimental kinetic plots suggested the occurrence of multiple and complex desorption mechanisms within the release processes observed in the test, possibly involving both electrostatically ruled non-specific bonds (outer-sphere complexes) and more energetic specific bonds (inner-sphere complexes) for arsenate and specific bonds only for arsenite. The occurrence of transport driven steps within the desorption processes might also be hypothesized because of the segmentation of the kinetic plots observed in the experiments. Although the assessed complex composition of the pyrite ashes does not allow to exclude the involvement of a combination of multiple processes at lower dimensional scale, the results of the experiments bring to identify the predominance of desorption processes from the surface of iron oxides in the phenomenological expression of arsenic mobility within the material.

Overall, the present study has illustrated the mobility of arsenic within the pyrite ashes at different experimental patters which could approximate actual conditions at the site scale, also casting light on some limits, in terms of environmental representativeness, of the leaching tests conducted solely using reagent water. The results of the study bring to remark the importance of conducting representative and site-modeled experiments for appropriately evaluate the potential environmental impact of this type of industrial residue and for designing effective protection and/or remediation plans.

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Povzetek

Študirali smo mobilnost arzena v piritnih pepelih in njegove možne efekte na vodne sisteme. Ekstrakcijska metoda je bila uporabljena za ocenitev kinetike in obsega izluževanja, ki ga povzroči kontakt tega materiala z deževnico ali s podtalnico. Območje pH-Eh vrednosti, ki se vzpostavi v sistemu piritni pepel/voda, povzroči, da sta As(III) in As(V) v vodni fazi prisotna kot nedisocirani arzenit H_3AsO_3 in anionski arzenat $HAsO_4^{2-}$. Testi reakcij z deionizirano vodo so pokazali, da sta hitrost in obseg izluževanja arzenita večja od arzenata. Celotna ravnotežna koncentracija arzena ([As] = 12 µg/L) rahlo presega Maksimalni EU koncentracijski nivo (MCL) za površinske in podtalne vode ([As] = 10 µg/L). Testi s podtalnico pa so nasprotno pokazali, da sta hitrost in obseg izluževanja za arzenat močno povečana v primerjavi z arzenitom. Kemijska sestava podtalnice torej vpliva predvsem na mobilnost arzenata; celotna koncentracija arzena skoraj vedno presega MCL vrednost in se blizu ravnotežnih pogojev močno poveča ([As] = 31 µg/L). Raziskava je pokazala kakšen pomen za okolje ima mobilnost arzena v piritnem pepelu. Opozorila je tudi na omejitve uporabnosti rezultatov izluževalnih testov v čisti vodi.