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Simultaneous leaching of arsenite, arsenate, selenite and selenate, and their migration in tunnel-excavated sedimentary rocks: II. Kinetic and reactive transport modeling

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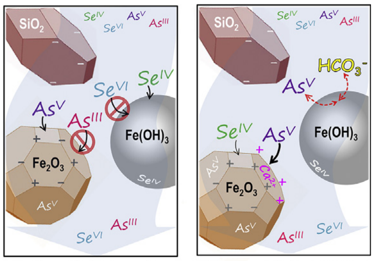
HIGHLIGHTS

- Evaporite salts were crucial in the geochemical evolution of effluents.
- Fe-oxyhydroxide phases were the dominant adsorbents of As and Se species.
- pH & Fe-oxyhydroxide phases were important in the migration of As^{III}, As^{V} & Se^{IV}.
- Preferential adsorption strongly affected As^{V} & Se^{IV} migrations.
- As^{V} adsorption was enhanced by Ca^{2+} but suppressed by HCO_3^-.

GRAPHICAL ABSTRACT



Preferential adsorption
Effects of Ca^{2+} & HCO_3^-

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ABSTRACT

Predicting the fates of arsenic (As) and selenium (Se) in natural geologic media like rocks and soils necessitates the understanding of how their various oxyanionic species behave and migrate under dynamic conditions. In this study, geochemical factors and processes crucial in the leaching and transport of arsenite (As^{III}), arsenate (As^{V}), selenite (Se^{IV}) and selenate (Se^{VI}) in tunnel-excavated rocks of marine origin were investigated using microscopic/extraction techniques, column experiments, dissolution-precipitation kinetics and one-dimensional reactive transport modeling. The results showed that evaporite salts were important because aside from containing As and Se, they played crucial roles in the evolution of pH and concentrations of coexisting ions, both of which had strong effects on adsorption-desorption reactions of As and Se species with iron oxyhydroxide minerals/phases. The observed leaching trends of As^{V}, As^{III}, Se^{IV} and Se^{VI} were satisfactorily simulated by one-dimensional reactive transport models, which predict that preferential adsorptions of As^{V} and Se^{IV} were magnified by geochemical changes in the columns due to water flow. Moreover, our results showed that migrations of As^{III}, Se^{IV} and Se^{VI} could be predicted adequately by 1D solute transport with simple activity-K'_d approach, but surface complexation was more reliable to simulate adsorption-desorption behavior of As^{V}.

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1. Introduction

Arsenic (As) and selenium (Se), trace elements with lethal and carcinogenic effects at elevated concentrations, are often released from tunnel-excavated sedimentary rocks of marine origin at amounts exceeding environmental standards (Li et al., 2016; Tabelin et al., 2012a, b; 2014a, b; Tamoto et al., 2015). Both elements are redox sensitive, a property that allows them to undergo reduction or oxidation reaction in nature and form several compounds with various oxidation states. In surface environments where conditions are mildly oxidizing, for example, As and Se exist as oxyanions with +3 (arsenite) or +5 (arsenate) and +4 (selenite) or +6 (selenate) oxidation states, respectively (Goldberg, 2014; Nakamaru and Altansuvd, 2014; Smedley and Kinniburgh, 2002). Speciation of As and Se is crucial in their final fates in the environment because their oxyanions tend to loss or gain protons with pH that change their ionic charges and adsorption-desorption behaviors (Goldberg, 2002, 2014; Raven et al., 1998; Savage et al., 2000). According to Wang and Mulligan (2006), As^{V} adsorption to positively charged surfaces of iron oxyhydroxide minerals/phases (e.g., hematite and hydrated iron oxyhydroxide ($Fe(OH)_3$)) is relatively extensive in soils and sediments because it exists as a negatively charged oxyanion ($HAs^{V}O_4^{2-}$) under geochemical conditions typically found in ground and surface waters (pH 6–8). In comparison, As^{III} adsorption is limited under these conditions because its uncharged $H_3As^{III}O_3$ oxyanion is dominant. At more alkaline pH, however, adsorption of As^{III} has been reported to increase slightly until the isoelectric point of iron oxyhydroxide minerals/phases (about pH 8.6) because of its deprotonation to a negatively charged oxyanion (Pierce and Moore, 1982; Wang and Mulligan, 2006). Similarly, the oxyanions of Se^{IV} have been reported to exhibit pH-dependent adsorption but those of Se^{VI} rarely adsorbed to common minerals/adsorbents regardless of the pH (Balistrieri and Chao, 1987; Börsig et al., 2017; Goldberg, 2002; Kang et al., 2002). Speciation of As and Se in dynamic systems commonly found in the environment is further complicated by two factors: (1) oxyanions with different oxidations states may coexist because of sluggish oxidation rates when only O_2 is present as an oxidant (Kim and Nriagu, 2000; Vesper et al., 2008), and (2) presence of other more abundant ions like Na^+, Ca^{2+}, SO_4^{2-} and HCO_3^- that could dramatically affect their adsorption-desorption behaviors. For example, Wilkie and Hering (1996) noted the enhanced adsorption of As^{V} to hydrous ferric oxide (HFO) due to favorable electrostatic effects of Ca^{2+} ions while Anawar et al. (2004) showed that As^{V} mobility in sediments at high HCO_3^- concentration increased because of competition between As and HCO_3^- for adsorption sites.

Although speciation is crucial in understanding how As and Se migrate in natural geologic media, majority of studies about the leaching and transport of As^{III}, As^{V}, Se^{IV} and Se^{VI} have been limited to one- or two-component systems (e.g., As^{III} or/and As^{V} only) that used pure mineral assemblages as adsorbents in batch experiments or media in column studies (Go and Lim, 2004; Gusman et al., 2016; Hyun and Lee, 2013; Kwon et al., 2016; Su and Wang, 2011; Tabelin et al., 2013, 2014c; Tao et al., 2006; Wang et al., 2008). Several studies have also evaluated the leaching and migration of As and Se in contaminated soils, rocks and sediments using laboratory experiments and in situ studies (Doherty et al., 2017; Tabelin and Igarashi, 2009; Tabelin et al., 2010; 2012c, d; Tamoto et al., 2015; Tatsuhara et al., 2012; Yolcubal and Akyol, 2008), but because of inherent difficulties in quantifying As and Se species, these studies generally ignored the effects of speciation. In other words, the roles played by pH and coexisting ions on the transport behaviors of As and Se species in natural geologic media remain poorly understood especially under dynamic conditions.

This paper is Part 2 of a two-part basic study on the leaching and transport of As and Se species in tunnel-excavated sedimentary rocks of marine origin under intermittent and unsaturated flow. In Part 1 of this study, simultaneous leaching of As^{III}, As^{V}, Se^{IV} and Se^{VI} was observed regardless of leaching duration and liquid-to-solid ratio, and their distributions relative to each other closely followed those predicted by equilibrium Eh-pH diagrams (Tabelin et al., 2017a). Rapid leaching of As and Se was attributed to the very high solubilities of evaporite salts containing these elements that were formed during diagenesis of the original rock. Once released, however, migrations of As^{III}, As^{V}, Se^{IV} and Se^{VI} were considerably different as illustrated by periods when As^{III} and Se^{VI} predominated in the effluents that were contrary to predictions of Eh-pH diagrams. A comparison of consecutive-batch and column speciation results indicates that species-dependent adsorption-desorption reactions were most likely magnified by water flow and accompanying changes in pH and concentrations of coexisting ions (Tabelin et al., 2017a). Although Part 1 pointed to preferential adsorption-desorption reactions as important mechanisms controlling the leaching and transport of As and Se species in the rocks under intermittent and unsaturated flow, how these reactions occurred, including the effects of pH and coexisting ions, remain unclear. In addition, the intertwining roles played by water flow, rock composition and effluent/pore water chemistry in these reactions were apparent but are still not well understood and should be evaluated in more detail.

These issues are tackled in this study using dissolution kinetics and one-dimensional (1D) reactive transport modeling whereby adsorption-desorption reactions of As and Se species were implemented using the activity-K'_d approach and two-site surface complexation model. Specifically, the objectives of Part 2 are as follows: (1) to identify the dominant minerals/phases involved in adsorption-desorption reactions, (2) to elucidate the roles played by major, minor and trace minerals in the geochemical evolution of effluents, and (3) to examine the effects of pH and coexisting ions in the leaching and transport of As and Se species. Although the first goal was partly addressed in Part 1 of this study when hematite was identifed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (Tabelin et al., 2017a), additional experiments (e.g., scanning electron microscopic observations and acidic oxalate extraction) were conducted in this part to determine other possible adsorbent minerals/phases in the rocks. The second and third objectives were elucidated by formulating several kinetically-controlled dissolution scenarios of mineral-evaporite salt mixtures as well as by constructing 1D reactive transport models that coupled advection-dispersion with adsorption-desorption reactions.

2. Materials and methods

2.1. Acidic oxalate extraction of amorphous phases

Amorphous Fe, Al and Si were extracted from the rocks using the procedure of McKeague and Day (1965), which was based on the method of Tamm (1922). Acidic oxalate extraction involves leaching of rock samples (<100 μm) in a 1:0.75 mixture of 0.23 M ammonium oxalate ($C_2H_8N_2O_4$) and 0.28 M oxalic acid ($C_2H_2O_4$) at 150 rpm in a temperature-controlled water bath shaker (25 °C). After 6 h, the suspensions were centrifuged at 3500 rpm for 20 min to collect the supernatant, which was then filtered through 0.45 μm Millex® membrane filters (Merck Millipore, USA) and analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES, ICPE-9820, Shimadzu Corporation, Japan). The margin of error