



Retention and transport of arsenic, uranium and nickel in a black shale setting revealed by a long-term humidity cell test and sequential chemical extractions



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ABSTRACT

The dispersion of acidic solutions with high levels of metals/metalloids, as a result of oxidative weathering of pyritic geomaterials, is a major environmental problem in areas where these materials are widely distributed and/or were historically mined. In this study, four types of materials encountered in an old black-shale mining area (unweathered black shale, weathered black shale, burnt black shale, and lime-mixed burnt black shale) were subjected to a long-term (up to 137 weeks) humidity cell test (HCT) combined with sequential chemical extractions (SCE), with the aim of examining geochemical controls on the release of Ni, U and As in this kind of pyritic settings. By combining the results of HCT and SCE as well as previously collected groundwater data, it is clearly shown that the degree of pyrite oxidation is the only major factor controlling the release of Ni, resulting in its highly elevated concentrations in acidic groundwaters. Although U followed a similar leaching pattern as observed for Ni and occurred abundantly in acidic groundwaters, a major decrease in the chemical fraction targeting exchangeable and carbonate phases, and a correlation of U concentrations with redox potential in groundwaters collectively suggest that the release of U was largely controlled by the solubilization of sorbed/carbonate U phases by oxidation to the highly soluble form (UO_2^{2+}). As compared to the HCT, the SCE procedures used in this study delivered equally good estimates of Ni, U and S cumulatively leached, suggesting the strength of the SCE in terms of quantification of these elements during the weathering of pyritic geomaterials. Arsenic X-ray absorption near-edge structure spectroscopy shows that during the HCT (oxidation and leaching) of unweathered black shale, As was oxidized from its reduced form (having the oxidation state of -1 and most probably occurs as arsenian pyrite) to $As(+5)$. Compared to the two cationic metals, As was released to a very limited extent and was not detectable in the leachates having pH between 6 and 3. This is because As was speciated exclusively as negatively-charged oxyanions in these leachates as predicted by MINTEQ modeling, thus was effectively attenuated by concurrently formed iron minerals. These minerals include mainly schwertmannite and K-jarosite as observed by SEM-EDS and also predicted by MINTEQ modeling. Elevated levels of As exclusively occurred in the groundwaters from one tube strongly impacted by seawater intrusion. This was regarded as a reflection of loosely-sorbed As oxyanions reliberated through ion exchange with seawater chloride. In this context, sea-level rise on a global scale as a potential driver for arsenic remobilization in low-lying coastal areas deserves further attention.

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1. Introduction

The release of large amounts of acidic weathering solutions with high levels of toxic trace elements, known as acid mine drainage (AMD) or acid rock drainage (ARD), from pyritic geomaterials (e.g., sulfide mine tailings or pyritic rocks) is one of the major environmental issues globally. It is mainly attributed to the oxidative weathering of iron sulfides such as pyrite (e.g., Peng et al., 2007; Forsberg et al., 2008; Seal et al., 2008; Peng et al., 2009; Tuttle et al., 2009; Claff et al., 2011). Once released,

the trace elements are generally subject to solubility control and/or surface interactions (adsorption or co-precipitation) with other solid fractions (Foster et al., 1998; Savage et al., 2000). Particularly important in the latter cases are secondary iron oxides (e.g., ferrihydrite and goethite) and iron oxyhydroxides (e.g., schwertmannite and jarosite), which occur abundantly as colloidal precipitates in AMD/ARD and mineral coatings on rock grains (Foster et al., 1998; Domènech et al., 2002; Acero et al., 2006; Burton et al., 2009; Parviainen et al., 2012).

As a common pyritic rock widely distributed in many areas of the world, black shale typically contains pyrite and trace elements (e.g., As, U, Ni, Cd and Cu) orders of magnitude higher than ordinary shale (Falk et al., 2006; Lavergren et al., 2009a,b; Tuttle and Breit, 2009). The

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dispersion of acidity and toxic trace elements from this rock has resulted in a long-term deterioration of ecological systems in many regions (e.g., Chon et al., 1996; Fang et al., 2002; Pašava et al., 2003; Peng et al., 2004; Lavergren et al., 2009b; Yu et al., 2012). Also, several studies have demonstrated that iron-oxide encrustations/aggregates on weathered black shales act as effective natural sinks for toxic elements at the microscopic scale, especially for As (Strawn et al., 2002; Fischer et al., 2009a,b; Tuttle et al., 2009). However, the extent and kinetics of natural attenuation processes involving these secondary iron minerals have been sparsely evaluated and characterized in terms of bulk black-shale materials in various oxidation and leaching stages.

To determine the chemical status of trace elements and thereby to better understand their retention/release mechanisms during weathering, sequential chemical extractions (SCE) have been widely applied on pyritic geomaterials as well as their weathering products (e.g., Domènech et al., 2002; Al-Abed et al., 2006; Lavergren et al., 2009a; Claff et al., 2011; Parviainen et al., 2012). Unfortunately, the performance of SCE is prone to a variety of inevitable pitfalls, including the incomplete dissolution of a target phase (Kim and Fergusson, 1991), the partial dissolution of non-target phases (Wallmann et al., 1993; Ostergren et al., 1999), as well as the incomplete removal of dissolved species due to re-adsorption or re-precipitation (Ostergren et al., 1999; Calmano et al., 2001). Therefore, chemical fractions of a certain element operationally defined by SCE may not entirely represent its chemical status in the tested samples.

Humidity cell test (HCT) characterized by alternating dry and humidified air cycles (US EPA, 1994) has been used to simulate the mobility of toxic trace elements as well as acid generation potential under natural weathering conditions (e.g., Newbrough and Gammons, 2001; Forsberg et al., 2008; Hakkou et al., 2008; Sapsford et al., 2009). Similar to other leaching tests, HCT itself provides limited information about the redistribution of trace elements inside pyritic geomaterials in the course of the HCT. In this context, HCT and SCE are complementary to each other and can ideally be combined as an integrated approach which could allow us to better constrain the geochemical processes controlling the release/retention of trace elements in pyritic settings.

In this study, we applied the integrated approach (HCT combined with SCE) on natural and processed black shale materials from an old mining area. The major aims were to: (1) define how these sulfidic geomaterials disintegrate and release As, U, Ni and major elements over time in terms of both absolute and relative leaching amounts and rates; (2) increase the mechanistic understanding of how As, U and Ni are released, retained and transported in such pyritic settings, and (3) assess how the HCT and SCE can be utilized as an integrated tool for improving the understanding of the behavior of oxyanion-forming metalloids (As) and cationic trace elements (U and Ni) in pyritic acidic environments.

2. Materials and methods

2.1. Site description and samples

On the island of Öland at Degerhamn in South East Sweden, a complex black shale setting including natural black shale and a variety of artificially oxidized shale materials occur and are a threat to the environment and groundwater resources (Falk et al., 2006; Lavergren et al., 2009a,b). The natural shale layer is approximately 15 m thick, outcropping in a belt of a few hundred meters width along the south-western coast of the island, with a total amount of c.a. six billion tonnes (Andersson et al., 1985). From the 18th century to 20th century, the shale was mined and burnt on site for production of alum and lime (Eklund et al., 1995), leaving behind c.a. 2,700,000 m³ of burnt shale deposits covering 1.2 km² from quarry walls towards the shoreline (Fig. 1). The deposits are to some extent mixed with lime residues, and occasionally with non-burnt shale. Also, over 60,000 m² mined black shale is exposed along the walls and floor of the old opencast

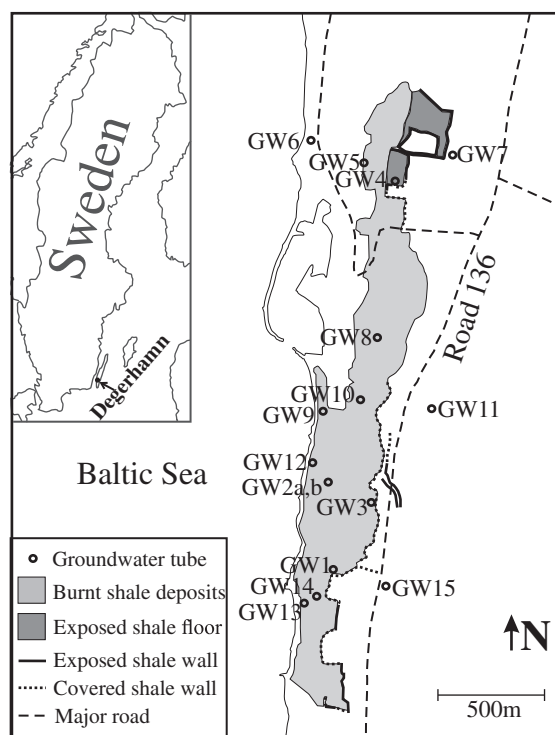


Fig. 1. Map showing the distribution of shale materials and the location of groundwater tubes included in a previous investigation (Lavergren et al., 2009b) in the study area, Degerhamn, Sweden.

mine, therefore directly exposed to weathering processes. Consequently, four types of shale materials occur at the site: unweathered black shale (henceforth shale), weathered black shale (weathered shale), burnt black shale (burnt shale), and lime-mixed burnt black shale (lime-mixed shale). For each of these materials, a composite sample was collected. Shale was taken from five drill cores. Weathered shale was sampled from six sites on the walls of the old shale quarry. Burnt shale and lime-mixed shale were gathered from the upper horizon (0–30 cm) at several sites in approximately 100-year-old waste deposits remaining after previous alum production and lime production, respectively. Each composite sample was crushed and thoroughly mixed, and sieved to get coarse-grained (0.5–2.0 mm) shale materials. The large grain size was chosen partly to represent the large-sized rock materials exposed to weathering in the field, and partly to facilitate the examination of secondary iron coatings/encrustations as found by Fischer et al. (2009a,b) and Tuttle et al. (2009). The water infiltrated in the mining deposits flows in a westerly direction, and eventually discharges into the Baltic Sea (Fig. 1). The total groundwater flow through the study area is estimated at 228,000 m³/year (Administrative Board of Kalmar County, 2005).

2.2. Humidity cell test (HCT)

Coarse-grained (0.5–2.0 mm) shale material (200.0 g) was placed in an enclosed plastic box with ports for input and output of air (Fig. 2). During a seven-day cycle, dry air was passed through the sample container for the first three days and humidified air for the next three days. On the 7th day, the material was mixed with 200 ml of deionized water by stirring. After one hour settling, the solution was decanted and filtered through a 0.45 µm filter. The retrieved volume was measured and recorded. pH and electrical conductivity (EC) of the leachate were measured immediately (WTW pH/Cond 340i/SET with WTW SenTix 41 pH electrode and WTW TetraCon 325 EC electrode). Thereafter, the leachate was acidified to pH < 2 with 1% HNO₃ to avoid any metal precipitation and stored at 4 °C before analysis.

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