



# Leaching of boron, arsenic and selenium from sedimentary rocks: I. Effects of contact time, mixing speed and liquid-to-solid ratio



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## HIGHLIGHTS

- B, As & Se leaching increased with time reaching equilibrium after ca. 48 h.
- Effect of L/S on B & As leaching was strong but not that much on Se.
- All leachates were alkaline regardless of the contact time, mixing speed & L/S.
- $\text{Na}^+ - \text{SO}_4^{2-}$  &  $\text{Na}^+ - \text{HCO}_3^-$  type leachates were produced depending on the L/S.
- Most of B, As & Se originated from soluble salts formed from Cretaceous seawater.

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## ABSTRACT

Sedimentary rocks of marine origin excavated in tunnel projects were recently identified as potentially hazardous because they could release significant amounts of toxic trace elements when exposed to the environment. This study investigated the leaching characteristics of B, As, Se and the major coexisting ions under various conditions to identify the factors and processes controlling their evolution in the leachate. In addition, we evaluated whether the parameters of the currently used leachability test for excavated rocks were adequate. Although the leachabilities of B, As and Se similarly increased at longer contact times, only those of B and As were influenced by the mixing speed and/or liquid-to-solid ratio (L/S). The majority of trace elements dissolved in the leachate originated from the dissolution of soluble salts formed from seawater of the Cretaceous trapped during the formation of the sedimentary rocks. Moreover, the alkaline pH of the leachates could be attributed to the simultaneous dissolutions at varying degrees of the mineral components of the rocks as well as the precipitation of clay minerals. In the leaching test of excavated rocks for regulatory purposes, the best values of contact time and mixing speed should represent conditions of the highest trace element extractabilities, which in this study were found at longer contact times (> 48 h) and the fastest mixing speed (200 rpm). The most appropriate L/S for the leaching test is 10 because it was around this L/S that the extractabilities and leaching concentrations of the trace elements were simultaneously observed at their highest values.

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## 1. Introduction

Tunnel projects for roads and railways require the excavation of huge amounts of rock, most of which is recycled as embankment material for road construction. In 2012, the Soil Contamination Countermeasures Law of Japan was amended and now covers naturally occurring contaminated soils (<https://www.env.go.jp/water/dojo/law/kaisei2009.html>). As a result, more scrutiny has recently been directed to the leachabilities

of hazardous trace elements found in tunnel excavated rocks, which were previously considered as non-hazardous. We have identified two kinds of rocks excavated from tunnels that could potentially contain and leach out substantial amounts of hazardous trace elements: hydrothermally altered rocks and sedimentary rocks of marine origin (Tabelin and Igarashi, 2009; Tabelin et al., 2012a, 2012b). Hydrothermally altered rocks usually contain arsenic (As) and heavy metals like lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) at amounts ca. two-orders of magnitude higher than the unaltered state (Tabelin et al., 2012a). In comparison, boron (B), As and selenium (Se) are the ones typically found in sedimentary rocks of marine origin at concentrations close or sometimes only slightly higher than background levels (Fishbein, 1983; Girling, 1984; Harder, 1970; Ishikawa and Nakamura, 1993; Smedley and Kinniburgh, 2002; Webster, 1999).

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Hydrothermally altered rocks are enriched with trace elements due to the physical and chemical changes associated with the interactions of the host rock and superheated hydrothermal fluid/solution containing high concentrations of dissolved solutes like metals and metalloids. In these rocks, the majority of As and heavy metals are preferentially partitioned in precipitated pyrite grains and not with the aluminosilicate mineral matrix of the host rock (Allen and Hahn, 1994; Halbach et al., 1993; Horton et al., 2001; Huston et al., 1995; Martin-Crespo et al., 2004; Tabelin et al., 2012a). On the other hand, the majority of hazardous trace elements in sedimentary rocks are transported by rivers from mineralized rocks found upstream or sequestered directly from seawater. For example, As in estuaries generally comes from rivers feeding the area, and its distribution in the sediments follows a distinct redox pattern. Solid-phase As is usually concentrated in the surface oxic layer of the sediments with hydrous Fe and Mn oxides while the bottom layers, which are more reducing, have pyrite grains enriched with As (Belzile and Lebel, 1986; Belzile, 1988). Similarly, As in deep marine sediments could largely be attributed to the sequestration of As from seawater by hydrous ferric oxides and pyrite or through the formation of ferric phosphate and ferric arsenate (Calvert and Price, 1970, 1977; Neal et al., 1979; Tourtelot, 1964).

Most of our works have focused on hydrothermally altered rocks because of their conspicuously higher contents of hazardous elements compared with the background levels (Tabelin and Igarashi, 2009; Tabelin et al., 2012a). However, two recent tunnels being constructed in Hokkaido, Japan have excavated sedimentary rocks leaching B, As and Se at concentrations higher than the Japanese environmental standards (B: 1 mg/L; As: 10 µg/L; Se: 10 µg/L) even though they only contain these hazardous trace elements at amounts close to background levels. Researches directed to the negative environmental impacts of sedimentary rocks are quite limited even in the literature probably because of the incorrect perception that rocks containing hazardous elements near background levels are safe. Thus, much is still unknown about the leaching behavior and release mechanisms of hazardous trace elements like B, As and Se in excavated sedimentary rock–water systems.

Standard leaching tests for soils and wastes (e.g., sludges, treated biowastes and fly ashes) have been used for regulatory purposes in countries like Japan (Environmental Agency of Japan Notifications No. 13 and 46), EU (ISO/AWI 21261-1 and 2) and the USA (USEPA method 1312). A summary of the parameters used in these standard tests is given in Table 1. Comparing them would show that even for soils/wastes, the parameters used in the determination of contaminant leachabilities are different most likely due to their site specific compositional variations. Therefore, it is also important to develop a leaching test specifically for excavated rocks, so they could be regulated and disposed of more appropriately. At the moment, a standard leaching test for excavated rocks is still non-existent anywhere in the world. In most cases, tunnel excavated rocks are directly recycled as embankment material for road construction without evaluating the leachabilities of toxic trace elements that they may contain. As a result, several problems

about acid rock drainage (ARD) and heavy-metal contamination have been reported from road embankments (Pye and Miller, 1990) and other road construction activities (Ji et al., 2007; Orndorff and Daniels, 2004). In the absence of a standard leaching test for excavated rocks, Japanese engineers and regulators have used a modified version of the standard leaching test for contaminated soils/wastes (Table 1). In this modified version, a similar liquid-to-solid ratio (L/S) of 10 is used, but at a lower mixing speed of 120 rpm and longer contact time of 24 h (Igarashi et al., 2008; Tabelin and Igarashi, 2009). However, whether these modifications are appropriate or not still remains unknown and has not been evaluated in detail.

This paper is Part 1 of a two-part basic research on the leaching of B, As and Se in marine sedimentary rocks excavated from tunnel projects. The general scope of Part 1 is three-fold: (1) to determine the effects of contact time, mixing speed and L/S on the leaching of B, As and Se from tunnel excavated rocks, (2) to identify the dominant processes responsible for the observed chemical properties of the leachates (e.g., pH), and (3) to evaluate the effectiveness of the currently used leaching test for naturally contaminated rocks. These objectives were achieved using batch leaching experiments, statistical analyses and geochemical modeling calculations. The follow-up paper (Part 2) investigated the effects of environmentally relevant factors like leachate pH, speciation and solid-phase partitioning on the mobilities of B, As and Se in sedimentary rocks and then proposed a comprehensive “picture” of the physico-chemical factors and processes controlling their release, which would be helpful in the design of possible countermeasures against this rapidly growing environmental problem.

## 2. Materials and methods

### 2.1. Sampling and characterization of the rocks

Two sedimentary rocks, both of marine origin, were collected from tunnel projects in the central and northern parts of Hokkaido, Japan. The rock from central Hokkaido is mainly composed of mudstone from the Cretaceous period (sample M). The other rock comes from the Cretaceous-Paleocene Yezo basin (sample O), which is a 10,000-m-thick forearc sedimentary sequence of sandstones and mudstones with subordinate conglomerate extending from offshore of northern Honshu, through Hokkaido, to Sakhalin island, Russia (Takashima et al., 2004). Since the excavated rocks leached out B, As and Se at concentrations higher than the environmental standards, they were placed in interim storage sites prior to their final disposal. We randomly sampled rocks with sizes varying from gravel (>20 mm in diameter) to silty clay (<2 mm in diameter) around these sites using hand shovels. The samples were brought back to the laboratory, air dried at room temperature, crushed using a jaw crusher, and sieved through a 2 mm aperture screen. The less than 2 mm fractions were collected, mixed thoroughly and stored in air-tight containers to minimize their exposure to moisture. The chemical composition and mineralogical properties of the samples were determined on pressed powders (<50 µm)

**Table 1**  
Standard leaching test procedures for soils and/or wastes in Japan, EU and the USA.

Test name	Environmental Agency of Japan Notification No. 13	Environmental Agency of Japan Notification No. 46	ISO/AWI 21268-1 and 2	USEPA method 1312
Type of test	Batch test	Batch test	Batch test	Batch test
Country	Japan	Japan	EU	USA
Type of waste	Industrial waste	Contaminated soil	Soils and wastes	Soils and wastes
Particle size	None	<2 mm	<4 mm	<10 mm
Leachant	Deionized water	Deionized water	Deionized water	60% H <sub>2</sub> SO <sub>4</sub> and 40% HNO <sub>3</sub> (pH 4.2)
L/S	10	10	10	20
Contact time	6 h	6 h	24 h	18 h
Temperature	20 ± 5	20 ± 5	20 ± 3	23 ± 2
Method of agitation	Lateral-reciprocating (200 rpm)	Lateral-reciprocating (200 rpm)	Tumbling (10 rpm)	Tumbling (30 rpm)
Filtration/filter size	1 µm	0.45 µm	0.45 µm	0.6–0.8 µm

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