



# Impact of organic carbon on the leachability of vanadium, manganese, iron and molybdenum from shale residues



Viktor Sjöberg\*, Stefan Karlsson

Man-Technology-Environment Research Centre, Örebro University, SE-70182 Örebro, Sweden

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## ABSTRACT

From 1942 to the 1966, oil was produced by pyrolysis of shale, in Kvarntorp, Sweden. This generated some 40 million m<sup>3</sup> of metal rich pyrolyzed shale and discarded fines that were piled on site with its original metal content almost intact. The present study focuses on the leaching of vanadium, manganese, iron and molybdenum from fines after addition of wood chips and steel slag, in outdoor 1 m<sup>3</sup> reactor systems at low liquid to solid ratio, in order to evaluate the potential environmental impact and recovery of the elements from the leachates. Seasonal variations were observed, with increased leaching during peak summer. For vanadium and molybdenum, high addition of wood chips decreased the leaching, probably due to adsorption. Manganese showed the opposite behavior while leaching of iron was almost independent of the amount of wood chips. Depending on the systems, up to 2200 µg L<sup>-1</sup> vanadium, 90 µg L<sup>-1</sup> molybdenum, 25 mg L<sup>-1</sup> manganese and 500 mg L<sup>-1</sup> iron was found in the aqueous phase. Applied to the 40 million m<sup>3</sup> pile, the annual leaching of those elements may reach 14 ton, 0.6 ton, 200 ton and 2400 ton, respectively.

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## 1. Introduction

During the Second World War the lack of oil for fuel in Sweden was significant and it was early decided by the government that domestic sources had to be explored. Many shale deposits containing hydrocarbons were identified and evaluated. Most promising was the Cambro-Ordovician shale deposit in Kvarntorp (N 59° 7.532', E 15° 15.202') outside Kumla in southern Sweden that contained up to 20% organic carbon. In 1940, shortly after the deposit was discovered, "Svenska Skifferoljeaktiebolaget" (the Swedish Oil-shale Corporation) was established and a processing plant was constructed on site. In 1941 the open pit mining of the shale began and the refinery was in operation from 1942 and onwards. To extract the oil, the shale was pyrolyzed under anoxic conditions in large furnaces and the hydrocarbons were recovered from the flue gases by condensation. After the oil-extraction the still glowing shale waste was immediately transported to a waste pile nearby the processing plant. Due to the construction of the furnaces not all shale sizes were suitable for processing. Material smaller than approximately 5 mm (called fines) caused the furnaces to sinter and was discarded together with the pyrolyzed shale on the waste pile. As a result of the high content of pyrite

the discarded fines still release acid upon oxidation. During pyrolysis most of the sulfur in the original minerals was lost to the air. Oxidation of the material also took place during the transport to the waste pile why the majority of the metals were transformed to oxides. Hence the pyrolyzed shale has slightly alkaline properties in contact with water. When the production ended in 1966 some 40 million m<sup>3</sup> of solid waste had been produced and the pile reached 100 m above ground covering about 50 hectares. Due to ongoing oxidation of remaining hydrocarbons and pyrite, the temperature in the pile is today up to 700 °C some 15 m below the surface (Holm, 2005, in Swedish).

Beside hydrocarbons the shale consisted of illitic clays (up to some 40%), quartz (up to some 35%) and pyrite (up to some 15%) (Armands 1972; cited in Allard et al., 2011, SGU 1972; cited in Gärtner, 2014, Andersson et al., 1985). It is rich in various valuable and precious elements such as vanadium and molybdenum, as well as the base metals aluminum and iron (cf. Fig. 1, data extracted from Karlsson et al., 2013b). None of the metals were recovered during oil extraction and based on existing literature data it can be estimated that the inventory of vanadium and molybdenum in the waste pile exceeds 10000 and 4000 ton, respectively (cf.: Holm, 2005, in Swedish, Bäckström, 2010; Karlsson et al., 2013a). Since the temperature in the pile is well above the boiling point of water there has been a negligible loss of water soluble metal species why the original content of these elements remains in

\* Corresponding author. Tel.: +46 19301264/19303000.

E-mail address: [viktor.sjoberg@oru.se](mailto:viktor.sjoberg@oru.se) (V. Sjöberg).

the pile. Annual quality measurements of the surface water that flows through the area supports this since the water entering the watershed has a slightly higher content of vanadium and molybdenum compared with the water near the pile (Jameson, 2013, in Swedish). The quality of the groundwater in the area shows elevated metal concentrations but it is not possible to conclude if it reflects the natural background or pollution from the pile (Svensson et al., 2005, in Swedish). In the future, however, with decreasing temperature in the pile as the fuel is consumed an increased percolation of rain water will increase the out flow of metals. In addition, lowered temperatures will also favor biological activity which also will increase the mobility of many metals in the waste. Since the closure in 1966, grasses and trees like birch (*Betula* sp.) and aspen (*Populus tremula*) have started to grow on the surface of the pile which in time will increase the organic content and with time produce a soil. These conditions also increase the potential for bioleaching of metals by heterotrophic microbial processes. Such interactions are known, although not always in detail, and used for controlled leaching of valuable metals from different kinds of solid waste (Kalinowski et al., 2004, 2006; Olson and Clark, 2008; Edberg et al., 2010; Sethurajan et al., 2012). By using microorganisms, the cost of the leaching operation is lowered and low-grade sources such as shale, slag and tailings can be processed (Mulligan and Kamali, 2003; Mulligan et al., 2004), even from an economic perspective. Depending on the type of microorganisms and carbon sources, different leaching agents are produced, such as organic acids (Schinner and Burgstaller, 1989; Bosshard et al., 1996; Krebs et al., 1997) and the mechanisms include acidolysis and/or complexolysis (Burgstaller et al., 1992). Depending on the purpose and raw material, bioleaching can be used in systems varying in size from tanks to heaps. However, in most cases the liquid to solid ratio (L/S) is kept fairly high with a few percent of the ore in a well-defined growth medium (Olson and Clark, 2008; Sethurajan et al., 2012). When considering potential negative environmental impact or keeping the cost for the operation to an extreme minimum the L/S should be kept at a minimum and the source of organic carbon must be cheap or preferably available on site to minimize transport.

In order to recover elements from aqueous leachates many different techniques are available. They may involve, depending on

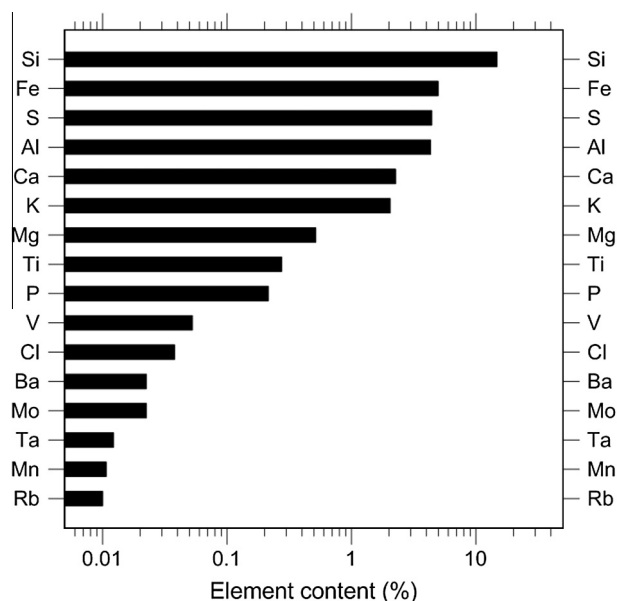


Fig. 1. Element content in the shale measured by XRF (X-ray fluorescence) (data extracted from Karlsson et al., 2013b).

the purpose and chemical conditions, adsorption/co-precipitation to metal (hydr)oxides formed in situ, precipitation, liquid–liquid extraction etc. (Luo et al., 2003; He et al., 2007; Naeem et al., 2007). The choice is usually made according to the properties of the target element and its concentration in relation to other elements and the general composition of the leachate matrix. Other factors to consider include the specificity for the target element, especially if its concentration is low and a high purity product is desired. For vanadium and molybdenum liquid–liquid extraction is widely used for recovery of the elements from a multitude of different liquid matrices (Zhang et al., 1996; Remya and Reddy, 2004; El-Nadi et al., 2009; Kumar et al., 2010; Biswas and Karmakar, 2013). Unfortunately it is less well explored how the technique works at low concentrations of the target element in relation to other elements.

In this study we try to mimic the natural conditions when discarded fines come in contact with a carbon source in the form of wood chips (*Salix viminalis*) at a low L/S, i.e. representative for rainfall. This carbon source is quickly utilized by microorganisms and it is readily available at low cost. Two different cases of mixing are evaluated where one deals with the effects when discarded fines are mixed with wood chips in thin layers in order to optimize the contact between the materials. The other consists of simply putting a 20 cm layer of wood chips on top of the waste. This would be the most cost effective way of adding the carbon source and it can also serve as a proxy for the production of litter from the plant community. The impact of the (bio)leaching on the target elements vanadium and molybdenum was evaluated from their concentrations in the aqueous phase as a function of time. Base metals with potential to interfere during recovery of vanadium and molybdenum i.e. iron and manganese were also determined as well as general hydrochemical conditions. The results allow for an evaluation of leaching efficiency for metal recovery as well as the potential environmental impact of the waste once the waste pile returns to ambient temperatures.

## 2. Materials and methods

### 2.1. Materials and characterization

In early September 2012 about 1.2 m<sup>3</sup> of discarded fines was collected with a wheel loader from the south slope of the waste pile in Kvarntorp. It was transported to the test site and unloaded on a polyethylene tarpaulin where five samples of about 1 kg each were collected randomly. The five samples were pooled and later used for characterization of the fines. From the pooled sample 0.1 kg was milled until some 70% passed a 0.56 mm sieve. This fraction was then used for estimating the metal speciation in the fines by a sequential leaching scheme modified after Tessier et al. (1979). In the original protocol the test is performed in sequence but for this study a parallel treatment was used where fresh material was exposed to each extractant. The following treatments were performed and their operational geochemical species are given in parenthesis:

- (i) De-ionized water (18.2 M $\Omega$ ) (water soluble elements).
- (ii) 1 M ammonium acetate at pH 7.00 (ion exchangeable elements).
- (iii) 1 M ammonium acetate at pH 5.00 (carbonates and amorphous hydroxides).
- (iv) 0.02 M nitric acid in 30% hydrogen peroxide followed by 3.2 M ammonium acetate in 20% nitric acid followed by double volume water (oxidizable elements).
- (v) Microwave assisted digestion in concentrated nitric acid (acid extractable elements).

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