



Leaching of U, V, Ni and Mo from Alum Shale Waste as a Function of Redox and pH – Suggestion for a Leaching method

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Abstract

Alum shale residues in the form of fines and ash were leached at different pH and redox conditions. Total concentrations and mineral analysis indicate loss of some elements in burned shale, and redistribution of others. Uranium and nickel were shown to be more leachable from fines than from ashes. Decreased pH favoured leaching of Ni, U and V, whereas increased pH resulted in increased leaching of molybdenum. Redox conditions affected leaching of Mo and V, but not U and Ni. Thus the method can be used as an estimate for leaching at different redox and pH conditions.

Keywords: Kvarntorp, alum shale, leaching, uranium, vanadium

Introduction

Alum shale in the Kvarntorp area, Sweden (figure 1), was used for oil production during 1942-1966. There is still untouched alum shale in the area, as well as remains from the production in the form of both burned shale (shale ash) and crushed but otherwise unprocessed shale (fines). The shale contains pyrite and forms acid rock drainage (ARD). It is of interest to increase the knowledge of the behaviour of the shale and the shale residues due to the risk of leaching of elements such as nickel and uranium. Examining only the total metal concentration will not necessarily provide information about the potential impact on the environment or metals available for leaching. The aim of this study is to gain increased information about the leaching behaviour of the material and to test the influence of pH and Eh on the leachability of elements.

Methods

Solid samples of both fines and two types of shale ash were collected and leaching was performed under laboratory conditions. The material was sieved and the fraction <2 mm was used in all tests. Manipulation of pH was done by addition of hydrochloric acid or sodium hydroxide, so that a pH range from 3 to at least 9.5 was obtained. Eh was varied by



Figure 1 Kvarntorp is located about 200 km to the west of Stockholm, Sweden.



addition of hydrogen peroxide or hydroxyl ammonium chloride. The redox experiments were not adjusted with respect to pH which implies that their pH was ruled by the redox reactions. For all materials a liquid to solid ratio of 10 was used and all samples were shaken intermittently. After 1, 7 and 28 days, pH (Metrohm 6.0257.000 with temperature compensation), electrical conductivity (Radiometer CDC836T-6, with temperature compensation), redox potential (Thermo Scientific REDOX/ORP 9678BNWP) and element concentrations were measured. For element analysis 100 µl was pipetted from the samples after centrifugation and diluted 100 times before analysis with ICP-MS (Agilent 7500cx).

Samples for total concentrations were sent to MS Analytical (Vancouver). Total concentrations were determined after alkaline fusion, aqua regia or four acid digestions followed by ICP-MS or ICP-AES. The materials were also examined by quantitative phase analysis by XRD.

Results and discussion

Total concentrations and mineral composition

Analysis of total concentrations shows that the fines have higher concentrations of uranium and nickel, but lower concentrations of vanadium and molybdenum than the shale ash (see table 1).

In the fines the sulfur content reached 7.9 % while the ashes contain 3.2 and 0.54 % sulfur respectively. The loss of some elements and redistribution of others due to the burn-

ing process is also reflected in the mineral differences between the fines and the ashes. As can be seen in table 2, no pyrite is present in the ashes and iron is instead found in goethite and hematite.

For the leaching tests in this study, measurements of pH and redox potential for the reference samples indicate that oxygen diffusion through the test tubes is not expected to influence the results to any greater extent, since no variation between day 1, 7 and 28 was observed.

Uranium

Highest concentrations of uranium (up to 9 500 µg/L) were found in leachates from fines. Even when considering the amount of uranium leached compared to the total content in the material, more uranium was leached from the fines than from the ashes (table 3). According to Armands (1972) the leachability of uranium in shale heated to 600°C or more is decreased, which is in line with the results of this study.

At low pH the leaching of uranium increased from both the fines and the shale ashes, while manipulation of the redox potential through the addition of hydroxyl ammonium chloride or hydrogen peroxide did not show any impact that could be distinguished from the accompanied pH change (figure 2). For fines, a pH above 4 gave lower aqueous concentrations than in leachates consisting of only deionized water. This indicates that pyrite weathering may enhance the leaching of uranium from the fines. For the ashes low

Table 1. Total concentrations for U, V, Ni, Mo and S in the different materials.

Sample	U, mg/kg	V, mg/kg	Ni, mg/kg	Mo, mg/kg	S, %
Fines	240	420	180	130	7.9
Shale ash (A)	200	660	51	210	3.2
Shale ash (B)	160	750	42	160	0.54

Table 2. Mineral wt. %

Sample	goethite	hematite	jarosite	gypsum	k-feldspar	pyrite	quartz	Illite/ musc
Fines	-	-	-	13	15.5	12.1	29.8	16.7
Shale ash (A)	5.9	11.2	4.6	19.2	18.2	-	34.2	6.0
Shale ash (B)	8.9	17.5	3.3	1.4	22.5	-	42.8	3.6



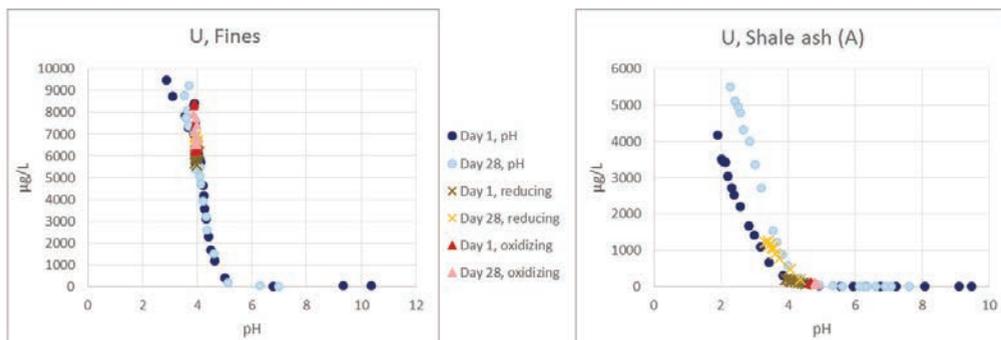


Figure 2 Leaching of uranium was increased with decreased pH for fines and ashes. Manipulation of the redox potential did not show any impact on leaching that could be distinguished from pH effects caused by redox-reactions.

concentrations of uranium were obtained unless the pH was below 4, which is below the natural pH for both ashes.

Vanadium

Accumulation of vanadium in sediments is favoured by good supply of vanadium from circulating seawater, slow sedimentation rate and a stratified partially anoxic water column (Breit and Wanty 1991). Organic materials can reduce V(V) to V(IV) but a stronger reducing agent, such as H_2S is needed for reduction of V(IV) to V(III) which is the least soluble redox state (Wanty and Goldhaber 1992). In alum shale it is believed that a series of reduction, adsorption and complexation reactions between V(V) and dissolved or particulate organic matter immobilized vanadium (Schovsbo 2001). Wright et al. (2014) also suggest that V(III) co-precipitation with Fe-oxides is a possible removal mechanism for vanadium under anoxic conditions.

For vanadium higher concentrations were found in the leachates from the ashes than from the fines (figure 3). Both pH and redox potential affected the leaching of vanadium and for the fines it was observed that the vanadium concentration increased with increased amount of hydroxyl ammonium chloride. This increase declined somewhat after day 1 and after 28 days, the difference from the control samples was small and rather indicated lower concentrations in the samples with added hydroxyl ammonium chloride than in those with only deionized water. For the ashes, increased amount of hydroxyl

ammonium chloride resulted in higher concentration of vanadium in the leachate, but contrary to the fines, these concentrations increased with time. Also higher amount of hydrogen peroxide added, resulted in increased V concentrations in the leachates for the ashes, but these concentrations decreased with time. For the fines, hydrogen peroxide did not increase the concentration of vanadium in the leachates. Both pH below 4 and above 9 increased the leaching. Even though there are different outcomes for the leaching efficiency, vanadium turned out to be not very leachable by the treatments in this test and in no sample more than 6 % was leached (table 3). The behaviour of vanadium indicates that vanadium is incorporated as vanadium(III) in iron(III) phases. Those are either dissolved during reducing conditions or oxidation of vanadium(III) increases its solubility. However the limited solubility of vanadium(III) and the poor attack of hydrogen peroxide on vanadium(III) in ordered iron(III) oxides limits the overall leaching of vanadium.

Nickel

As for uranium, the highest concentrations of nickel was found in leachates from fines, up to 8 000 µg/L corresponding to 43 % being leached (table 4). For nickel it has been suggested that in alum shale it is not concentrated in the pyrite as otherwise is the case for marine black shales (Armands 1972 and references therein) but probably bound organically. Lavergren (2008) suggests that nickel have a large abundance in sulfides more easily



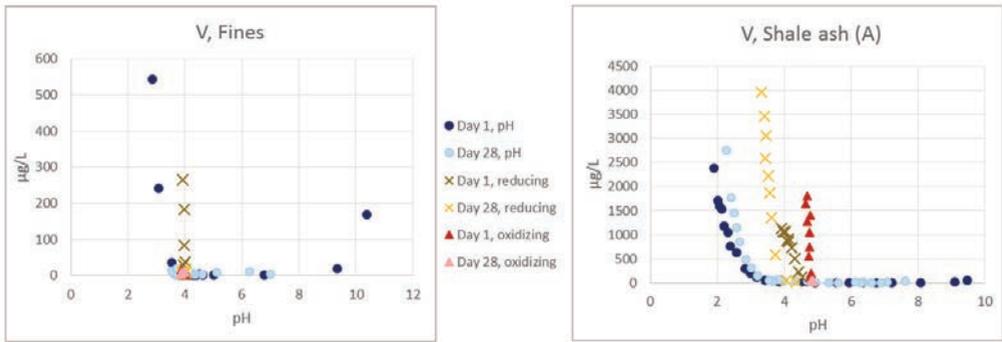


Figure 3 Leaching of vanadium was favoured by low pH, but also by high pH to some extent. The pH in the redox potential manipulated samples was controlled by redox reactions and were not pH manipulated. For shale ash both reducing and oxidizing conditions resulted in increased leaching that can be distinguished from the pH change.

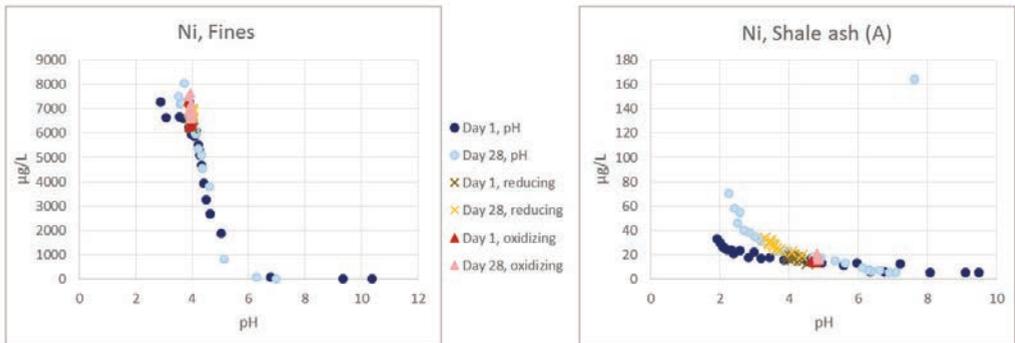


Figure 4 Leaching of nickel was favoured by low pH and showed no impact from manipulation of the redox potential.

oxidized than pyrite in e.g. the alum shale in Degerhamn, Öland. Schovsbo (2001) holds it for likely that nickel was immobilized within the sulfate reduction zone during shale formation. Whether present in pyrite or bound organically, nickel is expected to be affected by heating, either due to oxidation of pyrite or due to oxidation of organic phases. Higher total concentrations of nickel is found in fines than in the ashes. Nickel showed increased leaching by decreased pH but manipulation of the redox potential shows no impact that could be distinguished from the pH effect (figure 4). As the fines generate quite low pH, 35 % of the nickel was leached already with only deionized water.

Molybdenum

As for vanadium, higher concentrations of molybdenum were found in leachates from ashes than from fines. Studies of euxinic sediments have shown that molybdenum is not expected to mainly be found in molybdenite, but in other Mo(V)-S compound(s) (Dahl et al. 2013). Chappaz et al. (2014) argue that pyrite is not the primary host for Mo in euxinic sediments, but that there is a strong correlation between Mo and TOC that remains to be resolved. In this study, leaching of molybdenum increased with higher pH, both for the fines and the two ashes (figure 5). The fines did not show any impact from redox manipulation on molybdenum concentrations while



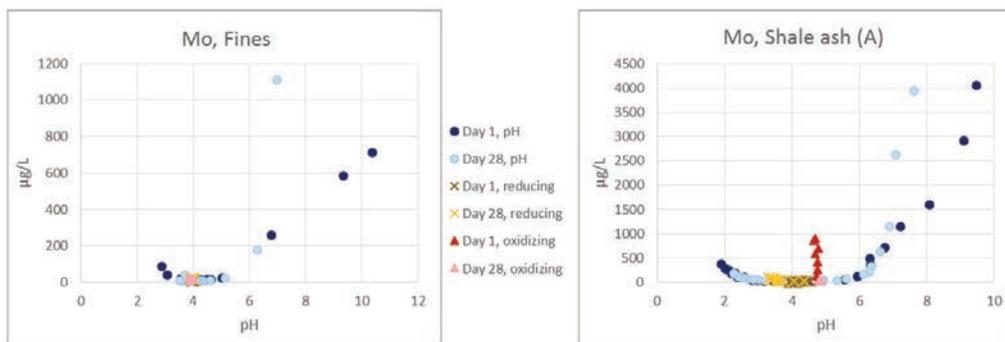


Figure 5 Leaching of molybdenum increased by increasing pH for both fines and ashes. For one of the ashes (A) also oxidizing conditions enhanced leaching that could be distinguished from pH changes, while ash B did not show any impact from redox potential manipulation (B is not included in the figure).

Table 3. Percentage of uranium and vanadium leached from fines and shale ash in deionized water (D.I.), and the range for the percentage leached in manipulated samples (pH or redox).

Uranium				Vanadium			
		% leached	pH			% leached	pH
Fines	D.I.	24	4	Fines	D.I.	0.02	4
	Range	0.04-38			Range	0.003-1.2	
Ash (A)	D.I.	0.23	4.82	Ash (A)	D.I.	0.03	4.82
	Range	0.002-26.5			Range	0.0065-5.7	
Ash (B)	D.I.	0.09	7	Ash (B)	D.I.	0.04	7
	Range	0.01-6.5			Range	0.02-3.6	

Table 4. Percentage of nickel and molybdenum leached from fines and shale ash in deionized water (D.I.), and the range for the percentage leached in manipulated samples (pH or redox).

Nickel				Molybdenum			
		% leached	pH			% leached	pH
Fines	D.I.	35	4	Fines	D.I.	0.09	4
	Range	0.1- 43			Range	0.03-8.0	
Ash (A)	D.I.	0.27	4.82	Ash (A)	D.I.	0.12	4.82
	Range	0.1-3.1			Range	0.04-19	
Ash (B)	D.I.	0.098	7	Ash (B)	D.I.	0.53	7
	Range	0.03-6.6			Range	0.06-30	

one of the ashes did. Added hydrogen peroxide resulted in increased leaching of molybdenum day 1 and 7, while the concentrations were back on the pH curve on day 28, i.e. did no longer show any increase.

Conclusions

Both fines and ashes showed increased leaching of uranium, vanadium and nickel at low pH, while leaching was increased for molyb-

denum at increased pH. The fines still contain pyrite and generate leachates with low pH which enhances further weathering and leaching of uranium and nickel, but not that much of vanadium. For the ashes, weathering with only deionized water added was not very important, whereas forced pH changes in some cases resulted in an increase of elements in the leachates. Nevertheless, even with forced decrease of pH, the ashes did not



reach the same release of uranium and nickel as the fines (nor in percentage leached nor in concentration). The impact that the shale residues have on the environment is dependent on the distribution of the varying types of waste and possible buffering materials (such as lime waste). Two ashes were analysed and even though they distinguish from the fines in the same way, they also display some mutual differences. This reflects the heterogeneity of the material, possibly both original differences in the shale and differences that emanate from inequalities in the treatment during the oil production process (e.g. different types of ovens).

The new method works as a fairly good estimate for leachate composition due to changes in pH and redox potential. It does not require any sequential leaching which makes it possible to also include time as a parameter.

Acknowledgements

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