Leaching of Sulfidic Alum Shale Waste at Different Temperatures

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Abstract
Four different alum shale waste products (unprocessed shale, weathered fines, processed shale and shale ash) from Kvarntorp, Sweden, were leached at different temperatures (-18°C, +22°C and +70°C) in order to elucidate the influence from freezing (frost wedging) and high temperatures (heat generated during sulfide oxidation). Unprocessed shale and the weathered fine fraction have an acidic pH while the processed shale and the shale ash have circum neutral pH. Leaching was performed at liquid solid ratio of 10:1 at room temperature followed by treatment at different temperatures for 24 hours (cycle repeated 10 times). pH, electrical conductivity, redox, alkalinity, acidity, sulfate, major cat ions and trace elements were measured.
pH was almost one pH unit lower in the heat treated shale ash samples compared to the samples kept in the freezer. No significant pH differences were observed for the other samples. Iron and sulfate concentrations were found to be higher in the heat treated samples still containing pyrite (unprocessed shale and weathered fines) indicating a higher rate of oxidation. When it comes to trace elements molybdenum, for instance, significantly higher concentrations were leached from the processed shale compared to the unprocessed shale indicating increased leachability due to transformation of the primary minerals.

Key Words: weathering, freezing, uranium, vanadium, molydenum

Introduction
Background
Shale is a sedimentary rock composed of silt and clay in different proportions. Shales generated in anoxic environments are often called sulfidic black shales due to their content of organic matter and sulfides. The high content of sulfur in sulfidic black shales may pose an environmental risk similar to that posed by base metal mine waste with lowered pH. Low pH will enhance the mobility of trace elements from the shale which may pose a severe environmental risk (Lavergen et.al. 2008).

From the beginning of the 20th century oil was retorted from the black shale at different localities in Sweden (Dyni, 2006).
Kvarntorp, a small community in Närke in the middle of Sweden, were one of the places where black shale was mined. Industrial operations in Kvarntorp have been conducted since the 1940s and the extraction of hydrocarbons ceased in the middle of the 1960s (SWECO VIAK, 2005). From 1950 to 1961 uranium was also refined from the shale in Kvarntorp. According to Dyni (2006) approximately 62 tons of uranium was produced during this period.
For the most part, in Närke, the layer of black shale, which was deposited during late Cambrium, is covered by Ordovician limestone. But in the area of Kvarntorp and its surroundings the black shale layer has been lifted due to faulting. This process has placed the black shale as the uppermost layer, making it possible to mine using open pits.

An important point source of heavy metals in the area is a large waste heap (around 40 Mm^3) containing processed material left over from a dry distillation process used on the ore. The waste heap is still warm due to the ongoing chemical reactions (pyrite as well a kerogen oxidation with temperatures reaching above 700°C) inside it. Because of this generated heat; relatively little water infiltrates the heap. But for

how long the waste heap will remain warm is unknown, however it is estimated that it will remain warm for around 50-100 years. When it cools elevated trace element concentrations in the area are expected since water will start to infiltrate the heap and thereby increase the mobility of trace elements.

The study described in this paper was designed to give an indication about how different elements will be leached from the waste heap once it cools and how the natural weathering of different seasons (heating and freezing/thawing cycles) may affect the waste material.

Materials and Methods

Selected samples

The study involves four materials which can be found in, or in the vicinity of, the heap:

- Black shale; unprocessed shale taken from an exposed (50 years) shale horizon in the area.
- Weathered fine fraction of black shale (hereby referred to as weathered fines); crushed and sieved black shale with a particle size of less than 1 cm. Samples collected at the base of the waste heap. These have been exposed to weathering for 50-60 years.
- Processed shale; black shale which have been processed by dry distillation. This processed shale was processed at temperatures below +500°C. This has removed all hydrocarbons in the material. These samples were collected at the base of the waste heap.
- Ash; black shale which have been exposed to heating. Samples collected at the top of the waste heap.

These materials were leached with water to simulate precipitation. The leaching process was carried out in cycles and in the beginning of each cycle the samples were temperature treated. Some samples were heated up to +70°C, which is a typical average temperature in the waste heap. Other samples were placed in a freezer at a temperature of -18°C to show how frost wedging might affect the materials. Remaining samples were placed in room temperature at approximately +22°C.
The importance of ice for this study is caused by the physical properties of water when it freezes. It is well known that ice has a lower density than water. The decrease in density for ice is caused by an increase in volume when the water molecules arrange themselves in the hexagonal structure of ice. This process generates a force strong enough to deform surrounding solid material. In geology this process is called frost wedging and is, as mentioned above, one of the aspects that are studied in this report.

Leaching process

All materials, black shale, weathered fines, ash and processed shale were crushed and sieved to a particle size of 0.25-0.55 mm prior to use.
For the study six samples of each material were prepared. These materials were then leached with ultra pure water at a liquid-solid ratio of 10:1 for 2-3 days in a turnover shaker. During sampling, which occurred twice a week, the samples were centrifuged at 10 000 g for 60 minutes, and their supernatants were extracted for different analyses. Thereafter the samples were treated at different temperatures by keeping them in an oven and in a freezer, respectively, for approximately 18 hours. The study involved three different temperatures in duplicates; +70°C, +22°C (room temperature) and -18°C. After temperature treatment water was added to the samples again and the samples were put in the shaker for another cycle.
At the beginning of the leaching process, two reference samples were extracted. The first was taken after only 1 hour of leaching. The second reference sample was taken after 1 day of leaching. When both references had been extracted the first temperature treatment commenced. The leaching process carried on repeatedly for 8 cycles. In total 10 sampling occasions.

Analytical

After samplings electrical conductivity, redox, pH and alkalinity/acidity were measured. Electrical conductivity, redox and pH were measured with suitable calibrated electrodes. Alkalinity and acidity were

measured by endpoint (pH 5.4) titration with either 0.02 M HCl or 0.02 M NaOH depending on the intial pH. Elements were analysed with ICP-MS using rhodium-103 as internal standard and sulfate was analysed using ion chromatography.

Results and Discussion

pH, electrical conductivity, redox and alkalinity

Electrical conductivity gives an indication of the total ion content in the leachates (Figure 1).

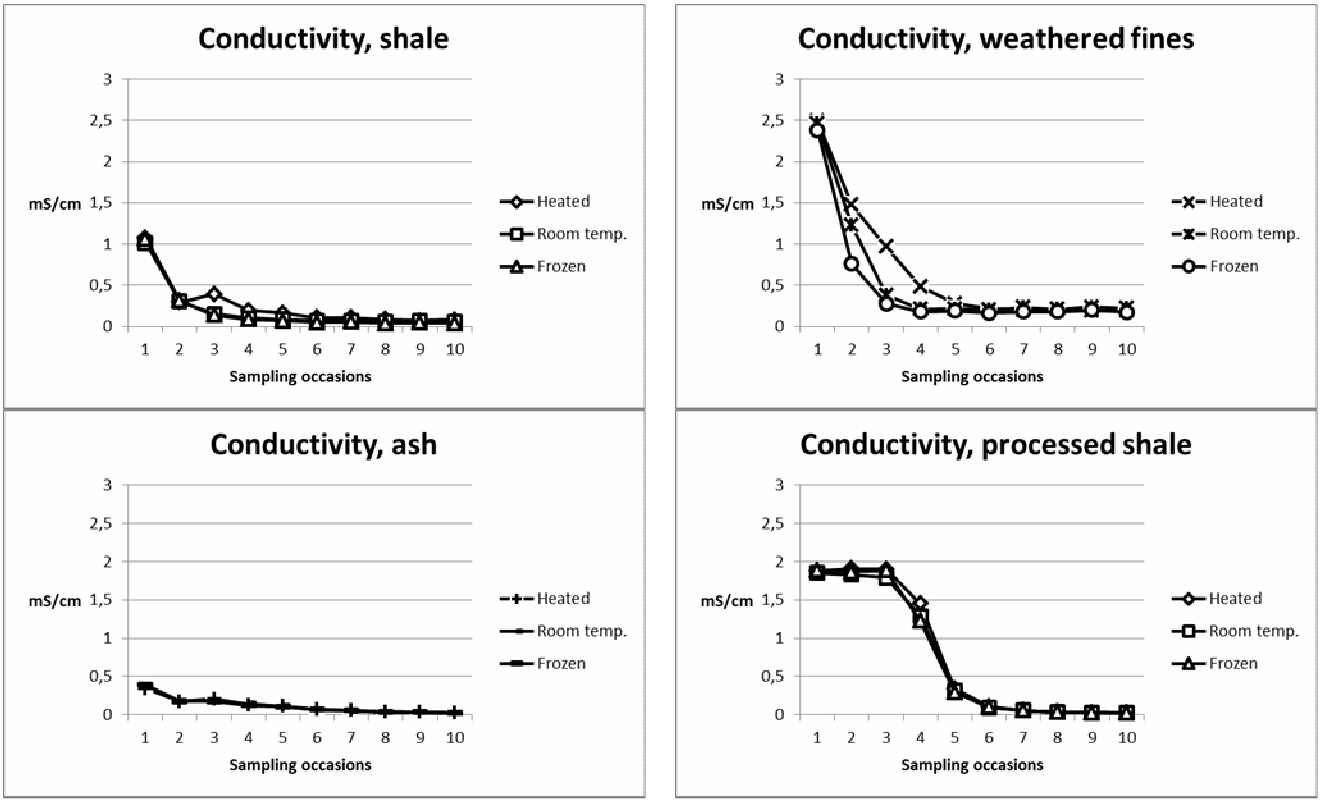

Figure 1. Electrical conductivity at leaching of four different materials at three different temperatures (frozen -18°C, room temp +22°C and heated +70°C).

The measured electrical conductivity of the first two days shows that ions leach quickly from the black shale, the weathered fines and the ash. This suggests that the particles contain coats of various elements which are easily leached (i.e. soluble salts). This is not the case for the processed shale, however. For the processed shale the electrical conductivity remains approximately the same initially indicating the presence of a mineral governing the solubility (Figure 1).
As for the temperature treatments effect on the electrical conductivity; two main patterns can be observed. Heating of shale and weathered fines increases electrical conductivity for the first and second cycle. This suggests that heating to +70°C open up more surfaces in these materials and enables more ions to be leached. For the ash and processed shale no obvious effect of either warming or freezing can be observed. During the last days of the leaching period, the weathered fines which had the highest electrical conductivity. This suggests that approximately 60 years of weathering of the fines may have weakened the mineral structure enabling a relatively easy leaching of ions.

pH of the leachates from the shale and the weathered fines are initially low; around 2.5 (Figure 2). The pH of the leachates increases slightly over time. The pH for the shale leachate stabilizes around pH 3.5 while

leachate pH for the weathered fines stabilized at approximately 3.0. This low pH is primary a result of the oxidation of pyrite, FeS_2 (equation 1; Sartz, 2010) initially followed by iron hydroxide buffering:

$$FeS_2(s) + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \quad (1)$$

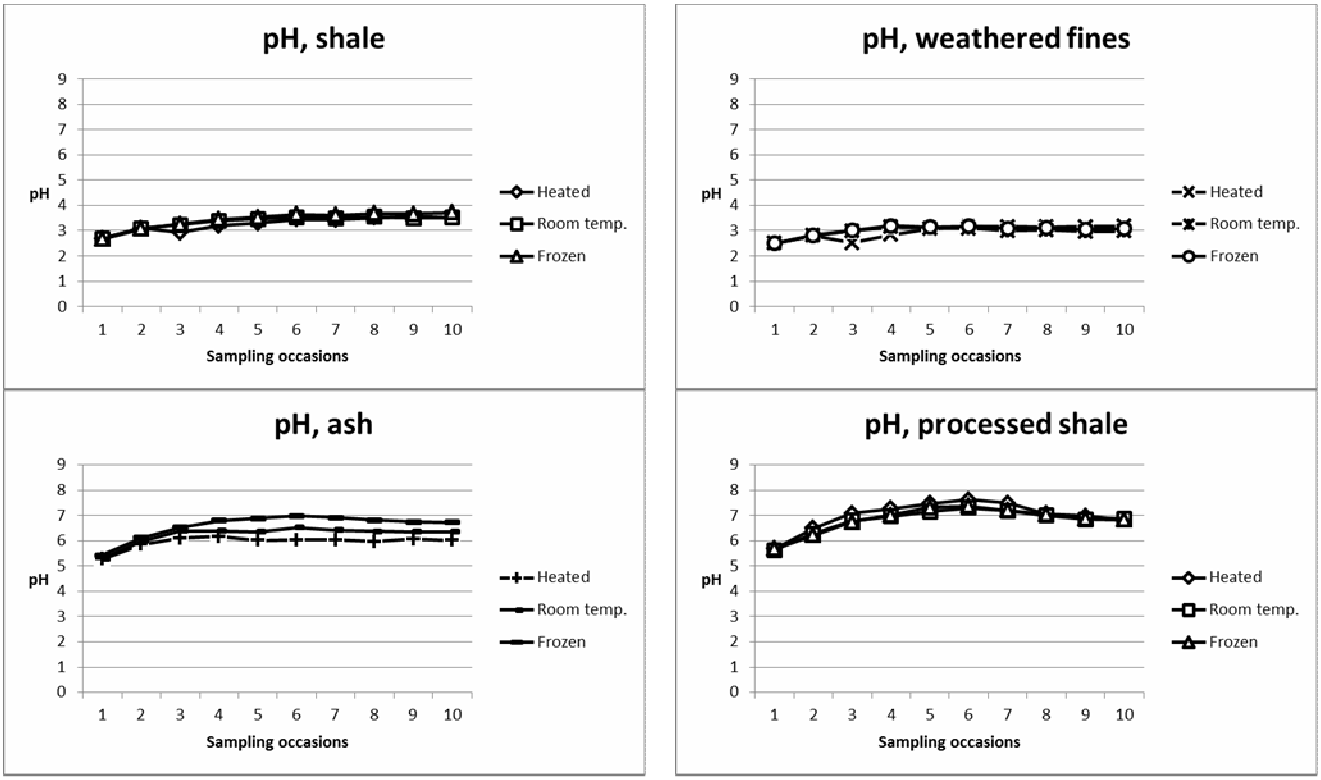

Figure 2. pH at leaching of four different materials at three different temperatures (frozen -18°C, room temp +22°C and heated +70°C).

The reason why the leachates from the weathered fines are more acidic than the shales is probably the same reason as in the case of its higher electrical conductivity, that is, the weathered surfaces and higher surface area.

A small decrease in pH was observed in the leachates from the heated shale- and weathered fines samples on sampling occasion 3. This indicates that the oxidation rate of pyrite, or the release of other pH lowering compounds, may increase as a result of higher temperatures. The dip in pH did not last long however before it once again increased in the same manner as the other samples did. Freezing did not seem to affect the leachates pH from shale or weathered fines.

For the ash and the processed shale the situation was different. Starting pH of their leachates was around 5.5 and an increase in pH over time occurred even in these samples. pH for the ash leachates did not exceed pH 7 while the maximum pH for the processed shale leachates reached approximately 7.5 before its pH slowly began to decrease.

In leachates for the ash such relationships can be observed. pH increases the most when the ash samples were continually frozen and thawed. This suggests that the expanding force of ice causes the exposure of new surfaces on the ash particles, possibly release of buffering minerals. Heating ash, on the contrary, generated the lowest pH increase of the three temperature treatments.

Acidity of shale and weathered fines share a similar pattern (Figure 3). Acidity is higher in the first reference compared to the second reference, suggesting that the species that is responsible for the acidity

covers the particles as a coating. Iron that contributes to acidity may originate from secondary iron sulfate minerals (possibly melanterite or schwertmannite).
For both shale and weathered fines the acidity increased when the samples were heated. Freezing seemed to have no effect on the samples acidity, however. Trace element analysis also shows that the heated samples leach iron to a higher extent than the room temperate and frozen samples (data not shown). This could explain why the acidity of the heated shale- and weathered fines samples increases during the first temperature treatment cycle.

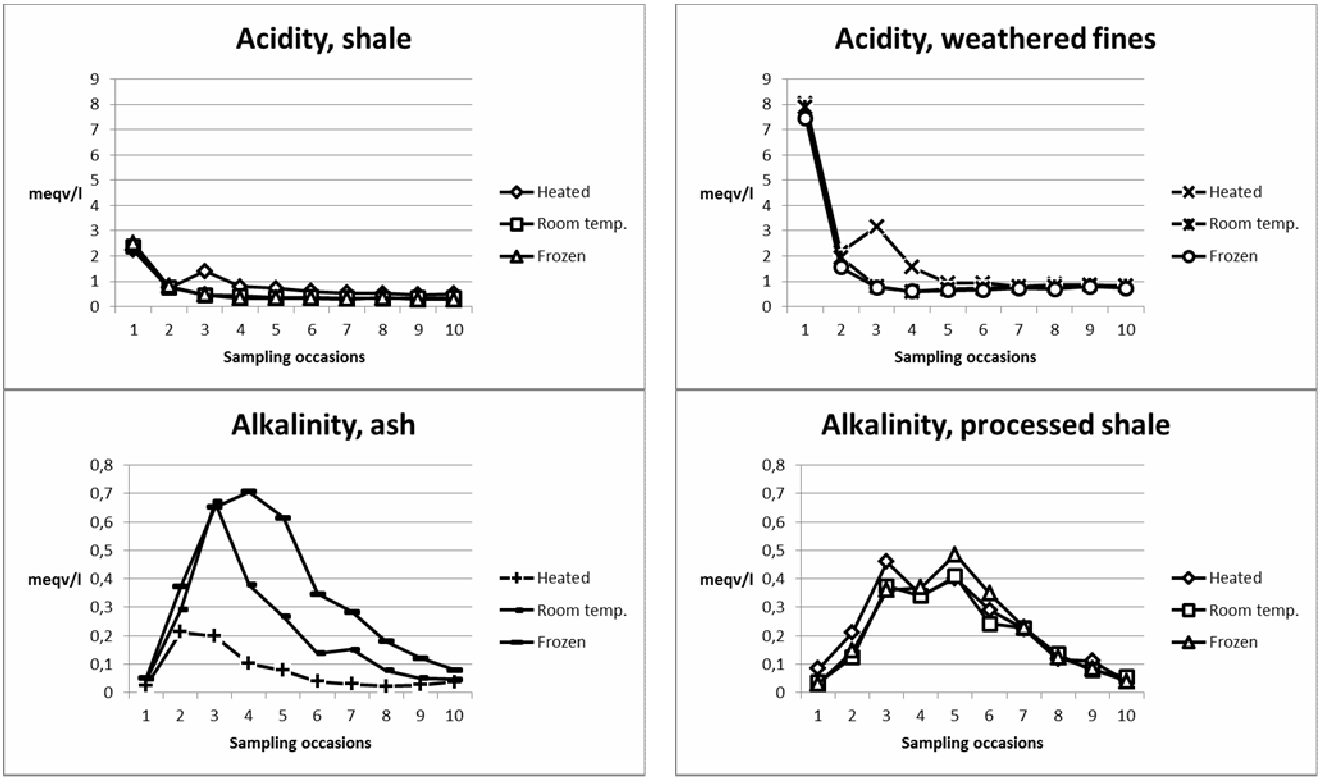

Figure 3. Acidity/alkalinity (meq/L) leaching of four different materials at three different temperatures (frozen -18°C, room temp +22°C and heated +70°C).

Alkalinity in leachates from ash and processed shale is low during the first two sampling occasions. This is probably caused by the release of acidic elements from the materials. Then the carbonates leach at a higher rate than the various acidic elements and cause the alkalinity effect noted in this study (Figure 3). The alkalinity for the samples of the processed shale shows a somewhat erratic pattern but is still quite similar between the different temperature treatments indicating that temperature does not affect the alkalinity, however for the ash, freezing seem to have a significant effect on the alkalinity.
Comparing the different materials, the leachates from the weathered fines have higher acidity than the leachates from the shale which is probably once again a result of previously weathered surfaces and higher surface area. The processed shale and the ash show quite similar alkalinities in their leachates but for occasion 3, 4 and 5 one may clearly see that the ash has higher alkalinity than the processed shale.

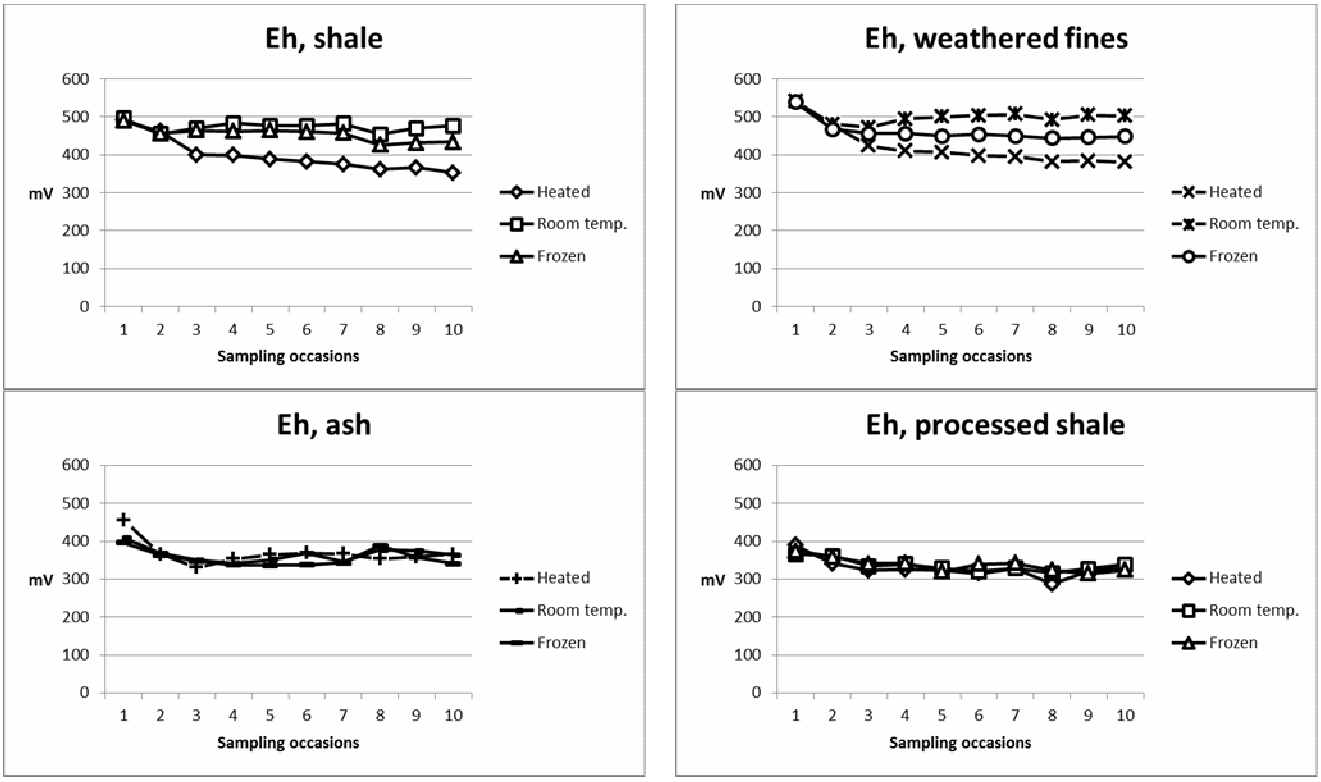

Figure 4. Redox (mV) at leaching of four different materials at three different temperatures (frozen -18°C, room temp +22°C and heated +70°C).

Measured redox values for shale and weathered fines leachates are higher than redox in the leachates from ash and processed shale (Figure 4). This corresponds to the relationship between redox and pH well shown by Eh-pH diagrams. Because the leachates from ash and processed shale have near neutral pH it is not surprising that their measured redox values are lower than those of shale and weathered fines with acidic pH.

Measured redox is lower in the leachates from the heated and frozen samples of shale and weathered fines than in the samples of shale and weathered fines which have been kept at room temperature.

In the leachates from the ash and processed shale no obvious change in redox can be observed as a result of temperature treatments.

Sulfate and base cations

Sulfate concentrations in the leachates from the first two sampling occasions of the shale, weathered fines and ash indicates that sulfate occurs as a coating or a secondary mineral precipitate on the particles and is easily leached by water (Figure 5). Heating shows a clear increase in sulfate concentration in the leachates from shale and weathered fines. As was discussed earlier, heating increases the oxidation of sulfides in these materials and therefore contributes to increased sulfate concentrations.

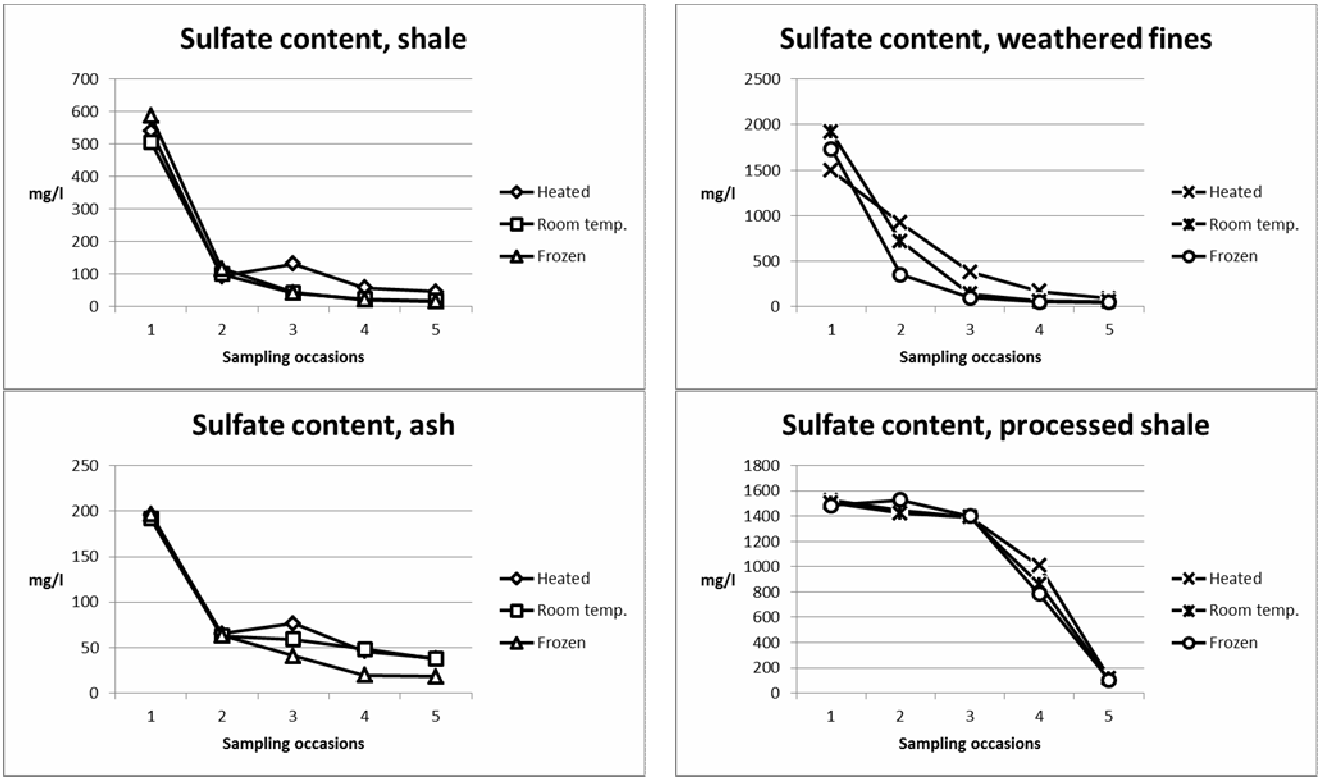

Figure 5. Sulfate (mg/L) leaching of four different materials at three different temperatures (frozen -18°C, room temp +22°C and heated +70°C).

Calcium reaches high concentrations in leachates of the different materials, at least during the first two sampling occasions (shale 150 mg/L, weathered fines 550 mg/L, ash 65 mg/L, processed shale 600 mg/L). After the initial sampling occasions calcium concentrations decrease relatively rapidly. Only in the processed shale the concentrations remain at 600 mg/L for several sampling occasions suggesting a mineral equilibrium.
No clear indication that the temperature treatments affect the leaching of calcium can be observed in the diagrams of shale and weathered fines.
In the ash and processed shale, calcium originating from calcite should possibly occur in the form of lime, CaO, due to the pyrolysis process.

Trace elements
A selection of trace elements will be discussed in this section. Trace elements with relatively high concentrations in the black shale are vanadium, molybdenum and uranium.

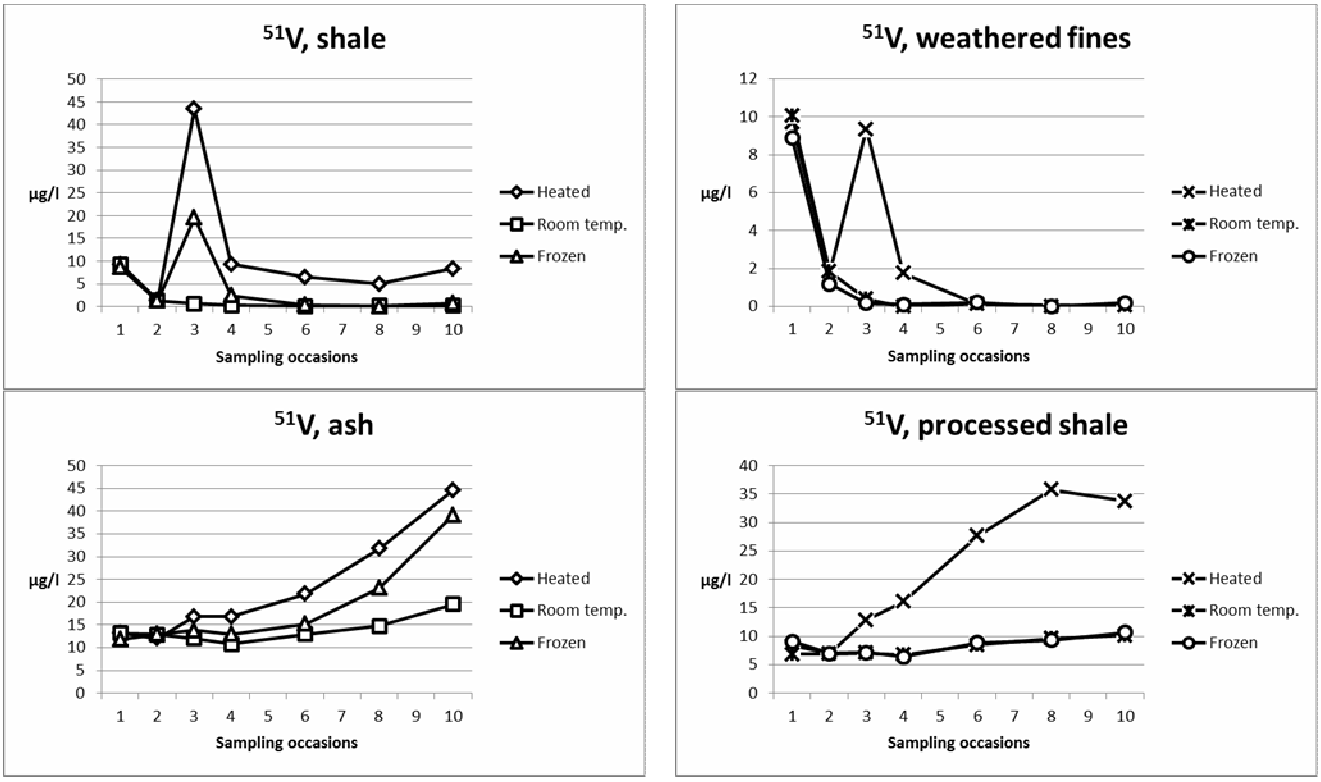

Figure 6. Vanadium (µg/L) leaching of four different materials at three different temperatures (frozen -18°C, room temp +22°C and heated +70°C).

Heating of shale and weathered fines causes a peak of vanadium concentration in the leachates (Figure 6). The vanadium concentration in the weathered fines leachates decreases to very low concentrations while continuous heating of shale stabilizes vanadium concentrations around 5-10 µg/L. Freezing of shale causes also a clear peak of vanadium concentration in the shale leachates.
The concentrations of vanadium are higher in the shale leachates than in the weathered fines leachates. This may indicate that the vanadium accessible through temperature treatments, primary the heating treatment, in the shale already has leached from the weathered fines during its approximately 60 years of exposure to weathering. Vanadium is very sensitive to redox conditions. Heating and freezing of shale and weathered fines lowers redox as was shown earlier.
Burning of shales alters its mineral structure into a composition which favors water leaching of vanadium as shown by the measured vanadium concentrations in the leachates from ash and processed shale. The samples from room temperature show steady vanadium concentrations until sampling occasion 8.
The partially processed ash shows an interesting response to heating and freezing. Vanadium concentration in these leachates increase and the maximum vanadium concentration do not seem to have been reached on sampling occasion 10 (8 temperature treatments). Even the ash samples at room temperature seem to increase vanadium concentrations in their leachates on sampling occasion 10.
The processed shale seems only to be affected by the heating treatment which causes a clear increase in vanadium leaching (maximum around 36 µg/L).

Vanadium does not seem to be affected by pH, at least to no great extent.

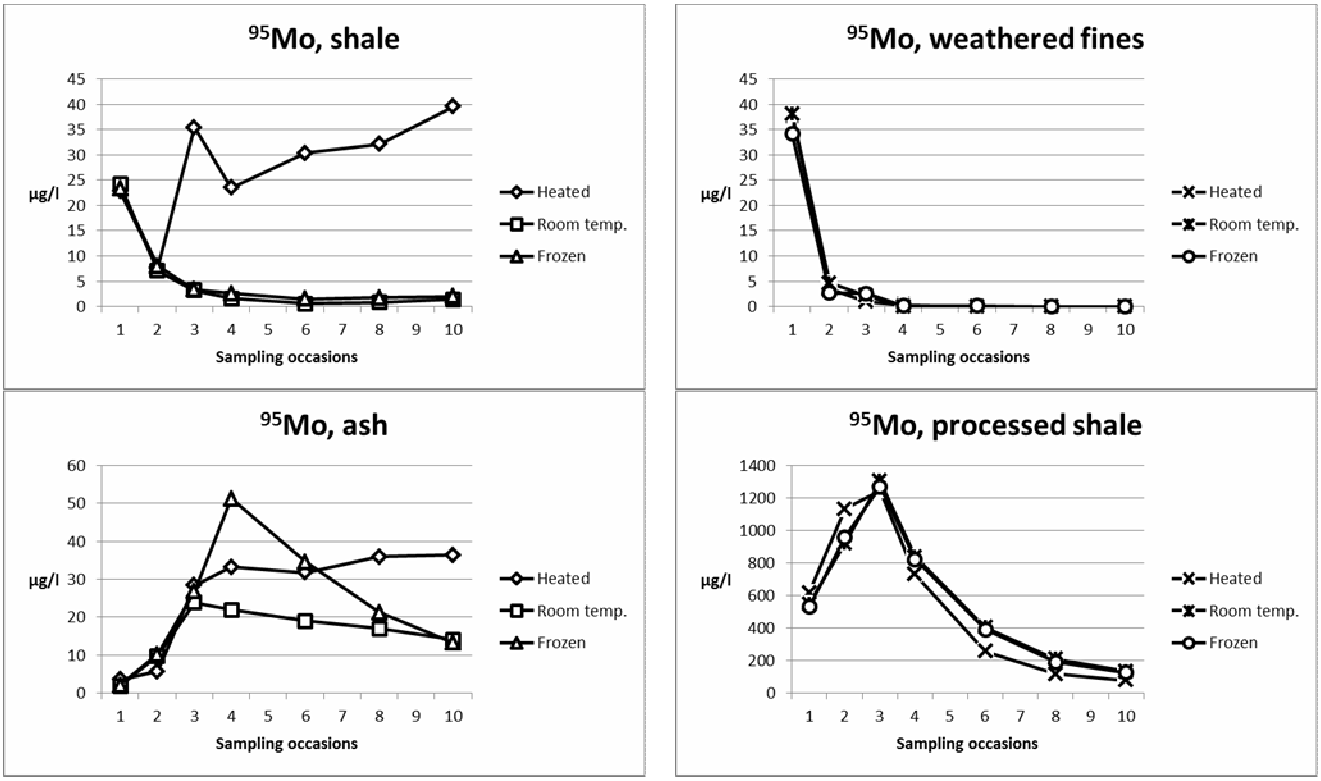

Figure 7. Molybdenum (µg/L) leaching of four different materials at three different temperatures (frozen -18°C, room temp +22°C and heated +70°C).

The temperature treatments do not seem to have any effect on the leachability of molybdenum from the weathered fines. This is not the case for the shale, however, where heating increases the concentration of molybdenum (Figure 7).
Once again different leachabilities caused by different grades of processing are apparent. Ash releases higher concentrations of molybdenum than the shale and weathered fines from sampling occasion 3 and forward. And the leachates from the processed shale contain very high concentrations of molybdenum. According to Cotton et al. (1995) the most common molybdenum containing mineral is molybdenite, MoS_2. When this is roasted it forms MoO_3. Differences in pH between ash and processed shale cannot explain the entire difference in molybdenum concentrations.

Another behavior of molybdenum in the processed materials is that it seems to leach quite slowly; this conclusion is drawn from the increasing concentration during the first three sampling occasions. When compared to pH a relationship between increasing leachability of molybdenum and increasing pH can be observed in the samples of ash and processed shale.

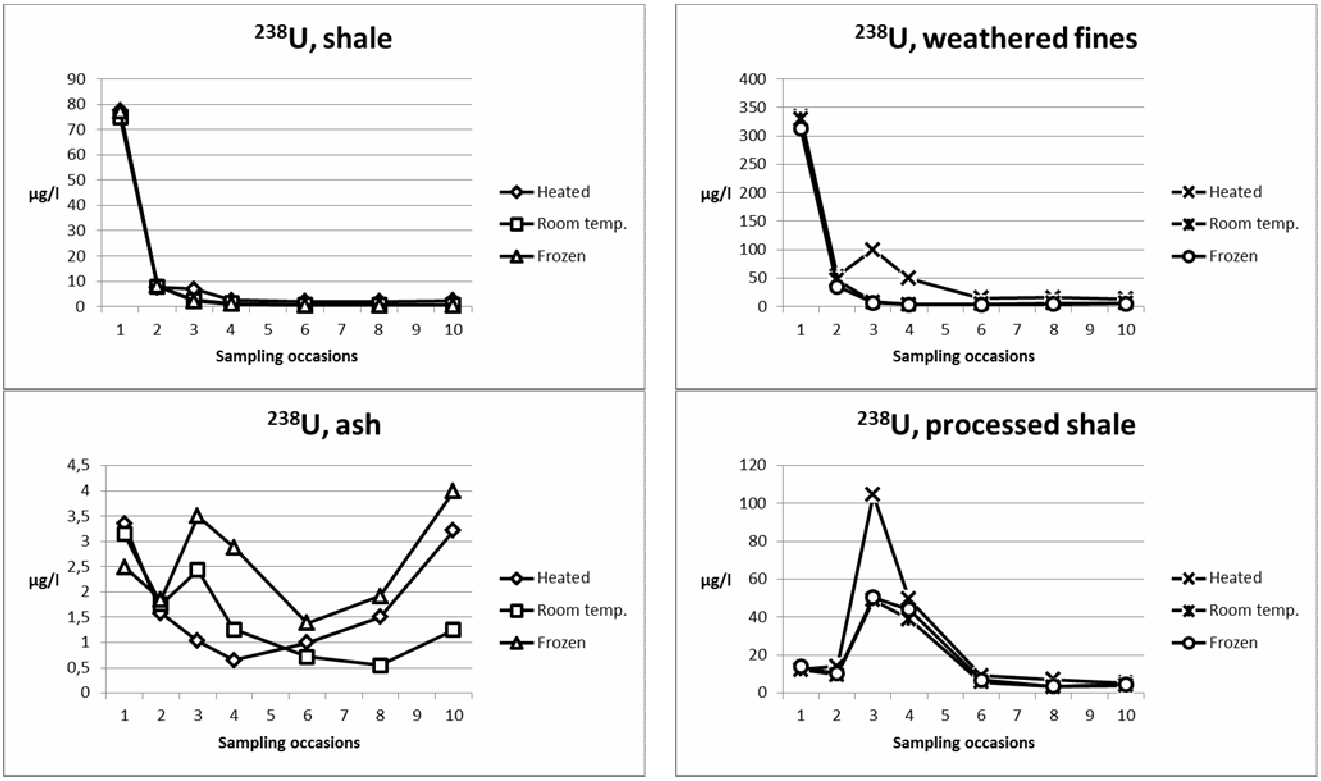

Figure 8. Uranium (µg/L) leaching of four different materials at three different temperatures (frozen -18°C, room temp +22°C and heated +70°C).

The concentration of uranium is higher in the leachates from the weathered fines than in the leachates from the shale (Figure 8). Heating causes a small increase in the leachability of uranium from the shale and weathered fines.
For ash the concentration of uranium in the leachates is down to background concentrations and the different temperature treatments shows no obvious patterns. The uranium concentrations in the leachates from the processed shale are also initially low, but increases on sampling occasion 3 and then drops again. Heating enhances the increase in uranium concentration on sampling occasion 3.

The uranyl ion, UO_2^{2+}, is capable of forming complexes with sulfate and carbonate depending on pH. At low pH uranium occurs as uranyl ion. When pH increases toward neutral or alkaline pH it will become hydrolyzed and if there is carbonate present; uranyl may form carbonate complexes.
Leaching curves for uranium in samples of shale and weathered fines follow a pattern very similar to that of sulfate which suggests a formation of uranyl sulfate complexes. Concentrations of uranium in leachates of processed shale increases during sampling occasions 3 and 4. This coincides with the observed increase in alkalinity for processed shale indicating a formation of uranyl carbonate complexes as well.

Conclusions

For most elements analyzed in this study, their concentrations in leachates from different black shale waste materials decreased during the leaching period. Many elements may have been present partly as soluble salts, which were easily leached with water (wash out). This should be confirmed by further mineralogical work on the samples.
Heating of the waste materials increased leaching of, for instance, vanadium, molybdenum, uranium and sulfate. This suggests a higher rate of oxidation is occurring at higher temperature, which is consistent with lower redox potential, higher acidity and slightly lower pH as observed in the heated samples still containing sulfidic minerals. Much higher molybdenum concentrations observed in the processed shale

suggest a greater leachability of molybdenum from shales may occur if the mineralogy has been changed at high temperatures. According to the analyses conducted in this study heating causes higher rates of leaching than frost wedging (freezing/thawing cycles). Frost wedging did not affect the leachability of elements as much as was initially suspected.

Acknowledgements

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