Natural weathering of shale products from Kvarntorp

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2011-06-19

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Chemistry C, 15 hp

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Abstract

A severe shortage of many, to mankind, valuable elements are to be expected in the near future. Therefor is it of utmost importance to find these deposits and a way to refine the elements with as little negative effect on the environment as possible.

One deposit of valuable elements such as U, V, Mo and Sr are the so called alum shale. Alum shale is a variety of sulfidic black shale which is rich in pyrite, FeS_2, and organic carbon. Primary due to its contents of hydrocarbons and uranium the alum shale has been mined at different sites throughout Sweden. One of these sites was Kvarntorp in the region of Närke. The shale which had have its contents of hydrocarbons extracted through dry distillation was dumped into a heap that is now known as Kvarntorpshögen.

The remaining hydrocarbons that this processed material still contain are to this day (2011) warm, with temperatures up to some hundred degrees Celsius. Due to this heat, infiltration of rainwater is held at a minimum. What no one knows however; is for how long Kvarntorpshögen will remain warm. Once it cools; many toxic elements will leak into the surrounding environment due to natural weathering caused by precipitation and frost wedging. The study also included a heating treatment of 70°C which is a temperature that the material of Kvarntorpshögen may be capable of generating by itself. This is assumed to be a good temperature for weathering processes; because it increases the kinetics of chemical reactions but also allows the presence of water.

The results of this study shows that summer will be the season that contributes the most to the leaching of elements, of which some are toxic. Newly exposed surfaces of various shale materials often contain elements that is easily leached by water. Once this coat is washed away however, further leaching of that element decreases. Exceptions from this pattern in some shale products were shown by for example vanadium and molybdenum.

The digestion data show that the completely processed shale, which makes up the majority of Kvarntorpshögen, still have a high content of rare and valuable elements. Making Kvarntorpshögen itself interesting for extraction processes in the future.

Innehåll

1 Introduction

1.1 Alum shale

Shale is a type of mudrock. Mudrocks are sedimentary rocks composed of silt and clay in different proportions. Mudrocks often contain organic matter; in truth approximately 95 % of all organic matter which occurs in sedimentary rocks can be found in mudrocks (Blatt *et.al.* 2006).

For the organic matter not to degrade due to oxidation, an anoxic environment is required. This occurs in water-filled basins with a very low rate of circulation. Shales generated in this type of environment are often called sulfidic black shales. The word black is derived from the high content of organic carbon which gives these shales their dark color. Due to the reducing properties of the sedimentary basins of these black shales, the sulfur in SO_4^{2-} (valence +6) will be reduced and form H_2S (valence -2). The reduced sulfur will then react with ferrous iron and form iron sulfide, FeS, and pyrite, FeS_2 (Blatt *et.al.* 2006).

The high content of sulfur in sulfidic black shales may pose an environmental risk similar to that posed by base metal mines. When leached from various sulfides, sulfur will oxidize into SO_4^{2-} and form sulfuric acid, H_2SO_4, which dramatically lowers the pH of the leachate. This low pH will enhance the mobility of cations (i.e. the majority of metals) from the shale which may pose a severe environmental risk depending on what kind of elements are present (Lavergen *et.al.* 2008).

The leaching of metals from sulfidic black shale is a serious problem due to the fact that these shales often contain high amounts of rare and often toxic heavy metals. These elements adsorbed to the clay particles during their sedimentation and then got trapped in the shale during lithification (Blatt *et.al.* 2006).

The sulfidic black shale occurring in Sweden has been given the name alum shale due to its contents of the mineral alum, $KAl(SO_4)_2$. Alum was important in the tanning and dyeing industries during the 18th and 19th centuries and therefor mined at several localities throughout Sweden during this period. At the beginning of the 20th century however the need for alum had ceased because of the discovery of other dyeing pigments and the use of cellulose paper instead of rag paper (Eklund *et.al.* 1995).

1.2 Kvarntorp; history and future problems

From the beginning of the 20th century oil was retorted from the alum shale at different localities throughout Sweden (Dyni, 2006). At a couple of these mine sites production of metals such as U, V, Ni, Mo and REEs also occurred.

Kvarntorp, a small society in Närke in the middle of Sweden, were one of the places where alum shale was mined. Industrial operations in Kvarntorp have been conducted since the 1940s. But the extraction of hydrocarbons conducted by SSAB (Svenska Skifferoljeaktiebolaget) ceased in the middle of the 1960s (SWECO VIAK, 2005). From 1950 to 1961 uranium was refined from the shale in Kvarntorp. According to Dyni (2006) approximately 62 tons of uranium was produced during this period.

For the most part of Närke; the layer of alum shale, which was deposited during late Cambrium, is covered by Ordovician limestone. But in the area of Kvarntorp and its surroundings the alum shale layer has been lifted due to faulting. This process has placed the alum shale as the uppermost layer, making it possible to mine in open pits.

Kvarntorp is today one of Sweden's most contaminated areas. The primary contaminants in the area are heavy metals and petroleum. But also a variety of secondary contaminants are present, such as detergents, PAHs, PCB and dioxins (SWECO VIAK, 2005).

The abundance of heavy metals in the area doesn't have to be only a result of industry. As mentioned by Lavergren *et.al.* (2008) the natural leaching process of alum shale contributes to significant amounts of heavy metals per year in groundwater. But the anthropogenic activity in Kvarntorp has had a large role in the contribution of heavy metal leaching due to the exposure of shale faces to various weathering processes.

Another crucial point source of heavy metals and probably also for many of the contaminating hydrocarbons in the area is Kvarntorpshögen. Kvarntorpshögen is the heap of processed material left over from the dry distillation process. Kvarntorpshögen is to this day (2011) still warm due to the ongoing chemical reactions inside it. Because of this generated heat; relatively little water manage to infiltrate the heap. But for how long Kvarntorpshögen will remain warm is a question without any absolute answer but the estimation is that it will remain warm for at least 100 years. When it cools elevated environmental problems in the area is to be expected since water may infiltrate the heap and thereby increase the mobility of heavy metals.

1.3 This study

This study is made to give an indication to how different elements will be leached from Kvarntorpshögen once it cools and how the natural weathering of different seasons may affect the heap. The study involves four materials which can be found in, or in the vicinity of, the heap. These materials are the following:

- Alum shale; unprocessed shale taken from a shale horizon in the Östersätter quarry. Been exposed to weathering for approximately 50 years.
- Weathered fine fraction of alum shale (hereby referred to as weathered fines); fractured alum shale with a particle size of less than 1 cm in diameter. Samples collected at the base of Kvarntorpshögen, at the southwest corner. Been exposed to weathering for 50-60 years.
- Processed shale; alum 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. Variations of processed shale may occur in the area due to the usage of different types of ovens. Samples collected at the base of Kvarntorpshögen, at the northwest corner.
- Ash; alum shale which have been exposed to massive heating. Was used as fuel for the production of processed shale. This material still contains hydrocarbons. Samples collected at the top of Kvarntorpshögen. At the time of sampling, which occurred during winter, this material held a temperature of approximately 50°C.

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 an approximate temperature that the material of the heap itself is capable of producing. Other samples were placed in a freezer at a temperature of -18°C to show how frost wedging affects the materials. The remaining samples were placed in room temperature of approximately 22°C.

Ice is important in this study and according to Nesse (2009) ice can be considered as an oxide mineral. It has the structural formula X_2O, which it shares with for example the mineral cuprite, Cu_2O. The water molecules in ice are held together by hydrogen bonds formed between positively charged hydrogen nuclei of one water molecule and the negatively charged oxygen nucleus of another water molecule. The coordination of each water molecule is tetrahedral, creating a hexagonal structure (Nesse, 2009).

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, allowing it to float. 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.

2 Materials and methods

2.1 Chemicals

- Hydrochloric acid 37%, purchased from VWR International
- Nitric acid 65%, purchased from MERCK
  - Distilled in clean room
- Ortho-phosphoric acid 85%, purchased from MERCK
- Potassium hydrogen phthalate, purchased from Scharlau Chemie S.A.
- Rhodium, ICP-MS standard solution, purchased from MERCK
- Sodium bicarbonate, purchased from Biochrom AG
- Sodium carbonate, purchased from VWR International
- Sodium hydroxide, purchased from Göteborgs Termometerfabrik
- Sulphuric acid 95-97%, purchased from MERCK

2.2 Solutions

- Mobile phase for ion chromatography

  1 ml of 0.5 M $NaHCO_3$ and 21 ml of 0.5 M Na_2CO_3 added to a 1 l volumetric flask. The solution was diluted to the 1 l mark with milli-Q water. The solution was then filtered through a polycarbonate filter with a pore size of 0.2 µm into another flask which were then placed in an ultrasonic cleaner for 15 minutes to drive off any air bubbles present in the mobile phase.
- Total carbon stock solution for TOC

  Some potassium hydrogen phthalate was dried at 105°C for approximately 2 hours and then placed in a desiccator overnight. Following day 2.125 g of this dried potassium hydrogen phthalate was weighted and placed in a 1 l volumetric flask. Milli-Q water was then added to the 1 l mark. The stock solution was mixed until all potassium hydrogen phthalate had been solved.

- Inorganic carbon stock solution for TOC

  Some $NaHCO_3$ was placed in a desiccator and some Na_2CO_3 was dried at 105°C and at a pressure varying between 0.1-0.3 bar for approximately 3 hours. The Na_2CO_3 were then placed in a desiccator overnight. Following day 3.50 g of dried $NaHCO_3$ and 4.41 g of dried Na_2CO_3 were weighted and placed in a 1 l volumetric flask. Milli-Q water was then added to the 1 l mark. The stock solution was mixed until all $NaHCO_3$ and Na_2CO_3 had been solved.

2.3 Subheading, Apparatus

- Centrifuge 5804
  Eppendorf AG
  - Rotor radius; 11.5 cm
- Conductivity electrode, 4-pole (platinum)
  Radiometer analytical S.A.
  Part No: E61M015, Type: CDC866T
- Digestion microwave oven, MARS5
  CEM
- Drying cupboard, Vacucell
  MMM Medcenter
- ICP-MS, Agilent 7500 cx, Japan
- Ion chromatography
  Metrohm
  - Column; IonPac AS12A 4mm(10-32)
    DIONEX
- pH electrode (used for pH measurement)
  Metrohm
  6.0257.000
  pH 0…13/0…60°C
- pH electrode (used for endpoint titration of alkalinity and acidity)
  Metrohm

6.0253.100
pH 0…13/0…60°C

- Redox electrode
  Thermo scientific
  Orion 9678BNWP
- Titrator, ABU93 TRIBURETTE
  Radiometer Copenhagen
  Coupled to a TIM900, Titration manager
  Radiometer Copenhagen
- TOC-U_{cph}
  Shimadzu
  Coupled to a ASI-V sampler
  Shimadzu
- Turnover shaker, REAX2
  Heidolph
- Ultrasonic cleaner
  VWR

2.4 The leaching process

Previous the beginning of this study, black shale, weathered fines, ash and processed shale had been crushed and sieved to a particle size of 0.25-0.55 mm by Häller, a PhD-student at Örebro University.

For the study 6 samples of each of the four materials were prepared. These materials were then leached with milli-Q water at an L/S ratio of 10. The samples were placed on a turnover shaker for 2-3 days. On sampling occasions, which occurred twice a week, the samples were centrifuged at 8230 or 10420 g (see heading; problems and mistakes, 3.1) for 60 minutes, and their supernatants were extracted for the different analyses. Thereafter the samples, i.e. the various shale materials and some remaining water, were treated at different temperatures for approximately 18 hours. The study involved three different temperatures; 70°C, 22°C (room temperature) and -18°C, 2 samples of each material were placed in each temperature.

At the beginning of the leaching process, two types of reference samples were extracted. The first type was taken after only 1 hour of water leaching. The second reference was taken after 1 day of water leaching. When both references had been extracted the first temperature treatment commenced. The leaching process carried on repeatedly for 8 cycles, which is equivalent to 4 weeks. This resulted in a total of 10 sampling occasions.

Table (2.4-1), Conversion table between different numbering systems on days throughout the leaching period

Sampling occasion	1	2	3	4	5	6	7	8	9	10
Temp. treatment cycle	Ref.	Ref.	1	2	3	4	5	6	7	8
Day of leaching period	1	2	5	8	12	15	19	22	26	29
Date	31/3	1/4	4/4	7/4	11/4	14/4	18/4	21/4	25/4	28/4

2.5 Digestions

Digestions in concentrated HNO_3 were conducted. The amount of elements which this method managed to release from the materials were then considered to be the total, i.e. 100%, of what was possible to leach from the materials. Particle fraction of 0.25-0.55 mm of each material were dried at 105°C over night. The next day the materials were pulverized with an electric hand mill and sieved to a particle size of <0.25 mm.

Each sample consisted of 50 mg material. Two replicates per material were prepared, meaning that the digestion process involved a total of 8 samples. The weighed samples were placed in teflon bombs and 5 ml of concentrated HNO_3 was added to each. The bombs were put in their holders and placed in the Mars5. The effect used was 1200 W and the run time was 60 minutes. The holding temperature was 180°C and the minimum pressure was 80 psi and may have varied up to a maximum of 180 psi.

After approximately 55 minutes of the run time had passed a pressure membrane on one of the bomb lids burst and thereby stopped the digestion process. But since it was only 5 minutes left of the run time the process was considered complete.

2.6 Analyses

2.6.1 Analyses conducted on sampling occasions

Various analyses of the leachate were conducted. On sampling occasions electrical conductivity, Eh, pH and alkalinity/acidity were measured. Electrical conductivity, Eh and pH were measured with electrodes. Alkalinity and acidity were measured by endpoint titration with either 0.02M HCl or 0.02M NaOH depending on the samples pH-value. As endpoint the pH-value 5.4 was chosen. This is one pH-unit lower than pKa_1 for H_2CO_3, which is 6.4. Above pH 5.4 carbonates is assumed to affect the buffering capacity. During titration the sample was degassed using an air pump which drove off any formed CO_2.

2.6.2 Metal analysis by ICP-MS

On sampling occasions, 1.5 ml of the samples leachates were extracted and placed in separate test tubes. Shortly thereafter 15 µl of concentrated HNO_3 were added to each. When opportunity presented itself these samples were diluted with an acid solution consisting of 1% of concentrated HNO_3. Three different dilutions of each sample were prepared; with dilution factors 10, 100 and 1000. To the dilutions with dilution factors 100 and 1000 an internal standard of rhodium (mass number 103) was added to a final concentration of 10 µg/l.

For the metal analysis it was the dilutions with dilution factor 100 which were selected because they had the best distribution of low- and high concentration elements. Only samples taken on sampling occasions 1, 2, 3, 4, 6, 8 and 10 were analyzed. The plasma effect used during the analysis was 1500 W, which is enough to ionize the elements into single positive ions.

2.6.3 Sulfate analysis by ion chromatography

The sulfate analysis was carried out after the leaching period had ended. The samples which had been extracted for sulfate analysis had been stored in a refrigerator in an attempt to decrease the chemical activity in the samples. Only samples taken on the first five sampling occasions were analyzed by ion chromatography. Because sulfate was known to be the dominating anion in the leachates (Karlsson, 2011) its concentration could be predicted very accurately by studying the samples electrical conductivity. And after sampling occasion 5 the electrical conductivity was considered to be too low for most materials to continue sulfate analysis.

2.6.4 Analysis of dissolved organic carbon by TOC

The samples extracted for organic carbon analysis was stored in a freezer to halter any microbial activity in the samples. The samples that were selected to be analyzed by TOC were filtered through a polycarbonate filter with a pore size of 0.2 µm some days prior to analysis. When the samples were once again thawed on the analysis´ day some samples contained a white precipitation which made it necessary to filter these samples once again before analysis. The precipitation occurred in all samples of processed shale from sampling occasions 1-4 and in some random samples of different materials from sampling occasions 1 and 2. The precipitation is believed to be gypsum, $CaSO_4$ (further discussion about gypsum can be found under heading; sulfate, 3.6)

The sampling occasions that were selected for DOC analysis were sampling occasions 1-4, 7 and 10. But many instrumental incidents happened; resulting in that half of the samples from sampling occasion 3 had to be stored in a refrigerator for 24 hours before the next analysis day. And most samples from sampling occasion 10 were not analyzed at all due to problems with the TOC and time shortage.

3 Results and discussion

3.1 Problems and mistakes

One of the most crucial problems which occurred during the laboratory work was the realization that the plastic test tubes which were used had quite a low quality. When the samples were centrifuged cracks appeared in the bottom of the test tubes and their sides where deformed. This made it necessary to move the samples to new test tubes between each cycle of leaching. Naturally this caused a small loss of shale material with each new test tube.

The rotation speed which the samples were centrifuged at was 8230 g at the beginning of the leaching sequence. After 3 temperature treatments fine fractions of the materials had accumulated in the samples. This was primary a problem in the heated samples of shale and processed shale and later on also in the frozen processed shale. The rotation speed was because of this increased to 10420 g but after only one more leaching cycle even this speed was insufficient to force all particles into a pellet. Due to the severe cracks that 10420 g caused on the test tubes any further increase in rotation speed was not done.

Due to the presence of fine particles in the supernatants, it could not be avoided that some particles were extracted with the pipette, especially the closer it came to the pellet. The last volumes that were extracted of the supernatants were the ones for total organic carbon analysis and those for electrode- and alkalinity/acidity analysis. With the latter volume; the presence of particles did not matter, but in the volume which were going to be used for analysis of total organic carbon content it was a serious problem. To avoid generating a plug of particles in the TOC-instrument all samples had to be filtered before analysis, making the analysis of total organic carbon an analysis of dissolved organic carbon instead.

A mistake was made in the beginning of the laboratory work in this study. The materials used for the samples were not dried before preparation. Resulting in that some percentage of the samples weights were water. However; previous experience with shale materials tells that these materials do not contain any larger amounts of water, especially if the material was dry enough to be sieved to the particle size used in this study. And compared to the material loss that each change of test tube caused, the margin of error that the absence of drying may have inflicted is considered to be a minor problem.

3.2 Electrical conductivity

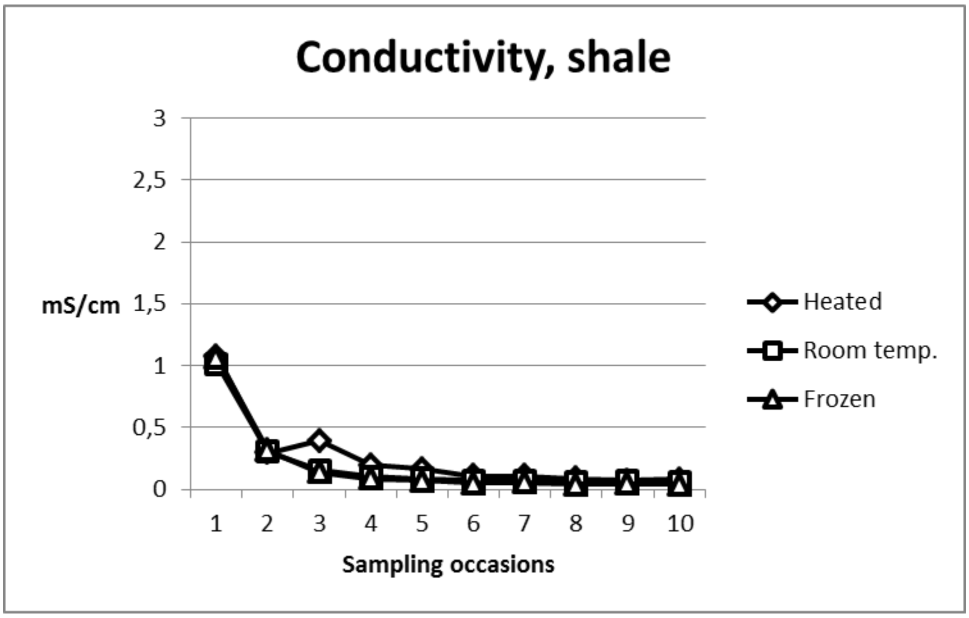


Figure (3.2-1), Electrical conductivity for samples of shale

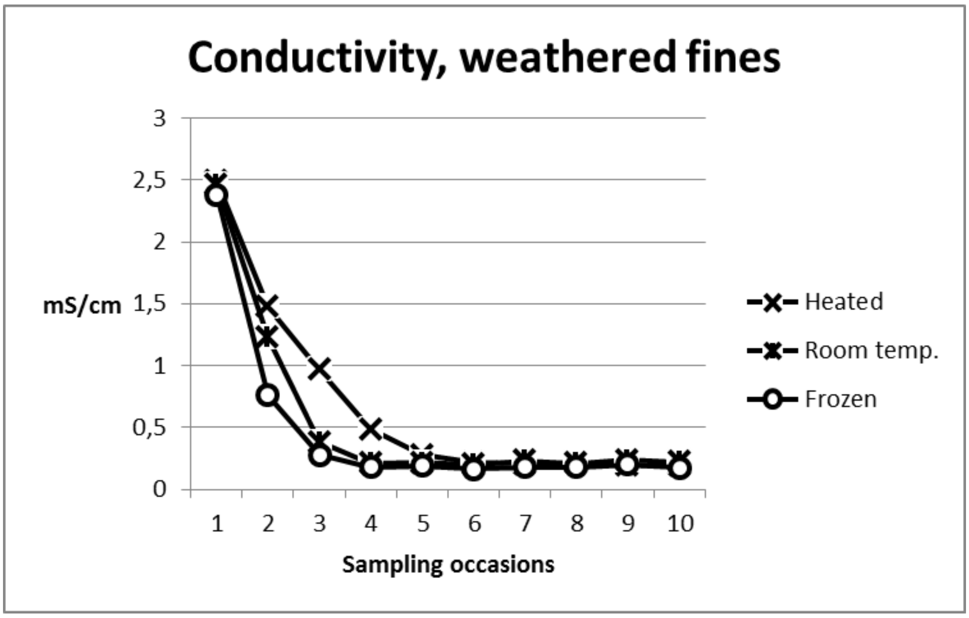


Figure (3.2-2), Electrical conductivity for samples of weathered fines

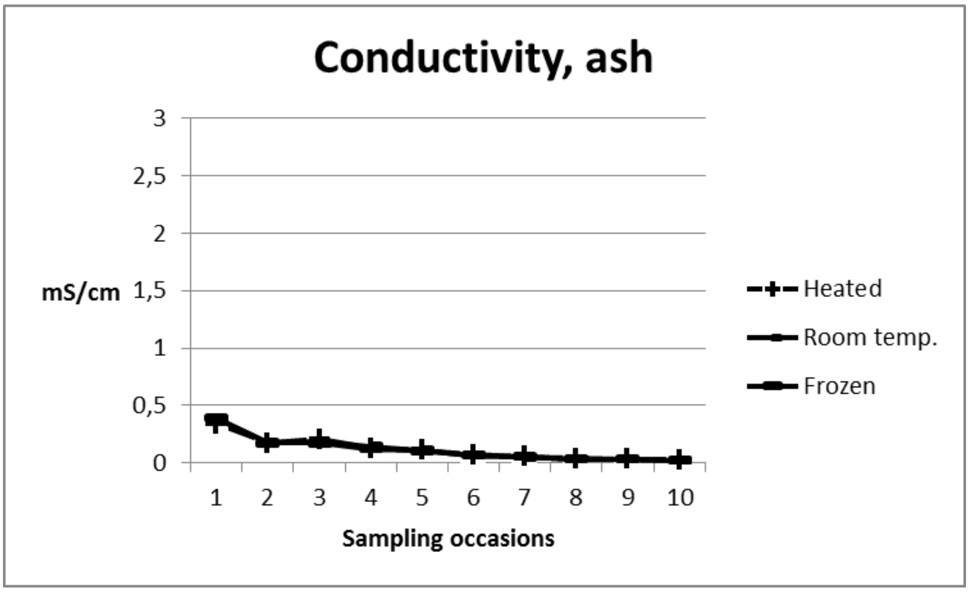


Figure (3.2-3), Electrical conductivity for samples of ash

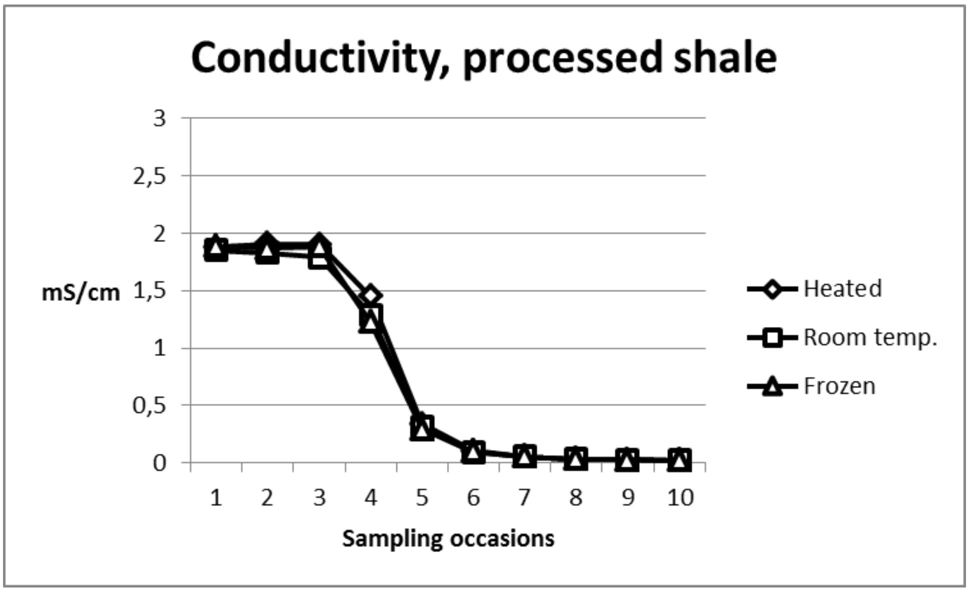


Figure (3.2-4), Electrical conductivity for samples of processed shale

Conductivity gives an indication of ion content in the leachates. The measured conductivity of the first two days, the reference days, shows that ions leaches fast from the black shale, the weathered fines and the ash. This is observed by comparing the higher conductivity in the samples after only 1 hour of leaching and in the samples after 1 day of leaching. This indicates that the materials particles contain coats of various elements which are easily leached. This seems not to be the case for the processed shale however. For the processed shale the conductivity remains approximately the same in both references indicating that the material releases ions in a large extent during a longer period of time.

As for the temperature treatments effect on the conductivity; two main patterns can be observed. The heating of shale and weathered fines increases conductivity for the first and second cycle. This indicates 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.

At the last days of the leaching period it was the weathered fines which had the highest conductivity. This implies that the approximately 60 years of weathering which the fines have been exposed to have weakened the mineral structure enabling a relative easy leaching of ions.

3.3 pH

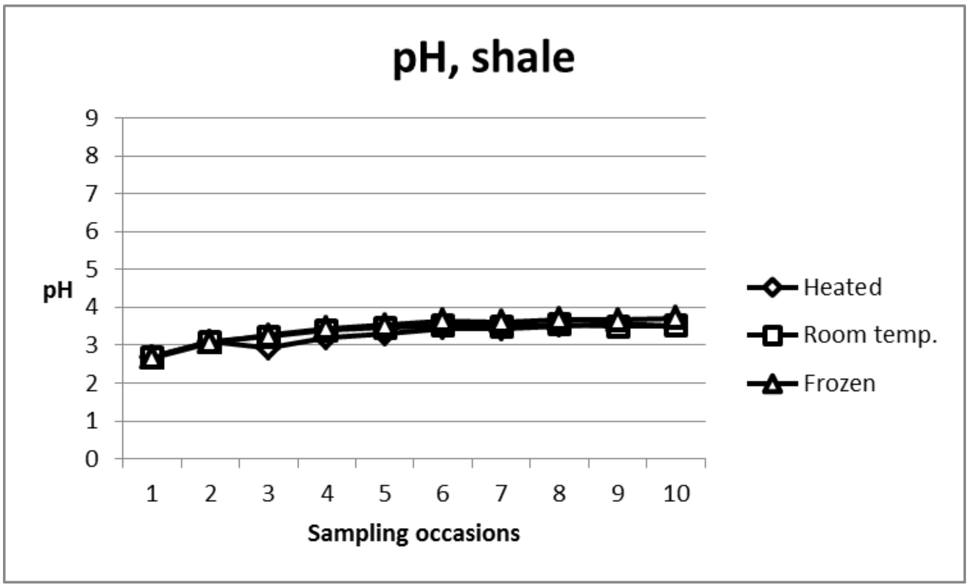


Figure (3.3-1), pH for the samples of shale

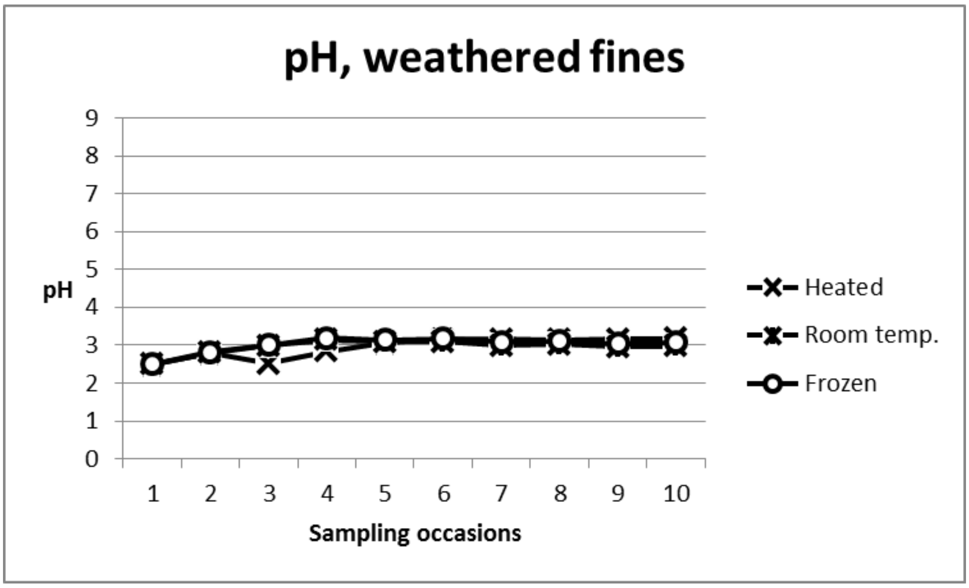


Figure (3.3-2), pH for the samples of weathered fines

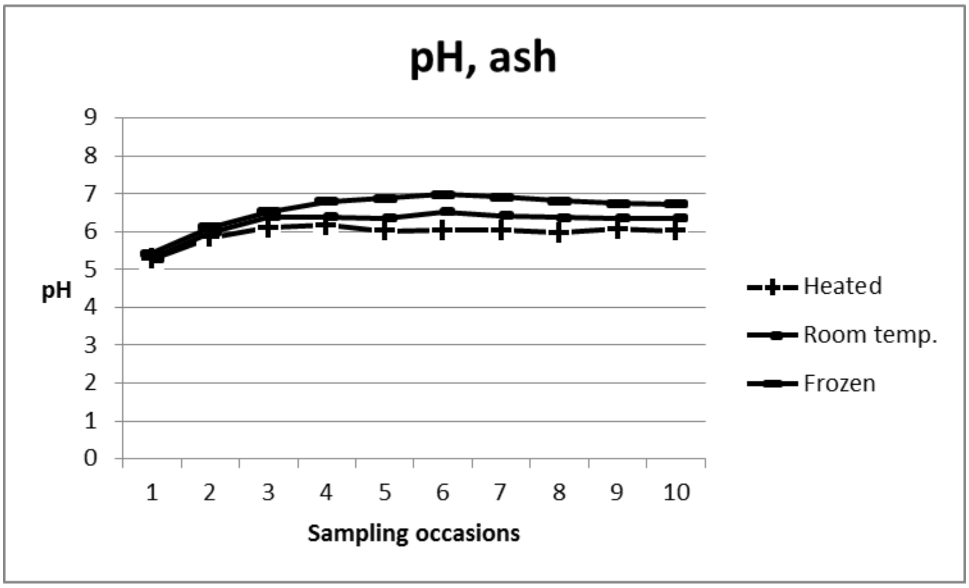


Figure (3.3-3), pH for the samples of ash

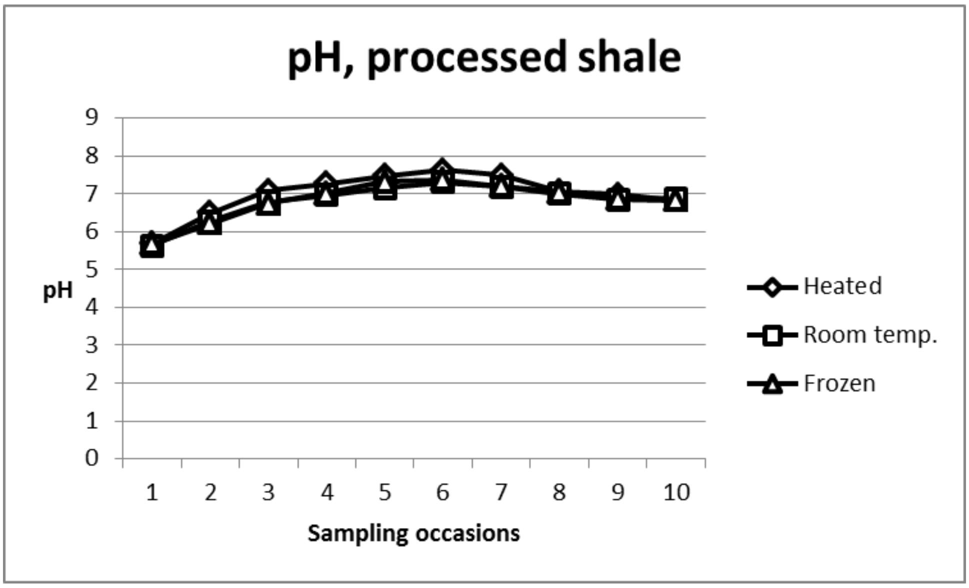


Figure (3.3-4), pH for the samples of processed shale

The pH values of the leachates from the shale and the weathered fines are initially low; around 2.5. The pH values of the leachates increases slightly over time. The pH for the shale’s leachates stabilizes around pH 3.5 while leachates from the weathered fines stabilized at approximately 3.0. This low pH is primary a result of the oxidation of pyrite, FeS_2 (Sartz, 2010):

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

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 conductivity, its weathered surfaces are more susceptible to react with the water.

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. The starting pH value of their leachates was around 5.5. An increase in pH over time occurred even in these samples. The pH for the ash´ leachates did not exceed pH 7 while the maximum pH value for the processed shale´s leachates reached approximately 7.5 before its pH slowly began to decrease. The reason why the ash and the processed shale causes such relatively high pH in their leachates, compared to the pH values in the leachates from the shale and the weathered fines, is the presence of various oxides.

Most of the oxides in processed shale and ash were created during their pyrolysis process. The heat drove off $CO_2(g)$ from carbonate minerals, forming oxides instead.
One of the occurring oxides in these materials is CaO, which is formed from $CaCO_3$:

$CaCO_3 + \text{heat} \rightarrow CaO + CO_2$

When exposed to water the oxides will form hydroxides, which increases the pH of the leachates:

$CaO + H_2O \rightarrow Ca(OH)_2$

No obvious relationship between temperature treatment and release of hydroxides from the processed shale can be seen from measured pH values. In the leachates for the ash such relationships can be observed. The pH increases the most when the ash samples were continually frozen and thawed. This indicates that the expanding force of ice causes the exposure of new surfaces on the ash particles. To these oxide surfaces protons may bind and thus increasing pH. Heating ash, on the contrary, generated the lowest pH increase of the three temperature treatments. Since ash is only partially processed material it may still contain some pyrite. And by heating ash, an oxidation of this remaining pyrite may be triggered, generating some H_2SO_4.

3.4 Acidity and alkalinity

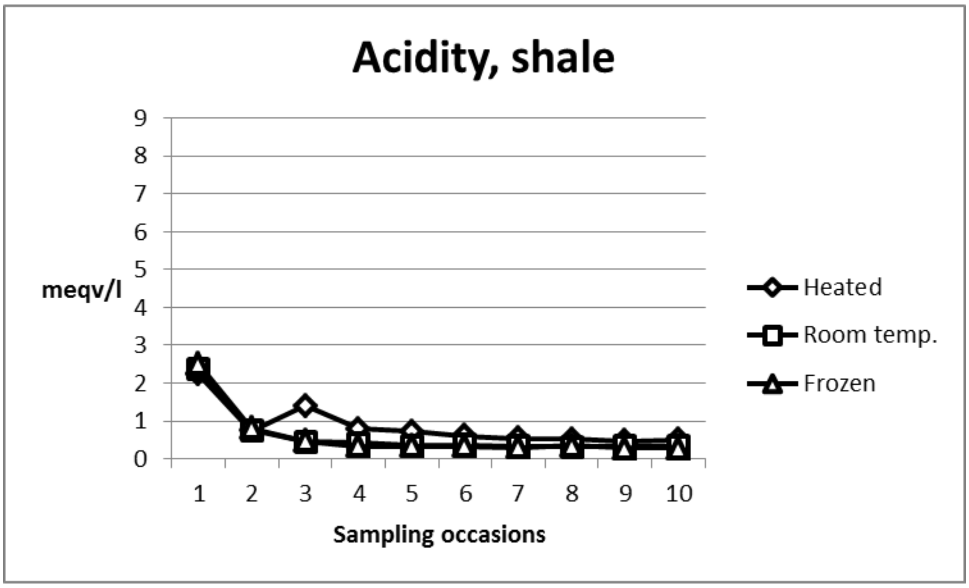


Figure (3.4-1), Acidity for the samples of shale

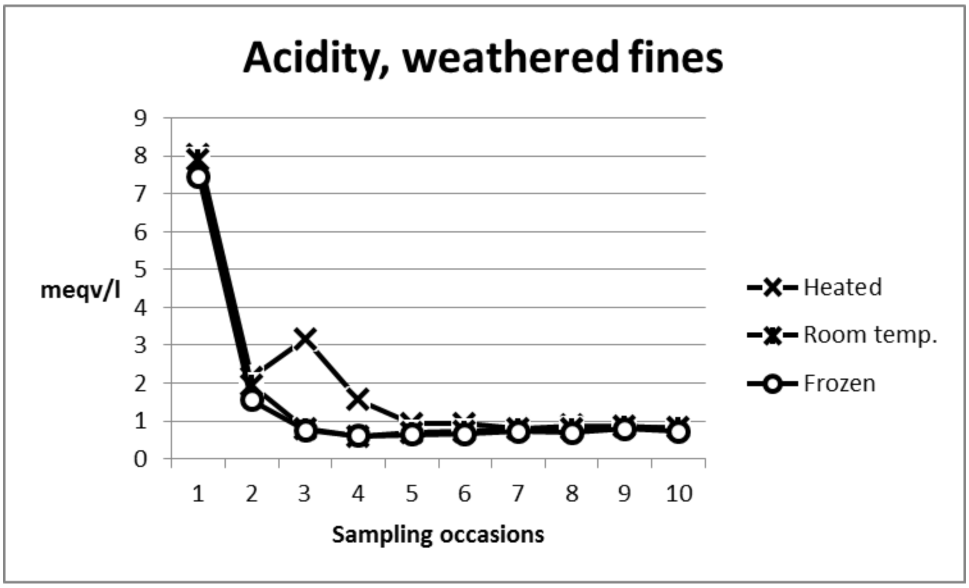


Figure (3.4-2), Acidity for the samples of weathered fines

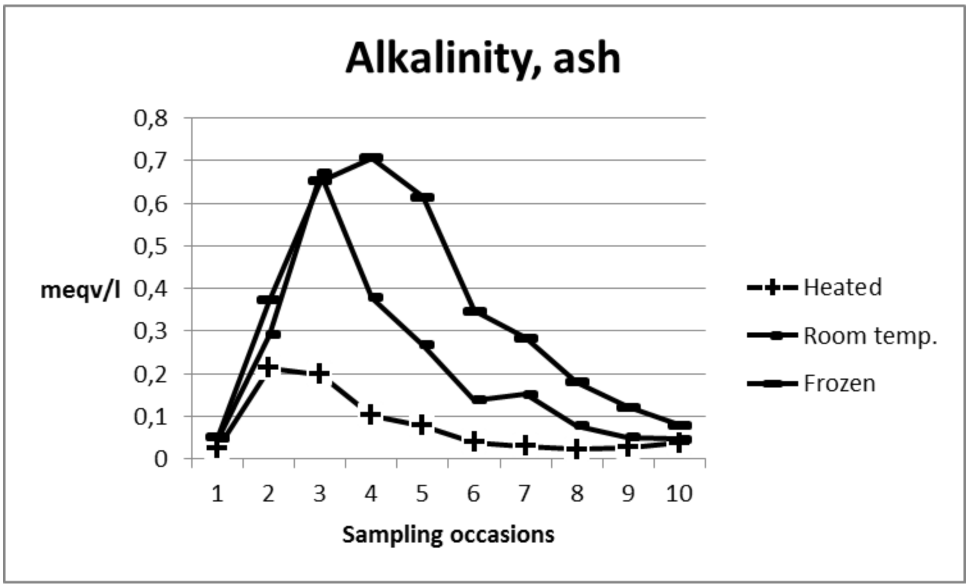


Figure (3.4-3), Alkalinity for the samples of ash

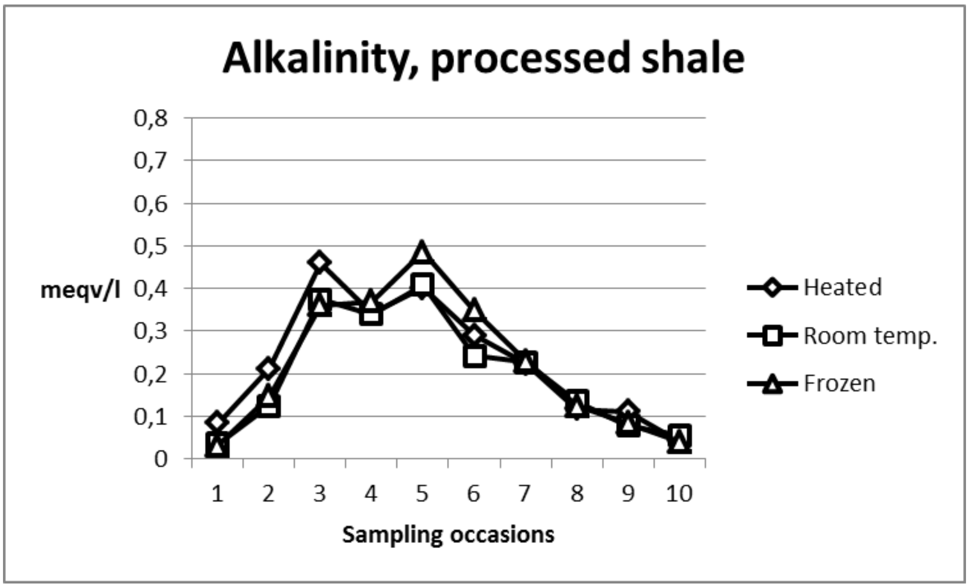


Figure (3.4-4), Alkalinity for the samples of processed shale

The acidity for the shale and the weathered fines shares a similar pattern. The acidity is higher in the first reference compared to the second reference, indicating that the species that is responsible for the acidity covers the particles as a coat. According to Drever (1997) aluminum and its hydroxides are the primary species which causes acidity. But as is shown by the metal analysis; also iron contributes greatly to acidity in these systems. The iron that contributes to acidity may originate from secondary iron sulfate minerals such as melanterite and schwertmannite.

For both the shale and the weathered fines the acidity increased when the samples were heated. Freezing seemed to have no effect on the samples acidity however. The results from the metal analysis (see tables (3.4-2) and (3.4-3) or headings 3.7.3 and 3.7.8) shows that the leachates from the shale and weathered fines contain high concentrations of aluminum. The metal analysis shows also that the heated samples leach iron to a higher extent than the room temperate and frozen samples. This could explain why the acidity of the heated shale- and weathered fines samples increases during the first temperature treatment cycle.

Table (3.4-1), Aluminum concentrations in the leachates of shale and weathered fines

Al content (µg/l)	**Sampling occasions**						
	1	2	3	4	6	8	10
Heated shale	5378.4	458.17	393.07	218.51	320.94	309.90	542.56
Room temp. shale	4993.5	504.47	209.18	176.52	174.03	167.79	165.93
Frozen shale	5202.0	521.13	203.68	165.65	168.82	164.33	170.74
Heated weathered fines	15147	2892.3	1534.8	781.80	381.35	470.92	417.67
Room temp. weathered fines	14746	2289.2	288.02	173.91	184.65	184.66	178.47
Frozen weathered fines	13952	1135.8	217.27	171.21	175.83	182.02	184.92

Table (3.4-2), Iron concentrations in the leachates of shale and weathered fines

Fe content (µg/l)	**Sampling occasions**						
	1	2	3	4	6	8	10
Heated shale	8130.6	1889.7	30268	11431	7265.9	5190.0	6027.5
Room temp. shale	7782.8	1892.9	597.74	199.97	144.08	174.20	212.86
Frozen shale	8070.2	2039.4	812.01	231.93	331.99	267.22	336.81
Heated weathered fines	84184	11422	42351	23078	9387.0	9916.8	8181.4
Room temp. weathered fines	82250	10094	2129.2	442.08	712.59	401.60	479.15
Frozen weathered fines	76601	6946.2	1904.4	1233.0	1419.2	1075.5	1185.0

The acidity was higher in the samples from the weathered fines compared to the samples from the shale. This, as it also was in the case of conductivity, implies that the weathered surfaces of the fines have easier to release aluminum and iron, and maybe other species that increases acidity, than the shale.

According to Drever (1997) low pH and high concentrations of sulfate may cause aluminum to precipitate as alunite, $KAl_3(SO_4)_2(OH)_6$, and/or jurbanite, $Al(SO_4)(OH)*5H_2O$. This might very well be the case in the leachates from the shale and the weathered fines because they both have low pH values (see figures (3.3-1) and (3.3-2)) and they do contain high concentrations of sulfate (see table (3.4-3) or heading; sulfate, 3.6).

Table (3.4-3), Sulfate concentrations in the leachates of all 4 materials

Sulfate content (mg/l)	**Sampling occasions**				
	1	2	3	4	5
Heated shale	540.9	93.11	131.1	57.86	45.68
Room temp. shale	506.9	99.37	42.34	23.52	18.20
Frozen shale	587.2	116.8	42.69	20.94	15.90
Heated weathered fines	1494	921.5	379.8	168.6	89.06
Room temp. weathered fines	1916	719.9	140.4	61.91	56.55
Frozen weathered fines	1732	349.7	95.89	50.25	47.21
Heated ash	195.3	65.00	76.63	46.01	37.89
Room temp. ash	191.4	62.85	59.08	48.16	37.56
Frozen ash	196.9	63.49	40.87	19.52	18.15
Heated processed shale	1526	1444	1391	1009	121.8
Room temp. processed shale	1506	1423	1393	861.7	112.9
Frozen processed shale	1484	1530	1399	783.4	105.3

The species that contributes to alkalinity is mainly bicarbonate and carbonate. Alkalinity in leachates from ash and processed shale is low during the first two sampling occasions. This is caused by the release of pH-lowering elements from the materials. Then the carbonates leach at a higher rate than the various pH-lowering elements and cause the alkalinity effect that is titrated in this study. Towards the end of the leaching period alkalinity decreases due to that the amount of leachable carbonates decreases. Heating does not increase alkalinity of the leachates from ash. This is probably caused by volatilization of carbonates in the form of CO_2(g).

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. Else can be said about the ash where 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. 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.

3.5 Redox

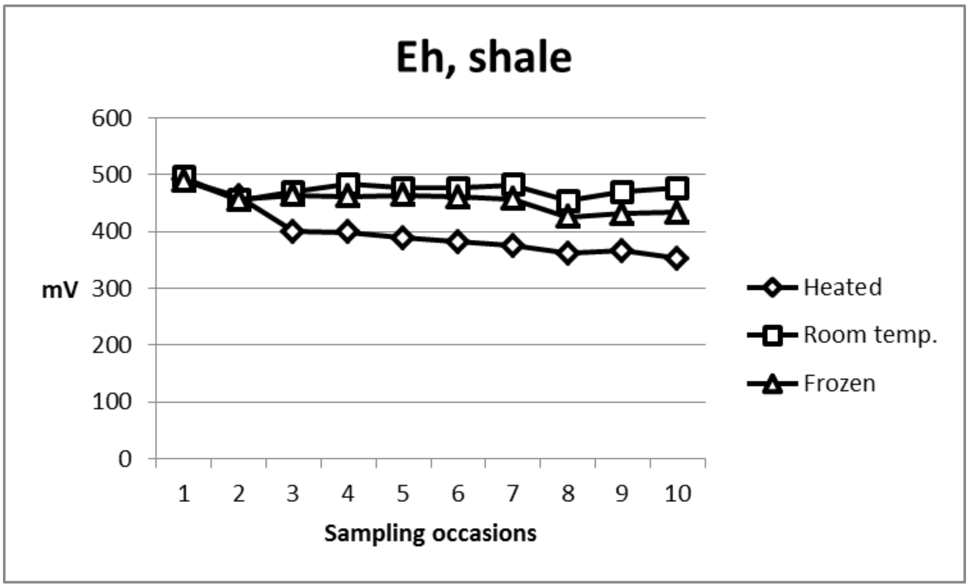


Figure (3.5-1), Eh for the samples of shale

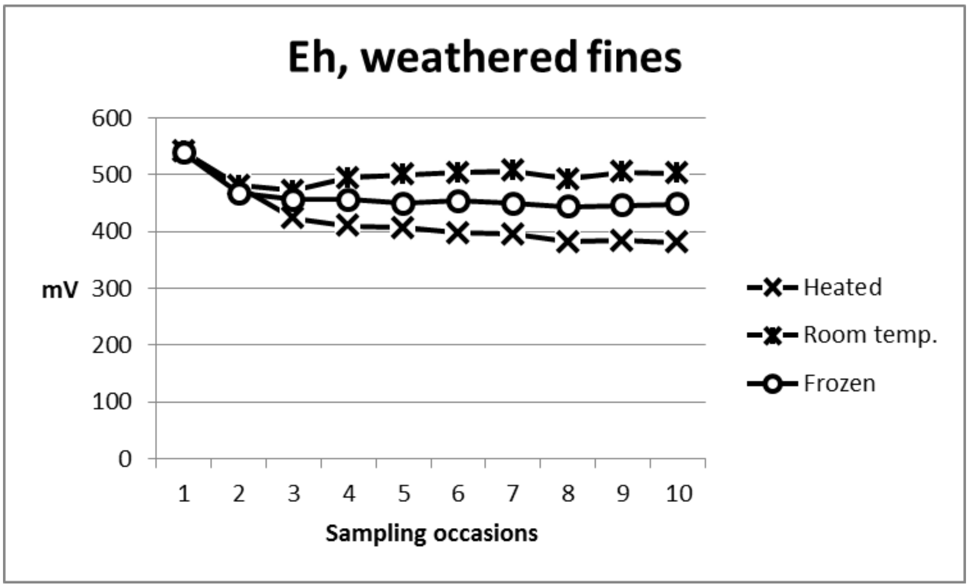


Figure (3.5-2), Eh for the samples of weathered fines

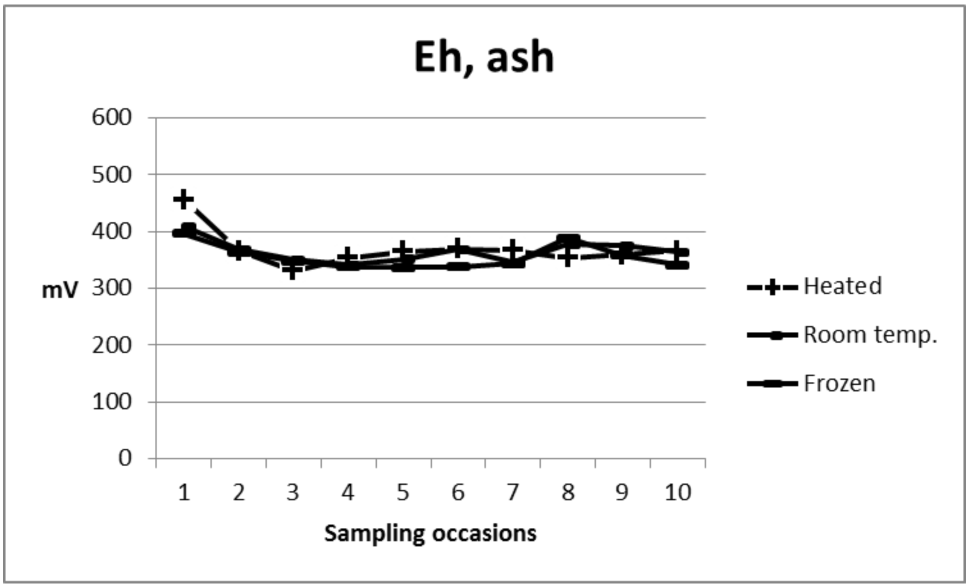


Figure (3.5-3), Eh for the samples of ash

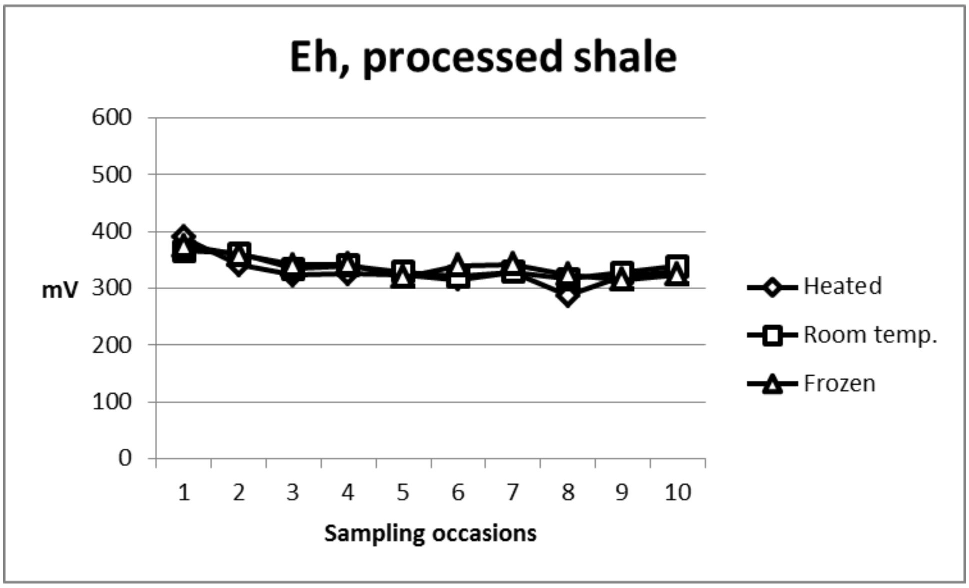


Figure (3.5-4), Eh for the samples of processed shale

There are two major groups of chemical reactions; the transfer of protons which drives acid-base reactions, and then it is the transfer of electrons which drives redox reactions. When speaking of redox and Eh the term redox pair is often used. If a solution contains only one redox pair it is easy to define Eh. But most naturally occurring solutions contain multiple redox pairs of which many will not be in equilibrium with each other. This makes it impossible to accurate define Eh in a solution (Drever, 1997). The Eh values measured with a redox electrode in this study is therefore just a crude estimation of the samples Eh values.

The measured Eh values for the shale´s and the weathered fines´ leachates are higher than Eh in the leachates from ash and processed shale. This corresponds to the relation of Eh and pH well shown by Eh-pH diagrams. A low pH corresponds to a higher Eh value due to the impact of oxygen buffering. As pH increases, Eh will decrease. And because the leachates of ash and processed shale have around neutral pH it is not surprising that their measured Eh values are lower than those of shale and weathered fines.

The measured Eh is lower in the leachates of the heated and frozen samples of shale and weathered fines than in the samples of shale and weathered fines which have stood in room temperature. This is probably caused by an increased sulfide oxidation brought on by the opening of new particle surfaces. With time, Eh will most likely increase once all sulfides have oxidized.

In the leachates from the ash and processed shale no obvious change in Eh can be observed as a result of temperature treatments. This is probably because most sulfide minerals already have been oxidized in these samples as a result of pyrolysis.

3.6 Sulfate

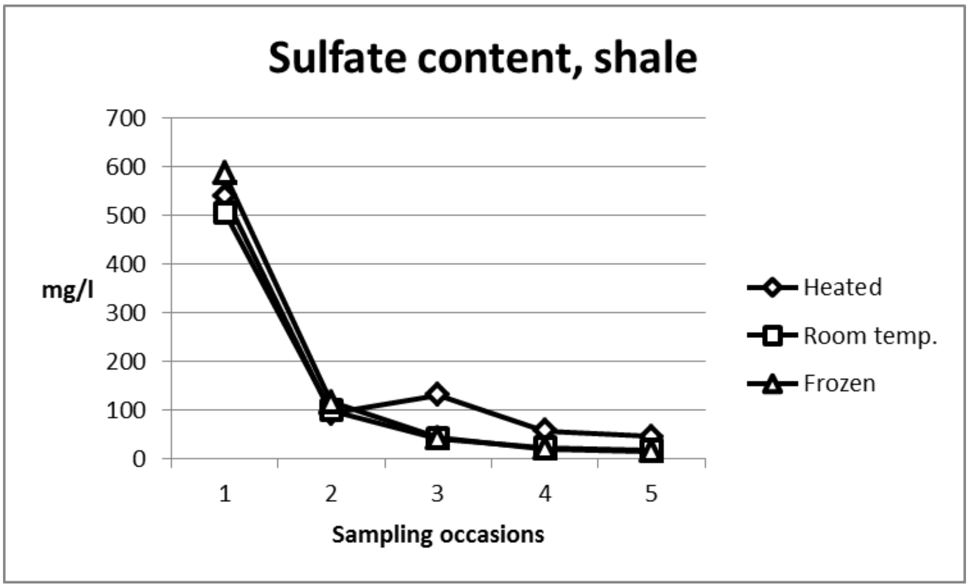


Figure (3.6-1), Concentrations of sulfate in the leachates of shale

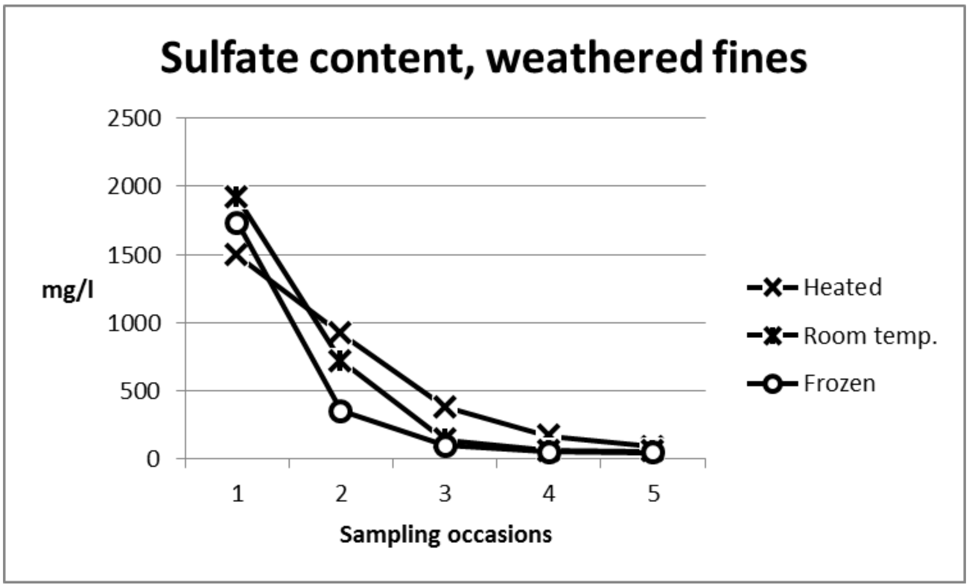


Figure (3.6-2), Concentrations of sulfate in the leachates of weathered fines

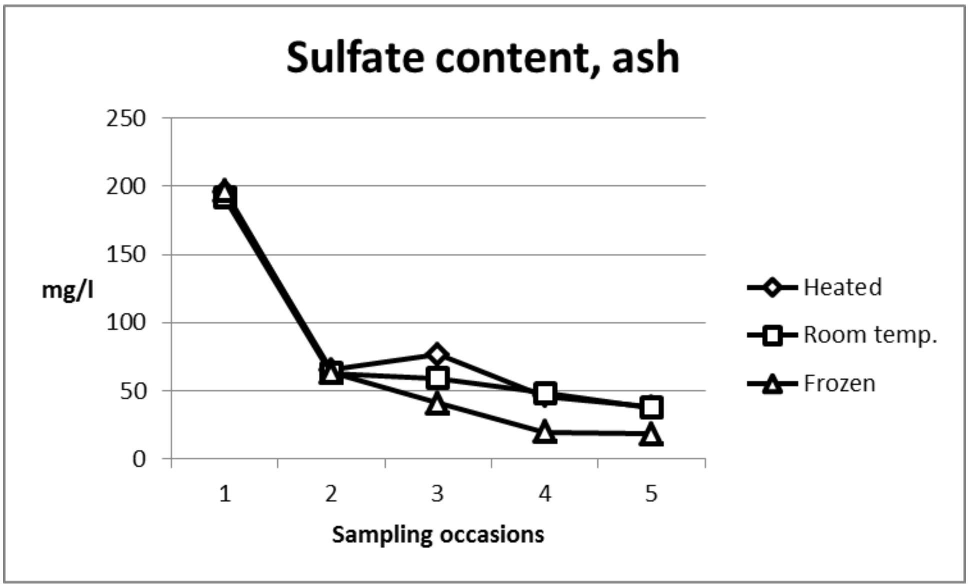


Figure (3.6-3), Concentrations of sulfate in the leachates of ash

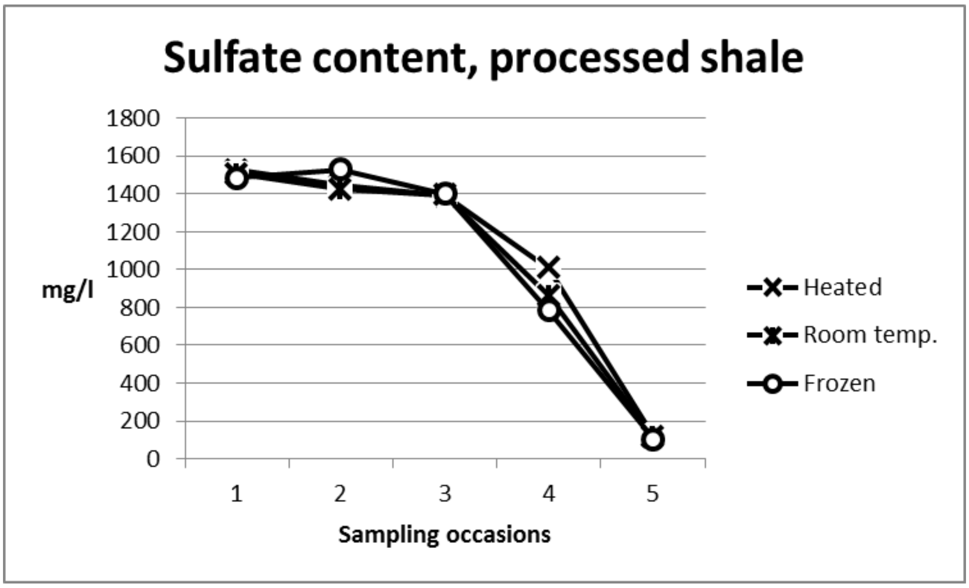


Figure (3.6-4), Concentrations of sulfate in the leachates of processed shale

Sulfate is the dominating anion in the leachates. Because of this, it was easy to predict the concentrations of sulfate by studying the samples conductivity. Therefore was only the first five sampling occasions analyzed by ion chromatography. After sampling occasion 5 the conductivity showed that the sulfate concentration in most samples would have decreased to such low concentrations which would not have been able to measure accurately.

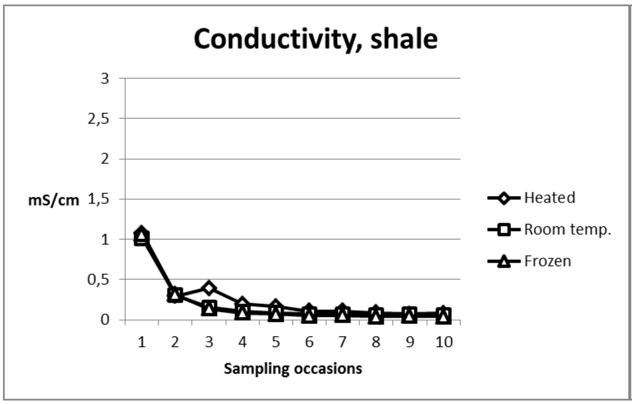


Figure (3.2-1), Electrical conductivity for samples of shale

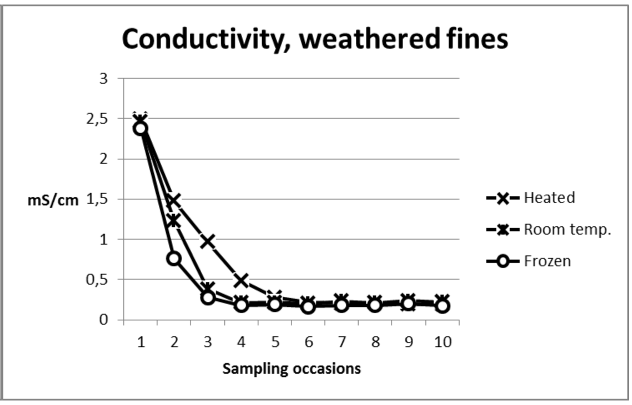


Figure (3.2-2), Electrical conductivity for samples of weathered fines

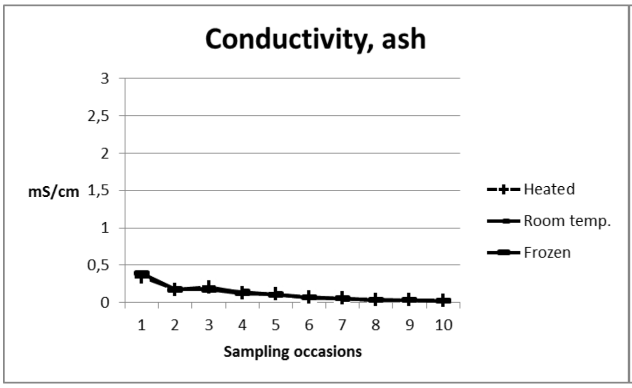


Figure (3.2-3), Electrical conductivity for samples of ash

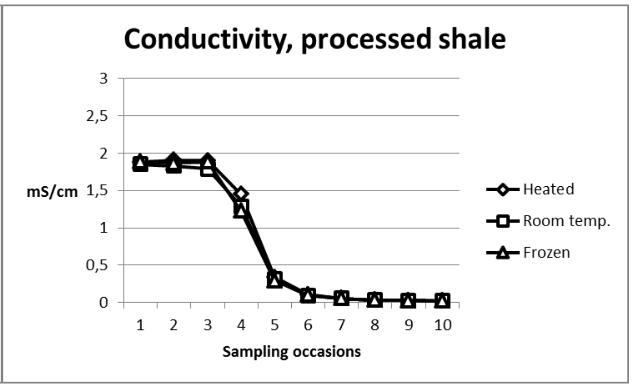


Figure (3.2-4), Electrical conductivity for samples of processed shale

The sulfate content in the leachates from the first two sampling occasions of the shale, weathered fines and ash indicates that sulfate occurs as a coat on the particles and is easily removed by water. Heating shows a clear increase in sulfate concentration in the leachates from shale and weathered fines. As was discussed under heading; redox 3.5, heating increases the oxidation of sulfides in these materials and therefore contributes to increased sulfate concentrations.

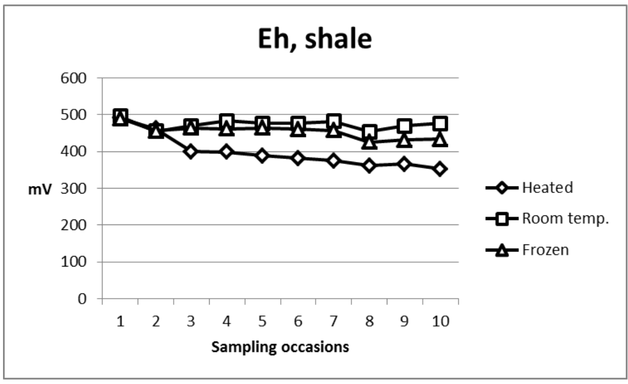


Figure (3.5-1), Eh for the samples of shale

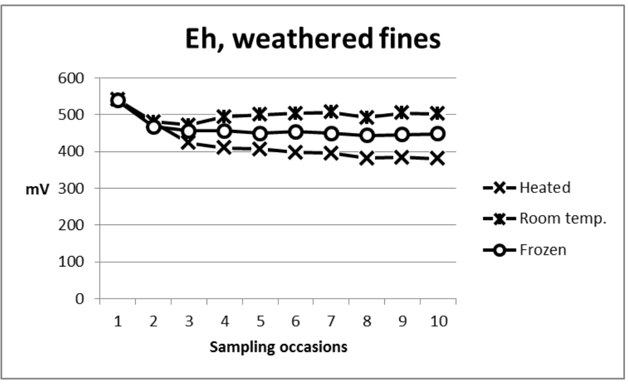


Figure (3.5-2), Eh for the samples of weathered fines

3.6.1 Fluoride

In the previous study made by Karlsson (2011) on the leaching of Kvarntorp shale; the fluoride- and chloride contents, also analyzed by ion chromatography, was found being low compared to the sulfate content. In this previous study, the measured chloride concentration was 0.98 mg/l in leachates from unprocessed shale and 0.56 mg/l in the leachates from processed shale. The fluoride contents were higher; 8.9 mg/l in the unprocessed shale´s leachates and 1.0 mg/l in leachates from the processed shale. Chloride seldom forms strong complexes or compounds with cations and especially not in such low concentrations. Fluoride on the other hand may be interesting as a complexing agent. But due to time limitation; the decision to only determine the sulfate content was made.

With the relatively high dilution factors that were used to quantify the samples sulfate concentrations within the concentration range of the standard solutions, no fluoride or chloride peaks were visible in the chromatograms. Not until the turn came to the samples collected on sampling occasion 5. In the samples of processed shale, following fluoride concentrations were determined.

Table (3.6.1-1), Concentrations of fluoride in the leachates of processed shale on sampling occasion 5 and their respective RSD values

	Fluoride content, ppm	RSD
Heated processed shale	2.43	0.120
Room temp. processed shale	1.92	0.0765
Frozen processed shale	1.97	0.118

These concentrations are higher than the concentration of 1.0 mg/l that was previously measured by Karlsson (2011) from leachate of processed shale. This is surprising because the samples presented in the table above are from sampling occasion 5, i.e. the 12th day of the leaching period (table (2.4-1)). If we neglect the possibility of heterogeneity of the different samples of processed shale, and assume that the method to leach in ultrasonic cleaner for 30 minutes equals leaching for 24 hours on turnover shaker; this would indicate that the fluoride concentration of the leachates have increased over time.

But since heterogeneity is a common phenomenon in nature, we cannot draw this conclusion. Without quantification of fluoride in the leachates from previous sampling occasions, it is impossible to say if the concentration of fluoride increases, decreases or have stayed the same throughout the leaching period. The only conclusion we may be able to make from these fluoride concentrations would be that heating could have a beneficial effect on the leach ability of fluoride.

3.7 Metal content

3.7.1 Sodium, Na

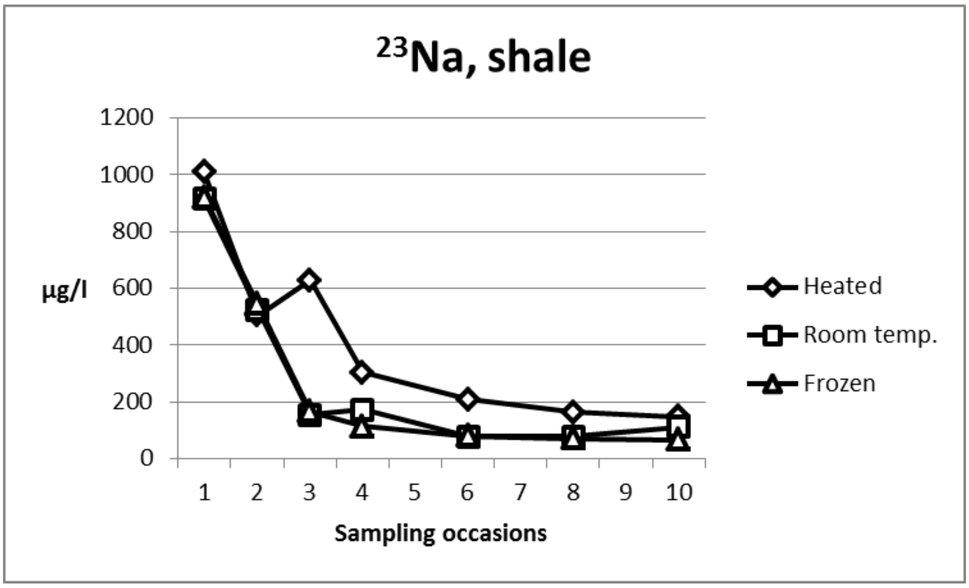


Figure (3.7.1-1), Concentrations of sodium in the leachates of shale

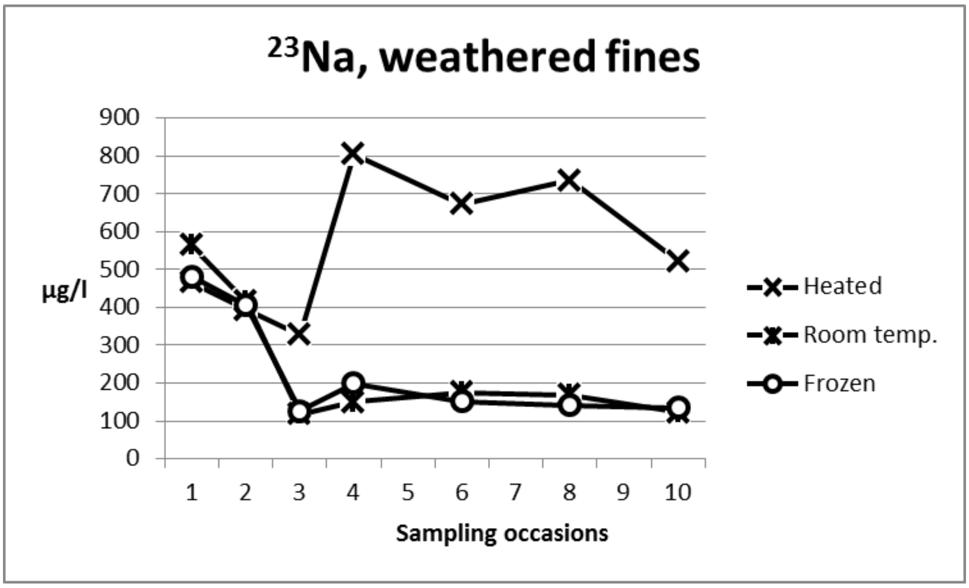


Figure (3.7.1-2), Concentrations of sodium in the leachates of weathered fines

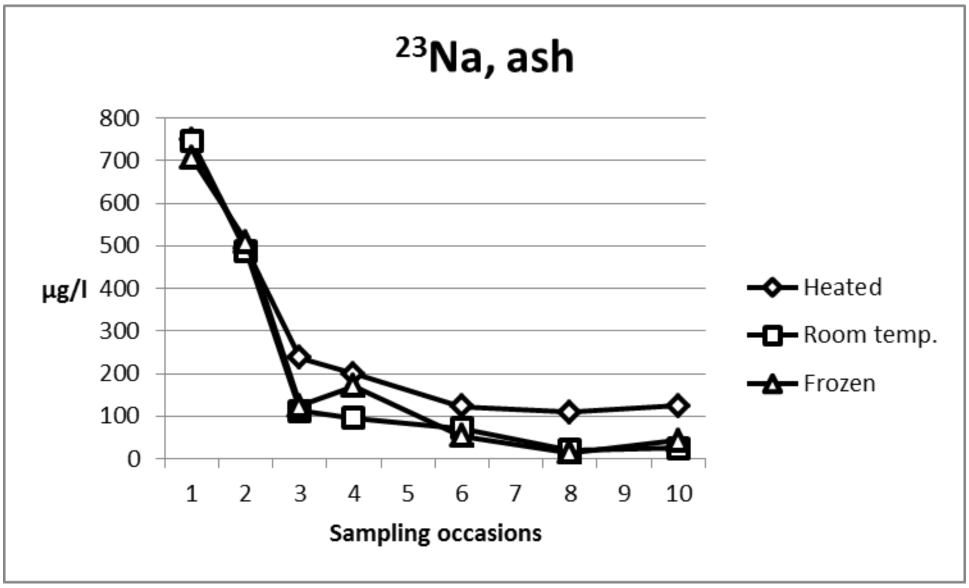


Figure (3.7.1-3), Concentrations of sodium in the leachates of ash

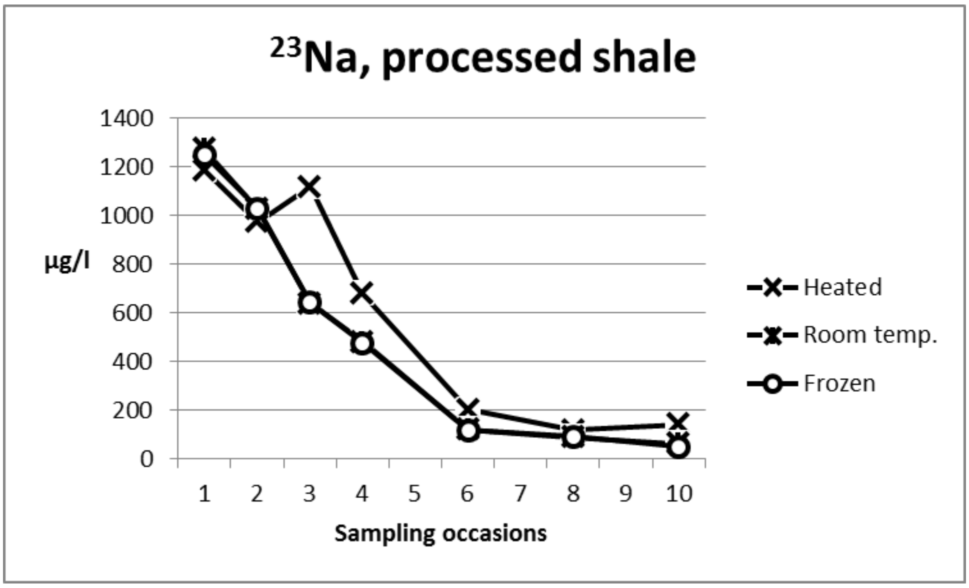


Figure (3.7.1-4), Concentrations of sodium in the leachates of processed shale

According to Cotton *et.al.* (1995) sodium makes up 2.6% of the lithosphere. In the leachates the sodium content was quite high, at least initially. For all materials the concentrations of sodium in the leachates decreased from sampling occasion 1 to sampling occasion 2. This indicates that the particles of all the materials possess a coat of sodium ions which are very soluble in water. Once this coat is dissolved the slower leaching process of the lattice bound sodium begins.

Heating of the materials seem to increase the leaching rate of sodium for all four materials. For the shale, the ash and the processed shale this increase is small but for the weathered fines the leach ability of sodium increases dramatically. Why heating has this effect on the release of sodium from the weathered fines and not from the shale is unsure. Maybe it is the smaller content of organic matter in the weathered fines which allows sodium to leach in a greater extent than it does from the shale.

3.7.2 Magnesium, Mg

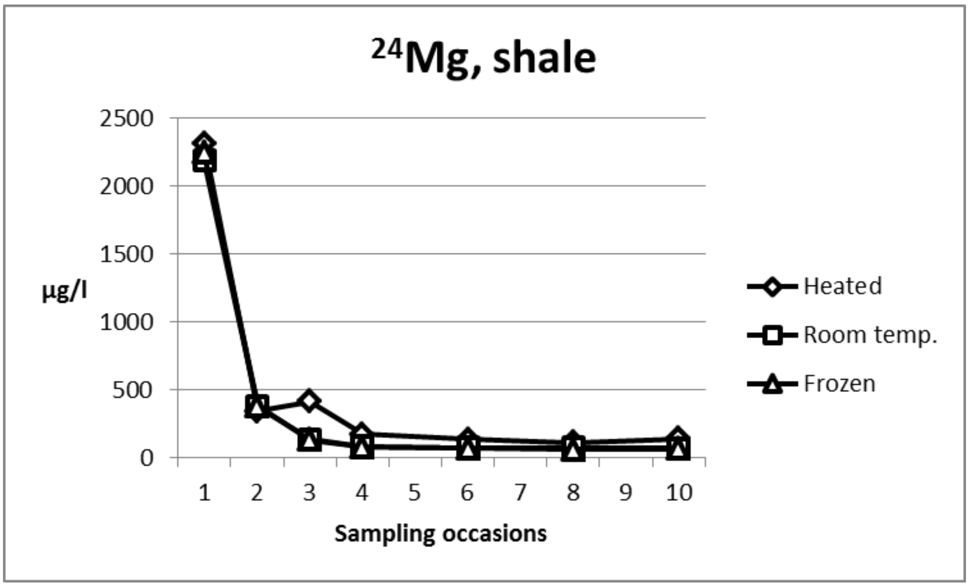


Figure (3.7.2-1), Concentrations of magnesium in the leachates of shale

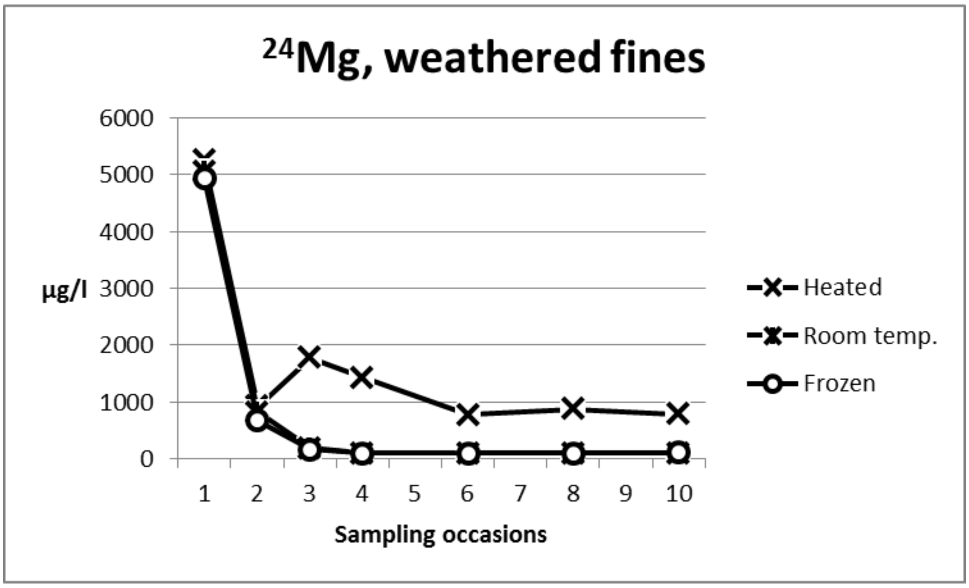


Figure (3.7.2-2), Concentrations of magnesium in the leachates of weathered fines

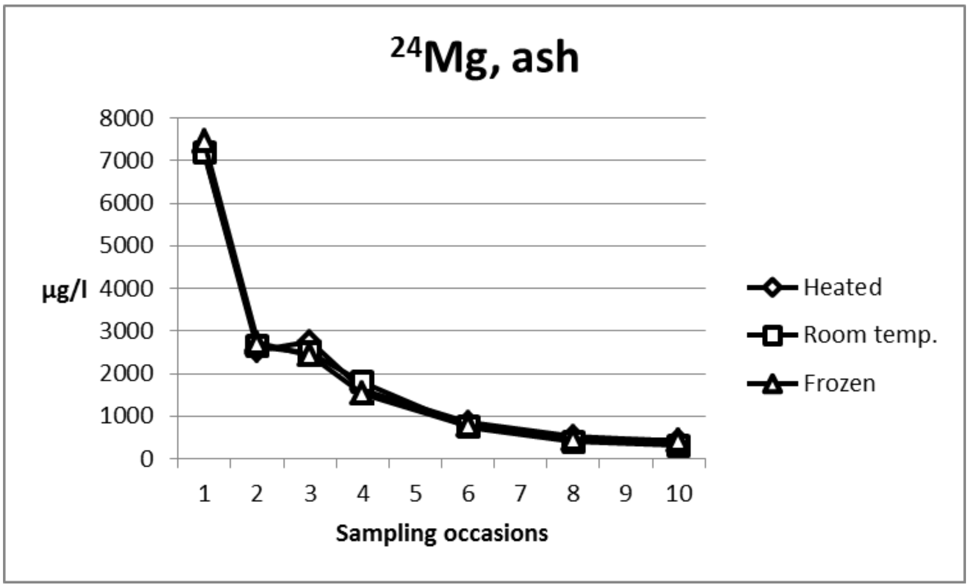


Figure (3.7.2-3), Concentrations of magnesium in the leachates of ash

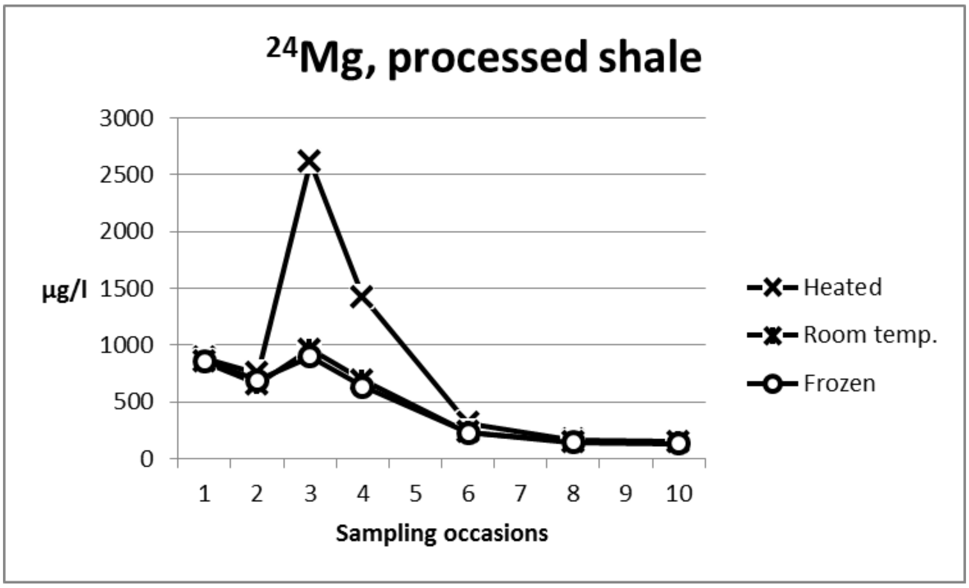


Figure (3.7.2-4), Concentrations of magnesium in the leachates of processed shale

Magnesium shows quite similar leaching patterns as sodium; with higher concentrations on sampling occasion 1 than sampling occasion 2 and an increase in leach ability in the heated samples (except for the ash). Even here higher concentrations of magnesium are observed in leachates from the weathered fines compared to the shale´s leachates, indicating once again that the weathered surfaces of the fines is more susceptible to water.

In the ash and in the processed shale, magnesium probably occurs in oxide form due to the pyrolysis. When hydrated, these oxides form hydroxides which contribute to the approximately neutral pH of their leachates. Though it must be mentioned that $Mg(OH)_2$, $K_s = 1,1*10^{-11}$, is not as soluble as some other hydroxides such as $Ca(OH)_2$, $K_s = 5,5*10^{-6}$ (Atkins & de Paula, 2009).

3.7.3 Aluminum, Al

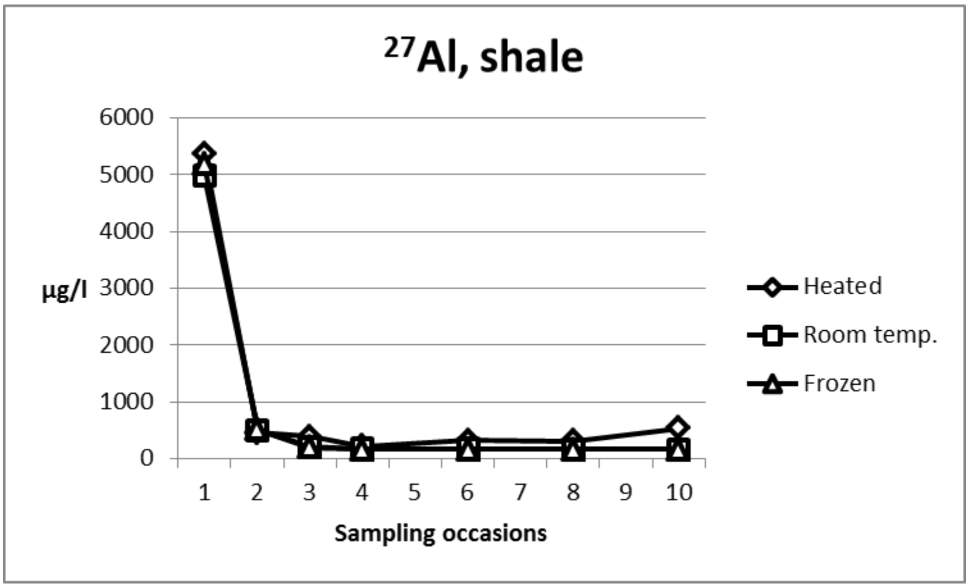


Figure (3.7.3-1), Concentrations of aluminum in the leachates of shale

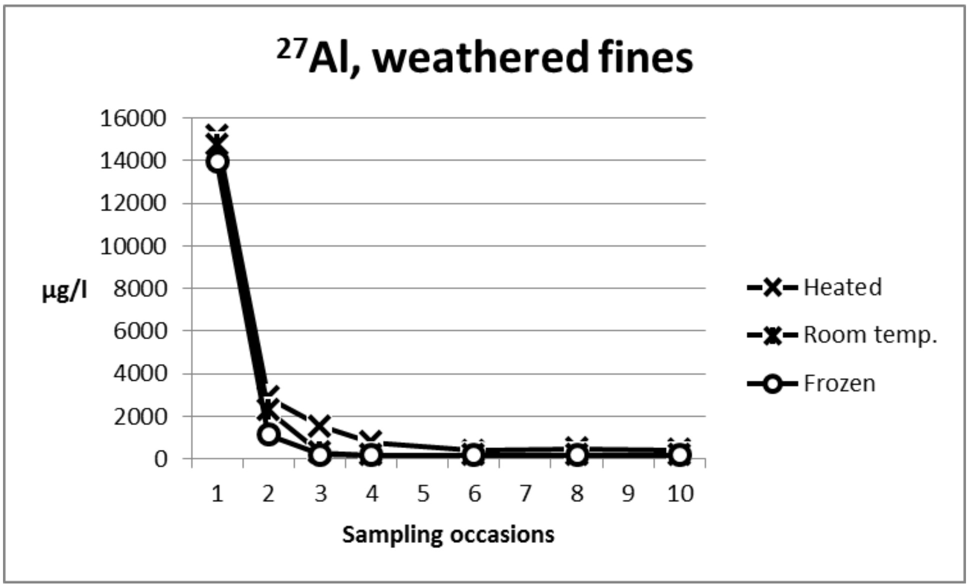


Figure (3.7.3-2), Concentrations of aluminum in the leachates of weathered fines

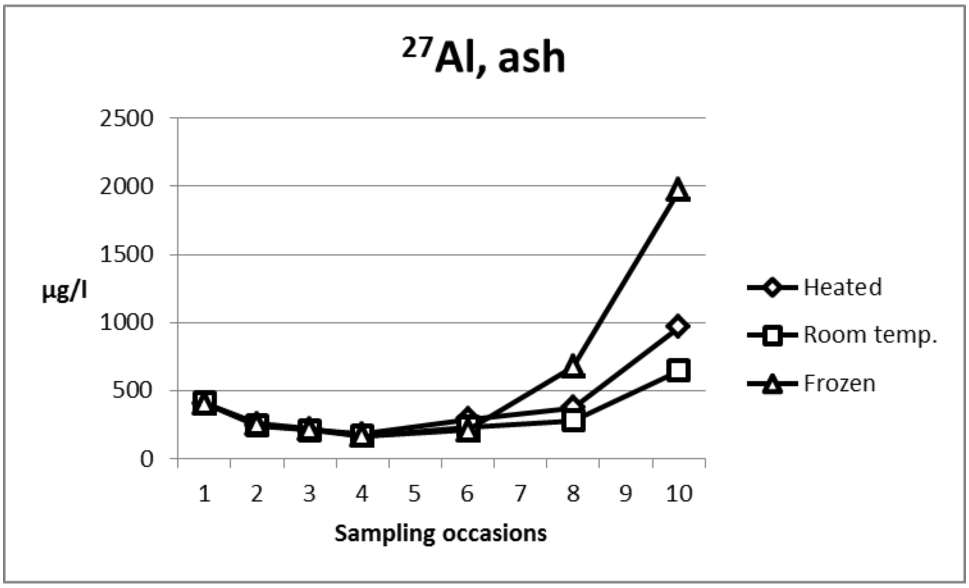


Figure (3.7.3-3), Concentrations of aluminum in the leachates of ash

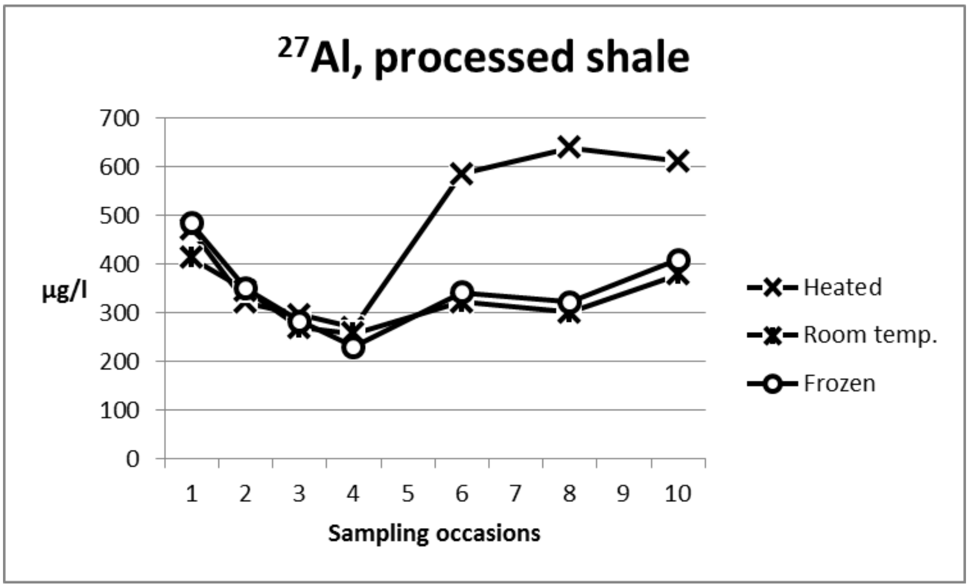


Figure (3.7.3-4), Concentrations of aluminum in the leachates of processed shale

Aluminum is the most abundant metal in the earth´s crust (Cotton *et.al.* 1995). But with this knowledge at hand, the measured concentrations in the samples leachates do not seem so high. This is probably because aluminum occurs in many stable and insoluble mineral structures, such as corundum, Al_2O_3.

Aluminum in water contributes to decreased pH by a series of reaction of which the first is:

$[Al(H_2O)_6]^{3+} = [Al(H_2O)_5(OH)]^{2+} + H^+$ (Cotton *et.al.*, 1995)

As mentioned under heading 3.4; the presence of aluminum increases the acidity of water. This is caused by aluminums ability to coordinate hydroxide ions as is shown by the reaction above.

The coat of aluminum on the particles of shale and weathered fines were removed by only one hour of water leaching. The different temperature treatments do not seem to affect the leach ability of aluminum from shale and weathered fines.

The leaching of aluminum from the ash and processed shale followed different patterns. Both of these materials lack the aluminum rich particle coat that is observed in leachates from the first sampling occasion from the shale and weathered fines.

Heating had a noticeable effect on the processed shale. The aluminum concentrations in the processed shale´s leachates increased after the third heating treatment and thereafter stayed at an even level with a concentration of around 600 μg/l. For the ash it was the freezing treatment which had the highest effect on the mobility of aluminum. The measured concentrations of aluminum on sampling occasion 8 and 10 show a clear increase of aluminum. And these concentrations probably would continue to increase beyond sampling occasion 10. During the pyrolysis process which these two materials have been subjected to their mineral structures may have changed making the completely processed shale more susceptible to heating while the only partly processed ash got a mineral structure more susceptible to frost wedging. Both of these examples are of course only valid from the leach ability of aluminums point of view. But the increase in aluminum concentration from these materials could also be a result of pH; see the discussion around table (3.7.3-3) and (3.7.3-4) below.

Table (3.7.3-1), pH and Al concentrations from samples of shale

	Heated shale		Room temp. shale		Frozen shale	
Sampling occasions	pH	Al (μg/l)	pH	Al (μg/l)	pH	Al (μg/l)
1	2.7	5378	2.7	4994	2.7	5202
2	3.1	458.1	3.1	504.4	3.1	521.1
3	2.9	393.0	3.2	209.1	3.3	203.6
4	3.2	218.5	3.4	176.5	3.5	165.6
6	3.4	320.9	3.5	174.0	3.6	168.8
8	3.5	309.9	3.6	167.7	3.7	164.3
10	3.5	542.5	3.5	165.9	3.7	170.7

Table (3.7.3-2), pH and Al concentrations from samples of weathered fines

	Heated weathered fines		Room temp. weathered fines		Frozen weathered fines	
Sampling occasions	pH	Al (μg/l)	pH	Al (μg/l)	pH	Al (μg/l)
1	2.5	15150	2.5	14750	2.5	13950
2	2.8	2892	2.8	2289	2.8	1136
3	2.5	1535	3.0	288.0	3.0	217.2
4	2.8	781.8	3.1	173.9	3.2	171.2
6	3.2	381.3	3.1	184.6	3.2	175.8
8	3.1	470.9	3.0	184.6	3.1	182.0
10	3.2	417.6	3.0	178.4	3.1	184.9

The high concentrations of aluminum in the leachates from shale and weathered fines at the first sampling occasion could be responsible for the initial pH. But it is more likely that this pH-value is a result from high concentrations of various elements. Because most of the elements analyzed in this study occurred as particle coats which were leached after just 1 hour of water leaching.

The decrease in pH observed at sampling occasion 3, i.e. at the first temperature treatment, in the heated samples of shale and weathered fines is not coupled to any increase in aluminum concentration. This indicates that it is the leaching of other elements that causes this pH decrease.

Table (3.7.3-3), pH and Al concentrations from samples of ash

	Heated ash		Room temp. ash		Frozen ash	
Sampling occasions	pH	Al (µg/l)	pH	Al (µg/l)	pH	Al (µg/l)
1	5.3	406.0	5.3	412.3	5.4	405.9
2	5.9	244.5	6.0	247.9	6.1	258.0
3	6.1	210.9	6.4	210.9	6.5	220.7
4	6.2	181.7	6.4	166.0	6.8	165.8
6	6.0	289.4	6.5	233.7	7.0	209.0
8	6.0	372.7	6.4	281.0	6.8	674.9
10	6.0	969.3	6.4	645.8	6.7	1972

Table (3.7.3-4), pH and Al concentrations from samples of processed shale

	Heated processed shale		Room temp. processed shale		Frozen processed shale	
Sampling occasions	pH	Al (µg/l)	pH	Al (µg/l)	pH	Al (µg/l)
1	5.7	470.3	5.6	413.0	5.7	483.6
2	6.5	321.2	6.3	346.0	6.2	349.7
3	7.1	295.2	6.8	269.4	6.7	282.5
4	7.3	269.4	7.0	257.2	7.0	230.6
6	7.6	584.8	7.3	321.9	7.4	341.6
8	7.1	638.8	7.0	300.8	7.1	322.5
10	6.8	611.1	6.9	379.3	6.8	408.4

In table (3.7.3-3) and (3.7.3-4) a comparison between pH and aluminum concentration in samples of ash and processed shale is shown. The concentrations of aluminum in the leachates from ash and processed shale decreases during the first 4 sampling occasions. After sampling occasion 4 the aluminum concentrations seem to increase again in samples from both materials and all temperature treatments. This leaching pattern of aluminum could explain the changes in pH in samples of ash and processed shale. The pH initially increases as concentrations of aluminum decreases and once the concentrations of aluminum increases; the pH decreases slightly. However, these pH changes are small so it is difficult to say if they really occur in relationship to the aluminum concentrations. Instead of being a result of changed mineralogy, as was discussed previously, the increased leach ability of aluminum could be triggered by formation of aluminum hydroxides. And since pH is higher in samples of frozen ash than in the samples of heated ash we see a greater increase of aluminum concentrations in these frozen samples. However heating still seem to favor the formation of aluminum hydroxides since the aluminum concentrations in heated ash samples are higher at sampling occasion 10 than the aluminum concentration in the room temperate ash samples. The same indication is also given by the aluminum concentration increase caused by heating in the samples of processed shale.

3.7.4 Potassium, K

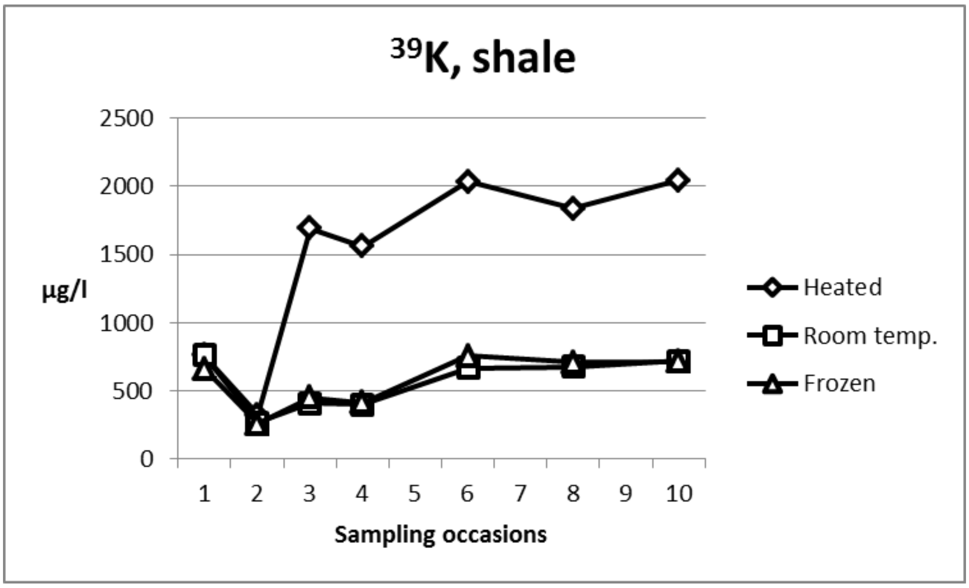


Figure (3.7.4-1), Concentrations of potassium in the leachates of shale

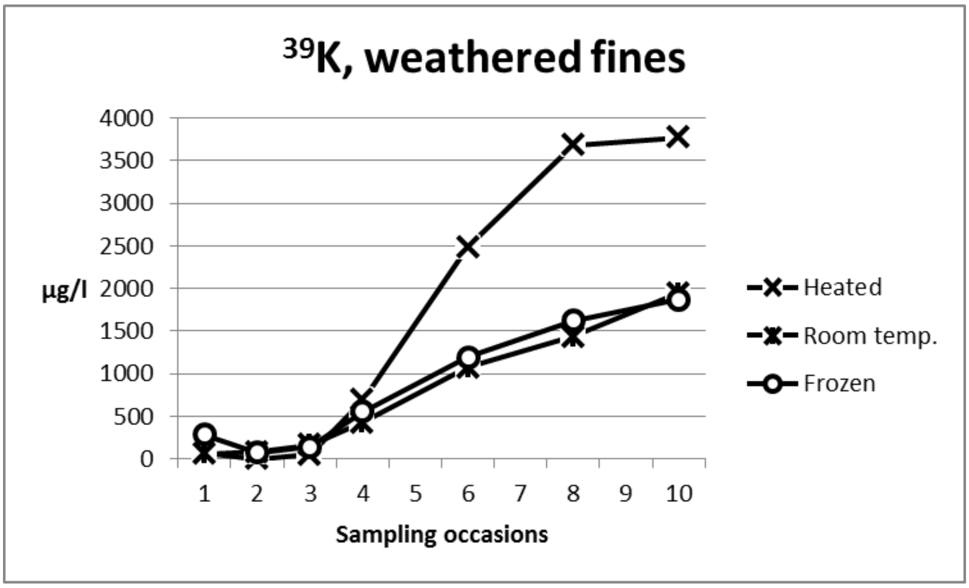


Figure (3.7.4-2), Concentrations of potassium in the leachates of weathered fines

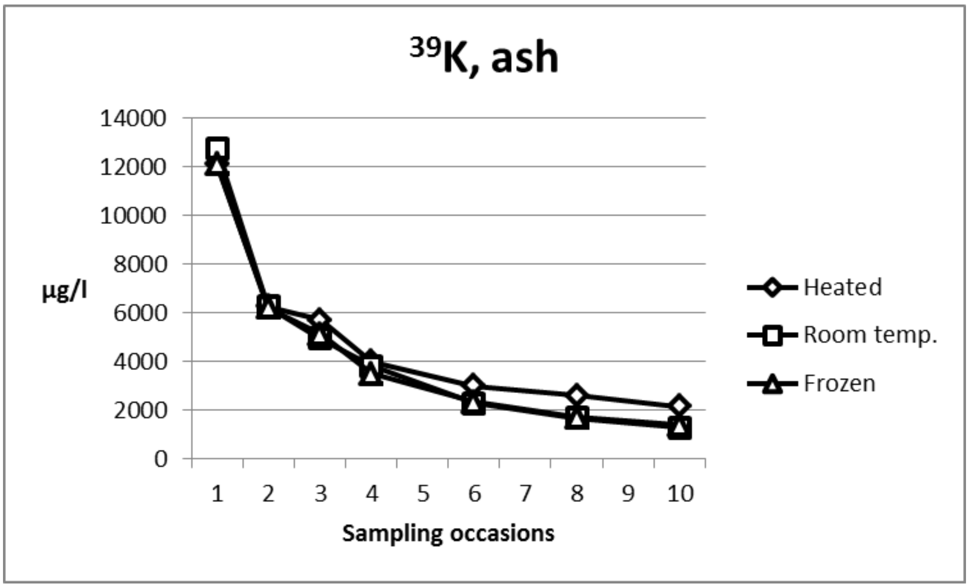


Figure (3.7.4-3), Concentrations of potassium in the leachates of ash

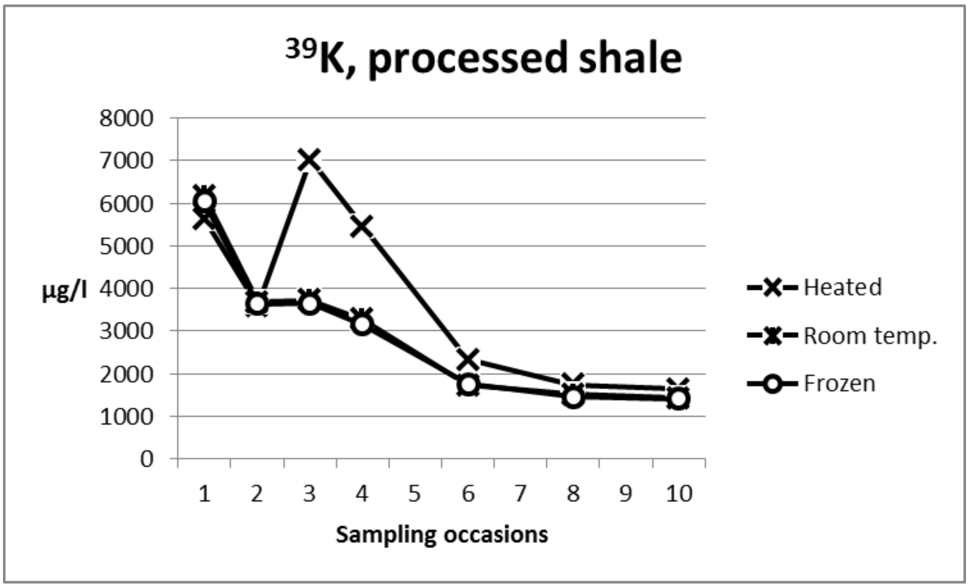


Figure (3.7.4-4), Concentrations of potassium in the leachates of processed shale

It is common that potassium occurs between layers in sheet silicate structures, giving these minerals charge balance (Nesse, 2009). These ions between the sheets are quite easily leached by water and, as one may clearly see by the results of the leachates from the shale and weathered fines, heating breaks open these thin sheets making the hollow spaces between them more accessible for water and leaching. The pyrolysis which the two processed materials been subjected to breaks the sheet silicates to an even greater extent, resulting in the high initial concentrations of potassium in their leachates. And for some reason additional heating of processed shale causes a short increase of potassium concentration in their leachates.

3.7.5 Calcium, Ca

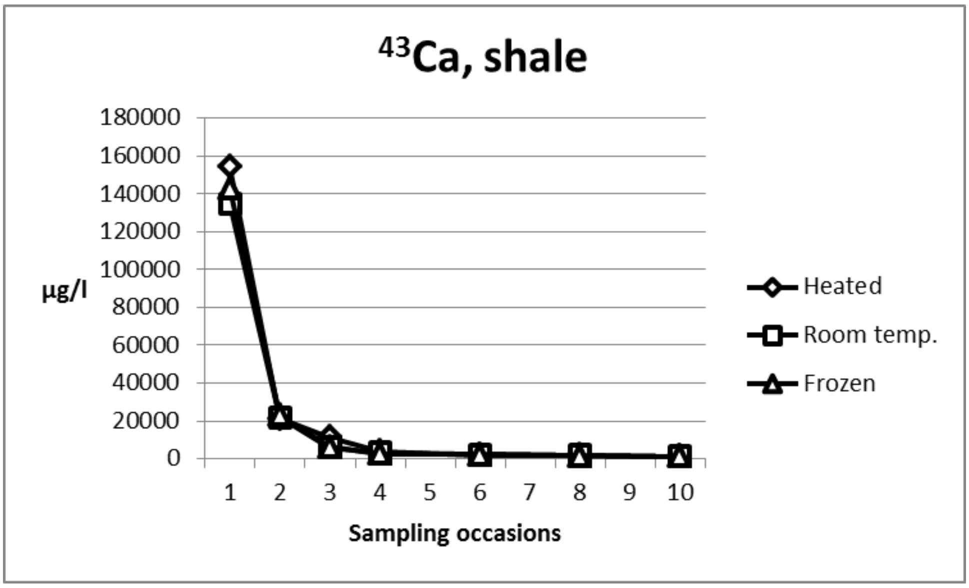


Figure (3.7.5-1), Concentrations of calcium in the leachates of shale

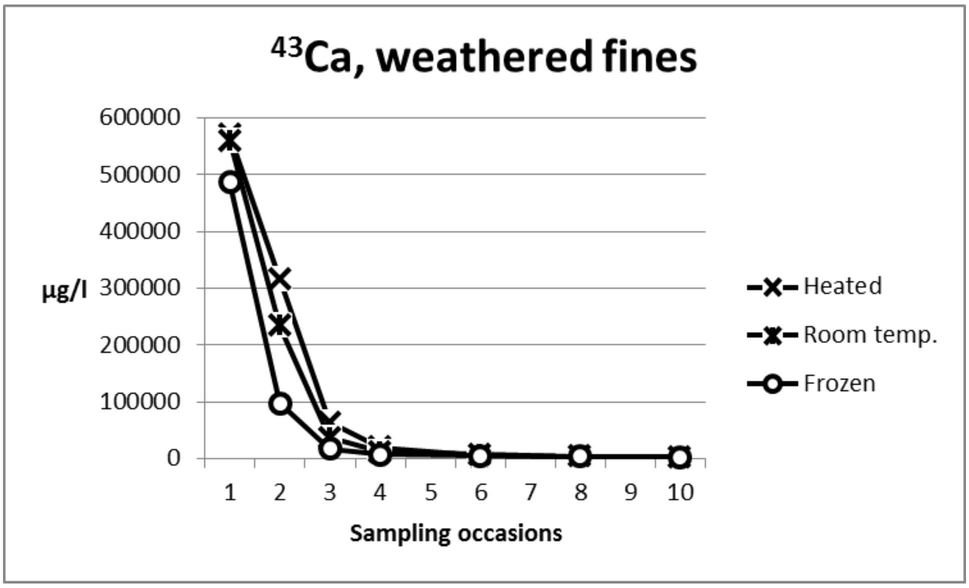


Figure (3.7.5-2), Concentrations of calcium in the leachates of weathered fines

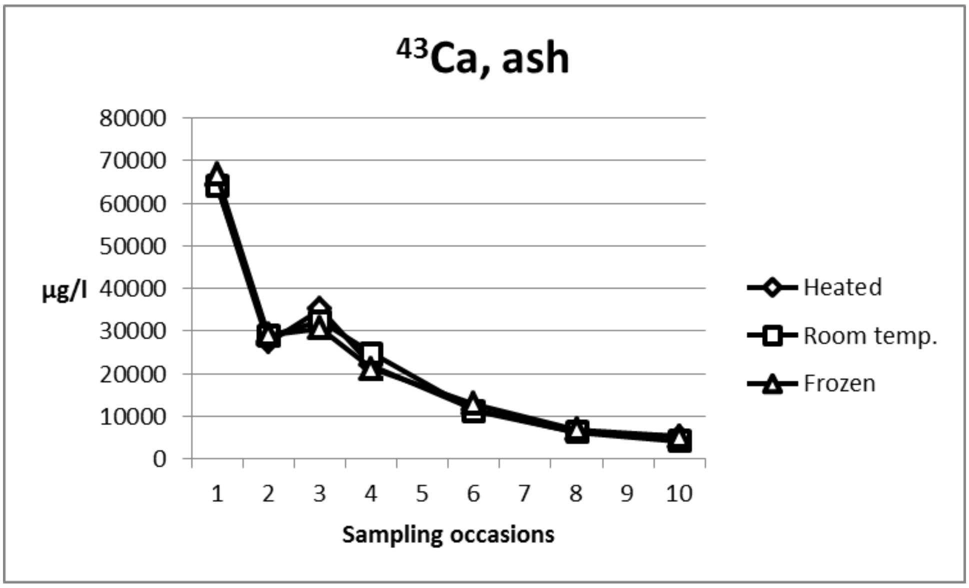


Figure (3.7.5-3), Concentrations of calcium in the leachates of ash

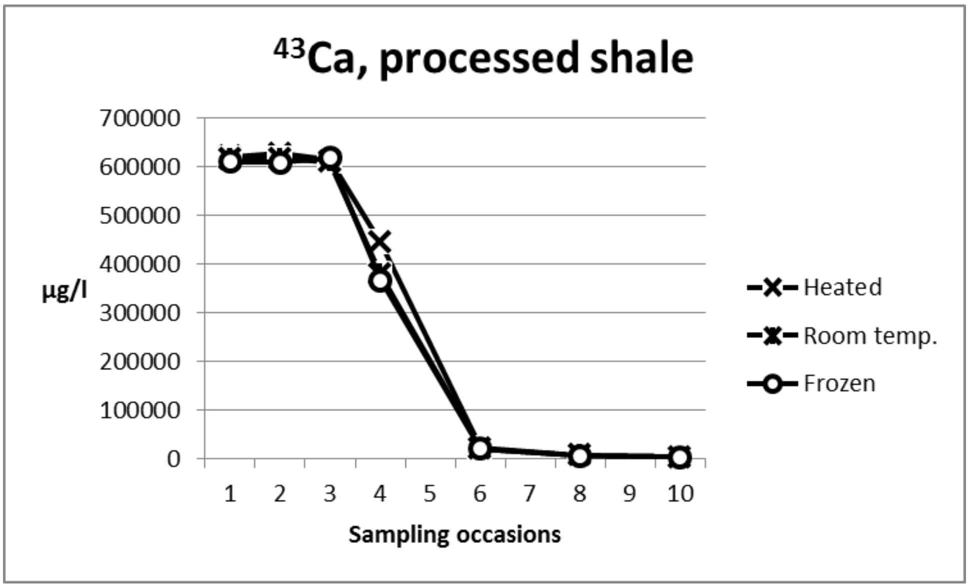


Figure (3.7.5-4), Concentrations of calcium in the leachates of processed shale

Calcium is the metal which reaches the highest concentrations in leachates of the different materials, at least during the first two sampling occasions. Calcium occurs in many minerals and one of the most common of these minerals is calcite, $CaCO_3$. Calcite is the primary mineral in the surrounding, and underlying, limestone layer in the area of Kvarntorp but the shale also contain a fair amount of calcite.

Once again we see a clear indication in the measured concentrations that the particles of shale and weathered fines contain a coat of, in this case, calcium which is easily loosened with water. 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 that originates from calcite should occur in the form of lime, CaO, due to the pyrolysis process (note the similarities with magnesium discussed in 3.7.2). The ash shows, as the shale and weathered fines, a clear indication of a particle coat of calcium the first sampling occasion. The processed shale however shows a quite different pattern of calcium leaching. This behavior indicates the formation of a mineral which saturates the system with calcium; and therefore it is not until sampling occasion 4 that the concentrations of calcium in the leachates decrease. Due to the high concentrations of sulfate in the leachates (table (3.4-4) or heading; sulfate, 3.6) this mineral is believed to be gypsum; $CaSO_4$. Gypsum may form as a result of oxidation of pyrite, FeS_2, in the presence of calcite, $CaCO_3$. The sulfuric acid generated by the oxidation of pyrite reacts with calcite and forms gypsum.

3.7.6 Vanadium, V

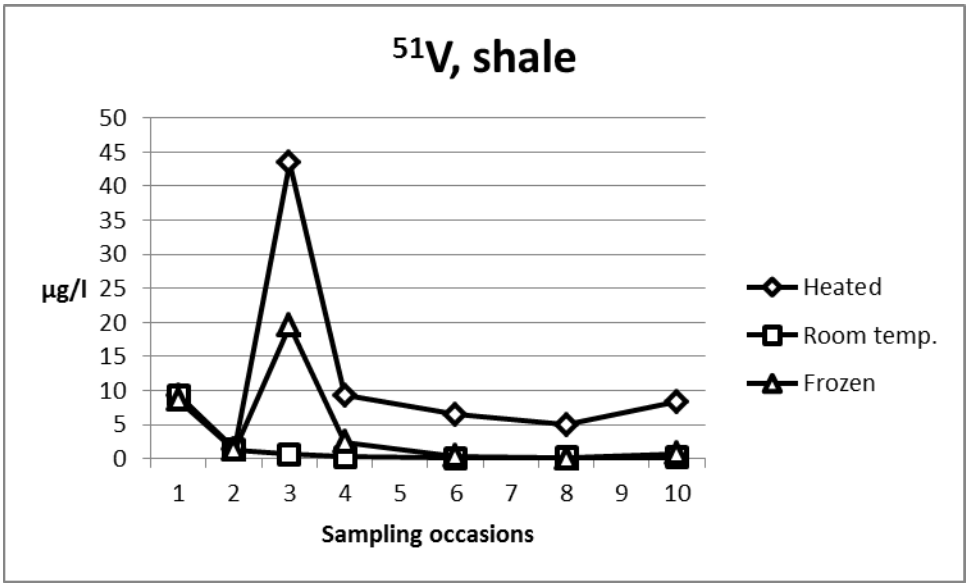


Figure (3.7.6-1), Concentrations of vanadium in the leachates of shale

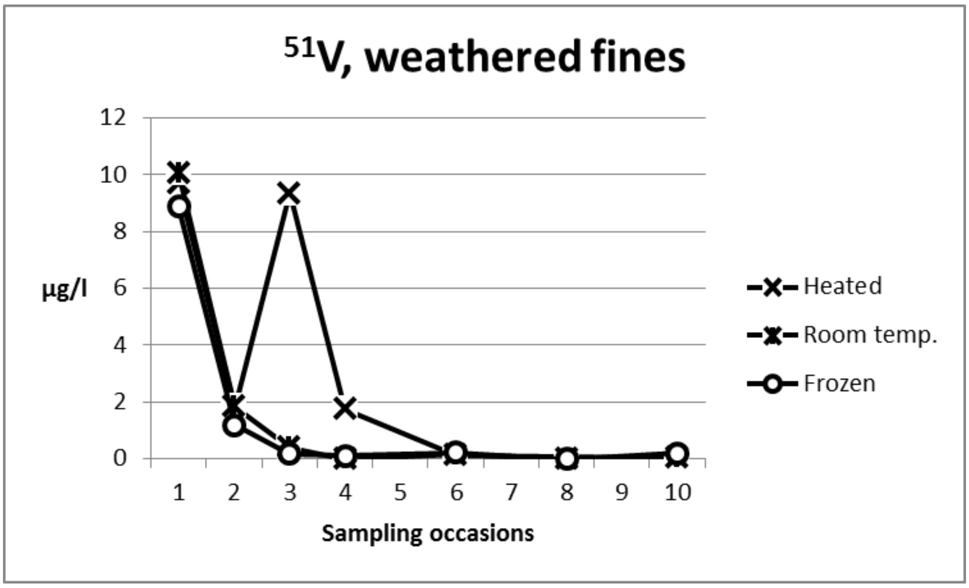


Figure (3.7.6-2), Concentrations of vanadium in the leachates of weathered fines

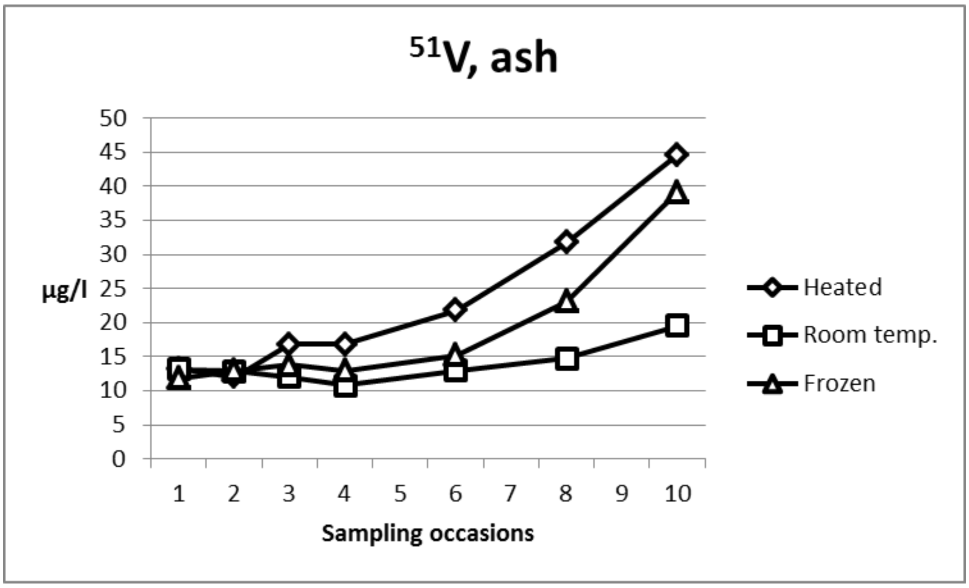


Figure (3.7.6-3), Concentrations of vanadium in the leachates of ash

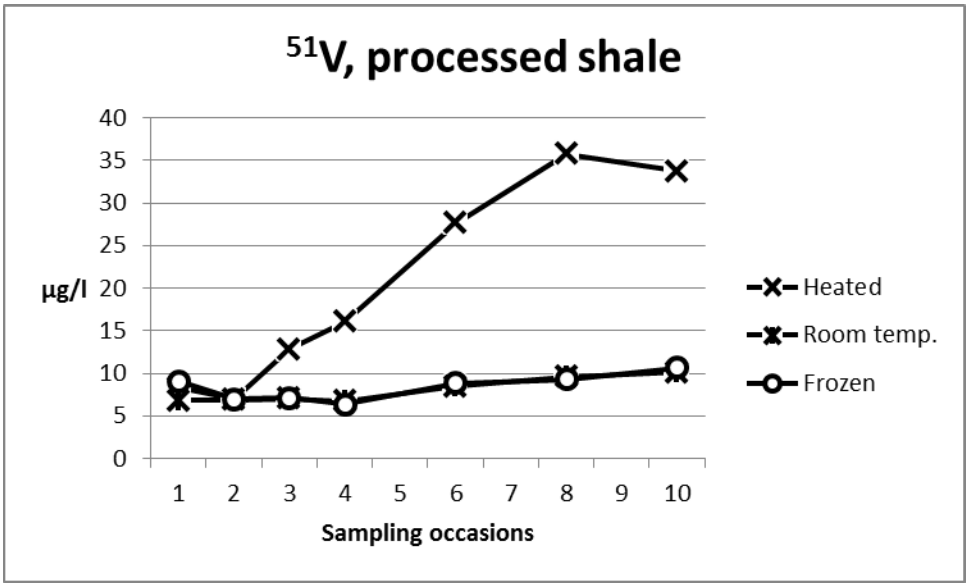
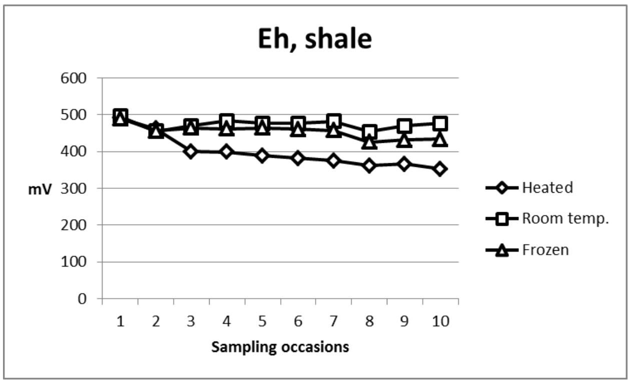


Figure (3.7.6-4), Concentrations of vanadium in the leachates of processed shale

Heating of shale and weathered fines causes a peak of vanadium concentration in the leachates. The vanadium concentration in the weathered fines´ leachates then decreases to almost 0 µg/l 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´s leachates.

The concentrations of vanadium are higher in the shale´s leachates than in the weathered fines´ leachates. This may indicate that that the vanadium that is 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. Or the vanadium from the weathered fines may have precipitated and therefore not being correctly quantified by the ICP-MS. Vanadium is very sensitive to redox conditions. Heating and freezing of shale and weathered fines lowers Eh as is shown under heading 3.5.



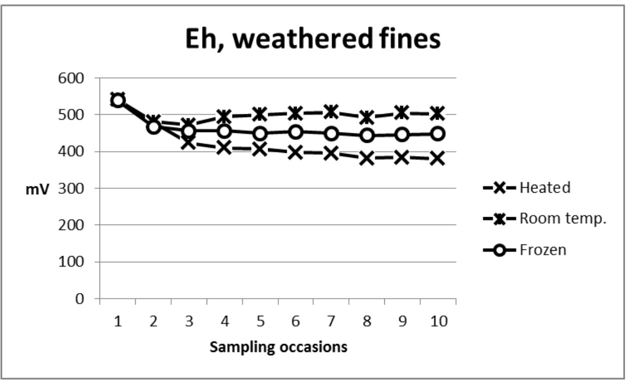


Figure (3.5-1), Eh for the samples of shale

Figure (3.5-2), Eh for the samples of weathered fines

The reason why Eh decreases was also discussed under heading 3.5 and is believed to be caused by increased oxidation rate of sulfides. This would then cause an increase in sulfate concentrations of the leachates as is shown in the following table:

Table (3.4-4), Sulfate concentrations in the leachates of all 4 materials

Sulfate content (mg/l)	**Sampling occasions**				
	1	2	3	4	5
Heated shale	540.9	93.11	131.1	57.86	45.68
Room temp. shale	506.9	99.37	42.34	23.52	18.20
Frozen shale	587.2	116.8	42.69	20.94	15.90
Heated weathered fines	1494	921.5	379.8	168.6	89.06
Room temp. weathered fines	1916	719.9	140.4	61.91	56.55
Frozen weathered fines	1732	349.7	95.89	50.25	47.21
Heated ash	195.3	65.00	76.63	46.01	37.89
Room temp. ash	191.4	62.85	59.08	48.16	37.56
Frozen ash	196.9	63.49	40.87	19.52	18.15
Heated processed shale	1526	1444	1391	1009	121.8
Room temp. processed shale	1506	1423	1393	861.7	112.9
Frozen processed shale	1484	1530	1399	783.4	105.3

The sulfate concentrations in leachates from heated and frozen shale may enhance the leach ability of vanadium, while the even higher concentrations of sulfate in leachates of weathered fines causes the formation of a solid vanadium sulfate which then precipitates.

Burning of shales alters its mineral structure into a composition which favors water leaching of vanadium. This is shown by the measured vanadium concentrations in the leachates from ash and processed shale. The samples which have stood in room temperature show steady vanadium concentrations until sampling occasion 8. The concentrations are 10-15 µg/l in ash samples and 5-10 µg/l in processed shale samples.

The partially processed ash shows an interesting response to heating and freezing. The 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 which have stood in room temperature seem to gain an increase in vanadium concentrations in their leachates on sampling occasion 10. If this is true however cannot be said with absolute certainty due to the short leaching period.

The processed shale seems only to be affected by the heating treatment which causes a clear increase in vanadium leaching. This increase seems to reach a maximum concentration of around 36 µg/l vanadium. But if this really is the maximum concentration that the heating treatment may cause in these leachates is unsure. A longer leaching period would be needed to gain this answer also.

Table (3.7.6-1), pH and V concentrations from samples of shale

	Heated shale		Room temp. shale		Frozen shale	
Sampling occasions	pH	V (µg/l)	pH	V (µg/l)	pH	V (µg/l)
1	2.7	9.325	2.7	9.248	2.7	8.670
2	3.1	1.425	3.1	1.283	3.1	1.297
3	2.9	43.42	3.2	0.6151	3.3	19.48
4	3.2	9.244	3.4	0.2973	3.5	2.379
6	3.4	6.508	3.5	0.09694	3.6	0.3426
8	3.5	4.974	3.6	0.1628	3.7	0.1158
10	3.5	8.372	3.5	0.2101	3.7	0.7229

Table (3.7.6-2), pH and V concentrations from samples of weathered fines

	Heated weathered fines		Room temp. weathered fines		Frozen weathered fines	
Sampling occasions	pH	V (µg/l)	pH	V (µg/l)	pH	V (µg/l)
1	2.5	9.697	2.5	10.08	2.5	8.872
2	2.8	1.794	2.8	1.853	2.8	1.196
3	2.5	9.350	3.0	0.3954	3.0	0.1790
4	2.8	1.750	3.1	0	3.2	0.1076
6	3.2	0.1208	3.1	0.1572	3.2	0.2263
8	3.1	0.05852	3.0	0	3.1	0
10	3.2	0.02904	3.0	0.02956	3.1	0.2057

Table (3.7.6-3), pH and V concentrations from samples of ash

	Heated ash		Room temp. ash		Frozen ash	
Sampling occasions	pH	V (µg/l)	pH	V (µg/l)	pH	V (µg/l)
1	5.3	13.27	5.3	13.13	5.4	11.85
2	5.9	12.02	6.0	12.83	6.1	12.98
3	6.1	16.78	6.4	11.99	6.5	13.75
4	6.2	16.79	6.4	10.78	6.8	12.98
6	6.0	21.82	6.5	12.96	7.0	15.21
8	6.0	31.71	6.4	14.74	6.8	23.13
10	6.0	44.63	6.4	19.55	6.7	39.21

Table (3.7.6-4), pH and V concentrations from samples of processed shale

	Heated processed shale		Room temp. processed shale		Frozen processed shale	
Sampling occasions	pH	V (µg/l)	pH	V (µg/l)	pH	V (µg/l)
1	5.7	8.303	5.6	6.837	5.7	9.069
2	6.5	6.979	6.3	6.880	6.2	6.988
3	7.1	12.83	6.8	7.061	6.7	7.134
4	7.3	16.04	7.0	6.777	7.0	6.402
6	7.6	27.68	7.3	8.442	7.4	8.887
8	7.1	35.78	7.0	9.571	7.1	9.317
10	6.8	33.75	6.9	10.11	6.8	10.66

Vanadium does not seem to affect pH, at least in no greater extent. The decrease in pH at sampling occasion 3 in leachates from shale and weathered fines is more probably caused by increased sulfide oxidation than by increased leaching of vanadium.

3.7.7 Manganese, Mn

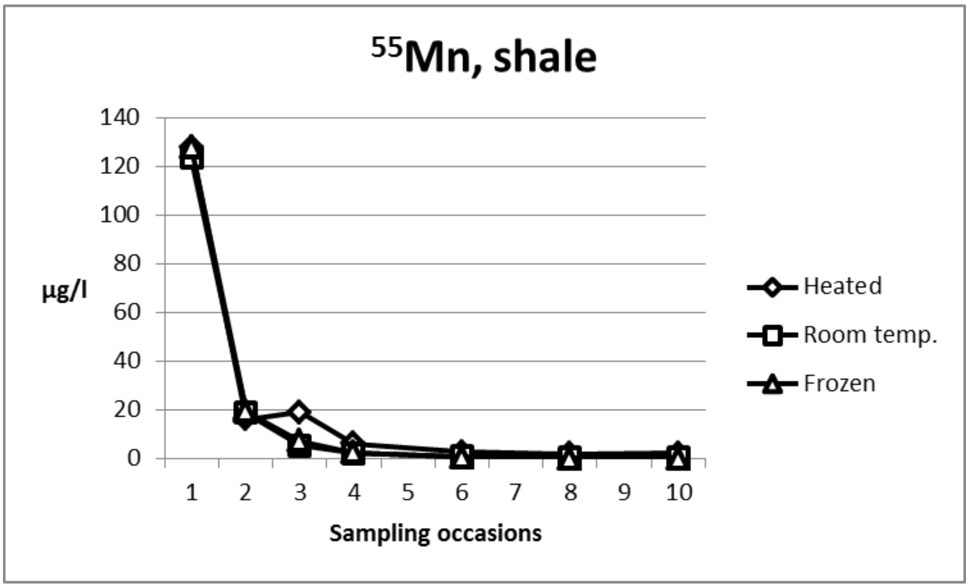


Figure (3.7.7-1), Concentrations of manganese in the leachates of shale

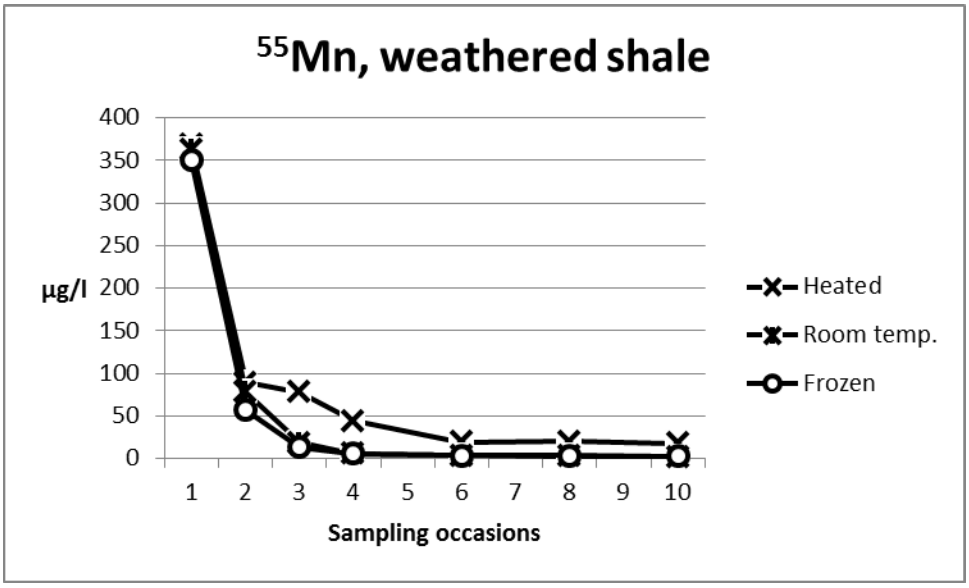


Figure (3.7.7-2), Concentrations of manganese in the leachates of weathered fines

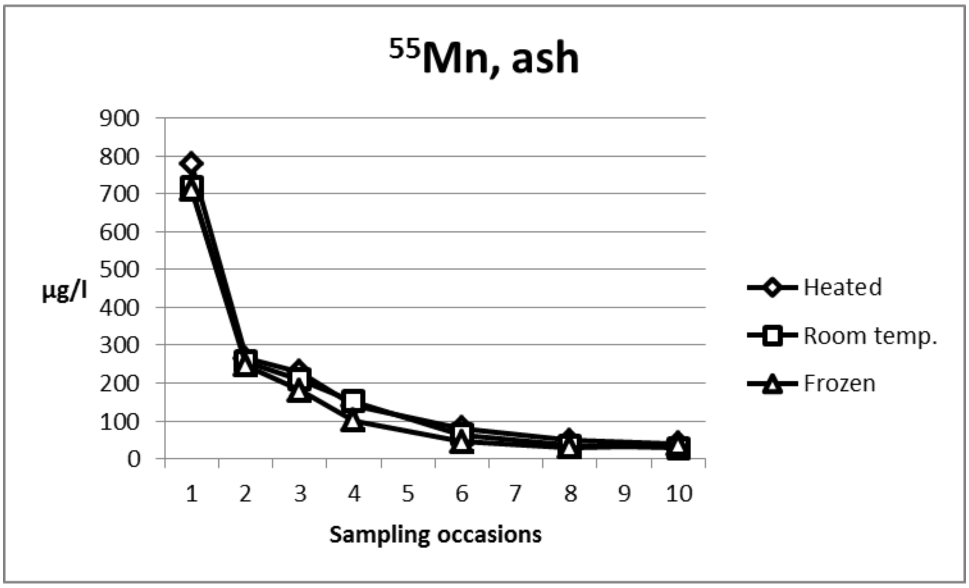


Figure (3.7.7-3), Concentrations of manganese in the leachates of ash

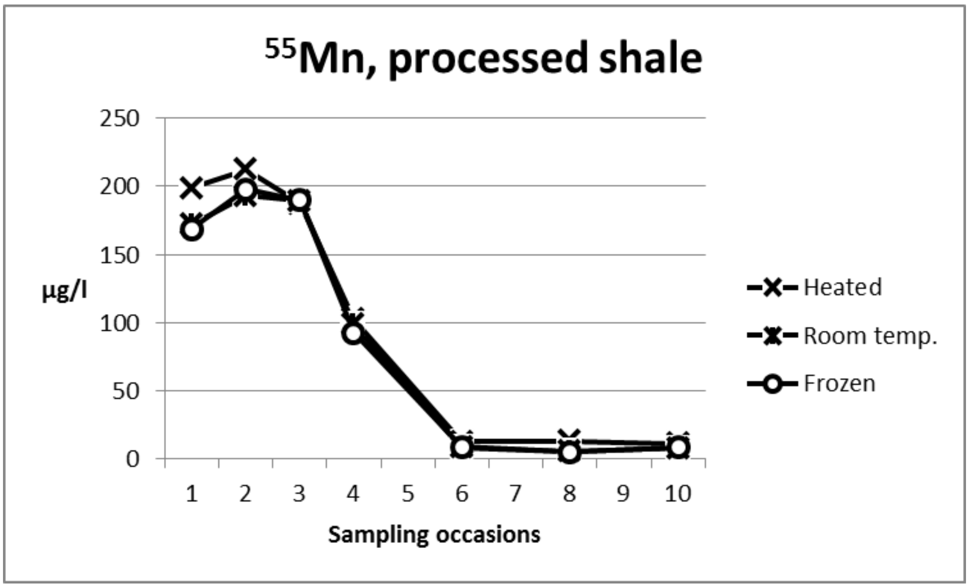


Figure (3.7.7-4), Concentrations of manganese in the leachates of processed shale

Once again clear particle coats present, this time of manganese, on shale-, weathered fines- and ash particles. The concentration of manganese is higher in leachates from weathered fines than in leachates from shale, but the highest concentration of manganese was found in the leachates from the ash. This indicates that partially processing of shale increases the leach ability of manganese.

Heating treatment increases leaching of manganese slightly in shale- and weathered fines samples. The ash- and processed shale samples remained unaffected by the temperature treatments. The concentration of manganese in the leachates from the processed shale shows a similar pattern to that of calcium; indicating the formation of a quite stable mineral which is not very soluble in water. It is hard to say for sure which mineral this is. It may even be more than one mineral. The most probable minerals are $Mn(OH)_2$ and MnOOH. It may also be $MnSO_4$, which is also a quite insoluble mineral according to Cotton *et.al.* (1995).

3.7.8 Iron, Fe

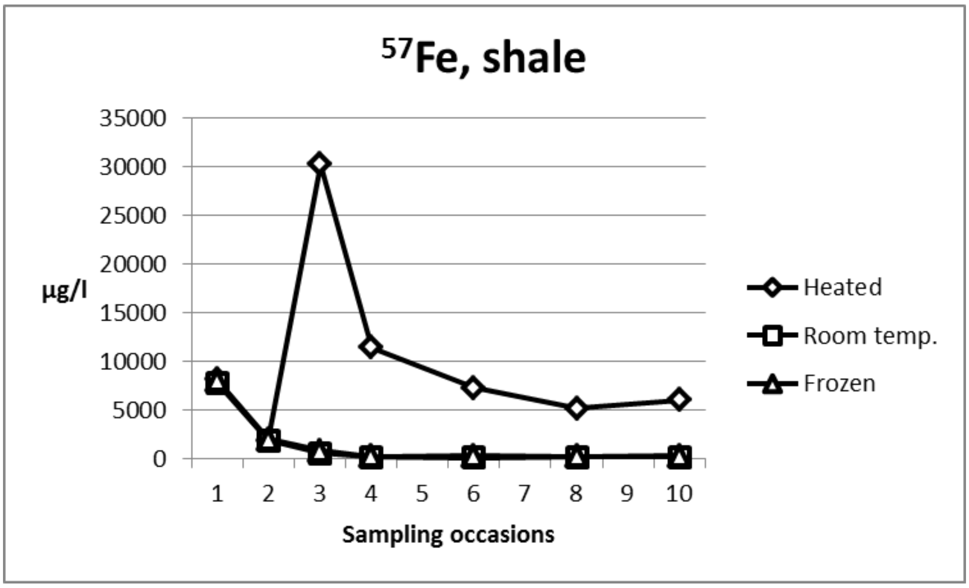


Figure (3.7.8-1), Concentrations of iron in the leachates of shale

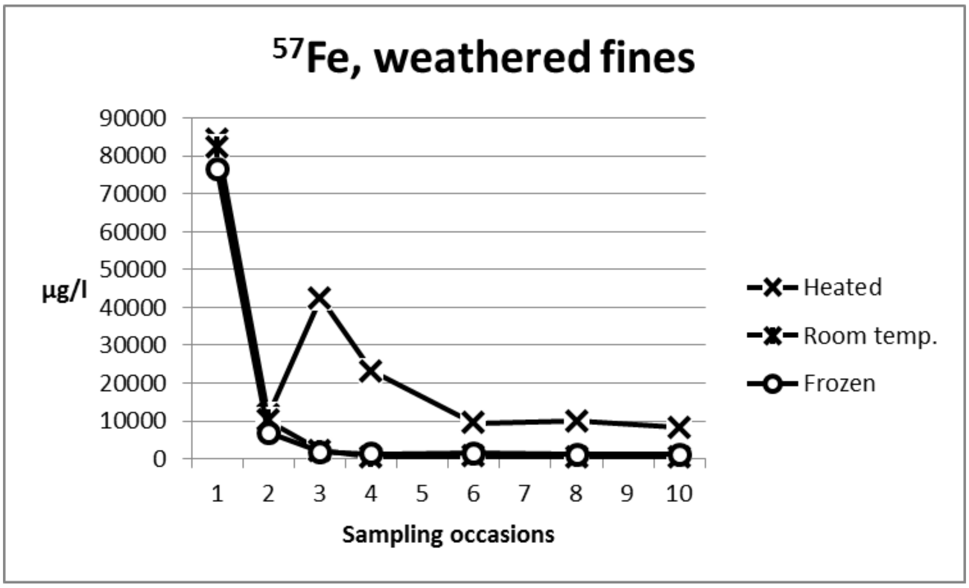


Figure (3.7.8-2), Concentrations of iron in the leachates of weathered fines

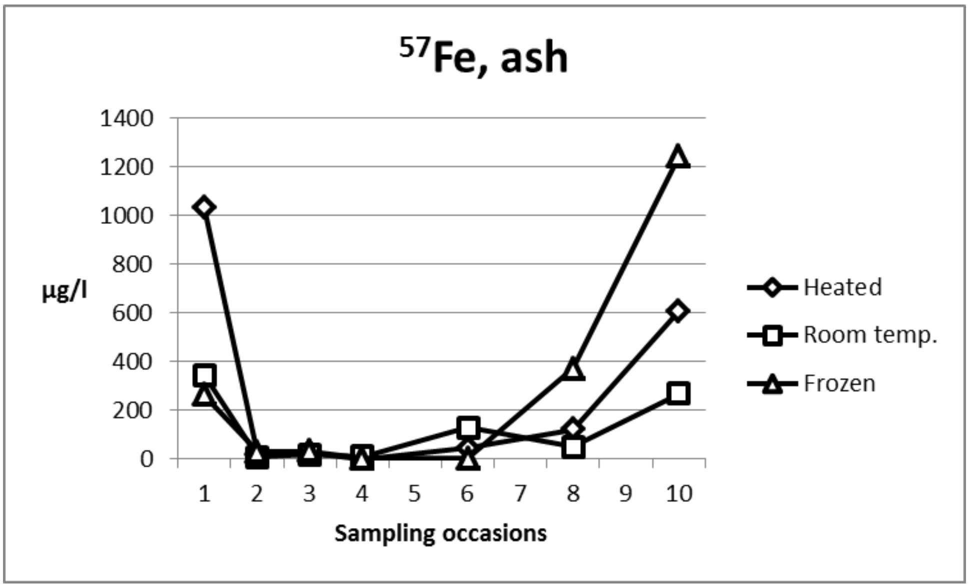


Figure (3.7.8-3), Concentrations of iron in the leachates of ash

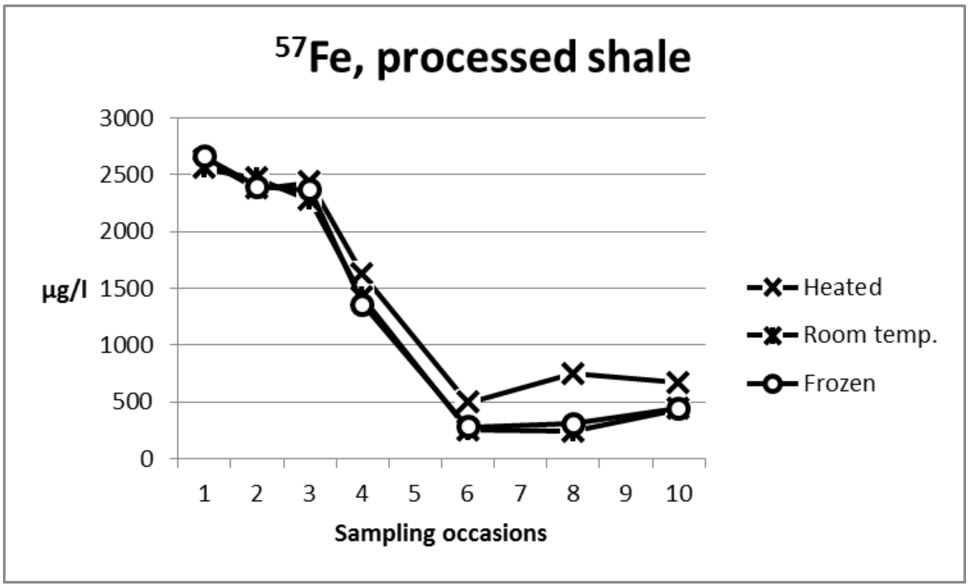


Figure (3.7.8-4), Concentrations of iron in the leachates of processed shale

Iron is the second most abundant metal in the earth´s crust (Cotton *et.al.* 1995) a fact that should be able to explain the high concentrations of iron in most of these samples. As in many previous cases; the concentrations of iron in the leachates from weathered fines are higher than in the shale´s leachates. A particle coat of iron is also present in the samples of shale, weathered fines and ash. Though the measured concentration of iron in the heated ash sample on sampling occasion 1 has a high RSD value and may therefore give a misleading impression. Heating treatment increases the leach ability of iron from shale and weathered fines.

Ash shows once again an interesting leaching pattern towards the end of the leaching period. This pattern is similar to the leaching of vanadium previously discussed under heading 3.7.6. All three temperature treatments seem to have a beneficial effect on iron leaching from ash but also here, on sampling occasion 10, are the RSD values for all treatments relatively high.

The samples of processed shale show once again the presence of a relatively insoluble mineral. A guess is that this mineral is ferrihydrite, $Fe(OH)_3$. This conclusion is drawn by an Eh-pH diagram presented by Drever (p. 153, 1997) showing the stability fields for the $Fe\text{-}O\text{-}H_2O\text{-}S\text{-}CO_2$ system. Due to the difficulty of measuring Eh, as was mentioned in 3.5, this is just a hypothesis. But the point generated by the processed shale´s Eh- and pH values coincides with the stability field of $Fe(OH)_3$. Ferrihydrite may, in turn, change into goethite, FeOOH. Iron hydroxides and oxyhydroxides are quite sensitive to changes in Eh. If Eh would decrease; ferric iron will be reduced to ferrous iron.

3.7.9 Nickel, Ni

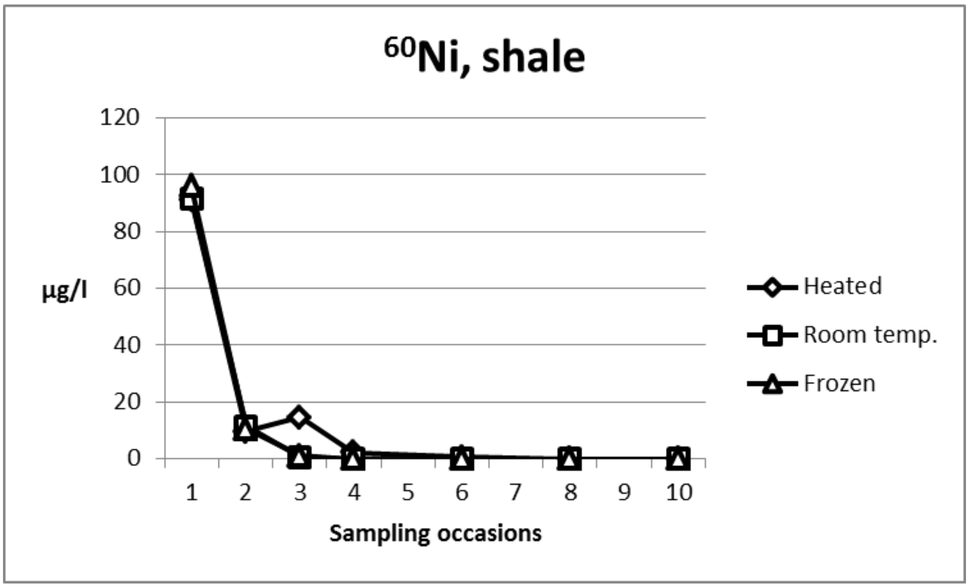


Figure (3.7.9-1), Concentrations of nickel in the leachates of shale

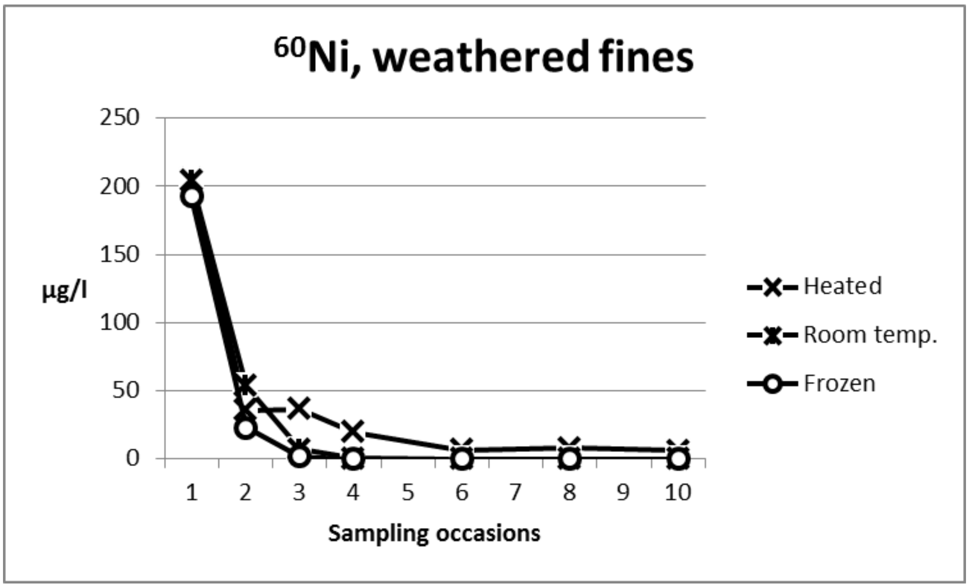


Figure (3.7.9-2), Concentrations of nickel in the leachates of weathered fines

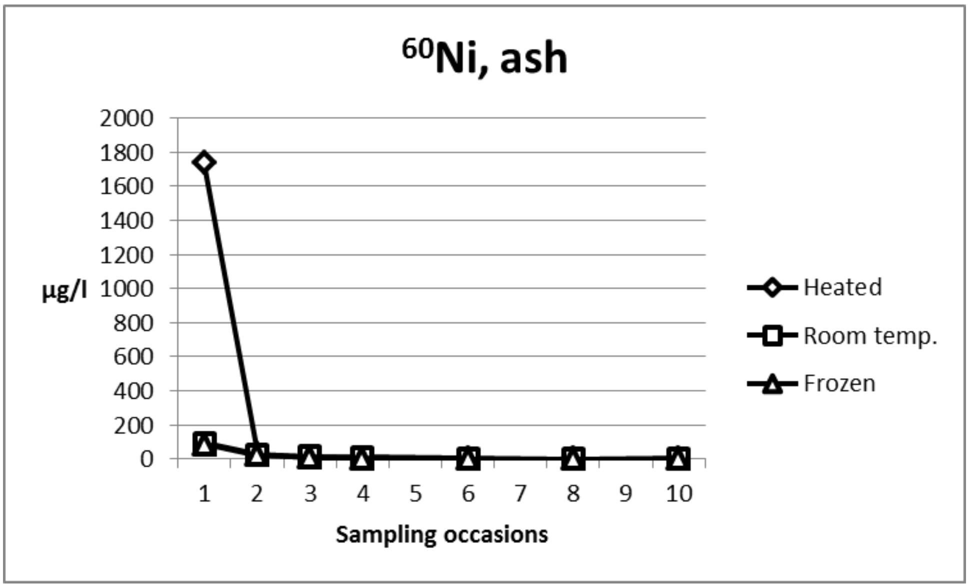


Figure (3.7.9-3), Concentrations of nickel in the leachates of ash

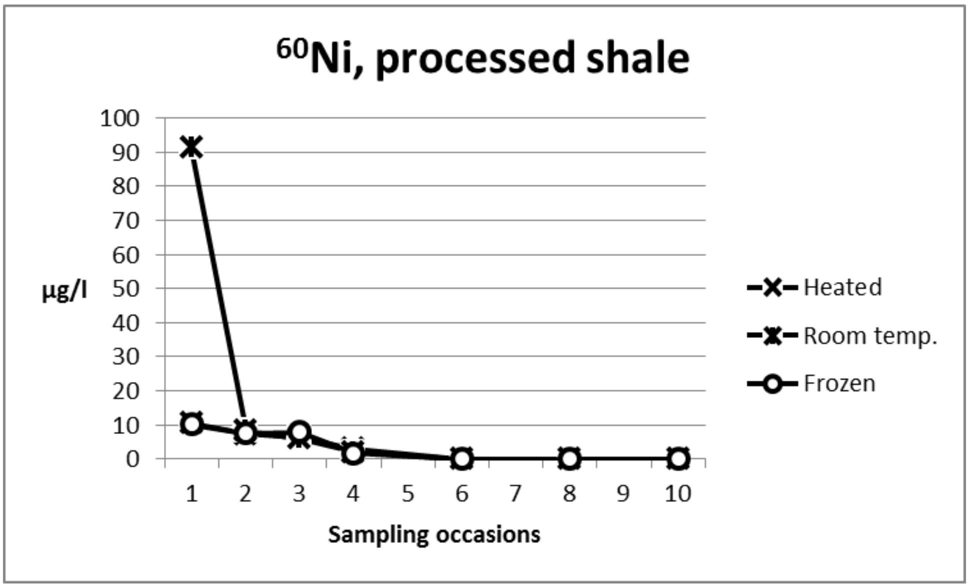


Figure (3.7.9-4), Concentrations of nickel in the leachates of processed shale

Nickel occurs as a coat on particles of shale and weathered fines. Once this layer is washed away with leaching water further release of nickel is very low and reaches concentration 0 µg/l (or almost) at the 6th sampling occasion in all shale- and weathered fines samples except for the heated weathered fines samples. A small increase in nickel leach ability can be noted in the heated samples of shale and weathered fines.

The nickel content in the leachates from the ash and processed shale was low and remained low until no more nickel were released from the material. The quantified concentration of nickel from the first sampling occasion in one heated ash and in one of the room temperate processed shale samples may be caused by some kind of contamination. But nickel may occur as individual mineral beads and can thus have resulted in these high concentrations during analysis.

3.7.10 Copper, Cu

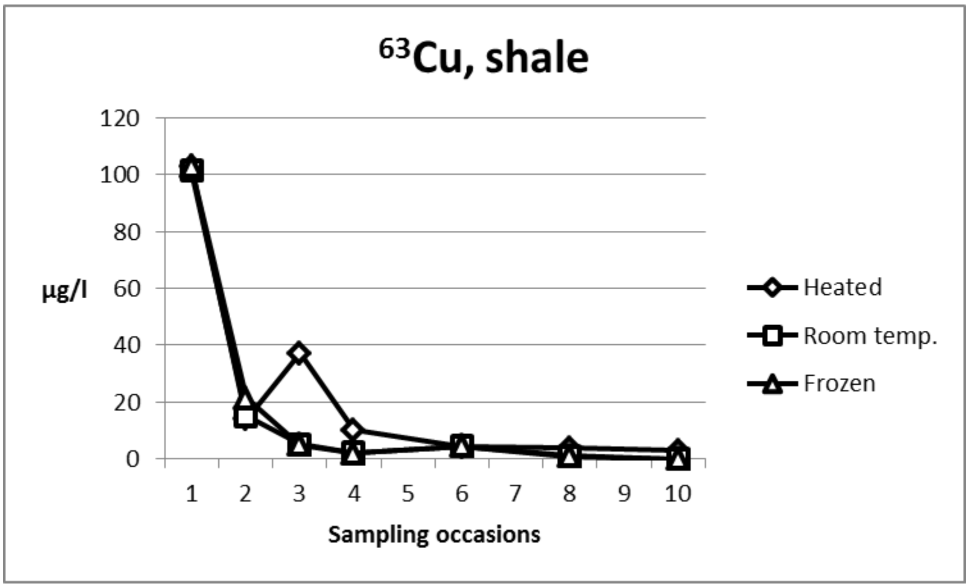


Figure (3.7.10-1), Concentrations of copper in the leachates of shale

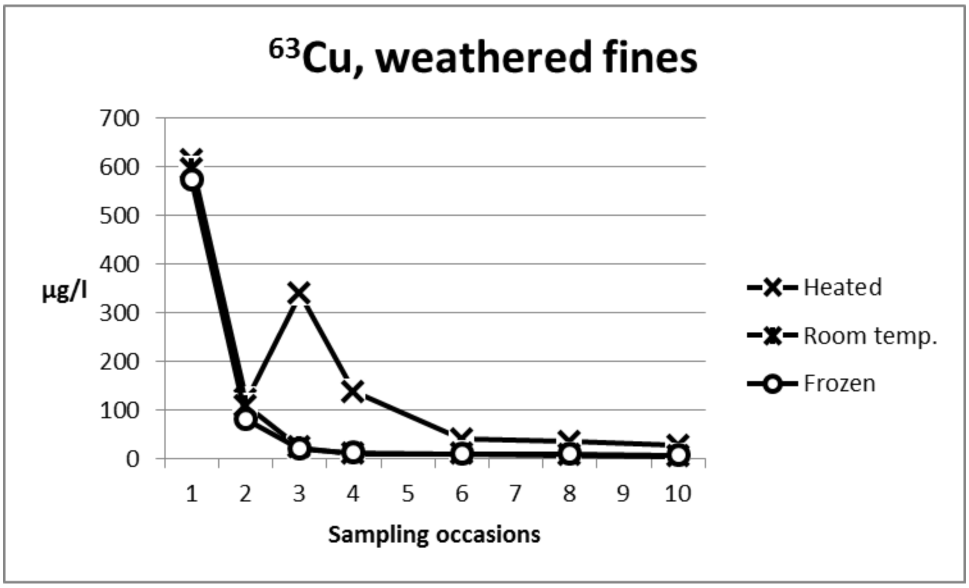


Figure (3.7.10-2), Concentrations of copper in the leachates of weathered fines

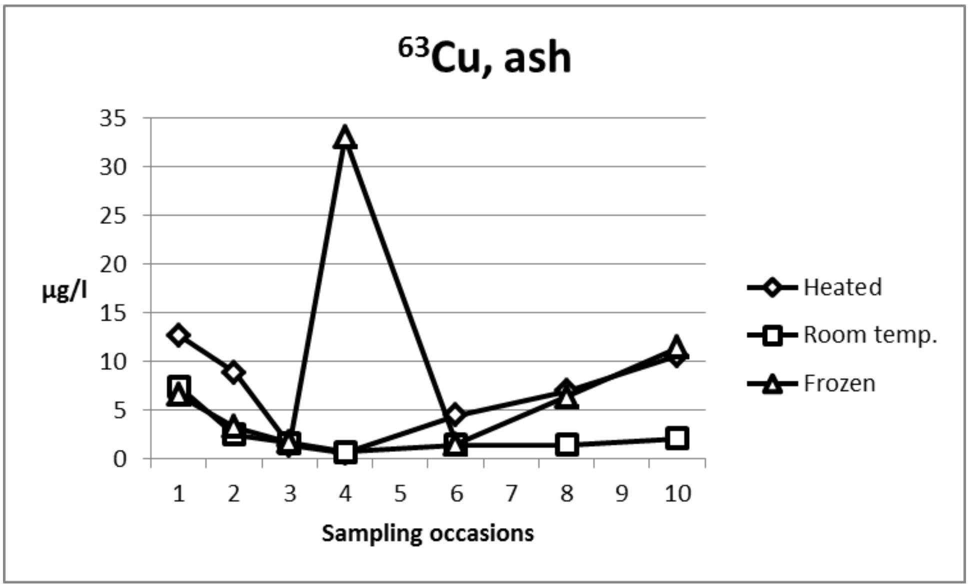


Figure (3.7.10-3), Concentrations of copper in the leachates of ash

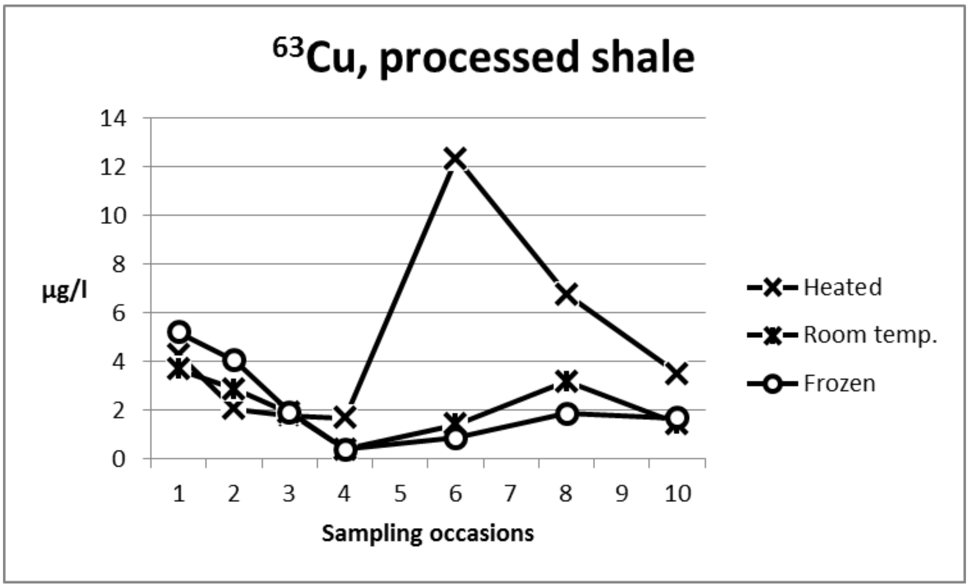


Figure (3.7.10-4), Concentrations of copper in the leachates of processed shale

The leachates from the weathered fines contain more copper than the shale´s leachates. Both of these materials show the presence of a particle coat of copper. Heating causes once again an increase in leach ability, this time of copper.

The leaching of copper from ash and processed shale is harder to predict. The peaks of copper concentrations in the frozen ash and heated processed shale have high RSD values (see table (7-15)) which indicate either contamination of samples or sample heterogeneity.

3.7.11 Zinc, Zn

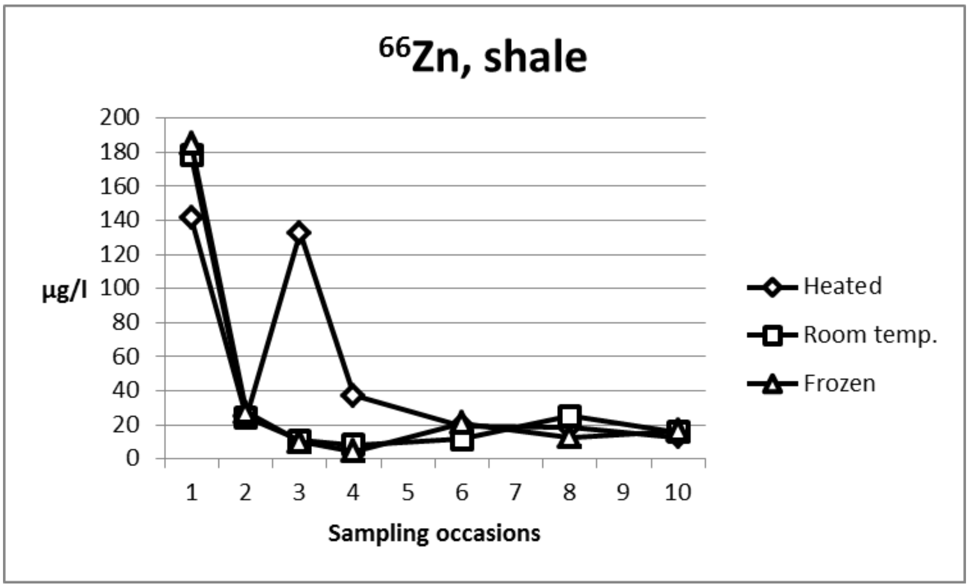


Figure (3.7.11-1), Concentrations of zinc in the leachates of shale

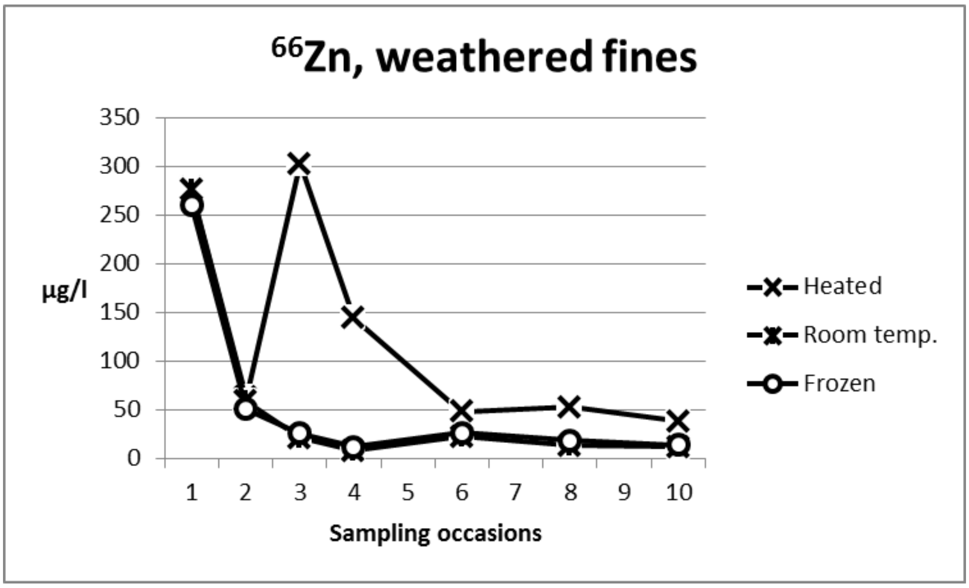


Figure (3.7.11-2), Concentrations of zinc in the leachates of weathered fines

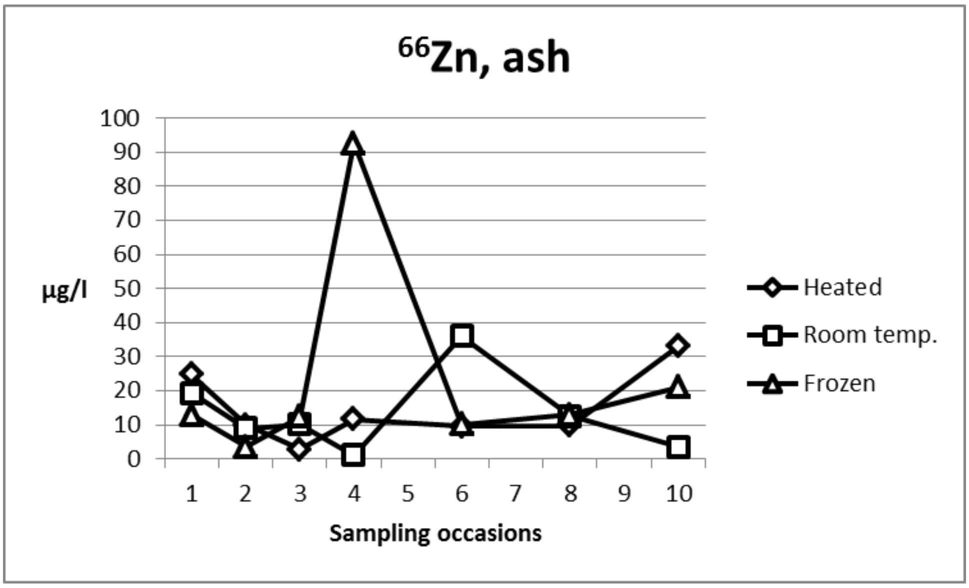


Figure (3.7.11-3), Concentrations of zinc in the leachates of ash

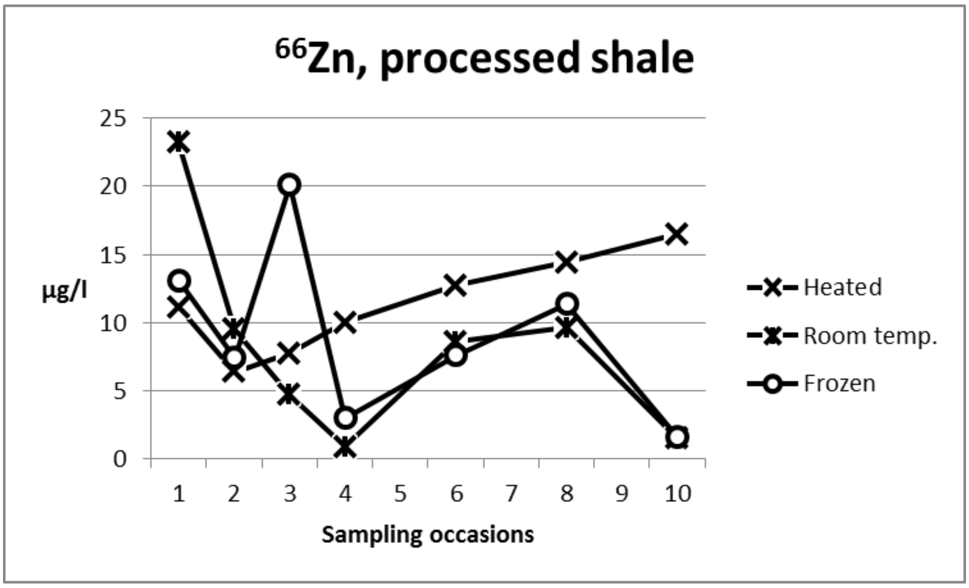


Figure (3.7.11-4), Concentrations of zinc in the leachates of processed shale

The leaching of zinc follows a pattern similar to that of copper. The zinc diagrams for shale and weathered fines indicates a particle coat and that heating causes an increase in leach ability of zinc. While the pattern of zinc leaching from ash and processed shale is erratic with many high RSD values shown by table (7-16).

3.7.12 Strontium, Sr

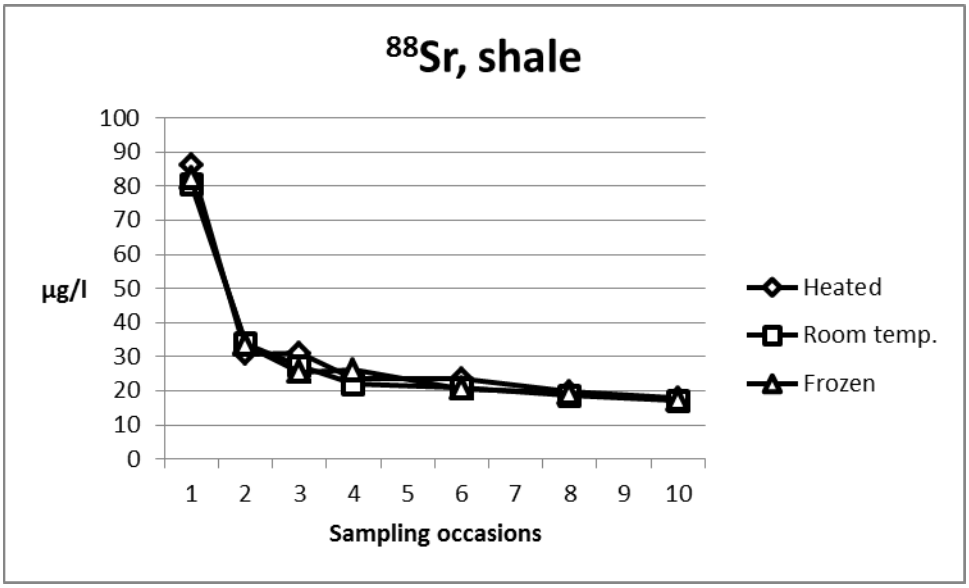


Figure (3.7.12-1), Concentrations of strontium in the leachates of shale

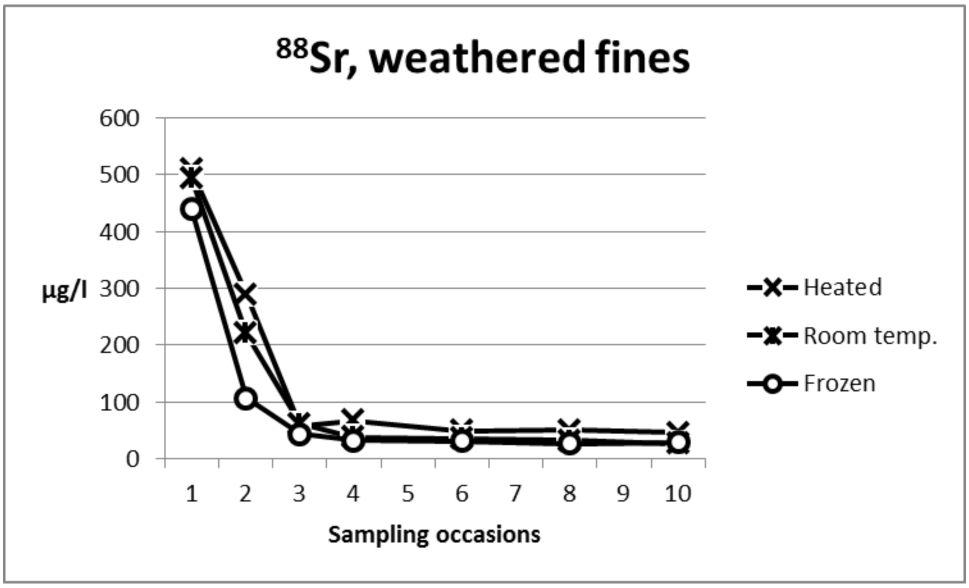


Figure (3.7.12-2), Concentrations of strontium in the leachates of weathered fines

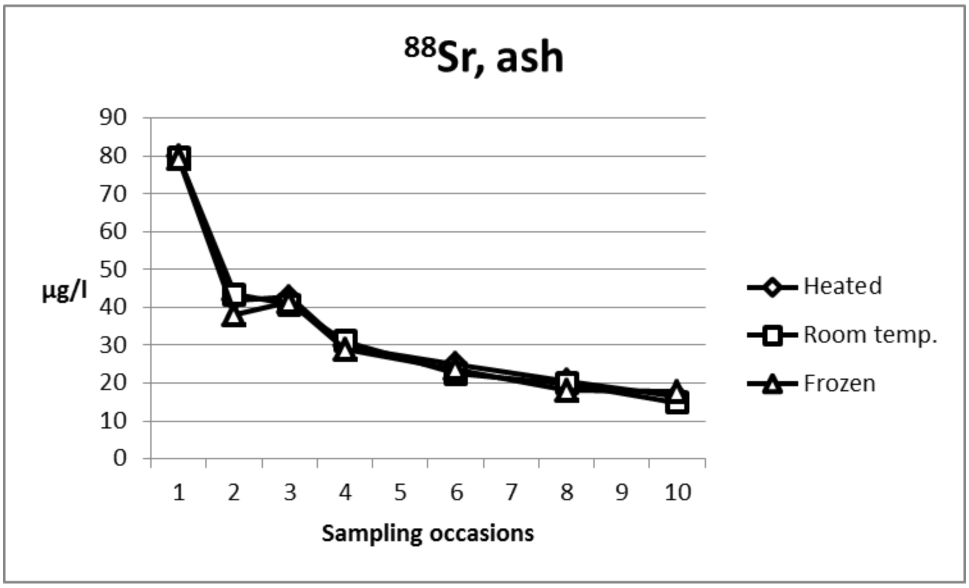


Figure (3.7.12-3), Concentrations of strontium in the leachates of ash

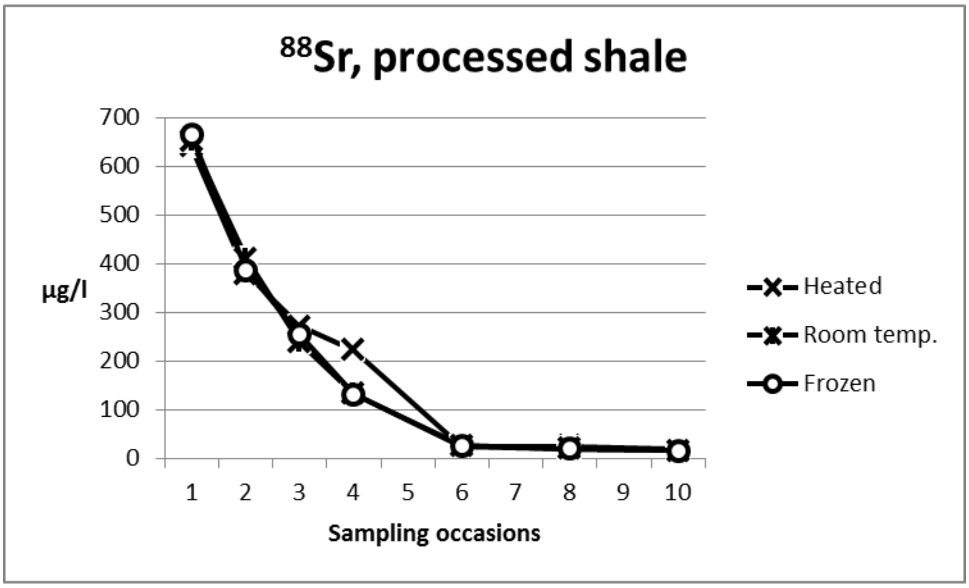


Figure (3.7.12-4), Concentrations of strontium in the leachates of processed shale

The concentration of strontium in the leachates is initially high and then decreases over time. No clear indication that any temperature treatment has a beneficial effect on the leaching of strontium can be observed.

The weathered fines have, as have been the case with most elements (an exception may be vanadium, 3.7.6.); higher concentrations of strontium in their leachates than the shale. By studying the concentration of strontium in the leachates from ash we can see that a partially processing of shale does not affect the amount of strontium that is accessible for water leaching very much. However, when the shale is completely processed, as is the case of the processed shale, strontium becomes easily available for water. And this causes higher concentrations of strontium in the leachates from processed shale than in the leachates of the weathered fines (from sampling occasion 1-4).

Table (3.7.12-1), sulfate and Sr concentrations from samples of shale

	Heated shale		Room temp. shale		Frozen shale	
Sampling occasions	Sulfate (mg/l)	Sr (μg/l)	Sulfate (mg/l)	Sr (μg/l)	Sulfate (mg/l)	Sr (μg/l)
1	540.9	86.24	506.9	80.65	587.2	82.35
2	93.11	30.70	99.37	33.74	116.8	33.50
3	131.1	31.04	42.34	27.27	42.69	25.58
4	57.86	23.58	23.52	21.86	20.94	25.99

Table (3.7.12-2), sulfate and Sr concentrations from samples of weathered fines

	Heated weathered fines		Room temp. weathered fines		Frozen weathered fines	
Sampling occasions	Sulfate (mg/l)	Sr (μg/l)	Sulfate (mg/l)	Sr (μg/l)	Sulfate (mg/l)	Sr (μg/l)
1	1494	509.1	1916	495.0	1732	441.0
2	921.5	289.9	719.9	220.8	349.7	106.5
3	379.8	57.30	140.4	61.42	95.89	43.26
4	168.6	67.96	61.91	37.57	50.25	32.51

Table (3.7.12-3), sulfate and Sr concentrations from samples of ash

	Heated ash		Room temp. ash		Frozen ash	
Sampling occasions	Sulfate (mg/l)	Sr (μg/l)	Sulfate (mg/l)	Sr (μg/l)	Sulfate (mg/l)	Sr (μg/l)
1	195.3	79.81	191.4	79.63	196.9	79.28
2	65.00	41.95	62.85	43.50	63.49	37.98
3	76.63	42.76	59.08	40.76	40.87	41.40
4	46.01	29.73	48.16	31.08	19.52	28.85

Table (3.7.12-4), sulfate and Sr concentrations from samples of processed shale

	Heated processed shale		Room temp. processed shale		Frozen processed shale	
Sampling occasions	Sulfate (mg/l)	Sr (μg/l)	Sulfate (mg/l)	Sr (μg/l)	Sulfate (mg/l)	Sr (μg/l)
1	1526	641.6	1506	654.2	1484	665.5
2	1444	380.3	1423	412.0	1530	387.4
3	1391	272.6	1393	238.7	1399	254.3
4	1009	223.9	861.7	134.1	783.4	132.8

Strontium and calcium belongs to the same group in the periodic table and one of the properties that they share is their ability to form quite insoluble minerals with sulfate. In the samples of shale, weathered fines and ash there is no obvious indication that any stable strontium sulfate mineral is formed. In the samples of processed shale however there is a relatively slow decrease in strontium concentrations from the first 4 sampling occasions. This could very well be an indication that there is strontium sulfate present.

3.7.13 Molybdenum, Mo

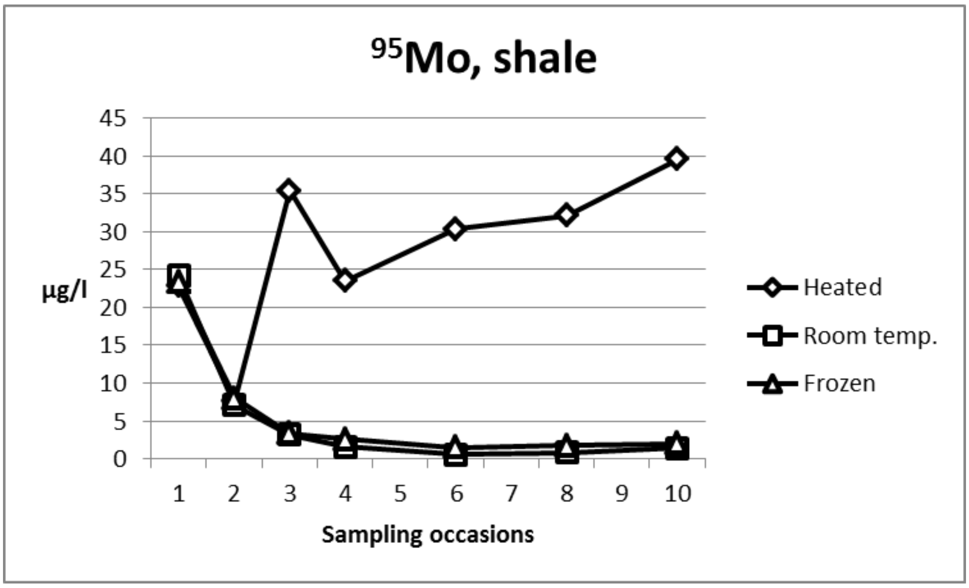


Figure (3.7.13-1), Concentrations of molybdenum in the leachates of shale

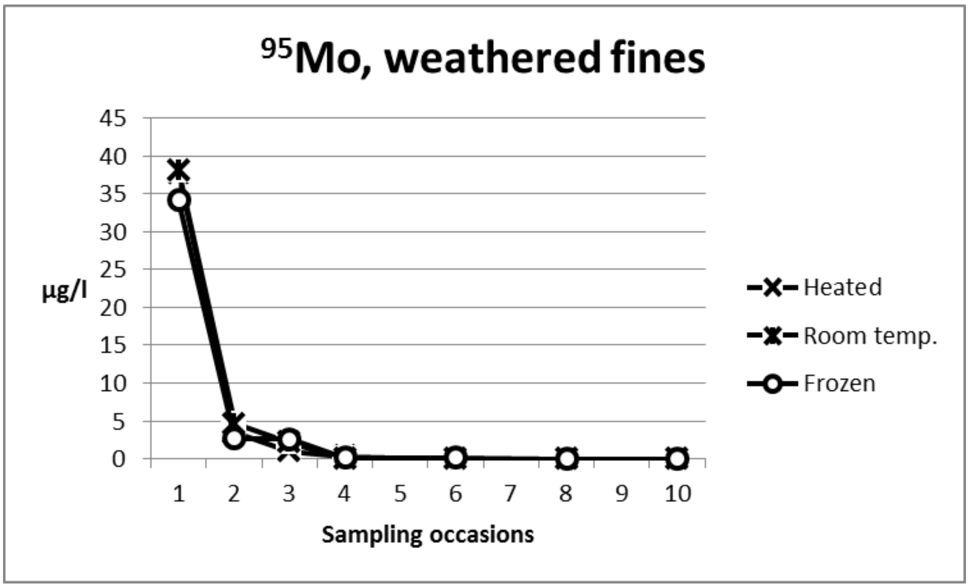


Figure (3.7.13-2), Concentrations of molybdenum in the leachates of weathered fines

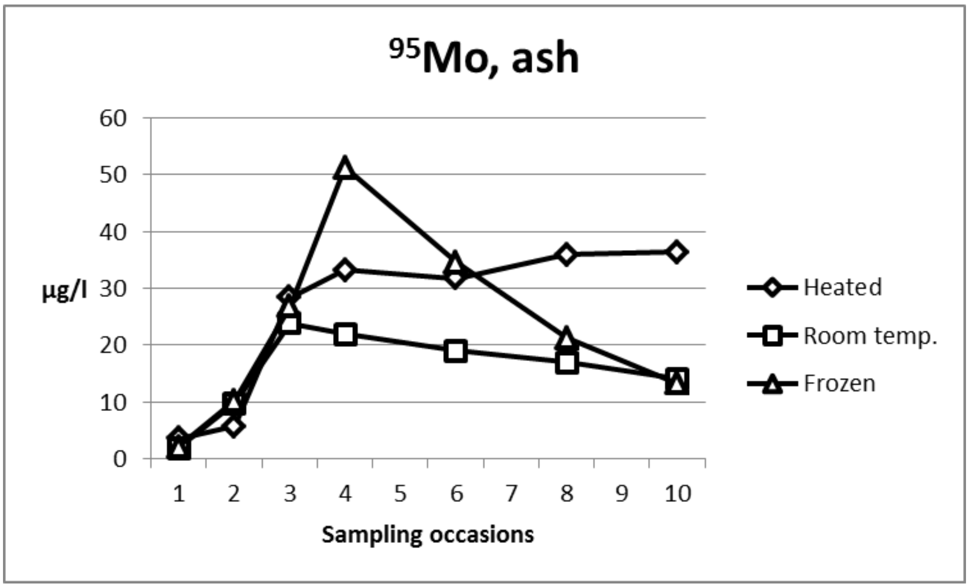


Figure (3.7.13-3), Concentrations of molybdenum in the leachates of ash

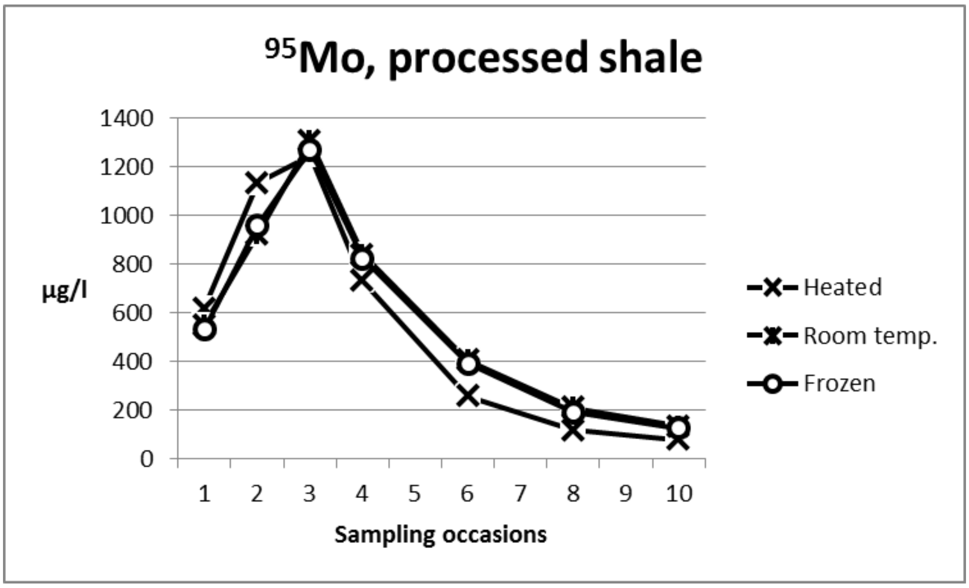


Figure (3.7.13-4), Concentrations of molybdenum in the leachates of processed shale

Coats of molybdenum are present on the particles of shale and weathered fines. The temperature treatments do not seem to have any effect on the leach ability of molybdenum from the weathered fines. This is not the case for the shale however, where heating increases the concentration of molybdenum the leachates. Why the leach ability of molybdenum in this relatively unweathered shale reacts this way in response to heating is unknown. Another thing that cannot be said for certain is if the maximum concentration of molybdenum that is possible to gain in the leachates has been reached during this relatively short leaching period.

Once again we see different leach abilities caused by different grades of processing. The 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 amounts of molybdenum. This is just a hypothesis, but according to Cotton *et.al.* (1995) is the most common molybdenum containing mineral molybdenite, MoS_2. When this is roasted it forms MoO_3 and maybe this oxide is more susceptible to water leaching than the sulfide mineral.

Table (3.7.13-1), pH and Mo concentrations from samples of shale

	Heated shale		Room temp. shale		Frozen shale	
Sampling occasions	pH	Mo (µg/l)	pH	Mo (µg/l)	pH	Mo (µg/l)
1	2.7	22.78	2.7	24.16	2.7	23.34
2	3.1	7.694	3.1	7.048	3.1	8.052
3	2.9	35.39	3.2	3.232	3.3	3.392
4	3.2	23.45	3.4	1.593	3.5	2.630
6	3.4	30.35	3.5	0.6056	3.6	1.533
8	3.5	32.16	3.6	0.8452	3.7	1.767
10	3.5	39.58	3.5	1.394	3.7	2.008

Table (3.7.13-2), pH and Mo concentrations from samples of weathered fines

	Heated weathered fines		Room temp. weathered fines		Frozen weathered fines	
Sampling occasions	pH	Mo (µg/l)	pH	Mo (µg/l)	pH	Mo (µg/l)
1	2.5	37.78	2.5	38.10	2.5	34.13
2	2.8	3.423	2.8	4.670	2.8	2.648
3	2.5	0.9955	3.0	2.213	3.0	2.560
4	2.8	0.3457	3.1	0	3.2	0.1280
6	3.2	0	3.1	0	3.2	0.1585
8	3.1	0	3.0	0	3.1	0
10	3.2	0	3.0	0	3.1	0

Table (3.7.13-3), pH and Mo concentrations from samples of ash

	Heated ash		Room temp. ash		Frozen ash	
Sampling occasions	pH	Mo (µg/l)	pH	Mo (µg/l)	pH	Mo (µg/l)
1	5.3	3.601	5.3	1.926	5.4	2.156
2	5.9	5.670	6.0	9.834	6.1	10.21
3	6.1	28.41	6.4	23.85	6.5	26.83
4	6.2	33.26	6.4	21.99	6.8	51.24
6	6.0	31.75	6.5	19.06	7.0	34.60
8	6.0	35.99	6.4	16.96	6.8	21.25
10	6.0	36.37	6.4	14.12	6.7	13.29

Table (3.7.13-4), pH and Mo concentrations from samples of processed shale

	Heated processed shale		Room temp. processed shale		Frozen processed shale	
Sampling occasions	pH	Mo (µg/l)	pH	Mo (µg/l)	pH	Mo (µg/l)
1	5.7	617.2	5.6	548.9	5.7	531.7
2	6.5	1134	6.3	924.2	6.2	960.6
3	7.1	1247	6.8	1306	6.7	1270
4	7.3	730.6	7.0	839.0	7.0	823.6
6	7.6	258.0	7.3	404.1	7.4	391.1
8	7.1	117.7	7.0	209.7	7.1	190.6
10	6.8	79.30	6.9	133.3	6.8	125.3

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 leach ability of molybdenum and increasing pH can be observed in the samples of ash and processed shale. This indicates that the molybdate ions are more soluble in water with higher pH, i.e. neutral or alkaline.

3.7.14 Barium, Ba

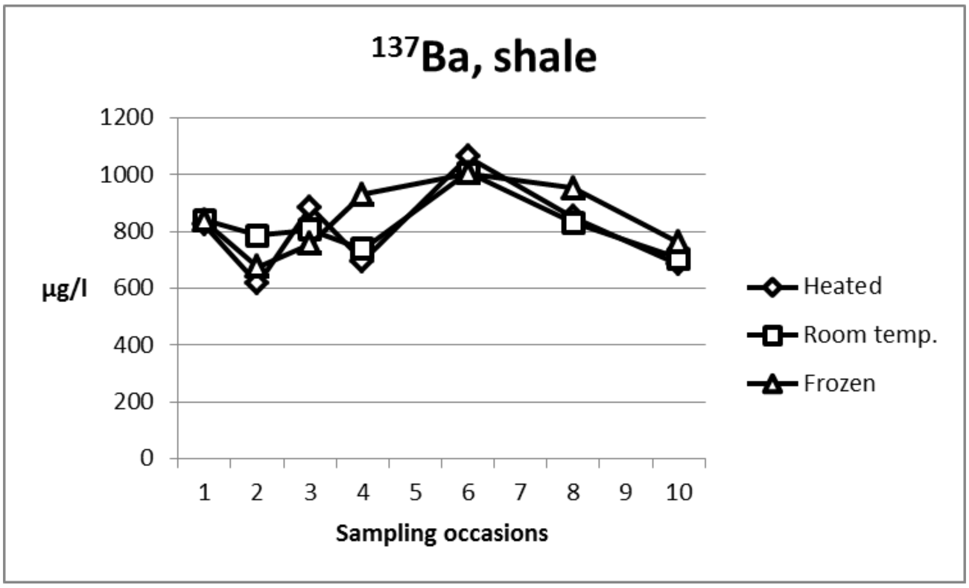


Figure (3.7.14-1), Concentrations of barium in the leachates of shale

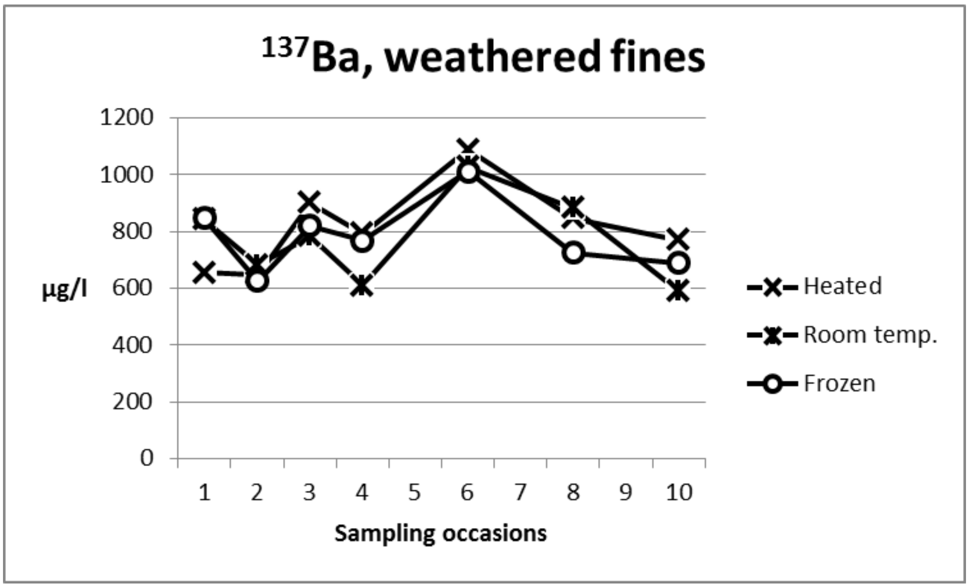


Figure (3.7.14-2), Concentrations of barium in the leachates of weathered fines

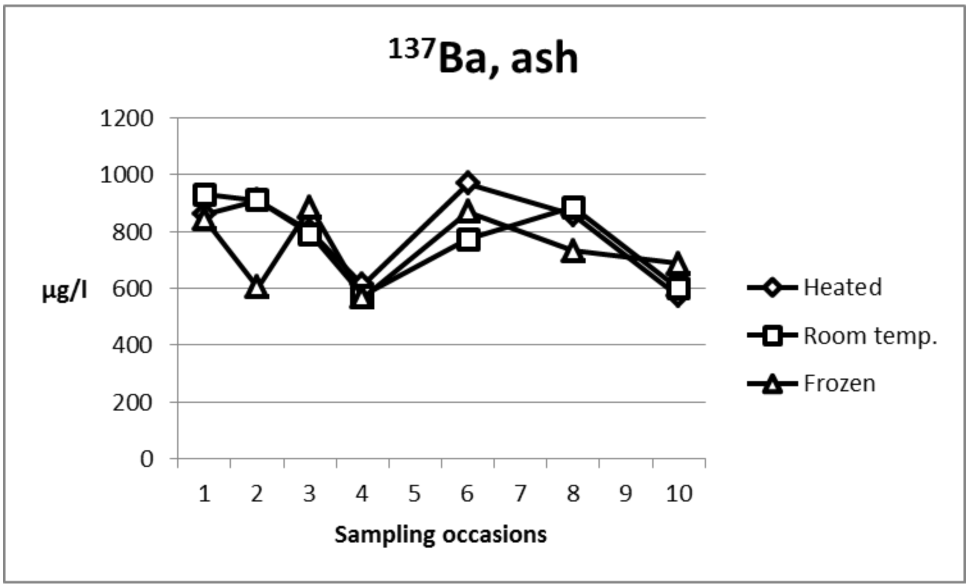


Figure (3.7.14-3), Concentrations of barium in the leachates of ash

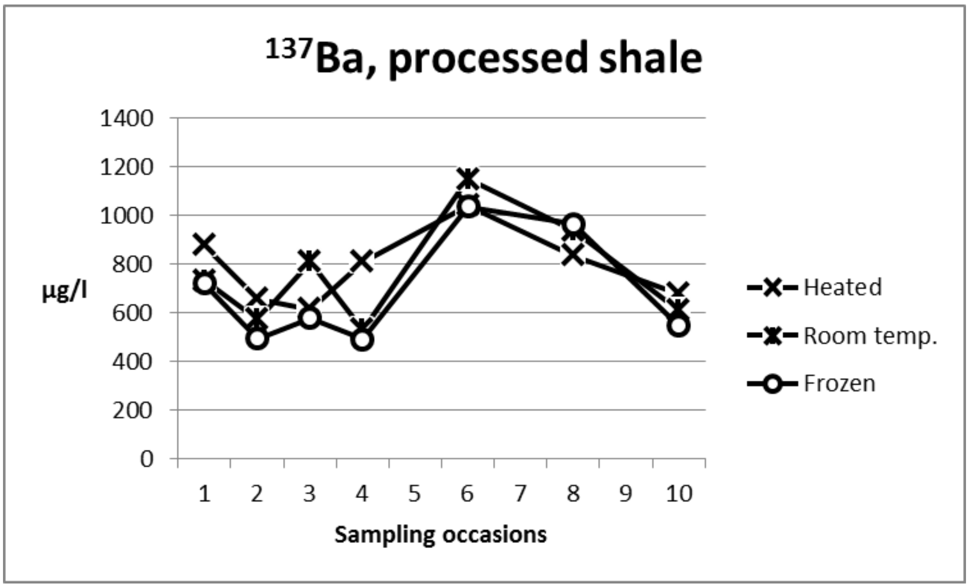


Figure (3.7.14-4), Concentrations of barium in the leachates of processed shale

The concentration of barium remains in approximately the same concentration in leachates from both the unprocessed and processed materials. No connection between temperature treatments and increased leach ability of barium can be drawn because all measured concentrations appear in an erratic pattern. Barium shares the same group as calcium and strontium in the periodic table and may also form insoluble sulfate minerals. The fact that the concentrations of barium do not decrease during the leaching period indicates that barite, $BaSO_4$, is very insoluble.

Table (3.7.14-1), sulfate and Ba concentrations from samples of shale

	Heated shale		Room temp. shale		Frozen shale	
Sampling occasions	Sulfate (mg/l)	Ba (µg/l)	Sulfate (mg/l)	Ba (µg/l)	Sulfate (mg/l)	Ba (µg/l)
1	540.9	825.6	506.9	840.3	587.2	838.7
2	93.11	617.8	99.37	786.7	116.8	676.4
3	131.1	886.0	42.34	807.7	42.69	756.9
4	57.86	695.5	23.52	738.6	20.94	930.1

Table (3.7.14-2), sulfate and Ba concentrations from samples of weathered fines

	Heated weathered fines		Room temp. weathered fines		Frozen weathered fines	
Sampling occasions	Sulfate (mg/l)	Ba (µg/l)	Sulfate (mg/l)	Ba (µg/l)	Sulfate (mg/l)	Ba (µg/l)
1	1494	656.2	1916	843.5	1732	847.3
2	921.5	648.8	719.9	682.8	349.7	627.3
3	379.8	902.1	140.4	783.7	95.89	820.3
4	168.6	794.3	61.91	611.2	50.25	769.7

Table (3.7.14-3), sulfate and Ba concentrations from samples of ash

	Heated ash		Room temp. ash		Frozen ash	
Sampling occasions	Sulfate (mg/l)	Ba (µg/l)	Sulfate (mg/l)	Ba (µg/l)	Sulfate (mg/l)	Ba (µg/l)
1	195.3	860.1	191.4	930.2	196.9	845.2
2	65.00	910.7	62.85	911.5	63.49	603.9
3	76.63	802.5	59.08	790.2	40.87	885.0
4	46.01	613.3	48.16	574.7	19.52	566.9

Table (3.7.14-4), sulfate and Ba concentrations from samples of processed shale

	Heated processed shale		Room temp. processed shale		Frozen processed shale	
Sampling occasions	Sulfate (mg/l)	Ba (µg/l)	Sulfate (mg/l)	Ba (µg/l)	Sulfate (mg/l)	Ba (µg/l)
1	1526	877.3	1506	732.5	1484	720.2
2	1444	656.0	1423	571.8	1530	495.3
3	1391	614.5	1393	810.4	1399	578.5
4	1009	810.7	861.7	531.1	783.4	491.6

3.7.15 Uranium, U

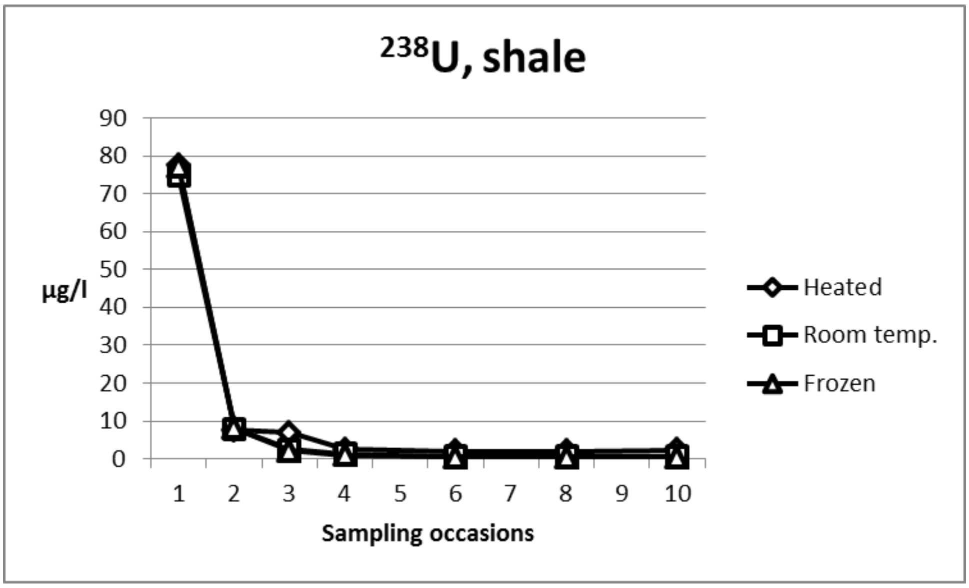


Figure (3.7.15-1), Concentrations of uranium in the leachates of shale

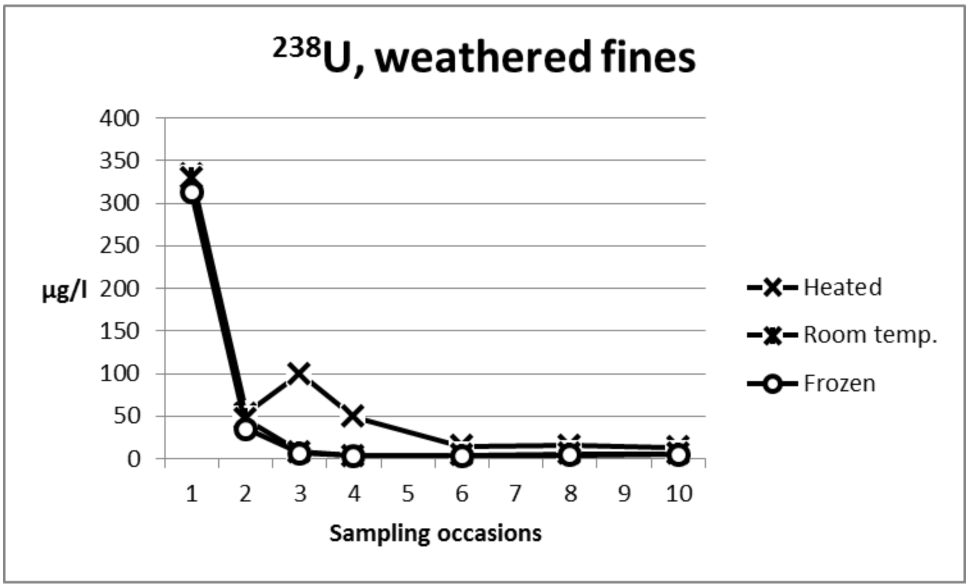


Figure (3.7.15-2), Concentrations of uranium in the leachates of weathered fines

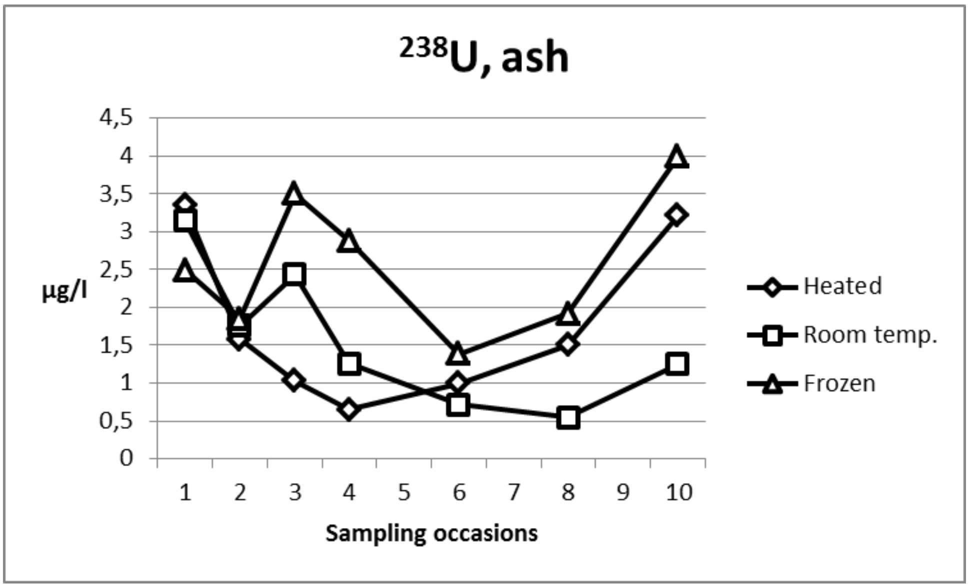


Figure (3.7.15-3), Concentrations of uranium in the leachates of ash

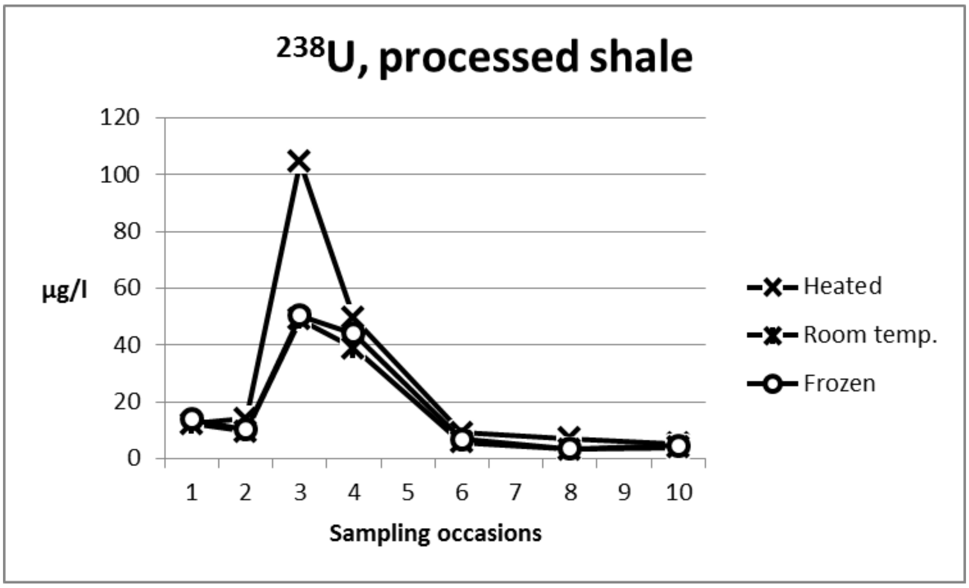


Figure (3.7.15-4), Concentrations of uranium in the leachates of processed shale

Uranium also occurs as a coat on particles of shale and weathered fines and the concentration of uranium is higher in the leachates from the weathered fines than in the leachates from the shale. Heating causes a small increase in the leach ability of uranium from the shale and weathered fines.

The fact that pyrolysis alters the mineralogy of shale can be observed by the concentration of uranium in the leachates of ash and processed shale (and will be discussed further under heading; digestion, 3.8). For the ash the concentration of uranium in its 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.

Table (3.7.15-1), pH, acidity and concentrations of U- and sulfate from samples of shale

	Heated shale				Room temp. shale				Frozen shale			
Sampling occasions	pH	Acidity (meqv/l)	U (µg/l)	Sulfate (mg/l)	pH	Acidity (meqv/l)	U (µg/l)	Sulfate (mg/l)	pH	Acidity (meqv/l)	U (µg/l)	Sulfate (mg/l)
1	2.7	2.2	77.45	540.9	2.7	2.4	74.98	506.9	2.7	2.5	77.34	587.2
2	3.1	0.73	7.490	93.11	3.1	0.76	7.857	99.37	3.1	0.81	8.131	116.8
3	2.9	1.4	6.852	131.1	3.2	0.45	2.447	42.34	3.3	0.47	2.170	42.69
4	3.2	0.78	2.467	57.86	3.4	0.42	1.336	23.52	3.5	0.33	0.9169	20.94
6	3.4	0.61	2.019		3.5	0.36	0.6901		3.6	0.33	0.4814	
8	3.5	0.52	1.980		3.6	0.31	0.5859		3.7	0.35	0.42316	
10	3.5	0.51	2.376		3.5	0.33	0.6063		3.7	0.28	0.3908	

Table (3.7.15-2), pH, acidity and concentrations of U- and sulfate from samples of weathered fines

	Heated weathered fines				Room temp. weathered fines				Frozen weathered fines			
Sampling occasions	pH	Acidity (meqv/l)	U (µg/l)	Sulfate (mg/l)	pH	Acidity (meqv/l)	U (µg/l)	Sulfate (mg/l)	pH	Acidity (meqv/l)	U (µg/l)	Sulfate (mg/l)
1	2.5	8.0	334.2	1494	2.5	7.9	329.2	1916	2.5	7.5	313.7	1732
2	2.8	2.2	53.49	921.5	2.8	1.9	46.08	719.9	2.8	1.5	35.37	349.7
3	2.5	3.2	99.94	379.8	3.0	0.80	8.035	140.4	3.0	75,00	6.641	95.89
4	2.8	1.5	49.58	168.6	3.1	0.59	3.613	61.91	3.2	0.60	3.377	50.25
6	3.2	0.92	14.50		3.1	0.72	4.566		3.2	0.66	3.658	
8	3.1	0.87	15.80		3.0	0.78	5.517		3.1	0.68	4.178	
10	3.2	0.82	13.40		3.0	0.82	6.049		3.1	0.72	4.855	

Table (3.7.15-3), pH, alkalinity and concentrations of U- and sulfate from samples of ash

	Heated ash				Room temp. ash				Frozen ash			
Sampling occasions	pH	Alkalinity (meqv/l)	U (µg/l)	Sulfate (mg/l)	pH	Alkalinity (meqv/l)	U (µg/l)	Sulfate (mg/l)	pH	Alkalinity (meqv/l)	U (µg/l)	Sulfate (mg/l)
1	5.3	0.025	3.348	195.3	5.3	0.048	3.141	191.4	5.4	0.052	2.496	196.9
2	5.9	0.21	1.579	65.00	6.0	0.29	1.753	62.85	6.1	0.37	1.852	63.49
3	6.1	0.20	1.033	76.63	6.4	0.67	2.436	59.08	6.5	0.65	3.498	40.87
4	6.2	0.10	0.6456	46.01	6.4	0.38	1.254	48.16	6.8	0.71	2.883	19.52
6	6.0	0.039	0.9931		6.5	0.14	0.7136		7.0	0.35	1.381	
8	6.0	0.023	1.506		6.4	0.079	0.5520		6.8	0.18	1.920	
10	6.0	0.037	3.210		6.4	0.046	1.249		6.7	0.079	3.991	

Table (3.7.15-4), pH, alkalinity and concentrations of U- and sulfate from samples of processed shale

	Heated processed shale				Room temp. processed shale				Frozen processed shale			
Sampling occasions	pH	Alkalinity (meqv/l)	U (µg/l)	Sulfate (mg/l)	pH	Alkalinity (meqv/l)	U (µg/l)	Sulfate (mg/l)	pH	Alkalinity (meqv/l)	U (µg/l)	Sulfate (mg/l)
1	5.7	0.084	12.33	1526	5.6	0.036	12.42	1506	5.7	0.032	13.90	1484
2	6.5	0.21	14.25	1444	6.3	0.13	9.668	1423	6.2	0.15	10.24	1530
3	7.1	0.46	104.6	1391	6.8	0.37	49.13	1393	6.7	0.36	50.38	1399
4	7.3	0.34	49.58	1009	7.0	0.34	39.00	861.7	7.0	0.37	44.23	783.4
6	7.6	0.29	9.140		7.3	0.24	5.792		7.4	0.35	6.936	
8	7.1	0.12	7.099		7.0	0.14	3.344		7.1	0.12	3.453	
10	6.8	0.042	5.274		6.9	0.055	4.091		6.8	0.041	4.656	

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 may even form complexes with hydroxide ions. If there is carbonate present; uranyl may form carbonate complexes at near neutral- or alkaline pH.

The leaching curves for uranium in samples of shale and weathered fines follow a pattern very similar to that of sulfate which indicates a formation of uranyl sulfate complexes. The 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.

3.7.16 Short comparison with a previous leaching study of Kvarntorp shale

In a previous study made by Karlsson (2011); unprocessed and processed shale from Kvarntorp were leached with milli-Q water for 30 minutes in an ultrasonic cleaner. Due to the difference in leaching methods is it somewhat difficult to compare the values from the metal analysis conducted in that study with the metal concentrations quantified in this study. The quantified metal concentrations in both studies; 30 minutes of leaching in ultrasonic cleaner compared to approximately 24 hours of leaching on turnover shaker (sampling occasion 1 + 2), were at least of the same magnitude.

3.8 Digestion

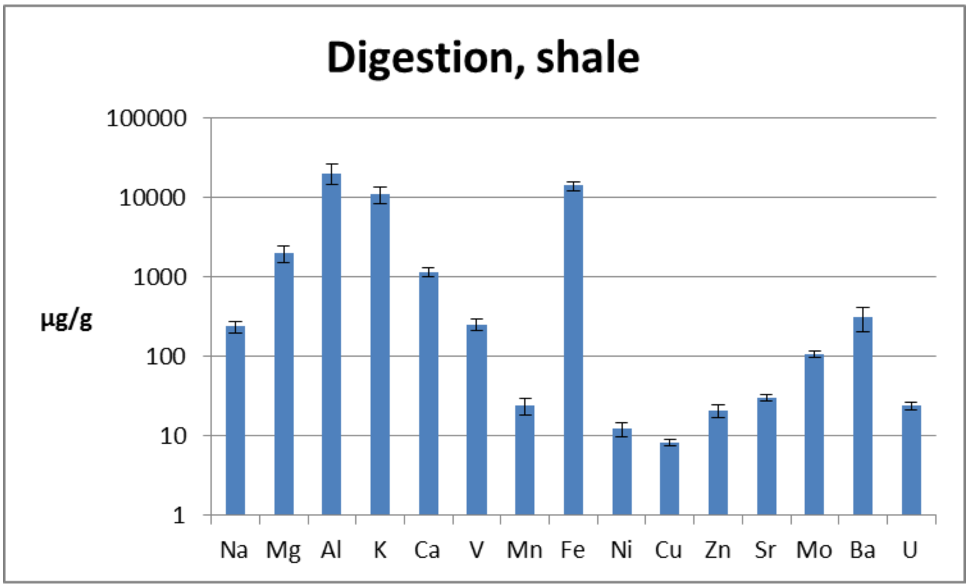


Figure (3.8-1), Assumed “total” content of selected elements in shale. Contents calculated from metal concentrations gained by digestion in concentrated HNO_3

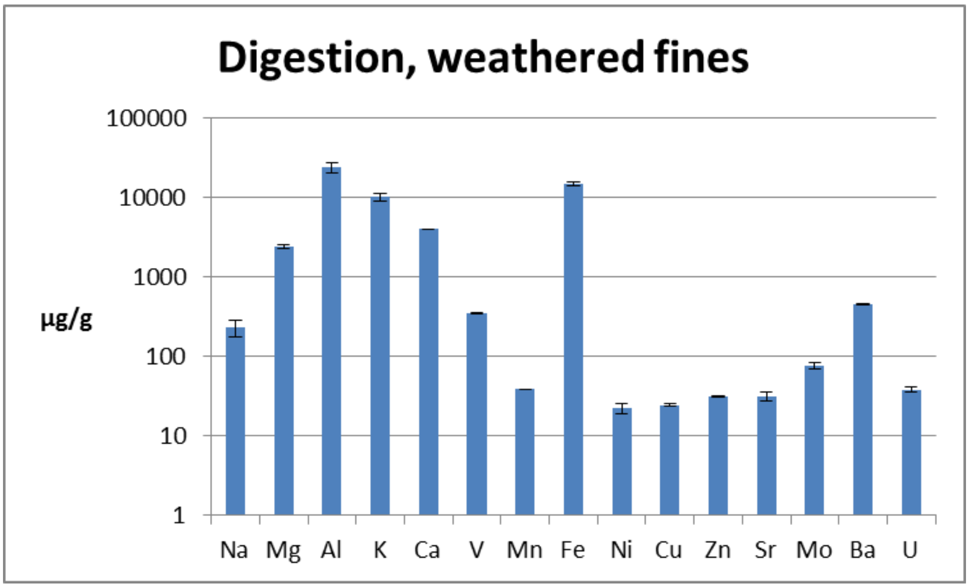


Figure (3.8-2), Assumed "total" content of selected elements in weathered fines. Contents calculated from metal concentrations gained by digestion in concentrated HNO_3

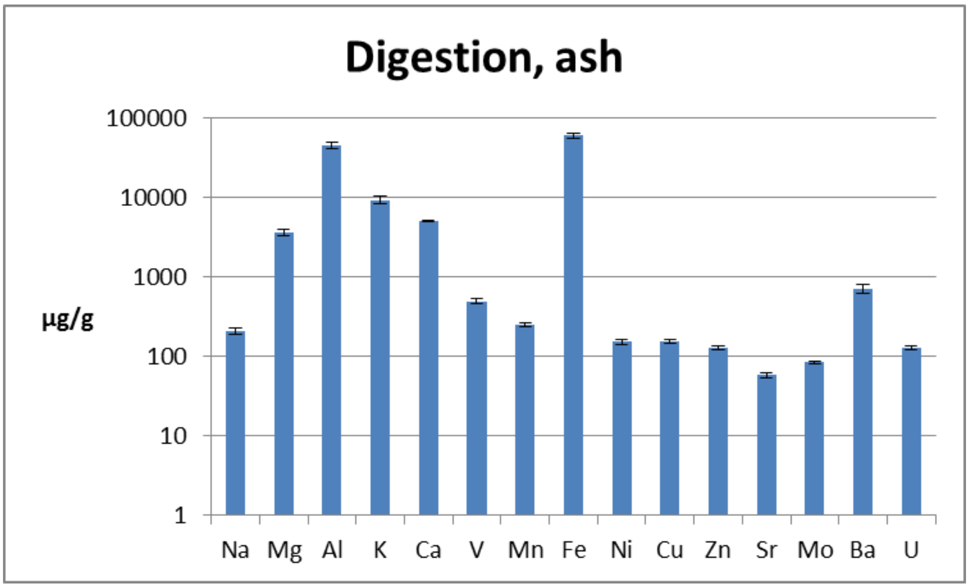


Figure (3.8-3), Assumed "total" content of selected elements in ash. Contents calculated from metal concentrations gained by digestion in concentrated HNO_3

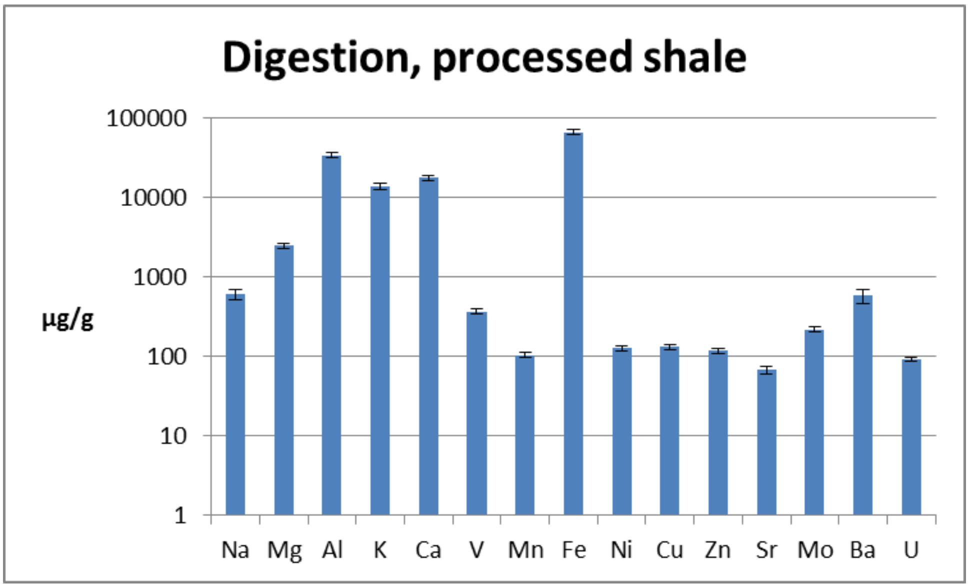


Figure (3.8-4), Assumed "total" content of selected elements in processed shale. Contents calculated from metal concentrations gained by digestion in concentrated HNO_3

Higher amounts of elements are leachable with concentrated HNO_3 from the ash and processed shale than compared to the original black shale. This proves that the high content of hydrocarbons in the shale prevents some of its containing elements to be leached. Even though the digestion is done with an oxidizing acid, HNO_3, its oxidizing capability is not enough to completely oxidize the film of hydrocarbons. If a "total leaching" of shale is sought a strong oxidizing agent must also be used. One example of such could be H_2O_2. If this oxidizing agent really manage to oxidize all hydrocarbons in the shale is however unsure.

During pyrolysis many elements may volatilize and leave the material. Examples of elements that become volatile during pyrolysis are lead and cadmium (Eklund *et.al.*, 1995). So the total content of elements in the unprocessed shale must actually be higher than in the ash and processed shale. The results of the digestions show also that the processed shale still contain many desirable elements which would be of great interest of refinement for mankind.

Table (3.8-5), Concentrations of elements quantified in leachates of shale, recalculated into µg/g of leached material. These recalculated contents and then compared as percentages to the "total" contents gained from digestion data. The results of the sampling occasions are added together throughout the leaching period. But it must be noted that this is not the total amount of elements that were leached during the leaching period; because not all sampling occasions were analyzed by ICP-MS

				Sampling days													
Shale		Total		1		2		3		4		6		8		10	
	Metal	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%
Heated	Na	238,0	100	10,10	4,2	15,15	6,4	21,44	9,0	24,47	10	26,56	11	28,20	12	29,68	12
Room temp.	Na	238,0	100	9,159	3,8	14,40	6,1	15,96	6,7	17,68	7,4	18,46	7,8	19,24	8,1	20,37	8,6
Frozen	Na	238,0	100	9,225	3,9	14,68	6,2	16,34	6,9	17,48	7,3	18,28	7,7	19,00	8,0	19,67	8,3
Heated	Mg	1997	100	23,13	1,2	26,57	1,3	30,75	1,5	32,49	1,6	33,84	1,7	34,98	1,8	36,38	1,8
Room temp.	Mg	1997	100	21,89	1,1	25,67	1,3	27,04	1,4	27,91	1,4	28,66	1,4	29,43	1,5	30,15	1,5
Frozen	Mg	1997	100	22,47	1,1	26,30	1,3	27,64	1,4	28,43	1,4	29,15	1,5	29,79	1,5	30,48	1,5
Heated	Al	20360	100	53,78	0,26	58,37	0,29	62,30	0,31	64,48	0,32	67,69	0,33	70,79	0,35	76,22	0,37
Room temp.	Al	20360	100	49,94	0,25	54,98	0,27	57,07	0,28	58,84	0,29	60,58	0,30	62,26	0,31	63,92	0,31
Frozen	Al	20360	100	52,02	0,26	57,23	0,28	59,27	0,29	60,93	0,30	62,61	0,31	64,26	0,32	65,96	0,32
Heated	K	11140	100	7,593	0,068	10,80	0,097	27,70	0,25	43,29	0,39	63,63	0,57	82,00	0,74	102,4	0,92
Room temp.	K	11140	100	7,624	0,068	10,29	0,092	14,36	0,13	18,36	0,16	25,00	0,22	31,75	0,29	38,94	0,35
Frozen	K	11140	100	6,624	0,059	9,176	0,082	13,69	0,12	17,80	0,16	25,35	0,23	32,42	0,29	39,54	0,35
Heated	Ca	1159	100	1542	130	1753	150	1868	160	1908	160	1927	170	1946	170	1959,636	170
Room temp.	Ca	1159	100	1350	120	1570	140	1630	140	1661	140	1683	150	1702	150	1715,227	150
Frozen	Ca	1159	100	1431	120	1659	140	1723	150	1750	150	1772	150	1788	150	1801,021	160
Heated	V	253,1	100	0,09326	0,037	0,1075	0,042	0,5417	0,21	0,6341	0,25	0,6992	0,28	0,7489	0,30	0,8326	0,33
Room temp.	V	253,1	100	0,09248	0,037	0,1053	0,042	0,1115	0,044	0,1144	0,045	0,1154	0,046	0,1170	0,046	0,1191	0,047
Frozen	V	253,1	100	0,08671	0,034	0,0997	0,039	0,2945	0,12	0,3183	0,13	0,3217	0,13	0,3229	0,13	0,3301	0,13
Heated	Mn	23,84	100	1,280	5,4	1,442	6,0	1,632	6,8	1,694	7,1	1,724	7,2	1,744	7,32	1,767	7,4
Room temp.	Mn	23,84	100	1,237	5,2	1,427	6,0	1,481	6,2	1,504	6,3	1,515	6,4	1,522	6,39	1,528	6,4
Frozen	Mn	23,84	100	1,282	5,4	1,477	6,2	1,549	6,5	1,574	6,6	1,581	6,6	1,583	6,64	1,584	6,6
Heated	Fe	14130	100	81,31	0,58	100,2	0,71	402,9	2,9	517,2	3,7	589,9	4,2	641,8	4,54	702,0	5,0
Room temp.	Fe	14130	100	77,83	0,55	96,76	0,68	102,7	0,73	104,7	0,74	106,2	0,75	107,9	0,76	110,0	0,78
Frozen	Fe	14130	100	80,70	0,57	101,1	0,72	109,2	0,77	111,5	0,79	114,9	0,81	117,5	0,83	120,9	0,86
Heated	Ni	12,27	100	0,9132	7,4	1,009	8,2	1,155	9,4	1,177	9,6	1,184	9,6	1,184	9,6	1,184	9,6
Room temp.	Ni	12,27	100	0,9175	7,5	1,032	8,4	1,039	8,5	1,039	8,5	1,039	8,5	1,039	8,5	1,039	8,5
Frozen	Ni	12,27	100	0,9601	7,8	1,065	8,7	1,074	8,8	1,074	8,8	1,074	8,8	1,074	8,8	1,074	8,8
Heated	Cu	8,246	100	1,031	12	1,171	14	1,543	19	1,645	20	1,688	20	1,725	21	1,754	21
Room temp.	Cu	8,246	100	1,014	12	1,164	14	1,215	15	1,236	15	1,281	16	1,292	16	1,292	16
Frozen	Cu	8,246	100	1,029	12	1,242	15	1,292	16	1,312	16	1,356	16	1,365	17	1,365	17
Heated	Zn	20,83	100	1,414	6,8	1,660	8,0	2,985	14	3,354	16	3,548	17	3,732	18	3,860	19
Room temp.	Zn	20,83	100	1,782	8,6	2,027	9,7	2,136	10	2,219	11	2,336	11	2,588	12	2,743	13
Frozen	Zn	20,83	100	1,848	8,9	2,121	10	2,219	11	2,263	11	2,472	12	2,597	12	2,761	13
Heated	Sr	29,90	100	0,8624	2,9	1,169	3,9	1,480	5,0	1,716	5,7	1,951	6,5	2,148	7,2	2,325	7,8
Room temp.	Sr	29,90	100	0,8066	2,7	1,144	3,8	1,417	4,7	1,635	5,5	1,843	6,2	2,028	6,8	2,200	7,4
Frozen	Sr	29,90	100	0,8235	2,8	1,159	3,9	1,414	4,7	1,674	5,6	1,880	6,3	2,074	6,9	2,248	7,5
Heated	Mo	107,0	100	0,2278	0,21	0,3048	0,28	0,6587	0,62	0,8933	0,83	1,197	1,1	1,518	1,4	1,914	1,8
Room temp.	Mo	107,0	100	0,2416	0,23	0,3121	0,29	0,3444	0,32	0,3604	0,34	0,3664	0,34	0,3749	0,35	0,3888	0,36
Frozen	Mo	107,0	100	0,2334	0,22	0,3139	0,29	0,3479	0,32	0,3742	0,35	0,3895	0,36	0,4072	0,38	0,4272	0,40
Heated	Ba	310,8	100	825,7	270	1443	460	2330	750	3025	970	4089	1300	4941	1600	5627	1800
Room temp.	Ba	310,8	100	840,3	270	1627	520	2435	780	3174	1000	4182	1300	5014	1600	5721	1800
Frozen	Ba	310,8	100	838,8	270	1515	490	2272	730	3202	1000	4208	1400	5162	1700	5923	1900
Heated	U	23,90	100	0,7745	3,2	0,8494	3,6	0,9179	3,8	0,9426	3,9	0,9628	4,0	0,9826	4,1	1,006	4,2
Room temp.	U	23,90	100	0,7498	3,1	0,8284	3,5	0,8529	3,6	0,8662	3,6	0,8731	3,7	0,8790	3,7	0,8851	3,7
Frozen	U	23,90	100	0,7734	3,2	0,8547	3,6	0,8764	3,7	0,8856	3,7	0,8904	3,7	0,8946	3,7	0,8986	3,8

Table (3.8-6), Concentrations of elements quantified in leachates of weathered fines, recalculated into µg/g of leached material. These recalculated contents and then compared as percentages to the “total” contents gained from digestion data. The results of the sampling occasions are added together throughout the leaching period. But it must be noted that this is not the total amount of elements that were leached during the leaching period; because not all sampling occasions were analyzed by ICP-MS

				Sampling days													
Weathered fines		Total		1		2		3		4		6		8		10	
	Metal	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%
Heated	Na	232,3	100	4,669	2,0	8,604	3,7	11,89	5,1	19,94	8,6	26,66	11	34,02	15	39,24	17
Room temp.	Na	232,3	100	5,653	2,4	9,817	4,2	11,00	4,7	12,49	5,4	14,26	6,1	15,95	6,9	17,18	7,4
Frozen	Na	232,3	100	4,810	2,1	8,866	3,8	10,14	4,4	12,14	5,2	13,66	5,9	15,08	6,5	16,43	7,1
Heated	Mg	2417	100	52,59	2,2	61,76	2,6	79,60	3,3	93,94	3,9	101,7	4,2	110,4	4,6	118,3	4,9
Room temp.	Mg	2417	100	50,52	2,1	58,67	2,4	60,55	2,5	61,50	2,5	62,47	2,6	63,45	2,6	64,40	2,7
Frozen	Mg	2417	100	49,53	2,0	56,29	2,3	57,99	2,4	58,99	2,4	59,96	2,5	60,97	2,5	62,04	2,6
Heated	Al	24070	100	151,5	0,63	180,4	0,75	195,7	0,81	203,6	0,85	207,4	0,86	212,1	0,88	216,3	0,90
Room temp.	Al	24070	100	147,5	0,61	170,4	0,71	173,2	0,72	175,0	0,73	176,8	0,73	178,7	0,74	180,4	0,75
Frozen	Al	24070	100	139,5	0,58	150,9	0,63	153,0	0,64	154,8	0,64	156,5	0,65	158,3	0,66	160,2	0,67
Heated	K	10270	100	0,7621	0,007	0,7621	0,007	1,273	0,012	8,165	0,080	33,06	0,32	69,92	0,68	107,7	1,0
Room temp.	K	10270	100	0,5790	0,006	1,376	0,013	2,999	0,029	7,283	0,071	18,03	0,18	32,40	0,32	51,87	0,51
Frozen	K	10270	100	2,842	0,028	3,610	0,035	5,006	0,049	10,53	0,10	22,45	0,22	38,66	0,38	57,39	0,56
Heated	Ca	3983	100	5705	140	8867	220	9509	240	9712	240	9766	250	9809	250	9839	250
Room temp.	Ca	3983	100	5602	140	7942	200	8309	210	8434	210	8506	210	8553	210	8588	220
Frozen	Ca	3983	100	4868	120	5851	150	6025	150	6099	150	6151	150	6190	160	6219	160
Heated	V	348,6	100	0,09698	0,028	0,1149	0,033	0,2084	0,06	0,2259	0,065	0,2271	0,065	0,2277	0,065	0,2280	0,065
Room temp.	V	348,6	100	0,1008	0,029	0,1194	0,034	0,1233	0,035	0,1233	0,035	0,1249	0,036	0,1249	0,036	0,1252	0,036
Frozen	V	348,6	100	0,08873	0,025	0,1007	0,029	0,1025	0,029	0,1036	0,030	0,1058	0,030	0,1058	0,030	0,1079	0,031
Heated	Mn	38,56	100	3,681	9,5	4,575	12	5,357	14	5,800	15	5,992	16	6,196	16	6,376	17
Room temp.	Mn	38,56	100	3,620	9,4	4,401	11	4,586	12	4,645	12	4,682	12	4,711	12	4,735	12
Frozen	Mn	38,56	100	3,513	9,1	4,083	11	4,218	11	4,275	11	4,310	11	4,344	11	4,371	11
Heated	Fe	14760	100	841,8	5,7	956,1	6,5	1380	9,3	1610	11	1704	12	1803	12	1885	13
Room temp.	Fe	14760	100	822,5	5,6	923,4	6,3	944,7	6,4	949,2	6,4	956,3	6,5	960,3	6,5	965,1	6,5
Frozen	Fe	14760	100	766,0	5,2	835,5	5,7	854,5	5,8	866,8	5,9	881,0	6,0	891,8	6,0	903,6	6,1
Heated	Ni	22,25	100	2,048	9,2	2,405	11	2,771	12	2,965	13	3,031	14	3,110	14	3,169	14
Room temp.	Ni	22,25	100	2,044	9,2	2,578	12	2,646	12	2,649	12	2,649	12	2,649	12	2,650	12
Frozen	Ni	22,25	100	1,927	8,7	2,155	9,7	2,173	9,8	2,173	9,8	2,173	9,8	2,174	9,8	2,174	9,8
Heated	Cu	24,38	100	6,133	25	7,336	30	10,73	44	12,11	50	12,5	51	12,88	53	13,15	54
Room temp.	Cu	24,38	100	5,955	24	7,041	29	7,272	30	7,368	30	7,466	31	7,548	31	7,601	31
Frozen	Cu	24,38	100	5,747	24	6,560	27	6,769	28	6,904	28	7,003	29	7,105	29	7,184	29
Heated	Zn	31,56	100	2,777	8,8	3,408	11	6,441	20	7,889	25	8,376	27	8,909	28	9,294	29
Room temp.	Zn	31,56	100	2,765	8,8	3,355	11	3,570	11	3,657	12	3,884	12	4,023	13	4,144	13
Frozen	Zn	31,56	100	2,612	8,3	3,126	9,9	3,386	11	3,509	11	3,780	12	3,968	13	4,109	13
Heated	Sr	31,74	100	5,091	16	7,991	25	8,565	27	9,244	29	9,740	31	10,25	32	10,71	34
Room temp.	Sr	31,74	100	4,950	16	7,159	23	7,774	24	8,149	26	8,507	27	8,827	28	9,101	29
Frozen	Sr	31,74	100	4,410	14	5,476	17	5,908	19	6,233	20	6,547	21	6,819	21	7,104	22
Heated	Mo	76,92	100	0,3779	0,49	0,4121	0,54	0,4221	0,55	0,4255	0,55	0,4255	0,55	0,4255	0,55	0,4255	0,55
Room temp.	Mo	76,92	100	0,3811	0,50	0,4278	0,56	0,4499	0,58	0,4499	0,58	0,4499	0,58	0,4499	0,58	0,4499	0,58
Frozen	Mo	76,92	100	0,3413	0,44	0,3678	0,48	0,3934	0,51	0,3947	0,51	0,3963	0,52	0,3963	0,52	0,3963	0,52
Heated	Ba	456,5	100	656,3	140	1305	290	2207	480	3002	660	4090	900	4939	1100	5710	1300
Room temp.	Ba	456,5	100	843,5	190	1526	330	2310	510	2921	640	3949	870	4833	1100	5424	1200
Frozen	Ba	456,5	100	847,3	190	1475	320	2295	500	3065	670	4078	890	4804	1100	5495	1200
Heated	U	38,00	100	3,343	8,8	3,878	10	4,877	13	5,373	14	5,518	15	5,676	15	5,810	15
Room temp.	U	38,00	100	3,293	8,7	3,754	9,9	3,834	10	3,870	10	3,916	10	3,971	10	4,032	11
Frozen	U	38,00	100	3,137	8,3	3,491	9,2	3,557	9,4	3,591	9,4	3,628	9,5	3,669	9,7	3,718	9,8

Table (3.8-7), Concentrations of elements quantified in leachates of ash, recalculated into µg/g of leached material. These recalculated contents and then compared as percentages to the “total” contents gained from digestion data. The results of the sampling occasions are added together throughout the leaching period. But it must be noted that this is not the total amount of elements that were leached during the leaching period; because not all sampling occasions were analyzed by ICP-MS

				Sampling days													
	Ash	Total		1		2		3		4		6		8		10	
	Metal	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%
Heated	Na	209,0	100	7,485	3,6	12,42	5,9	14,79	7,1	16,78	8,0	18,01	8,6	19,10	9,1	20,35	9,7
Room temp.	Na	209,0	100	7,463	3,6	12,34	5,9	13,46	6,4	14,42	6,9	15,14	7,2	15,34	7,3	15,59	7,5
Frozen	Na	209,0	100	7,084	3,4	12,17	5,8	13,42	6,4	15,13	7,2	15,67	7,5	15,82	7,6	16,25	7,8
Heated	Mg	3616	100	71,83	2,0	97,27	2,7	124,7	3,4	140,8	3,9	149,4	4,1	154,7	4,3	158,8	4,4
Room temp.	Mg	3616	100	71,99	2,0	98,47	2,7	123,4	3,4	141,4	3,9	148,9	4,1	153,0	4,2	156,2	4,3
Frozen	Mg	3616	100	74,53	2,1	101,7	2,8	126,0	3,5	141,4	3,9	149,2	4,1	153,8	4,3	158,2	4,4
Heated	Al	46040	100	4,061	0,009	6,507	0,014	8,616	0,019	10,43	0,023	13,33	0,029	17,06	0,037	26,75	0,058
Room temp.	Al	46040	100	4,123	0,009	6,602	0,014	8,712	0,019	10,37	0,023	12,71	0,028	15,52	0,034	21,98	0,048
Frozen	Al	46040	100	4,059	0,009	6,639	0,014	8,847	0,019	10,51	0,023	12,60	0,027	19,35	0,042	39,07	0,085
Heated	K	9325	100	121,1	1,3	183,7	2,0	240,7	2,6	280,5	3,0	310,4	3,3	336,2	3,6	357,8	3,8
Room temp.	K	9325	100	127,2	1,4	189,7	2,0	239,2	2,6	277,4	3,0	300,2	3,2	317,0	3,4	329,8	3,5
Frozen	K	9325	100	121,3	1,3	183,5	2,0	234,7	2,5	269,8	2,9	293,1	3,1	310,0	3,3	324,0	3,5
Heated	Ca	5070	100	641,7	13	915,0	18	1266	25	1485	29	1601	32	1663	33	1715	34
Room temp.	Ca	5070	100	641,7	13	929,6	18	1253	25	1501	30	1614	32	1676	33	1717	34
Frozen	Ca	5070	100	668,0	13	959,0	19	1266	25	1478	29	1607	32	1676	33	1729	34
Heated	V	495,8	100	0,1328	0,027	0,2530	0,051	0,4208	0,085	0,5887	0,12	0,8069	0,16	1,124	0,23	1,570	0,32
Room temp.	V	495,8	100	0,1314	0,026	0,2597	0,052	0,3797	0,077	0,4876	0,098	0,6172	0,12	0,7646	0,15	0,9601	0,19
Frozen	V	495,8	100	0,1186	0,024	0,2484	0,050	0,3859	0,078	0,5158	0,10	0,6680	0,13	0,8993	0,18	1,291	0,26
Heated	Mn	249,7	100	7,795	3,1	10,45	4,2	12,75	5,1	14,15	5,7	14,95	6,0	15,43	6,2	15,83	6,3
Room temp.	Mn	249,7	100	7,165	2,9	9,740	3,9	11,83	4,7	13,35	5,3	14,00	5,6	14,35	5,7	14,63	5,9
Frozen	Mn	249,7	100	7,121	2,9	9,581	3,8	11,38	4,6	12,39	5,0	12,85	5,1	13,15	5,3	13,52	5,4
Heated	Fe	60450	100	10,32	0,017	10,48	0,017	10,73	0,018	10,73	0,018	11,18	0,018	12,37	0,020	18,45	0,031
Room temp.	Fe	60450	100	3,449	0,006	3,531	0,006	3,700	0,006	3,796	0,006	5,085	0,008	5,571	0,009	8,253	0,014
Frozen	Fe	60450	100	2,638	0,004	2,928	0,005	3,236	0,005	3,264	0,005	3,283	0,005	6,981	0,012	19,42	0,032
Heated	Ni	153,0	100	17,35	11	17,65	12	17,70	12	17,71	12	17,71	12	17,71	12	17,71	12
Room temp.	Ni	153,0	100	0,921	0,60	1,190	0,78	1,350	0,88	1,459	0,95	1,491	0,97	1,492	0,97	1,496	0,98
Frozen	Ni	153,0	100	0,845	0,55	1,068	0,70	1,183	0,77	1,216	0,79	1,217	0,80	1,217	0,80	1,257	0,82
Heated	Cu	156,4	100	0,127	0,081	0,2155	0,14	0,2289	0,15	0,2350	0,15	0,2797	0,18	0,3495	0,22	0,4551	0,29
Room temp.	Cu	156,4	100	0,07406	0,047	0,09892	0,063	0,1152	0,074	0,1225	0,078	0,1366	0,087	0,1507	0,096	0,1716	0,11
Frozen	Cu	156,4	100	0,06594	0,042	0,09850	0,063	0,1155	0,074	0,4459	0,29	0,4609	0,29	0,5245	0,34	0,6391	0,41
Heated	Zn	127,4	100	0,2478	0,19	0,3471	0,27	0,3744	0,29	0,4910	0,39	0,5867	0,46	0,6841	0,54	1,015	0,80
Room temp.	Zn	127,4	100	0,1926	0,15	0,2826	0,22	0,3846	0,30	0,3957	0,31	0,7563	0,59	0,8826	0,69	0,9187	0,72
Frozen	Zn	127,4	100	0,1300	0,10	0,1655	0,13	0,2891	0,23	1,215	0,95	1,315	1,0	1,444	1,1	1,654	1,3
Heated	Sr	57,99	100	0,7981	1,4	1,218	2,1	1,645	2,8	1,943	3,4	2,193	3,8	2,399	4,1	2,565	4,4
Room temp.	Sr	57,99	100	0,7964	1,4	1,231	2,1	1,639	2,8	1,950	3,4	2,174	3,7	2,373	4,1	2,523	4,4
Frozen	Sr	57,99	100	0,7928	1,4	1,173	2,0	1,587	2,7	1,875	3,2	2,112	3,6	2,292	4,0	2,469	4,3
Heated	Mo	84,04	100	0,03602	0,043	0,09273	0,11	0,3769	0,45	0,7095	0,84	1,027	1,2	1,387	1,7	1,751	2,1
Room temp.	Mo	84,04	100	0,01926	0,023	0,1176	0,14	0,3561	0,42	0,5760	0,69	0,7667	0,91	0,9363	1,1	1,078	1,3
Frozen	Mo	84,04	100	0,02156	0,026	0,1237	0,15	0,3921	0,47	0,9045	1,08	1,251	1,5	1,463	1,7	1,596	1,9
Heated	Ba	714,0	100	860,1	120	1533	220	2573	360	3187	450	4157	580	5017	700	5590	780
Room temp.	Ba	714,0	100	930,2	130	1304	180	2632	370	3207	450	3980	560	4866	680	5465	770
Frozen	Ba	714,0	100	845,2	120	1216	170	2334	330	2901	410	3772	530	4504	630	5192	730
Heated	U	129,1	100	0,03348	0,026	0,04927	0,038	0,05961	0,046	0,06606	0,051	0,0760	0,059	0,09106	0,071	0,1232	0,095
Room temp.	U	129,1	100	0,03142	0,024	0,04896	0,038	0,07332	0,057	0,08587	0,067	0,09300	0,072	0,09853	0,076	0,1110	0,086
Frozen	U	129,1	100	0,02497	0,019	0,04350	0,034	0,07848	0,061	0,1073	0,083	0,1211	0,094	0,1403	0,11	0,1803	0,14

Table (3.8-6), Concentrations of elements quantified in leachates of processed shale, recalculated into µg/g of leached material. These recalculated contents and then compared as percentages to the “total” contents gained from digestion data. The results of the sampling occasions are added together throughout the leaching period. But it must be noted that this is not the total amount of elements that were leached during the leaching period; because not all sampling occasions were analyzed by ICP-MS

				Sampling days													
Processed shale		Total		1		2		3		4		6		8		10	
	Metal	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%	µg/g	%
Heated	Na	601,4	100	11,87	2,0	21,60	3,6	32,78	5,5	39,58	6,6	41,61	6,92	42,79	7,12	44,22	7,35
Room temp.	Na	601,4	100	12,72	2,1	22,98	3,8	29,37	4,9	34,18	5,68	35,37	5,88	36,25	6,03	36,89	6,13
Frozen	Na	601,4	100	12,49	2,1	22,77	3,8	29,19	4,9	33,93	5,64	35,12	5,84	36,02	5,99	36,51	6,071
Heated	Mg	2477	100	8,899	0,36	16,45	0,66	42,62	1,7	56,86	2,30	60,02	2,42	61,72	2,491	63,24	2,553
Room temp.	Mg	2477	100	8,540	0,34	15,13	0,61	24,74	1,00	31,67	1,28	34,00	1,372	35,52	1,434	36,95	1,491
Frozen	Mg	2477	100	8,633	0,35	15,54	0,63	24,57	0,99	30,91	1,25	33,22	1,341	34,65	1,399	36,01	1,454
Heated	Al	34180	100	4,703	0,014	7,914	0,023	10,87	0,032	13,56	0,04	19,41	0,057	25,80	0,075	31,91	0,093
Room temp.	Al	34180	100	4,130	0,012	7,589	0,022	10,28	0,03	12,86	0,038	16,07	0,047	19,08	0,056	22,87	0,067
Frozen	Al	34180	100	4,836	0,014	8,333	0,024	11,16	0,033	13,46	0,039	16,88	0,049	20,10	0,059	24,19	0,071
Heated	K	13780	100	56,40	0,41	92,26	0,67	162,4	1,18	217,0	1,57	240,3	1,74	257,7	1,87	274,1	1,99
Room temp.	K	13780	100	61,77	0,45	98,65	0,72	135,9	0,99	168,7	1,22	185,8	1,35	201,1	1,46	215,3	1,56
Frozen	K	13780	100	60,47	0,44	96,79	0,70	133,3	0,97	164,8	1,20	182,4	1,32	197,0	1,43	211,1	1,53
Heated	Ca	17740	100	6213	35	12490	70	18630	110	23070	130	23290	130	23360	130	23410	130
Room temp.	Ca	17740	100	6157	35	12490	70	18430	100	22220	130	22430	130	22500	130	22550	130
Frozen	Ca	17740	100	6104	34	12200	69	18370	100	22050	120	22250	130	22320	130	22350	130
Heated	V	367,2	100	0,08304	0,023	0,1528	0,042	0,2811	0,077	0,4416	0,12	0,7185	0,196	1,076	0,293	1,414	0,385
Room temp.	V	367,2	100	0,06838	0,019	0,1372	0,037	0,2078	0,057	0,2756	0,075	0,3600	0,098	0,4557	0,124	0,5569	0,152
Frozen	V	367,2	100	0,09070	0,025	0,1606	0,044	0,2319	0,063	0,2959	0,081	0,3848	0,105	0,4780	0,13	0,5847	0,159
Heated	Mn	104,0	100	1,987	1,9	4,108	4,0	5,984	5,8	7,006	6,74	7,132	6,86	7,262	6,98	7,372	7,09
Room temp.	Mn	104,0	100	1,719	1,7	3,648	3,5	5,541	5,3	6,527	6,28	6,612	6,359	6,667	6,412	6,744	6,486
Frozen	Mn	104,0	100	1,687	1,6	3,667	3,5	5,565	5,4	6,488	6,24	6,577	6,326	6,630	6,376	6,714	6,457
Heated	Fe	66470	100	26,33	0,040	50,12	0,075	74,48	0,112	90,72	0,136	95,66	0,144	103,2	0,155	109,8	0,165
Room temp.	Fe	66470	100	25,59	0,038	50,27	0,076	73,03	0,110	87,25	0,131	89,77	0,135	92,18	0,139	96,55	0,145
Frozen	Fe	66470	100	26,61	0,040	50,60	0,076	74,26	0,112	87,85	0,132	90,68	0,136	93,79	0,141	98,24	0,148
Heated	Ni	128,2	100	0,1045	0,081	0,1776	0,139	0,2411	0,188	0,2709	0,211	0,2709	0,211	0,2709	0,211	0,2709	0,211
Room temp.	Ni	128,2	100	0,9137	0,71	0,9957	0,777	1,055	0,823	1,076	0,839	1,076	0,839	1,076	0,839	1,076	0,839
Frozen	Ni	128,2	100	0,1014	0,079	0,1770	0,138	0,2551	0,199	0,2716	0,212	0,2716	0,212	0,2716	0,212	0,2716	0,212
Heated	Cu	132,9	100	0,04278	0,032	0,06317	0,048	0,08108	0,061	0,09775	0,074	0,2211	0,166	0,2887	0,217	0,3236	0,243
Room temp.	Cu	132,9	100	0,03682	0,028	0,06541	0,049	0,08428	0,063	0,08813	0,066	0,1024	0,077	0,1340	0,101	0,1484	0,112
Frozen	Cu	132,9	100	0,05202	0,039	0,09252	0,070	0,1117	0,084	0,1157	0,087	0,1243	0,094	0,1430	0,108	0,1598	0,12
Heated	Zn	119,0	100	0,1114	0,094	0,1754	0,147	0,2530	0,213	0,3528	0,296	0,4800	0,40	0,6242	0,52	0,7888	0,66
Room temp.	Zn	119,0	100	0,2319	0,19	0,3268	0,275	0,3735	0,314	0,3824	0,321	0,4683	0,393	0,5644	0,474	0,5793	0,487
Frozen	Zn	119,0	100	0,1310	0,11	0,2051	0,172	0,4060	0,34	0,4360	0,366	0,5120	0,43	0,6257	0,526	0,6414	0,539
Heated	Sr	67,41	100	6,416	9,5	10,22	15,2	12,95	19,2	15,19	22,5	15,44	22,91	15,70	23,29	15,90	23,58
Room temp.	Sr	67,41	100	6,542	9,7	10,66	15,8	13,05	19,4	14,39	21,3	14,66	21,75	14,87	22,06	15,04	22,32
Frozen	Sr	67,41	100	6,655	9,9	10,53	15,6	13,07	19,4	14,40	21,4	14,66	21,74	14,87	22,06	15,04	22,31
Heated	Mo	219,9	100	6,173	2,8	17,51	8,0	29,98	13,6	37,29	17,0	39,87	18,1	41,05	18,66	41,84	19,02
Room temp.	Mo	219,9	100	5,490	2,5	14,73	6,7	27,79	12,6	36,18	16,5	40,22	18,3	42,32	19,24	43,65	19,85
Frozen	Mo	219,9	100	5,318	2,4	14,92	6,8	27,63	12,6	35,86	16,3	39,77	18,1	41,68	18,95	42,93	19,52
Heated	Ba	579,4	100	877,4	150	1533	270	2148	370	2959	510	3999	690	4836	840	5514	950
Room temp.	Ba	579,4	100	732,6	130	1304	230	2115	370	2646	460	3795	660	4733	820	5344	920
Frozen	Ba	579,4	100	720,2	120	1216	210	1794	310	2286	400	3323	570	4288	740	4835	830
Heated	U	92,59	100	0,1234	0,13	0,2660	0,29	1,313	1,4	1,808	1,95	1,900	2,052	1,971	2,129	2,024	2,186
Room temp.	U	92,59	100	0,1243	0,13	0,2210	0,24	0,7123	0,77	1,102	1,19	1,160	1,253	1,194	1,289	1,235	1,333
Frozen	U	92,59	100	0,1391	0,15	0,2415	0,26	0,7453	0,80	1,188	1,28	1,257	1,358	1,292	1,395	1,338	1,445

By studying the leaching percentages we can see that the water leaching and temperature treatments that were used in this study are poor leaching methods compared to digestion in HNO_3. Exceptions are for calcium and barium. This may be because HNO_3 is an oxidizing acid. Its oxidizing capabilities may cause some elements to precipitate and to these precipitation particles calcium and barium may adsorb; and thus resulting in incorrect quantification of these elements in the digestions. This problem may be avoided by using less concentrated HNO_3 or some other type of acid.

The tables with the additive percentages from the leaching process gives the best indication on how effective the water and temperature treatments were in leaching elements from the different materials. But since not all sampling occasions were analyzed by ICP-MS; the percentage gained through addition on sampling occasion 10 is lower than what was actually leached from the materials. A short summary will follow of the elements with the highest leaching percentages gained over the whole leaching period, i.e. from sampling occasion 1 to sampling occasion 10. The presented value is a mean for all three temperature treatments.

- Shale
  - Cu 18%
  - Zn 15%
  - Na 9.6%
  - Ni 9.0%
  - Sr 7.6%
  - Mn 6.8%

- Weathered fines
  - Cu 38%
  - Zn 18%
  - Mn 13%
  - Ni 12%
  - U 12%

- Ash
  - Na 8.3%
  - Mn 5.9%
  - Sr 4.4%
  - Mg 4.4%

- Processed shale
  - Sr 23%
  - Mo 19%
  - Mn 6.7%
  - Na 6.5%

The presence of varying amounts of hydrocarbons in the different materials does affect the leach ability of elements but there is another attribute that has a key role in the materials susceptibility to weathering processes; their mineralogy. The impact of mineralogy was shortly mentioned under the heading; uranium, 3.7.15. Simply by studying the black, unprocessed shale and the red, processed shale one can clearly see that there has occurred a change in mineralogy between the two materials. The unprocessed shale has a bedded structure with the separate sheet layers that is typical for shales. This structure is totally gone in the processed, and even metamorphosed, shale. The result from the digestions and metal analysis enhances the evidence that a change in mineralogy was brought on by the pyrolysis process. The differences between concentrations of various elements in the samples of ash and processed shale also indicate that different grades of processing give rise to different mineralogy in the materials.

Even with all analyses which have been carried out in this study it is hard to get a clear and accurate picture of the mineralogy of the four materials. If further understanding of the materials mineralogy is desired; an analysis by XRD would be a good choice to gain this information.

3.9 DOC

Table (3.9-1), Concentrations of DOC in the samples leachates

	Sampling occasions											
	1		2		3		4		7		10	
	DOC mg/l	RSD	DOC mg/l	RSD	DOC mg/l	RSD	DOC mg/l	RSD	DOC mg/l	RSD	DOC mg/l	RSD
Heated shale	5,1	0,42	2,5	0,15	11	0,50	6,3	0,087	5,9	0,61		
Room temp. shale	5,3	0*	2,8	0,61	2,1	0,040	1,8	0,070	1,3	0,043		
Frozen shale	5,7	1,9	2,7	0,081	2,4	0,22	1,9	0,031	1,7	0,041		
Heated weathered fines	0,38	0**	1,4	0,24	5,8	0*	4,9	0,37	3,6	0,20		
Room temp. weathered fines	2,0	0,84	1,6	0,21	1,6	0,30	1,1	0,0086	1,2	0,060	1,2	0*
Frozen weathered fines	1,4	0**	1,3	0,18	1,8	0,029	1,2	0,014	1,3	0,092		
Heated ash	0,94	0**	2,0	0,13	4,0	0,072	3,3	0,25	3,6	0,14	2,8	0*
Room temp. ash	1,7	1,6	0,66	0*	1,5	0,14	1,2	0,02	1,2	1,3		
Frozen ash	0,57	0**	1,9	0,058	1,8	0*	1,4	0,12	1,3	0,13		
Heated processed shale	0	0**	0,50	0,37	2,0	0,52	2,5	0,059	2,7	0,038		
Room temp. processed shale	0	0**	0,38	0,27	1,5	0*	0,92	0,056	0,79	0,20		
Frozen processed shale	0,86	0**	0,021	0*	1,1	0,050	0,57	0,10	1,1	0,30		

*Only 1 out of 2 replicates analyzed

**1 or 2 replicate/-s with a negative DOC concentration due to greater quantified concentrations of inorganic carbon than total carbon concentrations. These DOC concentrations were therefore considered to be 0 mg/l

Many problems occurred during the DOC analyses which resulted in failed analyses of quite many samples. This was the case with all the samples from sampling occasion 10, except for 2 samples that were analyzed in a previous run. There is a great risk that the DOC concentrations in the samples from sampling occasion 1 are incorrect. Due to a fluctuating baseline; many of the measured inorganic carbon concentrations were higher than the measured total carbon contents, resulting in negative concentrations of organic carbon.

Overall, the samples contained low concentrations of DOC. The TOC have its best measurement accuracy of carbon concentrations in the span of 20-80 mg/l. The highest concentration of these samples was 11 mg/l , which was quantified in the leachates from the heated shale extracted on sampling occasion 3.

We have two known sources of organic carbon in these samples; one is due to biological activity and the other is the hydrocarbons which the materials contain. The materials that still contain hydrocarbons are shale, weathered fines and ash. Out of these three materials we see an increase in DOC in the leachates of the heated samples compared to the ones that have stood in room temperature or been frozen. The question is; is this increase caused by thriving microbial life or that the 70°C temperature treatment enhances the release of hydrocarbons from the materials? When the four different materials were collected from their different sites in Kvarntorp it was only the ash that was warm, with a temperature of approximately 50°C. With this fact in hand it seems unlikely that the microbes that live on materials other than the ash are very adapted to higher temperatures, such as 70°C. But in the samples of processed shale we see the same increase of DOC in the heated samples; and the processed shale is supposed to not contain any hydrocarbons. So the only conclusion that can be drawn is that the heating increases the leach ability of hydrocarbons but also that the microbes present on the materials are indeed adapted to 70°C.

As mentioned under the heading; materials and methods, subheading 2.6.4 a problem occurred with the TOC during an analysis which resulted in that some samples from sampling occasion 3 had to be stored in a refrigerator for 24 hours. This may have favored microbial growth in theses samples and therefore contributed to higher DOC concentrations quantified in samples from sampling occasion 3. The samples that were stored in refrigerator were:

- 1 replicate of heated shale
- 1 replicate of room temp. shale
- 2 replicates of frozen shale
- 1 replicate of room temp. weathered fines
- 2 replicates of frozen weathered fines
- 2 replicates of heated ash
- 1 replicate of room temp. ash
- 1 replicate of frozen ash
- 1 replicate of heated processed shale
- 1 replicate of room temp. processed shale

An interesting phenomenon is observed when comparing the room tempered and frozen samples. By studying the room tempered- and frozen samples one can see that the frozen samples of shale, weathered fines and ash contain more DOC than the samples that have stood in room temperature. If microbes were the primary source of the DOC; then the room tempered samples should have higher DOC than the frozen samples. Instead DOC increases in the frozen samples, probably due to that the freezing process generates new surfaces with hydrocarbons that can then be leached when the samples are thawed. It is hard to say if this increase occurs in the samples of processed shale. These quantified concentrations are so low so they have probably been very sensitive to any fluctuations of the baseline during analysis.

Another aspect that would indicate that hydrocarbons are the primary source for DOC in samples of shale, weathered fines and ash it that they reaches their highest quantified concentration on sampling occasions 2 or 3 and thereafter their concentrations of DOC decreases. This is a leaching pattern repeated by many metals. In the heated sample of processed shale however; the

DOC increases in the leachates even to sampling occasion 7. This continuing increase implies strongly that microbial growth is the primary source of DOC in these samples.

4 Conclusions

For most elements and compounds quantified in this study, their concentrations in leachates from different materials decreased as the leaching period transpired. Exceptions were Na from weathered fines, Al and V from ash and processed shale, K from shale and weathered fines, Fe from ash and Mo from shale. These exceptions increased in concentration and for some; the maximum concentrations were not even observed during this leaching period.

Many elements and compounds appeared as particle coats which were easily leached with water. This means that; if any force, natural or anthropogenic, would expose new surfaces in the various shale products for natural weathering; their leachates would initially contain high amounts of many elements. And since many of the elements that the shale products contain are toxic; this initial leaching will have a greatly negative effect on the environment around Kvarntorp.

According to the analyses conducted in this study heating causes higher rates of leaching than frost wedging. In fact; frost wedging did not affect the leach ability of elements and compounds as much as was initially suspected.

The data gained from the digestions shows that the ash and the processed shale still contain many valuable elements. And since the processed shale does not contain any hydrocarbons, any extraction attempt of elements from this material should be easier than compared to the black, unprocessed shale.

It is true that any anthropogenic activity conducted in Kvarntorp will have a negative effect on the environment. But as things are; negative effects on the environment are inevitable. Kvarntorpshögen cannot be ignored. If there are two options; and both of them have a negative environmental impact, why should we not choose the option that at least can bring us some profit? There is a shortage around the world for many of the elements that Kvarntorpshögen contain; why let it go to waste leaking out on its own into the surrounding environment?

4.1 Some future scientific projects

Lastly; some ideas for future projects involving Kvarntorp and its shale products will be presented. The projects will be varying in both size and purpose.

- Continued natural weathering – A small project suitable for being a side project. Continued natural weathering of those shale products that showed an increase in concentration of valuable elements at the leaching period’s latter occasions. Interesting materials, temperature treatments and elements would be; molybdenum from heated shale, vanadium from heated processed shale and vanadium from all three temperature treatments of ash.

  The aim would be to find out how the concentration curves develop beyond sampling occasion 10. How much, in percentage, of the materials “total” content gained from digestion is leachable by this natural weathering method?
- Leaching with adjusted pH and/or the addition of complexing agents – A medium sized project. Leaching test of shale products. The pH of the leaching fluid is adjusted to specific pH values. Which pH corresponds to the greatest leach ability of elements?

  Will the addition of various complexing agents have a beneficial effect on the leaching of elements? Examples on complexing agents could be organic acids from microbial metabolism or humic- and fulvic acids. Addition of anions could also be made in an attempt to compete with the shale products high sulfate contents. An example could be addition of carbonate; which is only possible if pH of the leachates is neutral or higher because a low pH would bind up the carbonate as H_2CO_3 and drive off some carbonate as CO_2.

  This project idea originated from prof. B Allard at Örebro University, Man Technology Environment Research Centre.
- Mineralogical changes caused by different grades of processing of black shale and their effect on the leaching of elements – A large project. Black, unprocessed shale from Kvarntorp is processed at different temperatures, with a varying access to oxygen and perhaps with the addition of some other compounds.

  The aim would be to find out how the different processing methods affect the mineralogy, which would be analyzed by XRD, of the shale. Then an attempt to find a connection between mineralogy and leaching pattern would be made. Try to figure out the different mineralogy’s susceptibility to various leaching methods in an attempt to find the best approach to extract the valuable elements in the shale.

  This project idea originated from prof. B Allard at Örebro University, Man Technology Environment Research Centre.
- How will the cooling of Kvarntorpshögen affect the surrounding plant life – A project of varying size, depending on its extent. A small model of Kvarntorpshögen which shares approximately its originals composition will be constructed. Plants of varying kind will be

planted around this miniature heap. This model would be constructed outdoors; leaving it exposed to the sun and precipitation.

Plants would be sampled at different time intervals and from varying positions. These would then be dried and digested in suitable acid. A metal analysis would be conducted to quantify their metal content. The results from different kinds of plants, their positions and their exposure time to the leachate will be compared to some kind of reference plants. The data should give an indication on the uptake and accumulation of elements in plants and their negative effect on plant life.

5 Acknowledgements

Thanks to Stefan Karlsson and Viktor Sjöberg for all instructions around the laboratory, for patiently answering all of my questions and for performing the metal analysis on the ICP-MS.

Thanks to supervisor Mattias Bäckström for answering my questions surrounding the written report.

Thanks to Bert Allard for showing great interest in my work and sharing of ideas and guidance.

Thanks to Sara Häller for crushing and sieving the materials used in this study.

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7 Supplement with RSD values

Table (7-1), RSD values for the samples electrical conductivity

Conductivity	**Sampling occasions**									
RSD for samples	1	2	3	4	5	6	7	8	9	10
Heated shale	0	0,013	0,025	0,0090	0,033	0,044	0,028	0,079	0,049	0,0070
Room temp. shale	0,080	0,027	0,0045	0,026	0,020	0,031	0,0060	0,018	0,0070	0,0010
Frozen shale	0,045	0,025	0,0020	0,0080	0,0085	0,0075	0,0080	0	0,018	0,00050
Heated weathered fines	0	0,11	0,15	0,085	0,025	0,011	0,023	0,045	0,043	0,065
Room temp. weathered fines	0,020	0,055	0,0025	0,0075	0,0015	0,0025	0,0085	0,0090	0,0010	0,021
Frozen weathered fines	0,23	0,085	0,016	0,0020	0,0050	0,033	0,049	0,0030	0,013	0,0040
Heated ash	0,0030	0,036	0,024	0,020	0,021	0,016	0,0040	0,00078	0,0065	0,015
Room temp. ash	0,0051	0,074	0,052	0,032	0,020	0,010	0,049	0,013	0,00073	0,0033
Frozen ash	0,0010	0,045	0,16	0,040	0,034	0,00050	0,035	0,036	0,019	0,0030
Heated processed shale	0	0,010	0,032	0,025	0,021	0,013	0,0075	0,0090	0,038	0,0088
Room temp. processed shale	0,00052	0,0020	0,019	0,012	0,0085	0,052	0,027	0,013	0,0041	0,0042
Frozen processed shale	0,0014	0,0085	0,033	0,032	0,042	0,043	0,024	0,017	0,021	0,0000050

Table (7-2), RSD values for the samples pH values

pH	**Sampling occasions**									
RSD for samples	1	2	3	4	5	6	7	8	9	10
Heated shale	0,0050	0	0,025	0	0,010	0,025	0,015	0,060	0,030	0
Room temp. shale	0,010	0,025	0,025	0,010	0,035	0,010	0,0050	0	0,0050	0,010
Frozen shale	0,0050	0,010	0,010	0	0	0,0050	0,010	0,030	0,010	0
Heated weathered fines	0,010	0,010	0,010	0,015	0	0,0050	0,0050	0,035	0,0050	0,055
Room temp. weathered fines	0,015	0	0	0,0050	0	0	0,0050	0,010	0,0050	0,015
Frozen weathered fines	0,015	0,0050	0,010	0,010	0,0050	0,015	0,010	0,0050	0,010	0,010
Heated ash	0,050	0,045	0,080	0,12	0,19	0,12	0,065	0,055	0,045	0,025
Room temp. ash	0,080	0,060	0,045	0,010	0,055	0,060	0,070	0,065	0,030	0,030
Frozen ash	0,040	0,025	0	0,010	0,035	0,040	0,040	0,035	0,080	0,025
Heated processed shale	0,16	0,050	0,020	0,0050	0,090	0,12	0,12	0,11	0,10	0,12
Room temp. processed shale	0,0050	0,025	0	0,020	0,030	0,030	0,075	0,070	0,045	0
Frozen processed shale	0,030	0,030	0,050	0,11	0,055	0,025	0,040	0,080	0,090	5,0E-02

Table (7-3), RSD values for the samples acidity and alkalinity

Acidity and alkalinity	**Sampling occasions**									
RSD for samples	1	2	3	4	5	6	7	8	9	10
Heated shale	0	0,013	0,025	0,0090	0,033	0,044	0,028	0,079	0,049	0,0070
Room temp. shale	0,080	0,027	0,0045	0,026	0,020	0,031	0,0060	0,018	0,0070	0,0010
Frozen shale	0,045	0,025	0,0020	0,008	0,0085	0,0075	0,0080	0	0,018	0,00050
Heated weathered fines	0	0,11	0,15	0,085	0,025	0,011	0,023	0,045	0,043	0,065
Room temp. weathered fines	0,020	0,055	0,0025	0,0075	0,0015	0,0025	0,0085	0,0090	0,0010	0,021
Frozen weathered fines	0,23	0,085	0,016	0,0020	0,0050	0,033	0,049	0,0030	0,013	0,0040
Heated ash	0,0030	0,036	0,024	0,019	0,021	0,016	0,0041	0,00078	0,0065	0,015
Room temp. ash	0,0051	0,074	0,052	0,032	0,020	0,0095	0,049	0,013	0,00073	0,0033
Frozen ash	0,0010	0,045	0,16	0,040	0,034	0,00050	0,035	0,036	0,019	0,0030
Heated processed shale	0	0,010	0,032	0,025	0,021	0,013	0,0075	0,0090	0,038	0,0087
Room temp. processed shale	0,00052	0,0020	0,019	0,012	0,0085	0,052	0,027	0,013	0,0041	0,0042
Frozen processed shale	0,0015	0,0085	0,033	0,032	0,042	0,043	0,024	0,017	0,021	5,0E-06

Table (7-4), RSD values for the samples Eh values

Eh	Sampling occasions									
RSD for samples	1	2	3	4	5	6	7	8	9	10
Heated shale	2,7	5,5	6,3	6,5	1,1	2,8	6,3	0,3	0,70	2,5
Room temp. shale	5,2	0,70	0,55	0,75	2,7	1,8	0,45	2,9	0,050	8,8
Frozen shale	0,15	2,3	0,15	0,15	1,7	1,0	1,2	4,8	4,1	2,2
Heated weathered fines	2,3	0,30	0,70	3,3	4,8	0,60	2,7	1,2	1,6	1,9
Room temp. weathered fines	1,3	3,2	6,2	3,1	3,8	0,050	1,4	1,4	2,1	0,60
Frozen weathered fines	0,30	14	2,1	1,4	3,1	2,5	4,1	0,90	1,0	1,2
Heated ash	27	0,60	7,7	0,65	2,2	7,4	12	3,1	13	7,2
Room temp. ash	15	0,70	3,9	18	13	11	9,1	25	4,3	5,1
Frozen ash	6,3	1,7	1,4	2,0	6,3	5,2	1,5	9,6	12	3,6
Heated processed shale	20	6,4	1,2	5,1	2,3	2,4	1,5	4,9	10	8,0
Room temp. processed shale	5,7	1,1	5,5	9,3	1,0	8,0	17	7,3	2,6	1,2
Frozen processed shale	18	1,2	0,45	0,40	1,2	11	1,4	2,2	10	19

Table (7-5), RSD values for the sulfate concentrations in the samples leachates

Sulfate content	Sampling days				
RSD for samples	1	2	3	4	5
Heated shale	93,3	4,89	0,0625	2,51	1,90
Room temp. shale	36,9	15,3	1,69	1,51	1,03
Frozen shale	7,19	3,83	0,838	3,77	0,187
Heated weathered fines	62,1	91,0	1,35	14,8	6,67
Room temp. weathered fines	9,53	52,1	17,2	2,70	6,04
Frozen weathered fines	116	75,9	12,7	2,18	0,463
Heated ash	3,63	2,85	1,01	6,51	0,0644
Room temp. ash	0,944	3,45	0,947	2,49	3,59
Frozen ash	6,78	0,653	0,858	0,702	0,921
Heated processed shale	29,2	47,5	39,8	161	10,6
Room temp. processed shale	11,4	65,3	32,0	115	11,9
Frozen processed shale	32,6	9,34	14,6	38,9	3,77

Table (7-6), RSD values for the sodium concentrations in the samples leachates

Na content	Sampling days						
RSD for samples	1	2	3	4	6	8	10
Heated shale	82,3	13,9	69,7	37,8	27,7	7,63	12,3
Room temp. shale	89,0	0,812	8,69	68,1	0,169	26,9	35,3
Frozen shale	80,4	15,1	12,4	2,58	13,7	8,24	8,16
Heated weathered fines	17,6	7,56	1,56	66,9	54,7	68,7	109
Room temp. weathered fines	72,5	5,38	9,00	0,388	8,13	54,9	0,682
Frozen weathered fines	37,8	3,97	10,7	32,2	7,79	2,33	16,1
Heated ash	44,0	0,164	8,66	40,1	19,5	9,56	61,9
Room temp. ash	36,2	6,06	2,92	17,1	20,0	5,49	8,10
Frozen ash	10,8	22,9	4,52	102	6,87	2,62	3,77
Heated processed shale	26,8	15,5	265	11,8	16,1	0,985	20,7
Room temp. processed shale	10,1	3,57	4,57	38,2	5,71	2,63	6,60
Frozen processed shale	24,1	36,6	13,9	18,5	2,41	30,4	1,23

Table (7-7), RSD values for the magnesium concentrations in the samples leachates

Mg content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	120	21,3	20,5	8,42	7,81	6,58	28,7
Room temp. shale	72,4	25,4	1,11	2,19	2,60	5,48	2,72
Frozen shale	49,4	27,4	3,61	0,336	6,07	0,53	12,0
Heated weathered fines	174	69,1	92,6	182	124	7,92	110
Room temp. weathered fines	55,9	21,4	0,83	2,40	0,81	5,87	1,87
Frozen weathered fines	123	23,4	0,445	5,97	5,04	0,72	6,91
Heated ash	202	46,0	2,67	101	11,9	12,9	14,4
Room temp. ash	89,8	33,2	37,8	36,7	20,8	2,39	9,28
Frozen ash	178	27,8	58,8	16,5	38,0	21,0	3,50
Heated processed shale	1,31	45,6	247	42,3	13,7	9,10	5,44
Room temp. processed shale	10,2	21,4	10,6	20,9	15,9	0,456	8,44
Frozen processed shale	15,7	14,6	10,7	1,26	7,63	1,66	3,65

Table (7-8), RSD values for the aluminum concentrations in the samples leachates

Al content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	933	15,7	5,66	2,81	59,6	26,7	120
Room temp. shale	459	60,1	8,37	0,115	9,71	3,03	10,3
Frozen shale	52,8	34,2	2,21	3,23	7,03	3,48	18,4
Heated weathered fines	58,5	264	36,0	109	25,3	7,38	50,8
Room temp. weathered fines	96,3	116	11,0	2,09	0,14	5,24	6,53
Frozen weathered fines	320	217	9,60	4,05	2,38	3,25	22,3
Heated ash	73,2	7,65	5,40	11,2	52,3	17,1	282
Room temp. ash	4,01	6,80	10,4	0,18	16,5	3,41	234
Frozen ash	95,9	40,1	4,39	9,29	20,0	121	118
Heated processed shale	29,8	30,6	14,0	6,86	102	45,7	28,3
Room temp. processed shale	2,33	21,6	12,8	8,00	14,8	2,20	4,98
Frozen processed shale	27,3	23,7	25,6	10,6	6,69	24,3	67,1

Table (7-9), RSD values for the potassium concentrations in the samples leachates

K content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	19,4	10,1	299	50,7	8,97	200	199
Room temp. shale	20,3	21,1	17,2	70,1	11,9	6,76	3,57
Frozen shale	0,978	8,37	42,6	32,2	37,9	66,5	25,1
Heated weathered fines	63,1	0	51,0	36,8	109	30,2	272
Room temp. weathered fines	7,31	22,0	7,33	54,0	55,7	3,82	268
Frozen weathered fines	225	67,9	5,53	50,3	21,3	16,7	103
Heated ash	115	272	87,9	316	18,8	47,1	78,2
Room temp. ash	518	39,3	47,0	8,08	32,1	71,2	15,7
Frozen ash	183	82,5	16,4	2,60	57,6	73,4	52,1
Heated processed shale	268	5,57	451	128	272	20,2	60,7
Room temp. processed shale	79,8	129	82,5	102	13,4	14,2	8,27
Frozen processed shale	70,4	84,6	2,49	27,1	56,4	2,23	25,3

Table (7-10), RSD values for the calcium concentrations in the samples leachates

Ca content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	40830	4347	2179	278,7	93,97	184,4	510,2
Room temp. shale	16110	3178	647,4	134,2	52,00	111,2	175,0
Frozen shale	1571	821,2	266,5	45,72	307,8	32,32	213,3
Heated weathered fines	935,0	24430	3009	1797	43,60	441,9	40,26
Room temp. weathered fines	221,0	28680	4903	838,80	427,4	101,2	147,5
Frozen weathered fines	45600	28440	3403	1084	599,9	409,4	62,10
Heated ash	2194	9,346	595,6	39,56	94,43	29,99	1038
Room temp. ash	493,2	511,7	109,0	61,24	614,5	234,6	11,10
Frozen ash	1807	494,6	1270	255,1	939,5	467,5	374,5
Heated processed shale	5241	3585	5719	71910	902,4	11,86	86,90
Room temp. processed shale	4353	3835	5566	36930	1422	51,04	61,96
Frozen processed shale	1638	6155	16,81	16940	1277	37,91	155,1

Table (7-11), RSD values for the vanadium concentrations in the samples leachates

V content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	0,248	0,0734	0,793	1,38	0,911	0,855	3,72
Room temp. shale	0,249	0,163	0,109	0,0876	0,0294	0,0714	0,117
Frozen shale	0,395	0,0462	19,0	2,12	0,129	0,0320	0,142
Heated weathered fines	0,225	0,0912	0,698	0,534	0,120	0,0416	0,013
Room temp. weathered fines	0,135	0,610	0,145	0	0,0794	0	0,0296
Frozen weathered fines	0,672	0,101	0,101	0,00389	0,116	0	0,164
Heated ash	1,33	0,197	1,32	0,657	1,59	0,377	4,11
Room temp. ash	0,975	0,114	0,0984	0,299	0,708	0,0885	2,50
Frozen ash	0,509	1,61	0,333	0,654	0,190	1,47	0,311
Heated processed shale	0,171	0,351	1,77	0,453	1,08	0,855	0,0228
Room temp. processed shale	0,134	0,599	0,510	0,00651	0,0455	0,413	0,00812
Frozen processed shale	0,426	0,346	0,102	0,612	0,431	1,56	1,99

Table (7-12), RSD values for the manganese concentrations in the samples leachates

Mn content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	7,69	0,717	0,585	0,181	0,716	0,513	0,0783
Room temp. shale	5,81	1,72	0,475	0,0183	0,299	0,0710	0,195
Frozen shale	1,37	1,53	2,56	0,665	0,391	0,101	0,143
Heated weathered fines	0,202	6,03	1,96	5,16	2,84	0,050	2,23
Room temp. weathered fines	1,59	0,601	0,858	0,237	0,435	0,308	0,191
Frozen weathered fines	5,95	2,50	0,454	0,335	0,256	0,485	0,202
Heated ash	60,7	6,36	17,7	20,7	6,96	3,60	4,40
Room temp. ash	2,16	3,03	3,31	8,15	4,48	1,55	0,508
Frozen ash	14,0	5,24	1,82	1,83	0,683	0,380	0,171
Heated processed shale	8,77	3,97	7,39	15,1	0,748	1,51	0,366
Room temp. processed shale	6,27	6,59	1,87	10,1	0,316	0,521	0,485
Frozen processed shale	2,03	9,08	6,83	9,00	0,879	0,0433	0,928

Table (7-13), RSD values for the iron concentrations in the samples leachates

Fe content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	405	15,2	688	490	681	1020	902
Room temp. shale	49,4	37,7	1,06	14,6	29,1	4,37	78,0
Frozen shale	234	71,5	129	23,3	61,1	15,1	54,0
Heated weathered fines	185	598	1390	2310	1130	512	1300
Room temp. weathered fines	1920	526	69,7	81,9	134,3	43,2	7,76
Frozen weathered fines	2150	444	8,49	105	60,1	51,0	287
Heated ash	565	11,2	2,95	0,00	45,1	3,02	262
Room temp. ash	44,8	2,88	3,90	9,57	78,1	26,8	151
Frozen ash	66,2	29,0	15,1	2,76	1,96	75,4	104
Heated processed shale	32,2	34,2	83,1	272	59,4	40,6	138
Room temp. processed shale	104	34,3	31,8	119	18,4	7,37	9,14
Frozen processed shale	56,6	91,9	39,5	40,6	63,3	37,5	65,6

Table (7-14), RSD values for the nickel concentrations in the samples leachates

Ni content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	6,90	0,0395	0,345	1,03	0,384	0	0
Room temp. shale	4,33	1,95	0,249	0	0	0	0
Frozen shale	2,21	0,261	0,346	0	0	0	0
Heated weathered fines	3,48	2,61	1,67	2,94	0,892	0,392	1,36
Room temp. weathered fines	3,59	23,13	2,64	0,326	0,0393	0	0,0414
Frozen weathered fines	3,56	0,520	0,0163	0	0	0,0971	0
Heated ash	1640	3,92	2,25	0,414	0	0	0,0796
Room temp. ash	3,15	2,87	1,24	1,55	0,865	0,0196	0,485
Frozen ash	0,760	0,788	0,148	0,614	0,184	0	0,580
Heated processed shale	1,14	0,0414	0,934	1,98	0	0	0
Room temp. processed shale	78,7	0,0144	0,509	0,281	0	0	0
Frozen processed shale	0,338	0,181	0,0803	0,784	0	0	0

Table (7-15), RSD values for the copper concentrations in the samples leachates

Cu content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	5,36	0,522	8,56	0,379	1,05	0,488	0,494
Room temp. shale	4,75	1,43	0,631	0,460	4,16	0,0274	0
Frozen shale	1,15	6,84	0,314	0,346	0,836	0,245	0
Heated weathered fines	1,79	5,47	2,47	13,9	2,55	4,44	5,57
Room temp. weathered fines	4,83	0,530	0,422	0,343	1,15	0,586	0,246
Frozen weathered fines	12,6	4,07	0,343	3,45	0,107	1,21	0,844
Heated ash	0,253	5,73	0,395	0,085	4,59	3,13	5,71
Room temp. ash	0,223	0,243	0,510	0,809	0,347	0,228	0,826
Frozen ash	0,263	0,225	0,474	32,6	0,850	0,454	0,196
Heated processed shale	0,269	0,106	0,615	1,51	7,44	0,193	0,0125
Room temp. processed shale	0,379	0,426	1,20	0,281	0,834	0,408	0,085
Frozen processed shale	1,52	0,297	0,068	0,398	0,713	0,002	0,373

Table (7-16), RSD values for the zinc concentrations in the samples leachates

Zn content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	6,50	1,73	12,4	7,83	3,51	0,377	7,06
Room temp. shale	21,2	1,05	0,844	4,31	5,63	17,6	11,6
Frozen shale	40,8	6,51	0,723	1,17	13,0	0,794	3,69
Heated weathered fines	8,50	4,52	8,46	2,38	0,288	0,846	0,535
Room temp. weathered fines	3,18	6,17	0,421	4,15	7,42	3,59	0,116
Frozen weathered fines	4,63	8,18	9,58	0,630	11,9	2,56	5,92
Heated ash	9,04	3,27	4,30	3,83	2,80	2,12	27,9
Room temp. ash	0,771	7,57	5,46	0,701	25,6	0,511	0,796
Frozen ash	0,522	0,648	11,7	80,1	6,99	2,59	2,05
Heated processed shale	2,24	2,12	5,37	7,07	6,27	1,13	10,6
Room temp. processed shale	7,29	2,42	1,90	0,887	2,10	5,61	0,317
Frozen processed shale	5,05	0,0884	1,54	3,00	0,784	0,721	1,57

Table (7-17), RSD values for the strontium concentrations in the samples leachates

Sr content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	18,1	1,88	2,30	2,29	0,402	0,849	1,83
Room temp. shale	5,08	2,12	0,250	2,91	0,708	0,902	0,795
Frozen shale	0,626	2,49	2,71	1,58	0,407	0,385	0,456
Heated weathered fines	1,80	22,3	0,938	6,25	0,271	3,27	6,46
Room temp. weathered fines	3,93	25,0	4,04	0,370	0,0226	0,464	0,859
Frozen weathered fines	38,0	23,4	6,11	0,175	1,35	1,90	0,410
Heated ash	2,41	2,15	1,28	2,35	0,451	0,395	1,94
Room temp. ash	0,874	0,516	1,66	1,08	2,48	0,679	0,569
Frozen ash	0,246	2,99	1,76	0,576	0,823	0,812	0,223
Heated processed shale	4,36	5,72	15,0	63,1	2,44	0,129	0,341
Room temp. processed shale	1,60	17,2	1,59	11,4	0,210	0,937	0,364
Frozen processed shale	9,45	5,47	8,01	7,42	0,0577	1,24	2,85

Table (7-18), RSD values for the molybdenum concentrations in the samples leachates

Mo content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	3,19	0,927	0,396	2,89	2,10	2,10	5,94
Room temp. shale	0,0716	0,551	0,114	0,278	0,221	0,436	0,150
Frozen shale	0,142	2,19	0,0242	0,227	0,569	0,223	0,018
Heated weathered fines	0,665	0,0144	0,169	0,346	0	0	0
Room temp. weathered fines	1,24	0,0255	0,838	0	0	0	0
Frozen weathered fines	1,31	0,936	0,630	0,128	0,159	0	0
Heated ash	1,73	1,05	5,04	4,91	0,239	1,34	2,28
Room temp. ash	0,251	0,560	1,63	2,80	0,521	1,13	0,157
Frozen ash	0,0683	2,55	1,63	12,3	0,757	0,521	1,09
Heated processed shale	11,3	57,1	49,8	25,5	35,1	1,29	0,878
Room temp. processed shale	8,51	49,9	4,42	0,483	1,25	3,90	1,15
Frozen processed shale	1,41	37,0	8,02	18,8	21,7	15,9	11,7

Table (7-19), RSD values for the barium concentrations in the samples leachates

Ba content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	85,5	17,8	4,44	37,6	78,6	32,6	152
Room temp. shale	54,6	6,73	25,2	150	52,1	44,3	66,7
Frozen shale	97,9	171	141	76,8	19,6	66,2	60,0
Heated weathered fines	128	52,3	19,8	127	25,0	75,6	164
Room temp. weathered fines	119	72,8	56,8	60,5	65,7	30,1	3,87
Frozen weathered fines	5,04	19,6	110	45,4	8,08	118	112
Heated ash	191	119	67,5	55,8	10,3	46,1	32,1
Room temp. ash	98,7	9,66	37,0	77,6	236	65,2	20,0
Frozen ash	136	128	84,1	37,2	57,1	57,5	19,2
Heated processed shale	36,2	128	86,1	54,6	243	155	57,6
Room temp. processed shale	176	30,0	45,6	34,5	97,3	44,2	8,07
Frozen processed shale	166	64,4	22,8	144	22,8	35,5	181

Table (7-20), RSD values for the uranium concentrations in the samples leachates

U content	**Sampling days**						
RSD for samples	1	2	3	4	6	8	10
Heated shale	3,14	0,162	0,194	0,192	0,154	0,0233	0,439
Room temp. shale	1,69	0,923	0,143	0,0570	0,0208	0,0310	0,0616
Frozen shale	2,27	0,670	0,0947	0,0276	0,0160	0,000890	0,0235
Heated weathered fines	0,784	3,55	3,66	7,22	0,725	1,37	2,58
Room temp. weathered fines	0,669	0,769	0,127	0,0906	0,156	0,119	0,0649
Frozen weathered fines	2,68	1,63	0,0767	0,187	0,0339	0,105	0,214
Heated ash	0,540	0,231	0,0326	0,0125	0,250	0,0721	0,0343
Room temp. ash	0,0871	0,0217	0,113	0,125	0,140	0,106	0,370
Frozen ash	0,0719	0,377	0,0717	0,331	0,120	0,233	0,0181
Heated processed shale	0,782	1,88	8,32	2,72	0,0960	0,512	0,0784
Room temp. processed shale	0,0700	0,565	0,176	4,78	0,00361	0,168	0,0447
Frozen processed shale	0,478	0,837	16,0	10,8	0,959	0,115	0,954