Release of metals from unprocessed and processed black shale due to natural weathering

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Abstract Black shale was mined and processed for recovery of hydrocarbons in Kvarntorp, some 200 km SW of Stockholm, Sweden, during 1942–66. Remains from the mining period is a deposit with 40 Mm^3 of crushed shale residues: Unprocessed fine-grained shale as well as processed shale. The deposit is still hot; oxidation of sulphides as well as burning of hydrocarbons are still in progress some 50 years after closure. Weathering of the shale leads to releases of metal-rich leachates which will increase with time. The release of metals from pristine shale as well as weathered shale (exposed to the atmosphere for 50 years) and two different processed shale residues have been studied using water of different pH as leaching solution, to simulate extreme pH-variations in environmental waters: 3.0 (determined by oxidation of iron sulphides), 5.5 (buffered by carbon dioxide), 8.5 (buffered by calcite) and 12.5 (buffered by calcium hydroxide). Extraction of cationic elements was substantial (several percent of the total content) for Ca and Mg, as well as Ni, Co and U at pH 3, and very high (up to 50–60 %) for anionic elements (V, Mo, As) at pH 12.5. Especially the high-temperature processed shale would be a potential source for As and Mo at high pH. The pH-dependence of the weathering processes should be considered when future remediation (or metal recovery) processes and strategies are designed.

Keywords Black shale, alum shale, weathering, leaching

Introduction

Black shale (alum shale) of Late Cambrium age is abundant in southern Sweden. The shale consists of K-feldspars (3–8 %), illite (24–41 %), chlorite (1–5 %), calcite (1–4 %), quartz (18–34 %), pyrite (5–17 %), organic carbon (5–20 %), and other mineral constituents (up to 8 %) (Andersson *et al.* 1985). Black shale was mined and processed for recovery of hydrocarbons in Kvarntorp, 200 km SW of Stockholm (N 59°08′, E 15°17′) during 1942–66. Remains from this period is a deposit (height 100 m, diameter 700 m) containing some 40 Mm^3 of shale residues of three categories: Unprocessed fine-grained shale, black processed shale (remains after recovery of hydrocarbons by dry distillation), and red processed shale (remains after pyrolysis or incineration, largely free from organic carbon as well as sulphides). The deposit is still hot; oxidation of sulphides and burning of hydrocarbons are still in progress 50 years after closure of all mining operations. Weathering of the shale leads to releases of metal-rich leachates, however still limited since large parts of the deposit are dry. Major releases of metals can be anticipated when the deposit has cooled and is water saturated, which will happen eventually. The weathering rate will be dependent on the chemical conditions created by the water that will percolate through the deposit. Most important would be pH, determined by the weathering process itself, or buffered by some other process or by agents present, notably carbonates associated with the shale. Also the presence of complexing agents, in particular organic acids (*e.g.* humic/fulvic substances, microbial exudates) would be of importance for the mobilisation of metals. The purpose of the present project is to assess the extent of natural weathering of shales and shale process residues when exposed to water at various pH, representing the maximum pH-range that may be anticipated under environmental conditions (but without the presence of potentially complexing ligands).

Previous studies of the black shale and this mining area are given by Bäckström (2010), Allard *et al.* (2011) and Karlsson *et al.* 2012, as well as in the MSc-thesis by Karlsson (2013).

Materials and methods

Shale samples

Four categories of shale residues were collected from the mining area:

1. Shale (S); pristine black shale, sampled from a block in the shale formation (0.5 × 0.1 m)
2. Weathered shale fines (WF); crushed already during the mining but deposited without processing, size <1 cm
3. Red processed shale (RPS); pyrolysed (incinerated) shale
4. Black processed shale (BPS); partially processed shale, remains after dry-distillation

The shale samples were dried (35 °C, 48 h), crushed and sieved, and two size fractions were selected for characterisation and for the leaching tests: 2.0–0.5 mm and <0.5 mm

Leaching tests

Batch-wise leaching tests (all four shale categories) were performed at constant L/S-ratio (10; 230 g/2.3 L) and at room temperature (ca. 20 °C) with water of different pH:

1. 3.0, representing sulphide (pyrite) oxidation
2. 5.5, representing carbon dioxide/water equilibrium
3. 8.5, representing calcite/water equilibrium
4. 12.5, representing calcium hydroxide/water equilibrium
5. pH set by the shale itself; no pH-adjustments and no buffer added

All of the selected pH-levels are observed at the mine site: pH 2.8–3.5 in leachates from pristine shale, pH 7.5–8.5 in carbonate dominated areas, pH 12–12.5 in an area where cement residues were deposited, and pH of 5–6 in most of the other areas at the site (surface waters with dissolved atmospheric CO_2). The shallow groundwater in the area is Ca-SO_4-CO_3-dominated with a pH around 8.

Adjustment of pH (with NaOH or HNO_3) was made at regular intervals, except for series (e). Samples of the aqueous phase were taken after 1 hr, representing starting conditions, 5 d, and 26 d: 40 mL of the aqueous phase was removed, centrifuged (10 000 rpm, 15 min) and analysed. Continued sampling and analysis will be made after 4 months and 20 months.

The selected L/S-ratio of 10 is high enough that no formation of sparingly soluble precipitates would be expected, except possibly after long exposure times.

Chemical analysis of leachates

Analysis of elements (ICP-MS, Agilent 7500), organic carbon (DOC, Schimadzu TOC-U; also spectrophotometry, HP 8453), sulphate (ion chromatography, Metrohm), as well as pH, were performed following standard procedures.

Characterisation of solid samples

The crushed and sieved shale samples were characterised:

- XRF (Spectro Xepos); chemical composition, major elements
- ICP-MS (after digestion); element composition
- XRD (PRO Powder, PANalytical); mineral phases

No analyses of the surface/mass ratios were made. However, the shale samples originate from the same shale horizon and are crushed and sieved to the same particle size, and no major differences in surface/mass ratios between the four materials are expected.

Results and discussion

Diffractograms (XRD) of the original samples, prior to the leaching, illustrate the presence of major minerals (fig. 1). Differences in phase composition between the materials are minor, except for S and RPS. The peaks corresponding to pyrrhotite and possibly ettringite (as well as pyrite, at 2 *Θ* around 33° and 37°) that are present in S have disappeared in RPS, and the peaks corresponding to calcite have been reduced. XRD before and after leaching (26 d) did not differ significantly.

The elemental composition of the shale, defined by the dominating minerals (*e.g.* feldspars, clays, quartz, as well as calcite, sulphides) is illustrated in fig. 2, based on elemental analysis of the solid materials (by XRF, two size fractions, and by ICP-MS, after digestion).

The four materials originate from the same shale formation, although not from identical locations. Concentrations of major elements are similar in S, WF and BPS, while the concentrations of Mg and Ca (as well as of S and P) are lower in RPS than in the others.

A summary of the concentration levels is given in table 1.

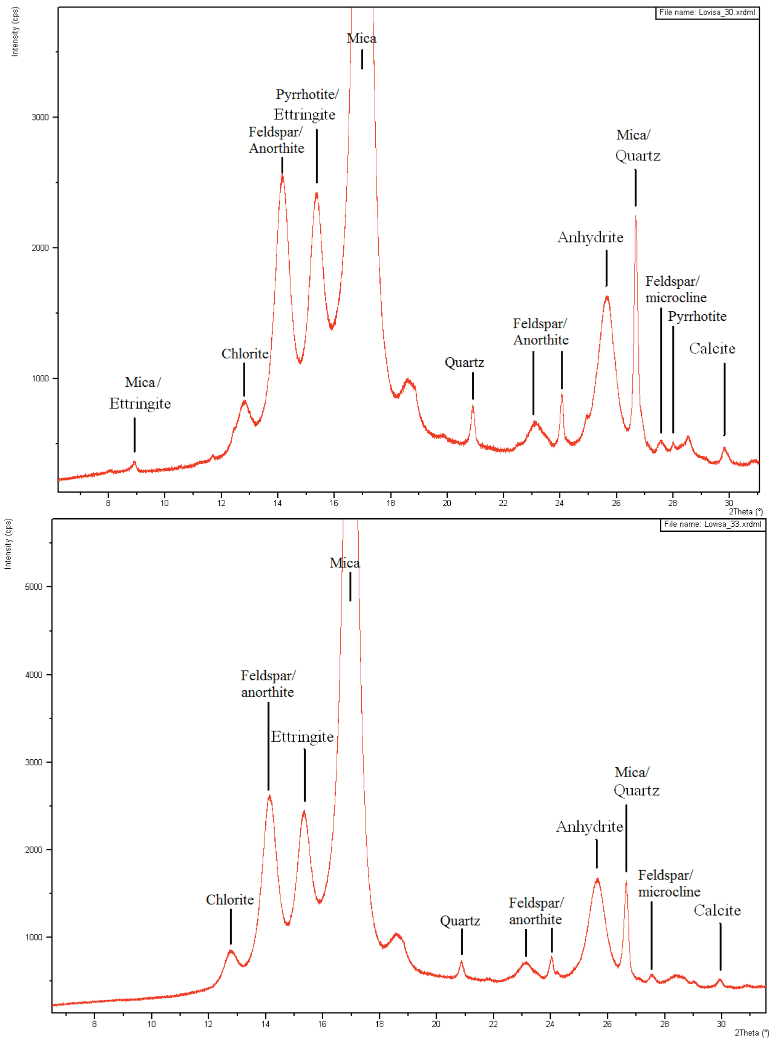

***Fig. 1** Diffractograms for shale S (top) and red processed shale RPS (bottom) (2 Θ from 5 to 30°)*

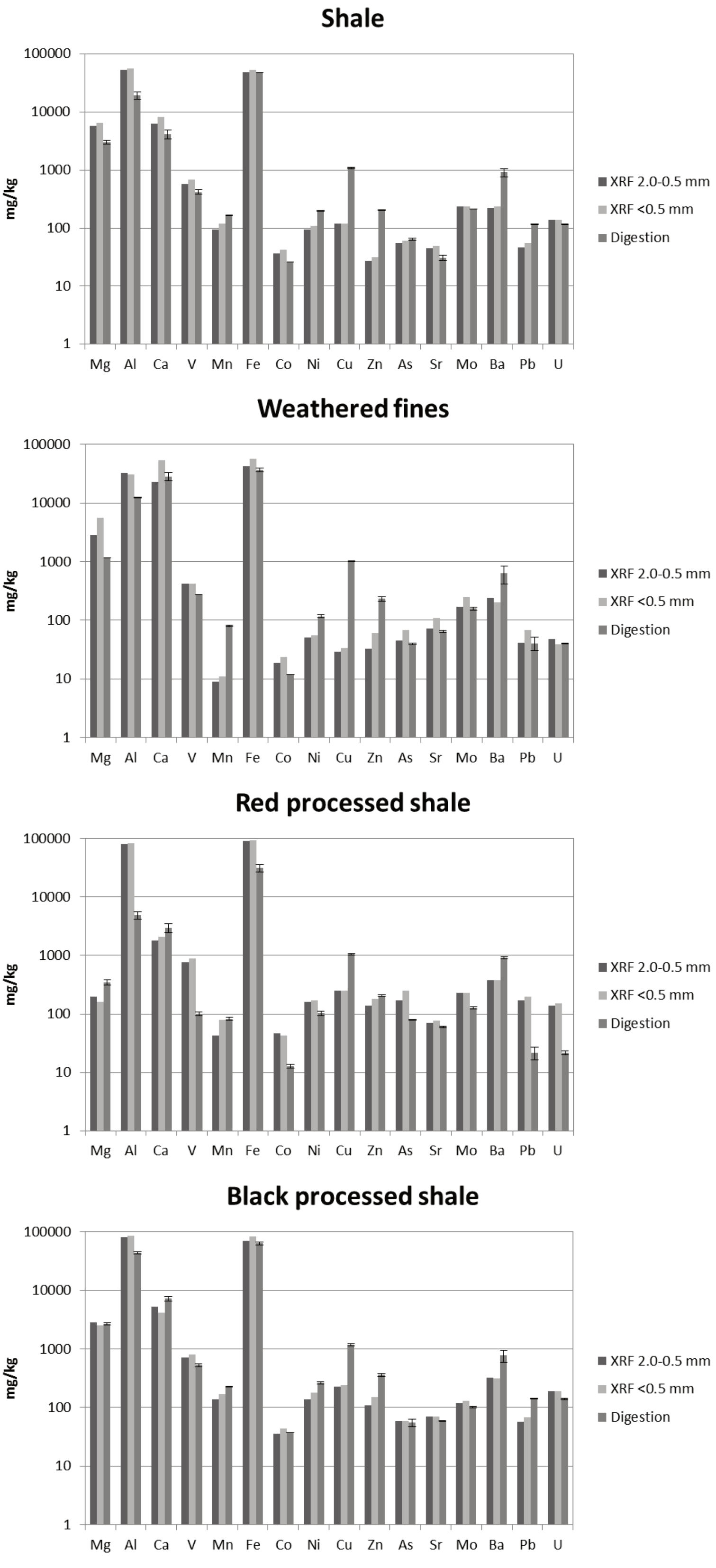

Fig. 2 *Major elements in the shale samples (by XRF, two size fractions, and by ICP-MS, digested samples)*

Conc.	Element
>10 %	Si, O, C
10 – 1 %	Al, Fe, S, K
1 – 0.1 %	Ca, Mg, Ti, P, Na
1000 – 100 mg/kg	V, Cl, Mo, Ba, Y, U, Ta, Cu, Rb
100 – 10 mg/kg	Ni, Mn, As, Ce, Pb, Sr, Ag, Co, Zn, Ga, La, Th, W

Table 1 *Concentration ranges (from XRF) for major and trace elements in the shale.*

Leaching tests

The releases of some major and minor elements from the pH-controlled systems, series (a)-(d), are summarised in table 2. In series (e), the resulting pH after 26 d was 3.0, 2.8, 6.1 and 5.4 for S, WF, RPS and BPS, respectively. The element releases from S and WF in (e) and at pH 3.0 in (a) were almost identical, as well as the releases from RPS and BPS in (e) and at pH 5.5 in (b). No formation of precipitates were observed after 26 days.

Evidently there were still non-oxidized Fe-sulphides in WF (as well as in S) giving pH around 3, but not in RPS or BPS, as confirmed by XRD. The presence of reactive sulphides in WF that had been exposed to the atmosphere and precipitation during some 50 years was unexpected. The minor amounts of carbonates in the processed shales RPS and BPS were not sufficient for buffering pH to levels around 8.

The high releases of Ca (as well as Mg and Sr) at pH 3.0 indicate a progressive dissolution of carbonates, when present, as well as weathering of feldspars and mica.

The release of cationic metals, originally present in the sulphide phase, was minor, except for Ni at low pH (S, BPS) and Co (S). Also the release of U was substantial at low pH. The releases of the elements V, Mo and As were high for all systems at pH 12.5, when the elements would exist predominantly as anions. This is particularly the case for the RPS-samples, where 28 %, 61 % and 55 %, respectively, of the total content were released after only 26 d.

Sulphate is the dominating anion that was released by leaching, besides carbonate. The fractions of the total sulphur content extracted after 26 d were 0.48 %, 1.2 %, 0.10 % and 2.0 % for S, WF, RPS and BPS, respectively. Besides the reduced sulphur (pyrrhotite) in both S and WF there was also sulphate (anhydrite) in all four shale categories.

Organic carbon was detected in all samples, including the pyrolysed (incinerated) RPS,

	S				WF				RPS				BPS			
pH	3.0	5.5	8.5	12.5	3.0	5.5	8.5	12.5	3.0	5.5	8.5	12.5	3.0	5.5	8.5	12.5
Al	0.65	0.14	0.01	0.64	0.42	0.02	0.01	0.02	3.7	0.08	0.08	2.0	0.08	0.01	0.01	0.14
Fe	1.1	0.04	0.01	0.02	0.23	0.01	0.01	0.03	0.02	0.03	0.04	0.21	0.02	<	<	0.01
Ca	**23**	**17**	**10**	0.11	**21**	**20**	**19**	**16**	**10**	3.9	1.0	0.37	**32**	**12**	**5.4**	0.16
Mg	4.1	3.4	1.8	0.04	0.77	0.70	0.55	0.03	2.3	1.2	0.41	0.18	**7.8**	3.9	1.7	0.09
V	0.17	0.01	<	0.69	0.02	<	<	0.26	0.12	0.10	0.15	**28**	0.02	0.03	0.08	**7.0**
Mo	0.35	0.13	0.85	**24**	0.06	0.01	1.8	**24**	0.04	0.19	1.3	**61**	<	0.12	1.0	4.1
Ba	0.80	0.91	0.75	1.0	1.0	1.3	0.92	1.4	0.79	0.90	0.91	1.1	1.2	1.2	1.3	1.4
U	4.5	0.91	0.02	0.22	1.6	0.03	0.01	0.01	2.6	0.14	0.27	0.94	0.13	0.01	0.07	0.19
Cu	0.32	0.06	0.01	0.03	0.12	0.01	0.04	0.06	0.08	0.01	0.02	0.15	0.06	<	0.02	0.32
Ni	**14**	**9.6**	1.3	0.12	0.50	0.37	0.03	0.06	0.13	0.03	0.06	0.04	2.8	0.45	0.05	0.08
Mn	3.2	2.7	0.92	0.04	0.95	0.62	0.01	0.02	**5.1**	0.65	0.13	0.22	**15**	3.8	0.70	0.13
As	0.21	0.08	0.01	**7.9**	0.09	0.01	0.01	1.2	0.16	0.19	0.38	**55**	0.03	<	0.05	4.2
Pb	0.26	0.07	0.02	0.02	0.01	<	0.03	0.02	0.02	0.05	0.07	0.27	<	<	<	0.02
Sr	**5.6**	4.0	2.1	0.54	**7.8**	**6.9**	0.88	**7.6**	3.0	0.47	0.39	0.50	**5.0**	1.5	0.92	0.39
Co	**18**	**13**			0.72	0.44							4.4	0.38		
Zn	1.0	0.64	0.07	0.05	0.31	0.06	0.04	0.07	0.34	0.05	0.05	0.07	0.31	0.04	0.02	0.03

Table 2 *Percentage leached of total element content after 26 d.*

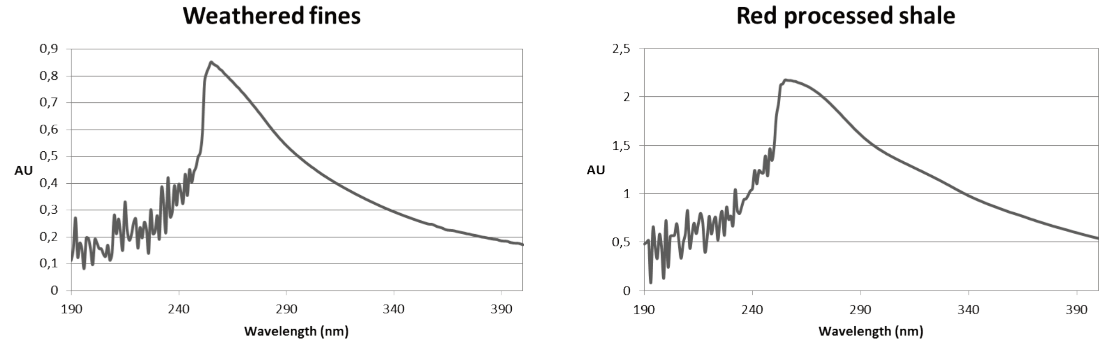

***Fig. 3** Absorbance spectra for WF (left) and RPS (right), (26 d, pH 12.5)*

as illustrated by the absorbance spectra of the leachates at pH 12.5 after 26 d, fig. 3. This organic material corresponded to a concentration (from DOC in solution) of some 30 mg C/kg for S and 100–150 mg/kg for WE, RPS and BPS. This is largely secondary carbon from coatings of biological origin that has been accumulated during more than 50 years of exposure to precipitation and the atmosphere. The highest level was obtained for RPS which evidently creates a local regime of pH around 6, to compare with pH<3 for WF.

Conclusions

Extraction of cationic elements was substantial (several percent of the total content) for Ca and Mg, as well as for Ni, Co and U at low pH, and very high (up to 50–60 %) for anionic elements (V, Mo, As) at pH 12.5. Especially the high-temperature processed shale would be a potential As and Mo source at high pH. The pH-dependence of the weathering processes must be considered when future remediation (or metal recovery) strategies are designed.

The continued release of metals, as well as the formation of secondary minerals (and alterations of the original phase composition) will be studied in the continuation of the project (sampling and analysis after 4 months and 20 months).

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