Stability of weathered shales at water field capacity in the presence of Aspen wood shavings

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Abstract Residues from weathered shales of different origins (Ronneburg, Germany and Kvarntorp, Sweden) were stratified with Aspen (*Populus tremula*) wood shavings as a carbon source in 50 mL test tubes and held at water field capacity during 12 weeks of incubation. Naturally occurring microflora was used, pH in the systems was not adjusted and samples were stored in the dark at room temperature. Results are showing that the overall metal recovery from Kvarntorp shale was generally higher than from Ronneburg shale and most elements analyzed follow the same leaching pattern, where increasing leaching rates could be seen after 6 weeks of incubation. An external carbon source appears to enhance metal dissolution over time, whereas metal dissolution from abiotic water leaching in general would decrease.

Key Words shale, weathering, heterotrophic leaching

Introduction

Historically, the industry has suffered from an excess over demand, but with increasing world demand and growing scarcity of high-grade ores, metal prices have increased immensely (Metals & Mining Industry Outlook 2011). Moreover, rising energy cost and environmental regulations make it urgent to develop sustainable solutions for mining, metal processing and also metal recovery. There exists large amounts of low-grade material which can be used as a source for metal recovery even though it is very expensive with conventional techniques. Microbial leaching technologies are being used for the recovery of copper, gold, uranium and zinc and mainly three groups of microorganisms are used in bioleaching: chemolitoautotrophic bacteria, heterotrophic bacteria and heterotrophic fungi (Brombacher *et al.* 1997).

The ability of microorganisms to leach metals from solid materials comprises several principles, (i) redox reactions, (ii) the formation of inorganic acid, such as sulphuric acid, and (iii) excretion of organic acids, as complexing agents (Krebs *et al.* 1997). Redox reactions are based either on electron transfer caused by direct physical contact between the solid phase and microorganism or on bacterial oxidation of Fe^{2+} to Fe^{3+} (acid or neutral solutions). Formation of inorganic acids, e.g. sulphuric acid, leads to lowering of pH and thus an increase in increased solubility for several elements. Low molecular weight organic acids, such as oxalic and citric acid, are known leaching agents excreted from fungi and they act as complexing agents as well as decreasing pH and therefore assisting in metal dissolution by two in principal different mechanisms.

Shales contain significant concentrations of organic carbon which may supply energy for heterotrohic microorganisms and hence mediating the chemical leaching process of the shale. Microorganisms play important roles in transformation of organic matter in geological environments, e.g. the weathering of shales (Anjum 2010). The fractured rocks display a broad diversity of microorganisms, for example strains of *Acinetobacter, Clostridium, Comamonas, Pseudomonas* (Petsch *et al.* 2005), *Bacillus* and *Microbacterium* (Matlakowska and Skodlowska 2009). The uranium-bearing black shale of Ronneburg, near Gera inThuringia, is rich in pyrite and organic matter and originates from Ordovician, Silurian and Devonian time (Witzke 2004).

Swedish black shale (commonly denoted alum shales) is from Cambrian to early Ordovician time. This organic-rich shale has been processed for petroleum and also for uranium (Dyni 2005). Here we report on the metal leaching from weathered shale from Kvarntorp, Örebro (Coordinates from where the shale has been retrieved: 59° 07' 12.02" N, 15° 16' 29.93" Ö) and from Ronneburg, Germany (Coordinates: 50° 51' 10.18" N 12° 10' 31.33" E) when they were supplied with aspen (*Populus tremula*) wood shavings as carbon source.

Methods

Air dried Kvarntorp shale (KT) and Ronneburg shale (RB) with particle size 0,55—0,9 mm were stratified with Aspen wood shavings (Asp) in 50 mL Sarstedt tubes. The Sarstedt tubes had been prepared with 5 holes (diameter 3 mm) in bottom and a hole (diameter 10 mm) in the lid for aeration and sampling. The holes were covered with a fine nylon net to avoid loss of material during the experiment. The aspen wood shavings were stored at -30°C before use and the dry weight was estimated to 54%. Four replicates were set up for each material as well as for controls with only aspen

wood shavings. Approximately 5 g of LD, KT and RB was used in each tube. Before put into a glass humidor and held at field capacity, the tubes were filled with deionized water, allowed to drain for 1 hour and the first sampling was conducted by letting 50 ml deionized water flow through the tubes by pouring through the net in the the top. The leachate was collected in new 50 ml Sarstedt tubes and adjusted to a volume of 50 ml for further analysis. The humidor was kept at room temperature in the dark and sampling was conducted once a week for the first 6 weeks of incubation and then at week 8 and 12.

Microwave assisted digestion of RB shale, KT shale and Asp was performed in concentrated HNO_3 for 1 h at 180 °C, 1200W and analyzed for metal content with ICP-MS (Agilent 7500 cx) as a reference for acid leachable metal concentrations (Sjöberg 2011).

Analytical procedures are given in Karlsson *et al.* (2011). In brief, after leaching, pH was measured in the aqueous phase and was then analyzed for metal concentrations sulphate, fluoride, chloride, nitrate (ion chromatography), dissolved organic carbon (Shimadzu TOC-V analyzer) and low-molecular weight organic acids (capillary electrophoresis). Leachates were checked for microorganisms by light microscopy both as live preparations and gram stained for bacteria.

Results and discussion

Metal dissolution from KT shale was generally higher than from RB shale. For the elements presented here, the highest release of took place at week 0 or 1 for 10 out of 11 elements for KT shale (Table 1). Highest release of metals from RB shale occurs at week 0 or week 1 for 9 out of 11 elements and for LD-slag at week 0 and 1 for 6 out of 11 elements (Table 1).

After a systematic decrease in metal dissolution, an increase could be observed after week 6 in both RB shale and KT shale for the elements Mn (Figure 1,2), Fe (Figure 3,4) and Zn (Figure 5,6). Also Mg, Al, V, Sr and U displayed the same leaching pattern as the elements shown in the graphs.

The initially high concentrations of soluble metals in the first leaching at week 0 is interpreted as a result of dissolution of secondary precipitates, possibly in combination with desorption. After this period in a truly abiotic water leaching system we should expect decreasing metal concentrations over time until the mineral/water equilibria are established. As demonstrated by Karlsson (2011b) this is what happens for KT shale. In this study with an external carbon source it is obvious that the phase with lowering of soluble metals is followed by an increased release. This might of course be related to changing mineral equilibria but there are no evidence for that according to the composition of general hydrogeochemical parameters in the leachates. For instance, the variations in pH were quite moderate in both systems and in the KT shales it increased slightly (Table 2). Further, increasing metal release was not observed by Karlsson (2011b) during abiotic leaching. Since the concentrations of DOC correlated rather well with the concentrations of aqueous metal species it seems more likely that the increased release of metals was related to this parameter. Under these conditions, the principal mechanism of solubilization would be of complexometric character, possibly in relation to changes in electron activity.

Live and gramstained samples from the RB shale and KT shale, respectively revealed a broad diversity of microbial forms (Table 2). An exten-

Element	RB shale (% of ref)	KT shale (% of ref)	Highest release from RB shale (week)	Highest release from KT shale (week)
Mg	2,88	4,24	1	0
V	0,02	0,2	0	0
Al	0,03	0,36	12	0
Cr	0,13	4,24	8	2
Mn	27,27	16,84	1	1
Fe	0,18	0,47	1	1
Cu	2,55	5,91	0	0
Zn	7,39	44,67	1	1
Sr	5,91	6,36	1	1
Ba	0,24	1,75	0	0
U	0,45	1,61	0	0

Table 1 Metal release (% of reference) and incubation week of highest release from RB shale and KT shale.

Table 2 Microbial growth in leachates from RB shale and KT shale, visible and by light microscopy.

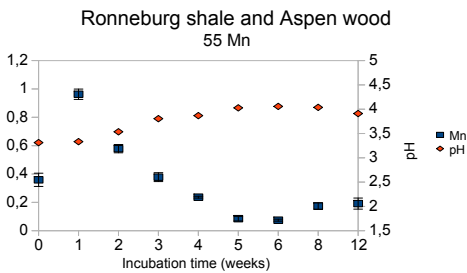| Material	Visible growth in Sarstedt tubes	Microscopic observations
RB shale	Dark green growth in solution at bottom of tube.	Fungus
		Bacteria: gram[+] and gram[-], cocci and rods, motile and non motile.
KT shale	Dark green growth in solution at surface, dark green and white growth in solution at bottom.	Fungus
		Bacteria: gram[+] and gram[-], cocci and rods, motile and non motile.

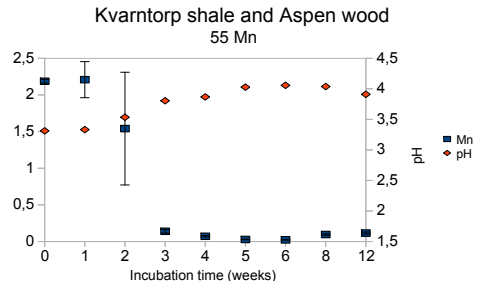*Figure 1 Concentrations of manganese in leachate from RB shale and Aspen wood as a function of time.*

Figure 2 Concentrations of manganese in leachate from KT shale and Aspen wood as a function of time.
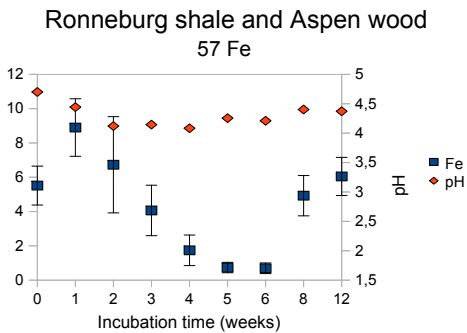

Figure 3 Concentrations of iron in leachate from RB shale and Aspen wood as a function of time.
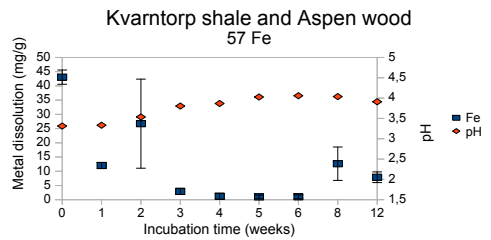

Figure 4 Concentrations of iron in leachate from KT shale and Aspen wood as a function of time.
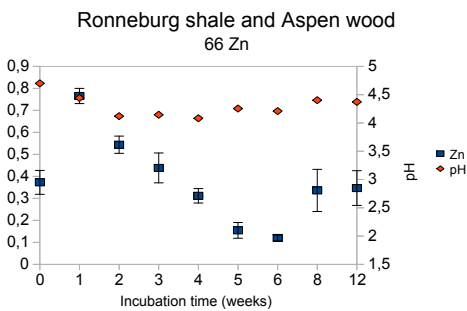

Figure 5 Concentrations of zinc in leachate from RB shale and Aspen wood as a function of time.
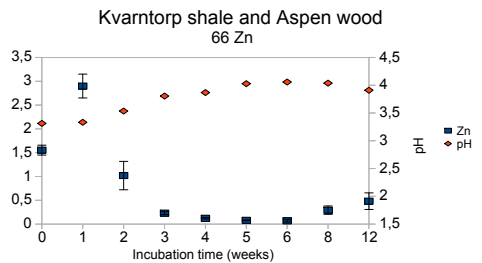

Figure 6 Concentrations of zinc in leachate from KT shale and Aspen wood as a function of time.

sive microbial growth was found in the leachate from incubation week 0 in all samples. Both fungi and bacteria were observed from week 0, but microscopy observations show that there is a lowered microbial diversity in the leachates from week 1—12 where no fungus could be observed. Bacteria were still observed, both gram$^+$ and gram$^-$ but not to the extent as from week 0. This behaviour indicates that the microbial diversity in the materials would either be influenced by the properties of secondary minerals or that it reflects a time dependent competition for some resource(s).

Shales are often rich in pyrite and other sulphides and their oxidation is dependent of O_2 supply, microbial activity, surface susceptibility and pH (optimum between 2—3) and the complete oxidation generates sulphate (Sartz 2010). The sulphate concentrations were approximately 10 times higher in the leachate from KT shale in comparison with the RB shale at week 1 (Table 3) which roughly corresponds to the S amount in the materials. As a result KT shale generates a lower pH in the leachates than RB shale, at least initially. With time, the difference is lowered and after week 6 they are within 0.5 pH unit. Thus, both systems contains buffering constituents in this pH range but they are not known in detail. It seems likely, however, that the production of DOC might be involved.

Changes in DOC concentrations follow, more or less, the same pattern in both shales. There is a slight difference in KT shale systems where a lower initial pH evidently leads to a higher degradation rate of the carbon source (Table 3). Although the pH might have a direct impact on the rate on cellulose/lignin hydrolysis in acidic systems other mechanisms might also be involved. For instance, if the original microbial communities were different this might also be reflected by the rate of hydrolysis and possibly also on the spectrum of products. Since the concentrations of DOC in leachates from the shales corresponds quantitatively to the release of most elements discussed here it is also essential to include the qualitative features of the DOC.

Table 2 Microbial growth in leachates from RB shale and KT shale, visible and by light microscopy.

Material	Visible growth in Sarstedt tubes	Microscopic observations
RB shale	Dark green growth in solution at bottom of tube.	Fungus
		Bacteria: gram$^+$ and gram$^-$, cocci and rods, motile and non motile.
KT shale	Dark green growth in solution at surface, dark green and white growth in solution at bottom.	Fungus
		Bacteria: gram$^+$ and gram$^-$, cocci and rods, motile and non motile.

Table 3 Dissolved organic carbon (DOC), sulphate, fluoride, chloride and nitrate from RB shale and KT shale.

material/analysis	week 1	week 2	week 3	week 4	week 5	week 6	week 8	week 12
RB/DOC (mg/L)	53,0	42,0	33,0	20,4	33,4	29,4	31,1	36,8
KT/DOC (mg/L)	85,5	66,9	38,7	32,2	38,1	31,4	35,0	29,7
RB/SO_4^{2-} (mg/L)	3,47	5,36	5,34	-0,71	5,33	4,02	4,97	5,20
KT/SO_4^{2-} (mg/L)	33,1	2,40	6,31	-0,05	3,06	3,50	5,44	7,51
RB/F^- (mg/L)	0,11	0,08	0,12	0,02	0,16	0,11	0,26	0,23
KT/F^- (mg/L)	0,15	0,01	0,14	0,06	0,11	0,13	0,09	0,13
RB/Cl^- (mg/L)	0,54	0,1	0,09	0,62	0,09	0,09	0,42	0,31
KT/Cl^- (mg/L)	0,5	0,09	0,18	0,18	0,14	0,24	0,56	0,38
RB/NO^{3-} (mg/L)	0,08	0,09	0,09	0,09	0,09	0,09	0,09	0,09
KT/NO^{3-} (mg/L)	0,26	0,09	0,09	0,09	0,09	0,09	0,09	0,09

Citric, oxalic, adipic and acetic acid were found in the leachates from both RB shale and KT shale and are well known for their complexing capacity. Organic acids can be produced by fungi in the presence of heavy metals and lead to immobilization of metals or to the formation of soluble metal complexes (Arwidsson Z 2009). Highest concentrations of organic acids was seen during the first two weeks of leaching followed by a decrease which might be explained by the high concentrations of DOC during week 0 and 1. Nutrient supply is crucial for the exudation of organic acids and also the prevention of degradation of exudates since they display an easily acessible carbon source for microorganisms.

Conclusions

Initially high metal concentrations in the leachates from the shales are attributed to the solubility of secondary precipitates, and possible desorption. In a second stage of the process the systems seem to go towards mineral equilibria but for most elements this is interrupted after some six weeks of incubation. Microbial mineralisation of the aspen wood shavings have then altered the hydrogeochemical conditions in favour of metal release through acid hydrolysis of the carbon source. As a consequence pH is within 0.5 unit in both systems but the leaching efficiency differs. Metal dissolution is generally higher from KT shale than from RB shale, indicating the impact from different mineralogies. The results show that heterotrophic leaching is a feasible alternative but needs to be optimised for different shales. Moreover, great care should be taken in remediation programmes where increased pools of carbon might get in contact with shale residues since results from this study show an impact of microbial use of easily accessible carbon sources, leading to changes in metal distribution in the environment. Nevertheless, there should be great possibilities to develop heterotrophic leaching systems for remediation of contaminated soils and waste materials but also for metal recovery that would be both environmentally and economically sustainable.

Acknowledgements

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