Retention of Fe-oxide colloids in a black slate environment

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Abstract Schwertmannite and ferrihydrite (Fh) colloids from an AMD system are characterized to elucidate their retention behavior in a black slate environment. The Fe-colloids are 3 to 300 nm in size. About 20 % of the Fe in the acidic suspension (incl. Fe-colloids) can be retained at the host rock's surface of the inside mine drainage. In the outside drainage, only 0.2 % of the released Fe can be precipitated and retained as Fh at black slate substrate. The remaining Fe remains in solution. The precipitated/retained Fh is very effective in removing Pb, U and Cd from the solution.

Key Words Black slate, Ferrihydrite, AMD, Colloidal retention, Fe-mass-balance

Introduction

This study is concerned with the retention of Fe-oxide colloids in an AMD system in a black slate environment. The retention of colloids is of particular interest, because colloids are well-known as carriers of hazardous elements (McCarthy and Zachara 1989). The following investigations are done to get insight in the natural retention potential: (1) Fe-oxide colloids, which are formed due to oxidative weathering of Fe-sulfides, are characterized concerning mineralogy, size, shape and surface charge. (2) The sorption behavior of Fe-precipitates is investigated with respect to abundant elements (Pb, U, Cd). (3) A Fe-mass-balance (sink/source) is calculated to contrast the amount of dissolved Fe inside the mine (low pH) with the outside released Fe (neutral pH). The difference of these Fe-concentrations provides information about the retained Fe inside the mine. (4) Retention experiments with structured particle collectors are performed to estimate the amount of retained Fe in the outside drainage system.

Geological Setting

The investigated mine and its drainage system is located in low-grade metamorphic rocks of the *Thüringisches Schiefergebirge* mountains in Germany (fig. 1). The mine was built in black slate strata of Silurian age. In the 17th to 19th century the mining was focused on the winning of vitriol and alum. In the 1950s the mine was explorated for uranium. Since the 90s it is open to the public (Müller 1994).

The drainage system of the mine consists of three parts (fig. 1). There is an inside drainage, comprising an acidic and a buffered part. At the adit mouth (AM) the inside drainage is released. Afterwards the outside drainage flows in a buffered creek to a tailings pond (TP). In the acidic part constant pH (≈ 3) and Eh (≈ 770 mV) conditions prevail with only slight local and seasonal fluctuations (tab. 1a). This indicates that the solution was in a metastable state concerning iron speciation. Aqueous Fe^{2+} and Fe^{3+} coexist with solid Fe^{3+}, e.g. as schwertmannite (Bigham *et al.* 1996). The drainage of the acidic solution/suspension occurs over three levels, which are linked in an adit system. The uppermost level is represented by sample site OS, the floor level by site TS. From site TS the drainage flows through the fractured black slate to the adit mouth. This part of the drainage is carbonate buffered due to an overlying limestone. In the fractured black slate the linear flow velocity is 16.4 m/d (Hoch 1999) (tab. 1a, b). Hence, the drainage needs 6.8 d for the distance TS-AM (112 m). At AM a clear solution of neutral pH (≈ 6.8) pours out. Only orange-red incrustations covering the black slate reveal precipitation of Fe-oxides. Furthermore, after collection of a clear water sample, precipitation occurs after a few minutes in the sample vessel. At AM, both redox potential (Eh ≈ 280 mV) and O_2 concentration (0.3 mg/L) are quite low. These are typical values for iron springs under neutral pH conditions. In such environments Fe(II) oxidizing bacteria are responsible for the precipitation of ferrihydrite (Konhauser *et al.* 2011). The drainage flows 50 m behind AM in a creek. Now the drainage contains clearly orange-red particulate matter. Suspended Fe-oxides and incrustations can be traced up to 500 m downstream. Then they thin out and are no longer observable near TP.

Methods

Mineralogical composition of precipitates was analyzed by XRD. Size and shape of precipitates were investigated by SEM and PCS (Photon Correlation Spectroscopy). Surface charge was measured by electrophoretic mobility. Chemical composition of the suspensions was analyzed by ICP-OES/MS. For the analytical background the reader is referred to the standard literature. Titration/precip-

Table 1 a) Physicochemical and b) hydrodynamic parameters of the Morassina mine (n.m. not measured).

a)

locality	OS		TS	AK	AM	SW	SS3	TP
d(AM) [m]	237		112	115	0	50	200	700
date 2000	09-10	01-03[a]	01-03[a]	09-10	09-10	09-10	09-10	
pH	2.9	3.4	3.3	6.3	6.8	7.0	7.2	7.9
Eh [mV]	775	764[b]	n.m.	n.m.	280	n.m.	276	491
Alk [mg/L]	0.5	n.m.	n.m.	n.m.	154.5	42.3	n.m.	n.m.
O$_2$ [mg/L]	n.m.	5.9[b]	n.m.	n.m.	0.3	n.m.	10.2	n.m.

b)

rainfall[c]	A$_{catch}$[d]	Q1$_{AM}$[d]	Q1$_{SW}$[d]	Q2$_{AM}$[e]	v$_f$(d)[d]
[mm/a]	[m²]	[L/d]	[L/d]	[L/d]	[m/d]
1200	300000	472399	50164	1537588	16.4

[a] Morassina Mine Data (Klaus Müller)
[b] Morassina Mine Data (Klaus Müller), 1992 - 1998, at different localities in the acidic drainage
[c] Schmiedefeld, DWD (average 1961 - 1990)
[d] Hoch (1999); Q values are mean values for 1999
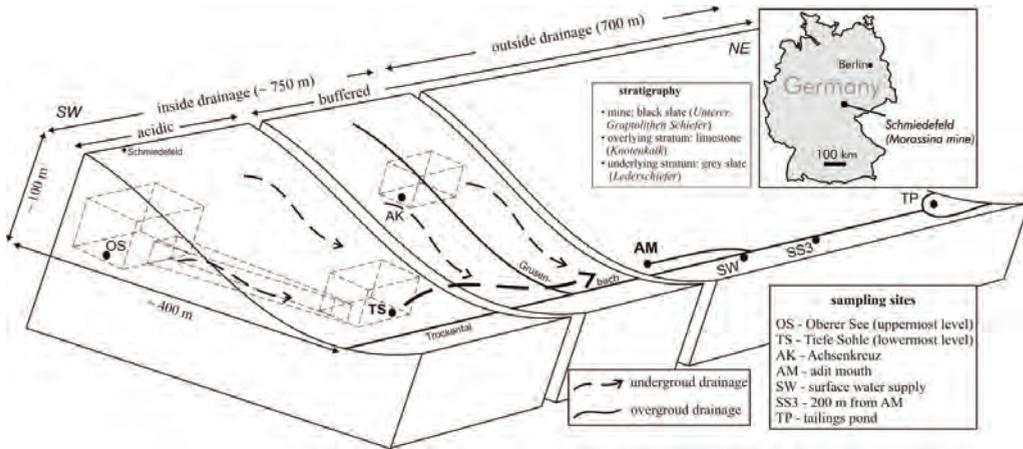[e] date of measurement 12/14/2010

Figure 1 Drainage system of the Morassina mine in Schmiedefeld (Thuringia, Germany) (not to scale).

itation experiments with acidic mine water were performed with 0.1 M NaOH up to pH values of 4.6 and 7.2. The chosen hydrolysis rate was 135 µmol OH/mmol Fe/min. VSI (Vertical Scanning Interferometry) was used for the quantification of deposited particles (Darbha *et al.* 2010).

Results & Discussion

Characterization of secondary Fe-oxide minerals: mineralogy, size, shape, surface charge

The secondary minerals inside the mine were characterized by Ullrich *et al.* (2005). There, schwertmannite (Sh) and diadochite are the dominant minerals. This study confirms this indirectly by precipitation experiments. At first, the primary ex situ precipitates of sample solution OS consist of 2-line ferrihydrite (2LFh). But within 2 months, the 2LFh converts into Sh in an unbuffered suspension (tab. 2).

The precipitates in the outside drainage consist mainly of 2LFh (tab. 2). This is primarily investigated at the orange-red incrustations covering the streambed. Directly at AM, where there is no influx of surface water (fig. 1), the incrustations consist of 2 and 6LFh as well as goethite (Goe). In the further drainage, now mixed with surface water (fig. 1, tab.1b), 2LFh is the main mineral forming incrustations. No better crystalline Fe-oxide-hydroxide was found. Precipitates from a suspension sample from AM, taken under a high

volumetric flow rate (Q2$_{BAM}$B, tab. 1b), consist as well of 2LFh. It follows that at least for the diluted drainage the rate of hydrolysis is sufficiently high to precipitate 2LFh only. The mineral assemblage at AM could be an indication for varying seasonal or past hydrolysis rates. On the other hand, the better-crystalline Fe-oxides could be a result of internal transformation (Kukkadapu *et al.* 2003).
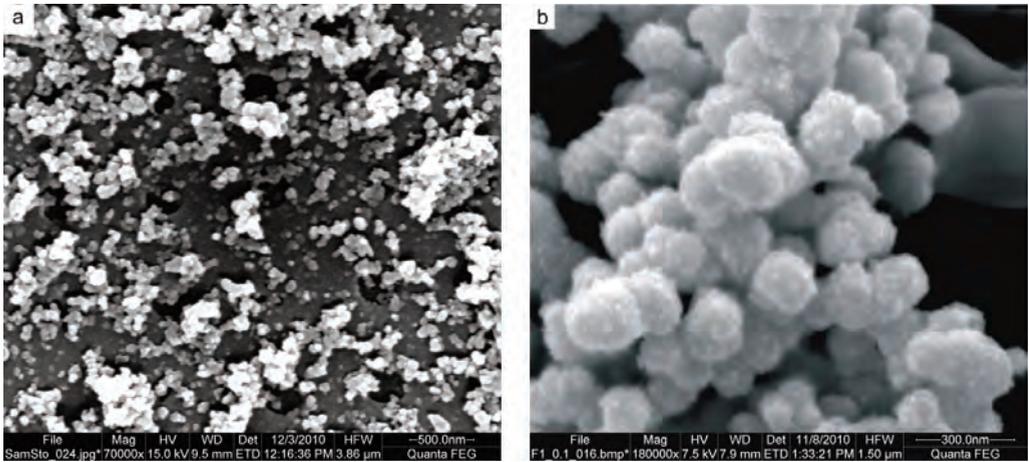
SEM analyses show that the smallest distinct particles in the acidic solution captured onto structured particle collectors and onto filters are of colloidal size. The smallest colloidal particles are about 10 nm in size (fig. 2a, tab 2). Maximum size of distinct particles is 120 nm. The size of aggregates is up to several hundred nm after 2 weeks of particle deposition on the traps. The shape of the colloids is nearly spherical. In aggregates the spheres are put together in a so-called pin-cushion structure. Such a structure is typical for natural Sh. Furthermore, the occurrence of colloids in the acidic solution can be confirmed by PCS size-analysis (tab. 2). Colloids of a raw (unfiltered) sample from site OS have an average hydrodynamic diameter - weighted by number - of 130 ± 20 nm.

The zeta potential of the suspended Fe-oxides at site OS is 7.5 ± 6.1 (tab. 2). It is assumed that the Fe-colloids are stable in the acidic solution with a tendency to agglomerate onto retaining substrates (fig. 2a).

Fh particles at AM and the subsequent outside

Table 2 Mineralogy, size and surface charge of the particulate drainage. (n.m. not measured, n.d. not detected).

			locality	OS	AA	AM	SS2	SS3	SS4	SS5
			d(AM) [m]	237	193	0	35	200	270	370
			pH	2.9	2.8	6.8	6.9	7.0	7.2	7.3
mineralogy	XRD			(2LFh, Sh)	(Sh)	2LFh, 6LFh, goe	2LFh	2LFh	2LFh	
size	SEM	upper limit	[nm]	80	120	70	n.m.	175	n.m.	200
of distinct		lower limit	[nm]	40	10	20	n.m.	25	n.m.	n.d.
particles	TEM	lower limit	[nm]	n.m.	n.m.	3 - 6	n.m.	n.m.	n.m.	n.m.
	PCS	raw	[nm]	130(±20)	n.m.	n.d.	n.d.	n.d.	n.d.	n.d.
		<1.2µm	[nm]	n.d.	n.m.	281(±46)	303(±49)	338(±53)	277(±43)	259(±40)
surface	zeta-	raw	[mV]	7.5(±6.1)	n.m.	−2.2(±5.2)	−1.1(±6.4)	−5.4(±4.8)	−5.9(±6.1)	n.m.
charge	potential	<1.2µm	[mV]	n.d.	n.m.	−2.7(±4.2)	−1.5(±5.8)	−5.7(±6.0)	−7.4(±5.7)	n.m.

Figure 2 a) Sh colloids onto structured collector between OS – TS. b) Fh colloids onto a membrane filter (AM).

drainage are also of colloidal size and spherical in shape. SEM analyses show that the smallest spheres have diameters of about 20 nm (fig. 2b, tab. 2). A TEM study of Fh from AM reveals that the smallest Fh particles are 3 – 6 nm in size. Both methods show that biggest spheres have diameters up to 300 nm. Moreover, SEM images (c.f. fig. 2b) show that bigger spheres are built up of smaller once, giving the agglomerates, like in the case of Sh, pin-cushion structure. At artificial particle collectors the spherical Fh aggregates agglomerate to aggregates of tens of microns in 16 h. This agglomeration tendency at AM is supported by zeta potential data of precipitates around 0 mV. PCS analyses of the Fh suspensions reveal no reliable results for unfiltered samples, because of the presence of large aggregates. Filtrates of the suspensions (< 1. 2 µm), analyzed after gentle disaggregation with an end-over-end turner, provide more conclusive results. Their number weighted diameters range around 290 nm (tab. 2). A clear gradient for the investigated distance down-stream (370 m) could not be identified. The PCS results match up well to the SEM-identified pin-cushion Fh, whose maximum size is up to 300 nm. Furthermore, the feasibility of PCS analyses indicates that aggregates in the outside drainage can be easily disaggregated. Hence, very turbulent flow in the drainage may be sufficient to disaggregate the Fh agglomerates. This could enhance the colloidal mobility in the suspension.

Coprecipitation/adsorption

Pb, U and Cd occur in high concentrations in the Morassina mine drainage (fig. 3). These elements were chosen to study their coprecipitation and adsorption behavior with respect to the Fe-oxide precipitation.

In ex situ precipitation experiments with acidic solution from site OS, Fe is completely precipitated (fig. 3a). Although the primary precipitates consist of Fh, S is strongly associated with the solid phase (4.4 %). The Fe/S ratio of the solid is 12.3. This is indicative for Sh. However, in the pre-
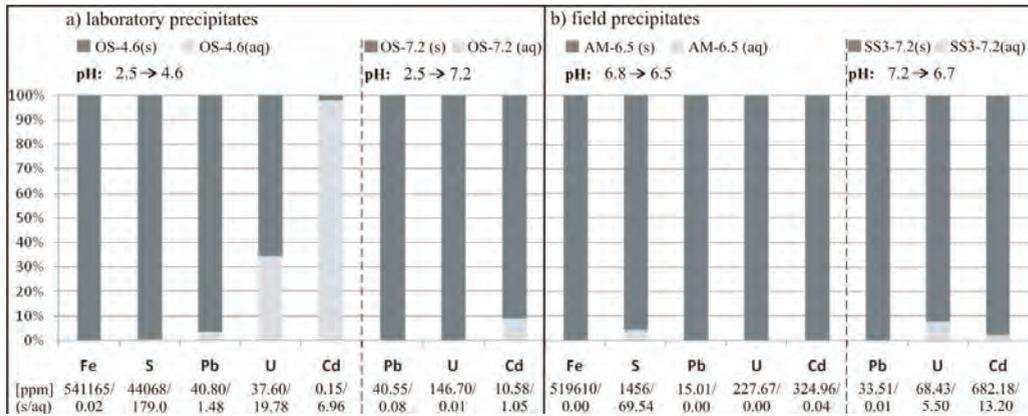
Figure 3 *Fractions of precipitated vs. dissolved elements for Fe, S, Pb, U and Cd (for explanation see text).*

cipitation experiment up to pH 4.6 Pb is almost completely enriched in the Fh phase (95.5 %). 65.5 % of the U is associated with Fh, while Cd remains almost completely in solution (97.9 %). If the precipitation experiment is accomplished up to pH 7.2, both Pb and U are completely removed from the aqueous phase. Only a considerable fraction of Cd stays in solution (10.6 %). These results suggest that most of the Pb is precipitated alongside with Fe and S, while U and mainly Cd adsorb at higher pH values to the Fe-oxide surfaces. These findings are in accordance with previous studies of Webster *et al.* (1998) and Zänker *et al.* (2003).

Undiluted outside drainage solution can be precipitated as Fh in a sample vessel. This precipitation is accompanied by a pH decrease (6.8 to 6.5) due to hydrolysis (fig. 3b). The Fh precipitates are different from laboratory ones. Only a small fraction of S is associated with the Fh surface (0.15 %). Like in the laboratory experiment all Pb and U is removed from the aqueous phase under neutral pH conditions. In addition, Cd is precipitated entirely with the Fh. The tendency that Cd can effectively be removed in SO_4-rich solutions by natural Fe-oxides at neutral pH is shown by Webster *et al.* (1998). Interestingly, also U is completely sorbed to the Fh. In the presence of carbonate (tab. 1a) U-carbonate complexes impede partly the U adsorption. Nevertheless, it was shown by Katsoyiannis *et al.* (2006) that as well under alkaline conditions the main fraction of U can be effectively adsorbed

to Fe-oxides-hydroxides. Moreover, the surface charge of Fh at AM ($\approx$ 0 mV) may favor U adsorption.

It is assumed that even in the diluted outside drainage (tab. 1a) not all Fe is entirely precipitated in the creek itself. This is also indicated by a pH drop (7.2 to 6.7). In this precipitation process a considerable fraction of U and Cd remains dissolved. The occurrence of dissolved U can be explained by the presence of increasingly negatively charged U-carbonate complexes up to higher pH values and the increase of negative surface charge at the Fh surface. The presence of dissolved Cd is difficult to explain. Maybe this phenomenon can also be explained by increasing electrostatic repulsion between Fh and Cd-complexes.

Fe mass-balance

The Fe mass-balance compares the amount of dissolved Fe available in the entire mine complex due to Fe-sulfide oxidation and the amount of Fe released at the AM. The difference between the two provides information about the amount of Fe retained inside the mine complex.

Based on measured Fe/S ratios in the acidic drainage an initial $Fe_{(aq)}$ concentration inside the mine related to the Fe/S ratio in pyrite can be determined (tab. 3). The flow time (t_f) of the suspension from TS to AM is used to calculate a maximum potential precipitation rate ($PR(Fe_{(aq)})$). This precipitation rate is linked to an average daily

Table 3 *Comparison of the amount of dissolved Fe inside the mine and Fe released at AM (for explanation see text).*

$Fe_{(aq)}$ [mg/L]	t_f(TS, AM) [d]	$PR(Fe_{(aq)})$ [mg/(L*d)]	$Q1_{AM}$ [L/d]	$PR(Fe_{(aq)}, Q1_{AM})$ [kg/d]	$Fe(Fh_{vessel})_{AM}$ [mg/L]	$Fe(Q1_{AM})$ [kg/d]	$Fe_{retained}$ (%)
157.5	6.8	23.1	472399	10.9	13.4	6.4	40.9

volumetric flow rate (Q1$_{BAM}$B). The resulting precipitation rate gives the maximum amount of dissolved Fe that could be precipitated (PR(Q1$_{BAM}$B)). PR(Q1$_{BAM}$B) is then compared with an average daily Fe release at AM (Fe(Q1$_{BAM}$B)). According to this calculation 40.9 % of the dissolved Fe could be retained in the inside mine complex.

It is clear that the calculated retention potential provides a maximum value, since it is determined by the shortest flow time t$_{brb}$(TS, AM). This is the time to neutralize the bulk of the acidic solution. A minimum retention potential is given by the situation that all Fe dissolved in the inside drainage is released at AM. Then no Fe would be retained in the inside mine complex. Both cases provide boundary values for the Fe retention. It is assumed that the actual retention potential lies clearly away from these boundaries and is rather located around the mean (20 % retention).

Retention of Fh colloids in the outside drainage

Volumetric flow rate was very high during retention experiments (Q2$_{BAM}$B, tab. 1b). According to this the Fe output was very high (Fe(Q2$_{BAM}$B) = 21.0 kg/d). The volume of retained Fh particles at artificial particle collectors and a black slate mounted at AM is shown in table 4a. The amount of retained particles was extrapolated to get a retention rate for the substrate (black slate) in the outside drainage. Taking a retention rate for black slate of 148 mg m^{-2} d^{-1} it can be assumed that in a streamed area of 500 × 0.5 (m^2) a total of 37 g Fe is retained per day. This corresponds to ≈ 0.2 % of the released 21.0 kg Fe. All the other Fe would not be retained. Future investigations have to clarify the further fate of the Fe in the creek.

Regarding the interaction of the negatively charged collectors and the ≈ 0-charged Fh colloids, the retention is more effective for the substrates with a higher specific surface area, expressed here as the surface area ratio F (tab. 4a). Furthermore, on the wafer sample with the higher pore density a higher volume of Fh particles was deposited. But this is only effective taking the relation between pore and particle diameter into account. Fh col-

loids of a diameters up to 300 nm attach preferentially to the edges of spherical holes of a similar diameter (AMO I collector, hole diameter 400 nm). Thus, such a collector is appropriate to retain Fh colloids. A comparative laboratory adsorption experiment with uncharged 1 μm polystyrene particles shows that the particles preferentially adsorb to 1 μm holes (AMO II collector) (tab. 4b). This is proven for a stagnant and a turbulent system. In both retention experiments (field and laboratory) the black slate has a higher retention potential than the two artificial collectors. This cannot be explained with the clearly higher specific surface area of the slate, because depending on the F-value the quantity of adsorbed particles decreases considerably. For this reason further studies will focus deeper on surface heterogeneities of slate-substrates. Furthermore, the development of the Fe-oxide multilayer will be considered. In this sense the interaction of Fe-oxide particles and Fe-oxide incrustations could enhance insight in the natural retention potential of comparable AMD systems.

Acknowledgements

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Table 4 a) Fh quantification at AM. b) Quantification of polystyrene particles in an overhead dip experiment.

traps 4 x 4 (mm²)	a) field retention exp. (16 h), trap AM				b) lab dip retention exp. (1 h, 200 rpm)		
	AMO I[a]	AMO II[a]	black slate		AMO I	AMO II	black slate
pore density [pores/μm²]	1.56	0.16	n.d.		1.56	0.16	n.d.
F (FOV: 93x93 (μm³))	1.23	1.06	5.94		1.23	1.06	6.11
θ (%)	14.41	6.82	20.4		0.868	1.029	1.272
Vol Fh [μm³]/μm²	0.034	0.013	0.049[b]	no I μm	0.011	0.013	0.016
retention rate Fe [mg m^{-2} d^{-1}]	104	39	148				

[a] Si-wafer. AMO I: spherical holes, diam. 0.4 μm, depth 0.115 μm, period. 0.8 μm; AMO II: spherical holes, dia. 1.0 μm, depth 0.115 μm, period. 1.5 μm
[b] The volume of Fh results from a comparison of the θ-values (% of Fh-coverage) obtained from SEM images of slates and AMOs.

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