Mass transport of hydraulically stowed residues in adjacent aquifers in the Ruhr Area, Germany

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Abstract Metal-containing residues were stowed in hard coal mines of the Ruhr Area. Induced by mine flooding highly mineralized groundwater can come into contact with these underground stowed residues. As known from laboratory tests – especially single fracture tests – the mobility of zinc, lead and cadmium increases when adding sodium chloride. In absence of sodium chloride, zinc has the highest mobility, followed by cadmium and lead. With addition of sodium chloride the mobility of cadmium enhanced and becomes higher than the mobility of zinc, this is due to the influence of chloro-complexation which is stronger for cadmium than for zinc. Moreover, it was ascertained that the mobility for oxyanions has an inverse behaviour.

Key words residues, mine flooding, metals, oxyanions, sodium chloride, single fracture experiments

Introduction

From the mid-1980s to 2006 large amounts of residues were used for stowing in hard coal mines of the Ruhr Area, Germany. A mixture of water and fine-grained residues were pumped directly into the goaf, i.e. into the collapsed material of the hanging wall beyond the shield. In case of a contaminant release of these residues the transport initially takes place via flow in fractures. The flow is orientated towards the next receiving level (e.g. nearest gate road). The distance from the stowed residues to the receiving level is at least 100 m in the investigated mining area. A flow through the goaf and country rocks takes place. A major challenge is to find out whether metals can be released from the stowed materials and, in case they were released, the country rocks are able to retard or even hinder their transport. Without retardation or barrier function of the country rocks there is a risk that pollutants reaching the surface via mine water drainage. For this purpose, laboratory tests such as column tests, single fracture experiments and flow cell experiments with typical country rock samples and waters of differing chemical composition were carried out.

Which components are the key players in this investigation of mass transport from the stowed residues?

It is necessary to assess the **country rocks** of the area of stowed residues, in order to make reliable statements on their barrier effect. The Ruhr Carbon depositions are characterised by a regular sequence of mudstone and sandstone as well as seams with an underclay. Especially fine-grained rocks such as clay- and siltstones break in the cavities created by the mining of coal (goaf). Mainly due to the high rock load, the hydraulic permeability is very low. A Carboniferous Ruhr-Sandstone, which outcrops in a quarry in the city of Herdecke in the south of the Ruhr Area was used for laboratory tests. This so-called "Kaiserberg-Sandstein” occurs as a country rock of the coal seams even in very large depths. The effective porosity is low (4.4 %). The mineralogical composition of the sandstone was determined by X-ray diffractometry: main components are 65 weight % quartz and 15 weight % feldspar. The calculated proportion of clay and mica minerals is 19.6 %.

Deep groundwater is water, which existed already in fractures and pores before coal mining started. While mining it still seeps into the mines and in long term, after flooding the mines, it will be the water which comes into contact with the stowed residues. This deep groundwater is always highly mineralized and in general mineralization increases with depth. The NaCl concentration for example already reaches in a depth of about 500 m below ground level the concentration of seawater (approx. 35 g L^{-1}) and the concentration increases steadily to values of up to 200 g L^{-1} at depths of more than 1000 m (Jäger et al. 1990, Wedewardt 1995).

A total of approximately 1.6 million tons of **residues** were stowed; like residues from hard coal-, special waste-, household waste- and sewage sludge incineration, foundry sand and sludges from the chemical industry. Most residues were stowed at least 800 m deep in the underground. Before these residual substances were compressed into the goaf, they were mixed with cement-like additives and water. All data show that the mixture has hardened in the underground (AHU 2017). As seen from elution experiments, high pH-values were found in the case of a reactive contact with water (Jäger et al. 1990, RAG 1993-2004, Klinger 1993, Pass 1997). Since the metal compounds are usually nearly immobile at high pH values, their discharge is prevented. However, remobilization can occur with decreasing pH values and this will occur in the long run (centruries) by mineral transformation e.g. from ettringite to brucite and further mineral dissolution. Analysis of metals, present in filter dusts, showed that both zinc and lead are the dominant metals in a proportion of 80 weight % of the average total metal content. Cadmium has a proportion of approx. 1 weight % (AHU 2017). Due to the large proportions in the residues, due to the toxicity, and the large masses which can be eluted, these metals receive special attention in the risk assessment.

Experimental methods

All experiments were carried out with specimens of sandstone. They were flowed through with a solution of ultrapure water with a concentration of $2{,}5 * 10^{-4}$ mol L^{-1} of the metals lead, cadmium and zinc. The hydraulic gradient was kept constant. Reaching the breakthrough of the metals, the solution was enriched with 100 g L^{-1} sodium chloride. The concentration was analysed in the effluent. Additionally behaviour of oxyanions (vanadate, molybdate and arsenate), the effects of changes in pH and the flow in fractures per se were investigated. Specific electrical conductivity, oxygen content and pH, except the flow cell experiments (due to low flow rates), were measured continuously. In most of the cases the fluorescence tracer sodium naphthionate was used as a conservative tracer. Table 1 shows the boundary conditions for the various experimental setups.

***Table 1** Boundary conditions for the various experimental setups.*

	Flow cells	**Column tests**	**Single fracture**
Rock material	Sandstone cylinders (with and without a single fracture) 0.075 x 0.050 m	8 kg of crushed sandstone	sandstone block with a single fracture 0.30 x 0.30 x 0.10 m
Adsorption surface [m²]	2 x 0.0042 (3D-scan)	20,000 (BET)	2 x 0.096 (3D-scan)
Flow rate [$m^3 s^{-1}$]	undamaged: $5*10^{-12}$ split: $1*10^{-10}$	$2.5*10^{-08}$	$3*10^{-08}$
Temperature [°C]	20	20	17
pH range [-]	-	5.9 – 9.2	5.2 – 7.0
spez. conductivity range [$\mu S\ cm^{-1}$]	-	160 – 135,000	160 – 130,000
Oxygen range [$mg\ L^{-1}$]	<1 $mg\ L^{-1}$	<2 $mg\ L^{-1}$	<2 $mg\ L^{-1}$
Redox range [mV]	-	-	195 – 330
Ø Saturation of samples [d]	50	25	60
Ø Duration of experiment [d]	100	30	14

Flow cell experiments

For Flow cell experiments a latex sheath is pressurized to the surface of the sample in order to suppress edge circulations. Solutions passed through the sample from the bottom to the top with constant pressure. Two different samples were installed in the cells. On the one hand, undamaged sandstone cylinders were used. On the other hand, rock cylinders were scarified with a diamond saw 3 mm on both sides along the longitudinal extension and then split in a controlled manner. The incisions of the saw blade was then sealed with silicone.

The hydraulic conductivity coefficient (K) of the unbroken sandstone ($1.5*10^{-11}$ m s^{-1}) is very low. The sandstone cylinder with the single fracture has the same K-value regarding the matrix, but due to the fracture a faster flow takes place. The K-value is about 3,500 times higher. On the basis of these K-values only the flow through fractures is relevant for the spreading of pollutants in the underground. The spreading through the pore system can be neglected.

Column tests

Crushed sandstone up to a predominant grain size of coarse sand was used as columns filling. The silt fraction was removed by sieving. It was attempted to pack and solidify the material as similar as possible to the original storage density. Three series of experiments were carried out in three different columns (fig. 1).

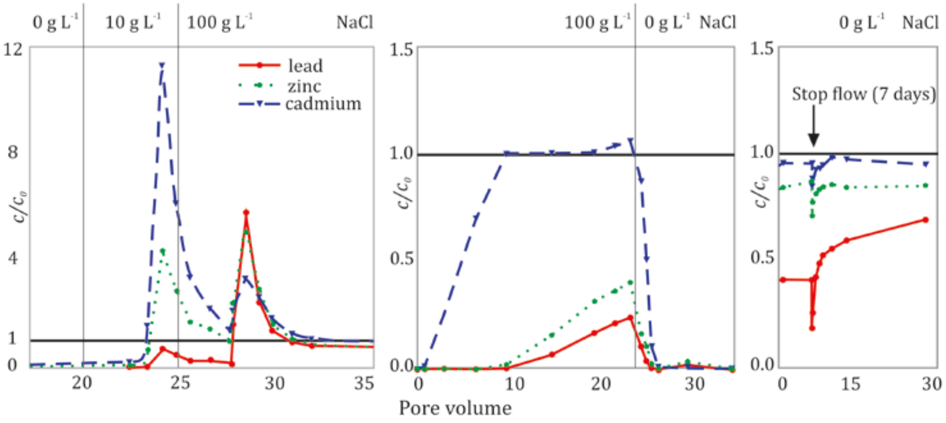

Figure 1 *Metal concentrations in the effluent of the various column tests.*

The first sorption experiment proceeded without NaCl addition. The metal concentrations were normalized to 1, i.e., in the first phase without NaCl, the starting concentration of the input solution was not reached in the effluent. After an exchange of 20 pore volumes, NaCl was added with a concentration of 10 g L^{-1}. As a result, the mobility of all metals was increased significantly (see also: Acosta et al. 2011). The mobility of cadmium increased more than that of zinc and lead. The concentration of cadmium in the effluent even rose to a value 11 times as high as the inflow concentration. This means that the addition has led to extreme desorption processes in the column. The metals sorbed in the first phase were released to a large extent by the addition of NaCl. A further increase to 100 g L^{-1} NaCl leads to a repetition of this effect. Once again the metal concentrations in the effluent increased. By increasing the NaCl concentration to 100g L^{-1} metals not yet desorbed at 10 g L^{-1} were mobilized.

Another sorption experiment was carried out in reverse order. Starting with a NaCl concentration of 100 g L^{-1} resulted in a rapid increase of the metals. Zinc and especially lead do not quite reach the concentration of the input solution. Without NaCl the concentrations in the effluent decreased abrupt to almost zero. From this point the concentrations increased slowly.

As a further experiment, an intermittent flow test without NaCl was performed. The flow was stopped for 7 days. After the stop, significantly lower concentrations in the effluent were measured then before the stop.

Single fracture experiments

In order to investigate the transport of metals in fractures, sandstone blocks were split parallel to the layering. Each half of the split block has the dimensions of 30 cm x 30 cm x 10 cm. So that the diffusion and sorption processes are not superimposed by advective processes due to the suction voltage of an only partially saturated rock matrix, a broadest saturation of the rock matrix was attempted before the tests. The rocks were saturated for 2 months by flowing degassed ultrapure water. In the inlet basin of the experimental setup, the gradient can be adjusted with a threaded rod. Due to the difference in pressure to the outlet basin, in which the water level is fixed, a flow through the artificial single fracture takes place (fig. 2). The outlet basin was limited to a width as small as possible of about 4 mm in order to minimise dead volume of the solution behind the fracture flow.

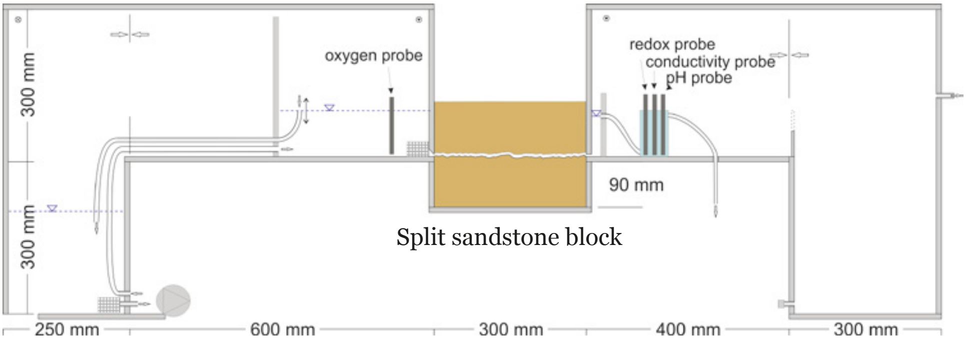

Figure 2 *Setup for the single fracture experiments (side view).*

For a preliminary run degassed ultrapure water was used. For the experimental run this water was replaced by a solution containing fluorescent tracers and metals (cadmium, lead and zinc). The single fracture test without NaCl shows the same phenomenon as the column experiment. Lead sorbs in larger amounts than cadmium and zinc. This was also observed by Himmelsbach & Wendland (1999). By addition of 100 g L^{-1} NaCl an extreme increase in metal concentrations in the effluent was observed. It is interesting to note that the increase of lead in the effluent is almost 13 times higher than the inflow concentration of the metal solution. This is explained by the high sorbed mass of lead in the run-up to the addition of NaCl. Additionally this experiment was carried out for oxyanions (arsenate, vanadate, molybdate). As a result, it was found out that the mobility for oxyanions has an inverse behavior in comparison to the metals of the first experiment A decrease was observed for a rising salinity (fig. 3). In the case of a pH reduction of the input solution to pH 3, due to the buffer capacity of the rock a very slow lowering of the pH value takes place in the effluent of the fracture. Because of this phenomenon, there is no sudden increase in the metal contents.

Experimental results

The sorbed metal concentrations decrease with increasing **salt concentrations** (tab. 2, fig. 4). Cadmium shows the most pronounced effect of 179 mg kg^{-1} to only 5 mg kg^{-1} in the column tests. In the case of zinc and lead, the values are almost three times higher without NaCl in the aqua regia digestion of the column material. It is noticeable that without addition of NaCl cadmium sorbs in larger quantities than zinc. After the addition of 100 g L^{-1} NaCl, it is sorbed significantly less than zinc. This means that the influence of NaCl is most evident for the cadmium mobility. Modeling of the speciation of metals with the software PHREEQC showed that there are mainly free ions during experiments without the addition of NaCl. By adding NaCl the metal-chloro compounds, especially dichloride and trichloride,

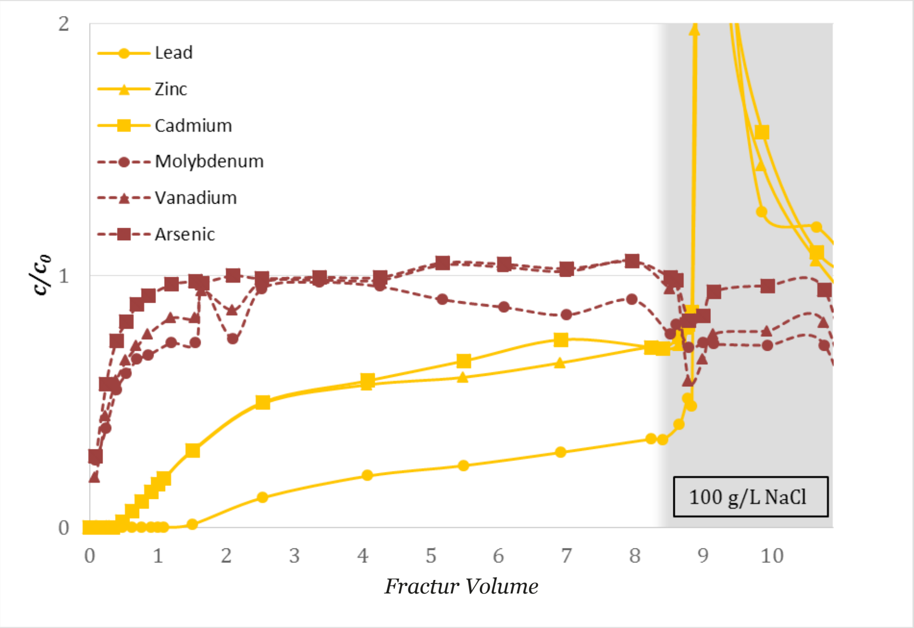

Figure 3 *Metal concentrations in the effluent of the single fracture experiments.*

dominate for lead and cadmium. The neutral to even negative charge of these complexes leads to the higher mobility. Against that, oxyanions are generally negatively charged. On the other hand zinc is mainly present as Zn^{2+} when NaCl is added.

Table 2 *Retardation factors observed in the experiments.*

	R (Cd)	R (Cd +NaCl[1*])	R (Pb)	R (Pb +NaCl)	R (Zn)	R (Zn +NaCl)	R (As)	R (As +NaCl)	R (Mo)	R (Mo +NaCl)	R (V)	R (V +NaCl)
Flow cell	-[3*]	-	-	-	-	-	-	-	-	-	-	-
Column tests[2*]	23	2	55	14	22	9	-	-	-	-	-	-
Single fracture	6.4	1	22	1	6.4	1	1.0	-	1.2	-	1.1	-

[1*] +NaCl -> 100 g L^{-1} NaCl [2*] calculated for the first quarter of the column [3*] still in progress

At the end of a stop flow experiment of 7 days, the concentrations decrease visibly. These experiments showed that in addition to the sorption at the directly accessible sorption sites of the mineral surfaces, **intra-particle diffusion** took place and so a long-term retention of the metals is given. Furthermore low flow rates lead to a significantly higher sorption due to the length of the solution's contact time.

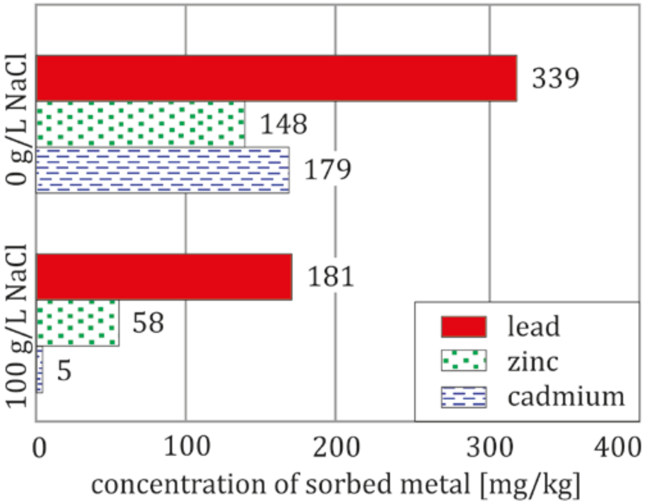

Figure 4 *Sorbed metal concentrations examined of the filling material of the columns.*

The retardation factors for the single fracture experiments are significantly lower than for the column tests (tab. 2), which is due to the much lower **rock surface** exposed to the solution when passing through (tab. 1). For crushed sandstone material, the retention capacity (also in the case of highly mineralized groundwater) is good for Cd, Pb and Zn. Under laboratory conditions (extremely high flow rates!) 23 mio. tons of the material would be sufficient to hold back the entire Cd, Pb, Zn inventory of an investigated mine – 19 t Cd, 403 t Pb and 1321 t Zn (AHU 2017) -. For the worst case of a fracture flow under laboratory conditions with 100 g L^{-1} NaCl and with significantly high flow rates, a fracture surface of 10,000,000 m^2 would be sufficient. It should be noted that the values were determined by Zn because Zn has the largest metal content in the residues. The values for Cd and Pb are more than 10 times lower.

The **pH value** is a “master variable” for the mobility of the metals. A change in the pH value from a basic to an acidic milieu results in metal mobilization. The behavior of the different metals due to pH changes is different. With decreasing pH values, the metal mobility increases in the order Cd > Zn > Pb. Since H^+ is desorbed while metal sorption, a gradual drop in the pH value occurs, this is diminished only by the buffer properties of the rock. The dominant buffer substances are, in addition to variable charge exchangers, silicate phases (Paas 1997).

Summary and Conclusions

This research work, with its experimental approach, refers to the current topics of expiring coal mining in Germany, associated mine flooding and the problem of stowed metal-containing residues. Due to mine flooding, highly mineralized groundwater with several tens of grams per litre of sodium chloride can come into contact with the residues.

Transport tests – especially single fracture experiments – performed with constant concentrations of metals (zinc, lead and cadmium) and variable sodium chloride concentrations showed an increasing mobility of these metals influenced by high sodium chloride concentrations. With the absence of sodium chloride, zinc has the highest mobility, followed by cadmium and lead. With addition of sodium chloride the mobility of cadmium is more enhanced than the mobility of zinc as the influence of chloro-complexation is stronger for cadmium than for zinc. Moreover, it was ascertained that the mobility for oxyanions (arsenate, molybdate and vanadate) has an inverse behaviour in comparison to these metals and a decrease was observed in the case of a rising salinity. Intermittent flow experiments showed that in addition to the sorption at the directly accessible sorption sites of the mineral surfaces intra-particle diffusion also took place and so a long-term retention of the metals is given. With a higher mineralization of groundwater the viscosity is rising. Increasing viscosities cause lower flow rates and lower flow rates cause a higher sorption of metals.

Owing to the decreasing mobility of the oxyanions for high salt contents and the overall low content, no risk is likely. Due to a very low permeability, the spreading of zinc, lead and cadmium through the pore system can be neglected. For country rocks, crushed in small pieces, in the goaf retardation and hinder capacity are very high, so spreading is also unlikely. For the fracture flow, a slight mass transport, to the at least 100 m away receiving level, can take place, because of a higher permeability and a lower amount of rock surfaces in contact with the solution. To enable reviews and predictions of mass transport into adjacent aquifers – based on the experimental results – a modelling of contaminant transport for a single fracture will be performed.

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