







## 20 Pyrite Weathering in the Unsaturated Zone of Lignite Mine Tailings: Release of As, Cd, Ni and Pb in a Soil Column Experiment

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### Abstract

In a column experiment on pyrite decomposition in the vadose zone of overburden material of an open cast lignite mine the release and the leaching characteristics of As, Cd, Ni and Pb were examined. In the experiment, the formation of acid mine drainage results in seepage water pH between pH 1.6 and pH 2.4 and  $E_H$  values between 575 mV and 880 mV. Seepage waters with concentrations of up to 5500  $\mu\text{g/l}$  As, 420  $\mu\text{g/l}$  Cd, 47 000  $\mu\text{g/l}$  Ni and 1000  $\mu\text{g/l}$  Pb are found. 100 % of the arsenic is released during pyrite decomposition. Arsenic is not completely leached from the column, but about 70 % remains sorbed to the solid phase. Under the experimental redox conditions the sorption of arsenic becomes smaller with decreasing pH. At the beginning of the experiment lead is leached from easily soluble phases. Despite the extreme geochemical conditions only 5 % of the initial lead was mobilized, while 95 % of the lead still remains in the system at the end of the experiment. Ni is released to 78 % from easily soluble phases or by desorption. The remaining 22 % originates from the dissolution of pyrite. Nickel shows a high mobility under the experimental pH- $E_H$  conditions. 75 % of the total nickel is leached from the column. The mobility of cadmium is even larger. Only 5 % remains in the material. 6 % of the released cadmium originates from pyrite weathering, while 94 % is released from easily soluble phases and by desorption processes. The species distributions of the elements are mainly determined by the high sulfate concentrations and the low pH.

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## 20.1 Introduction

The load of seepage water and groundwater with heavy metals and arsenic represents an endangerment for many ecological systems. Large quantities of trace elements are released in systems, which are affected by the formation of acid mine drainage. The extreme geochemical conditions with in some cases pH below pH 1 (Williams 2001) and different redox conditions result in various reactions, which affect or control the release and the mobility of heavy metals and arsenic. The most important factors are the pH- $E_H$  conditions, the amount and the distribution of the elements in easily oxidizable or soluble phases, the availability of suitable sorbents and the solution composition (Aström 1998). The latter can influence the mobility by solution, precipitation and complexation processes, which can again strongly affect sorption processes. Since the different factors strongly interact, general predictions for the behavior of the heavy metals or the arsenic are difficult. Williams (2001) describes the extremely variable boundary conditions in arsenic-loaded mine waters. Concentrations of more than 1000  $\mu\text{g/l}$  As are reported for waters with pH values between pH 0.52 and pH 10.0 at  $E_H$  values between 135 mV and 634 mV.

The large number of publications on the distribution of trace elements in abandoned mine sites or sites with recent mining activity show the importance of the problem. Many investigations were made to clarify the processes that are responsible for the behavior of trace elements under particular geochemical conditions (e. g. Aström 1998; Benvenuti et al. 1997; Clark et al. 2001; Li and Thornton 2001; Lin and Herbert Jr. 1997; Roussel et al. 2000; Williams 2001). Also within areas not affected by mining activities pyrite decomposition can be identified as a cause for increased trace element concentrations in the groundwater and in the vadose zone (Larsen and Postma 1997).

The majority of papers dealing with the mobility of trace elements in conjunction with acid mine drainage do not deal with the temporal investigation of dynamic systems, but with momentary situations and the spatial distribution of elements in various mineral phases. These phases are examined mineralogically and the potential mobilization of the specific element is determined by extractions. Mineralogical and extraction data do not necessarily provide information on element mobility in a dynamic flow system. The column experiment was originally focused on the quantitative description of pyrite decomposition processes and the oxygen recharge within the soil. The results of these investigations are published elsewhere (Hecht and Kölling, 2002). This paper does not focus on mineralogical investigations but on the release and the mobility of As, Cd, Ni and Pb in an acid mine drainage system. The elements were chosen after an element screening was driven out with a few samples. These four were identified as most relevant for the examined system. Cu and Zn could not be measured with sufficient standard

deviations. By the way, electron microprobe analysis that were carried out by Friedrich et al. (1999) showed contents of Co, Cu and Zn below the limit of detection within the tested pyrites. Comprehensive overviews of pyrite decomposition and subsequent secondary processes are given by Appelo and Postma (1994), Evangelou (1995), Lawson (1982) and Nordstrom (1982).

## 20.2 Methods and Materials

A column experiment on pyrite weathering in the unsaturated zone was performed. Figure 20.1 shows the experimental setup. The column was constructed from a Perspex tube with a length of 1 m and a diameter of 10 cm. The tube is equipped with a frit at the lower end, which holds the pyrite bearing overburden material (thickness 87 cm) over a sampling chamber. The upper end of the column is open to the atmosphere to allow gas exchange. The seepage water is sampled in the chamber at the bottom of the column.

The overburden material used in the experiment for pyrite decomposition in the unsaturated zone originates from the lignite open mine Garzweiler, Germany (Neurather Sand 6D). The column was irrigated once a day with tap water (oxygen saturated, not buffered) and the effluent was sampled once a week. The infiltration quantity (average 2475 mm/a) is higher than in natural systems resulting in an average sample quantity of approximately 36 ml/d. The total duration of the experiment was 800 days. The pH and  $E_H$  values in the effluent were monitored and the concentrations of Fe, S, Na, K, Ca, Mg, Mn and Al were determined by measurement with an ICP-OES (Perkin Elmer, Optima 3000). The trace elements As, Cd, Ni and Pb were determined by measurement with an GF-AAS (Unicam Solaar 989QZ). Additional information on the instruments and methods used may be found under [http://www.geochemie.uni-bremen.de/koelling/lab\\_instruments.html](http://www.geochemie.uni-bremen.de/koelling/lab_instruments.html). Total solid concentrations of Na, K, Ca, Mg, Al, Fe, As, Cd, Ni and Pb were determined at the end of the experiment by microwave digestion (MLS Ethos 1600) with hydrofluoric acid (Zabel et al 2001). Subsequent analysis of the digestion solution was made using an ICP-OES and an GF-AAS. Due to an error in the digestion method, there are no reliable data concerning the starting conditions. Since weathering occurs even in frozen aliquot samples stored under argon, the measurements could not be repeated at the end of the experiment. Therefore, the initial solid concentrations were estimated due to exact investigations on release of reaction products and final solid concentrations.

The overburden material is a silty (to clayey) fine sand with an initial pyrite content of 1.2 wt%, a porosity of 0.44 and an average diffusion effective porosity of about 0.2 (Hecht and Kölling, 2002). Mineralogy and trace

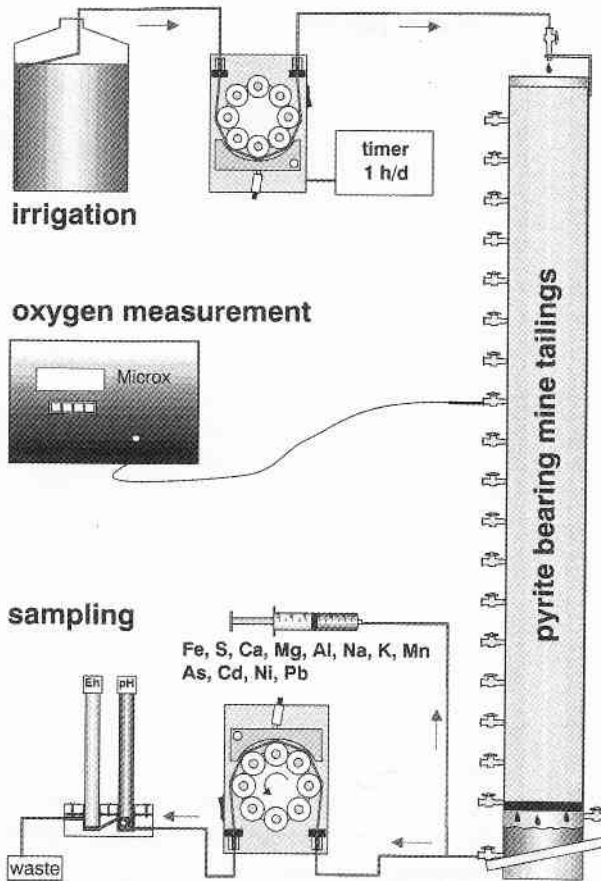


Figure 20.1: Experimental setup soil column experiment (modified after Hecht 1998).

element distribution in the Neurather Sand were studied by Friedrich et al. (1999). The sands contain pyrite (mostly framboidal; As, Ni, (less Co, Cu, Zn)) and other detrital heavy minerals (ilmenite, garnet, tourmaline, titanomagnetite, chromium spinel). Other minerals like feldspars, clay minerals, micas, and carbonates also contain trace elements (Pb, Zn).

The description of the pyrite weathering occurring in this experiment and the behavior of the major elements are published elsewhere (Hecht and Kölling, 2002). This paper focuses on the behavior of the trace elements within a system with a progressing pyrite weathering front which determines the change in pH- $E_H$  conditions and the release of sulfur and iron with time (Fig. 20.2).

The experimental column is open above to ambient air. With the beginning of the experiment, oxygen enters the column from above by diffusion and it is consumed by pyrite decomposition. The diffusive oxygen recharge

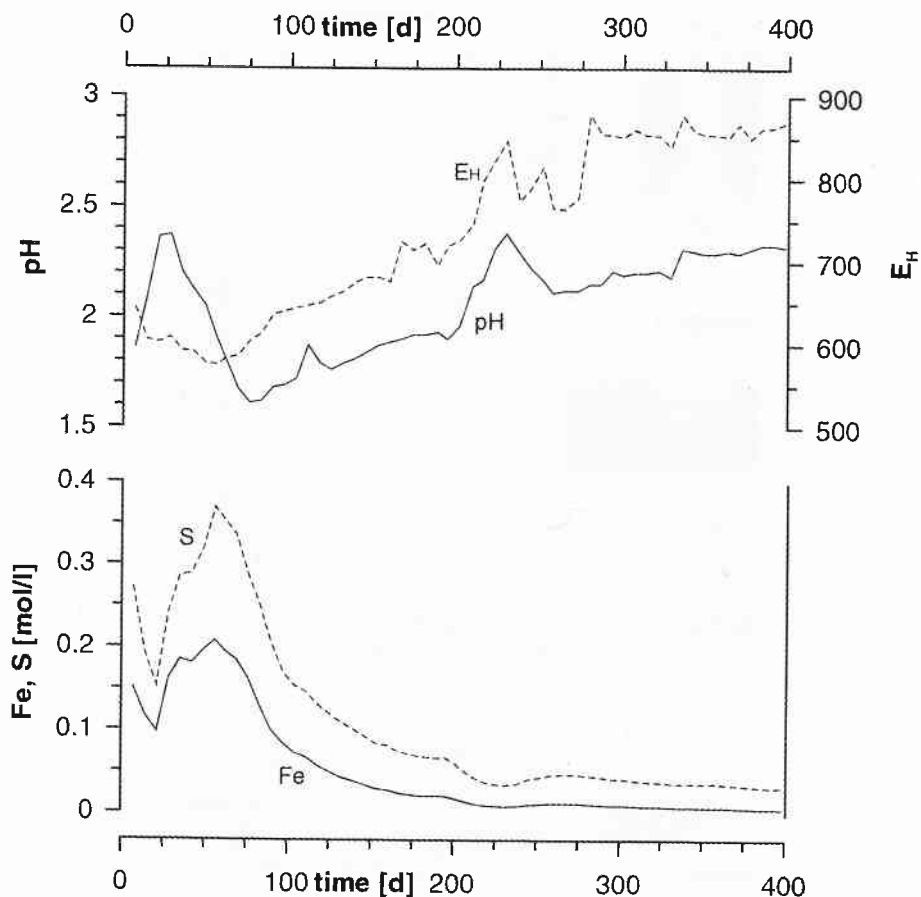


Figure 20.2: Effluent pH and  $E_H$  over time (Hecht and Kölling, 2002); release of S and Fe over time.

is smaller than the potentially possible consumption, so that at the beginning only in the upper part of the column pyrite decomposition occurs. With decreasing pyrite content of the upper zone the oxygen penetrates deeper into the column. After approximately 200 days the pyrite is decomposed in all depths. The reaction products of pyrite weathering and secondary reactions are transported with the seepage water and partly released with the effluent. At the beginning of the experiment buffering processes and gypsum precipitation take place. Silicates are dissolved in dependence on the pH. The slowly rising pH and the rise of the  $E_H$  show that the rate of the pyrite decomposition decreases with time. A steep increase of the  $E_H$  value around the 220<sup>th</sup> day and the strong decrease of the iron and sulfur discharge indicate the end of pyrite decomposition. Furthermore the development of oxygen concentrations indicates the end of pyrite decomposition (Hecht and Kölling, 2002).



ling, 2002). The high concentrations of iron and sulfur at the beginning of the experiment are not led back on present pyrite weathering processes but due to the washout of reaction products already available in the column material. The release of sulfur occurring after the pyrite decomposition has ended is the result of the dissolution of previously precipitated gypsum.

## 20.3 Results

The releases of the trace elements with the effluent are represented in Fig. 20.3. The graphs show both the concentrations and the cumulative release over time. Fluctuations of the quantity of effluent (see Fig. 20.4) and starting conditions are balanced within the cumulative presentation.

The initial solid concentrations of the trace elements were homogeneous over depth. The total solid concentrations are listed in Tab. 20.1.

## 20.4 Discussion

During the first 200 days of the experiment, where intensive pyrite weathering occurs, all examined elements show an increased release. Subsequently, both the concentrations and the relative concentration changes are much smaller. Shortly after the beginning of the experiment a large quantity of heavy metals is leached from the column (represented by the initial values of the cumulative curves). Arsenic and lead show a pH dependent mobility, while nickel and cadmium indicate a direct correlation with the quantity of effluent.

The behavior of nickel is controlled by two main processes. The first process is the release of easily mobilizable nickel by solution or desorption. The second process is the release of nickel from pyrite. The discharge of nickel can be divided therefore into two phases. Phase I is marked by very high concentrations, which strongly decrease with time. At the beginning of the experiment the highest concentrations occur. In connection with a large quantity of effluent (Fig. 20.4) 35 % of the total discharge takes place during the first week. The nickel concentrations of up to 0.8 mMol/l result from the release of easily mobilizable nickel from unstable mineral phases or from desorption. Throughout the experiment, the pH is below pH 2.4. Under these conditions cation sorption is strongly limited, since the surfaces of potential sorbents are positively charged. Calculations with PhreeqC show that under the experimental conditions the major Ni-species are  $\text{Ni}^{2+}$  and

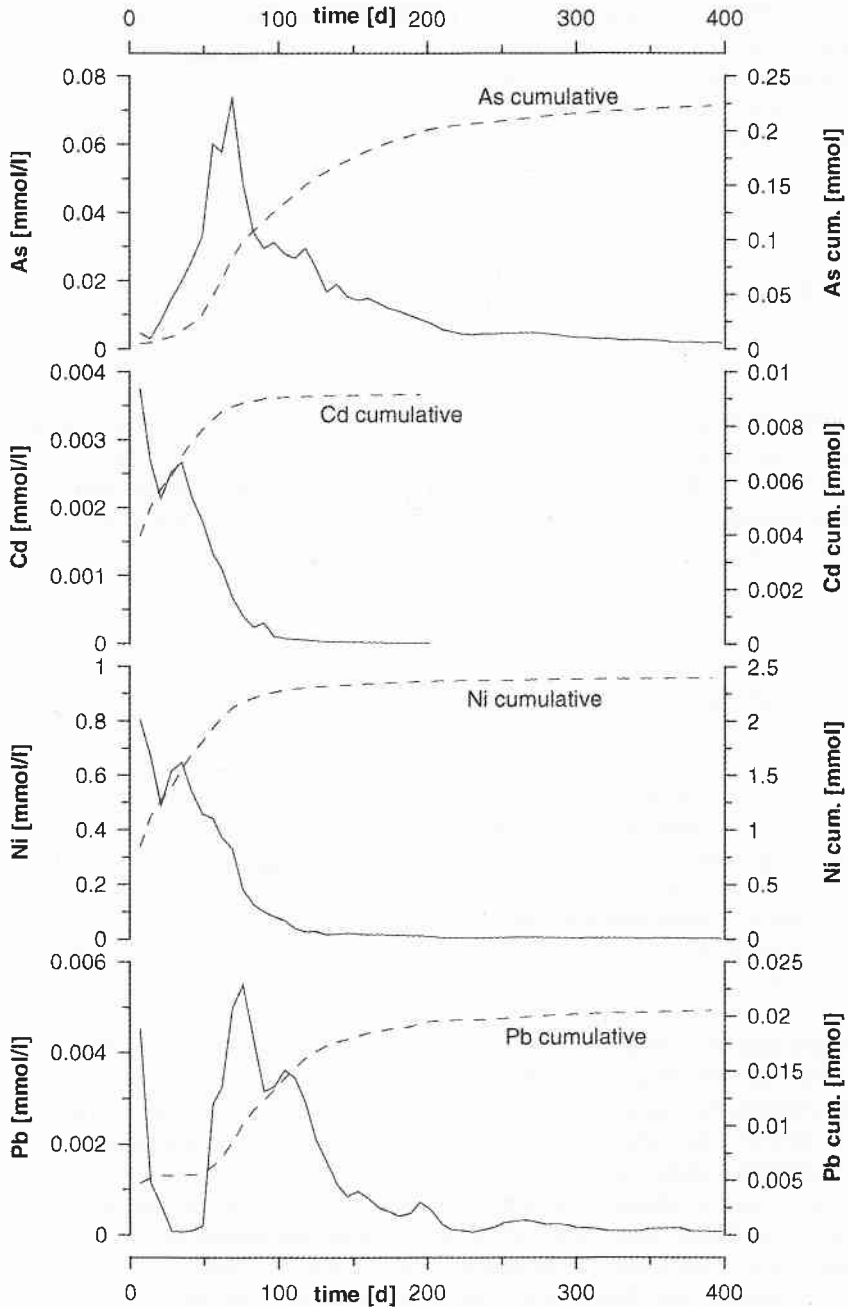


Figure 20.3: Concentrations and cumulative release of As, Cd, Ni and Pb over time.

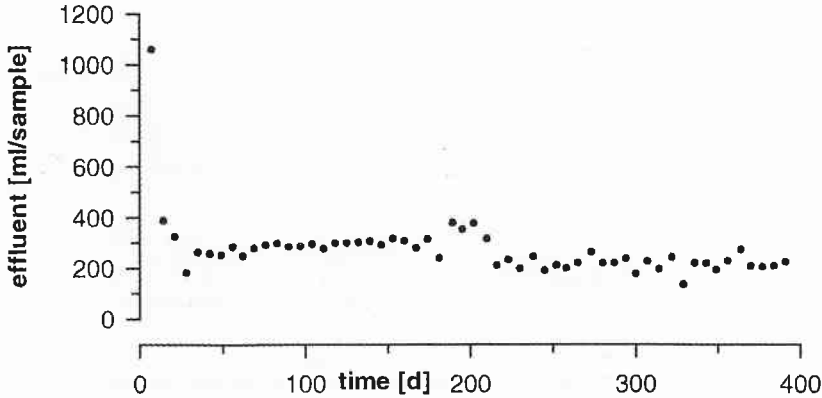


Figure 20.4: Effluent quantity over time.

Table 20.1: Final solid concentrations of As, Cd, Ni and Pb in different depth. Initial solid concentrations (\*estimated from final conc. in conjunction with cumulative release).

Column depth [cm]	As [ $\mu\text{mol/kg}$ ]	Cd [ $\mu\text{mol/kg}$ ]	Ni [ $\mu\text{mol/kg}$ ]	Pb [ $\mu\text{mol/kg}$ ]
2.5	56.6	0.086	90.6	45.5
12.5	48.1	0.085	100.5	41.7
22.5	41.0	0.085	65.6	41.2
42.5	108.1	0.087	67.1	51.4
62.5	99.1	0.207	89.3	56.9
82.5	101.5	0.165	73.6	48.4
initial conc.*	98.2	1.02	318.4	49.6

$\text{NiSO}_4^0_{(\text{aq})}$ . Therefore sorption of negatively charged nickel complexes is of no importance.

In addition to the release of the large quantities of nickel during the first 50 to 100 days, a release of Ni from pyrite decomposition takes place. In phase II this process is the only source for nickel. Figure 20.5 shows the changes in the nickel-iron-ratio within the effluent over time. After the 110<sup>th</sup> day of the experiment this ratio stabilizes at a value of  $7 \cdot 10^{-4}$ . The constant ratio indicates that in this phase the major source for Ni is pyrite dissolution. This ratio suggests that the pyrite contains 0.034 wt% Ni. Friedrich et al. (1999) found values between 0.01 and 0.05 wt% for different pyrites within the Neurather Sand. We found no indications for a Ni retardation. Using the nickel-iron-ratio from the second phase it is possible to calculate the nickel quantity, which was released from pyrite during the entire experiment. In Fig. 20.5 (bottom) this proportion is represented in comparison to the

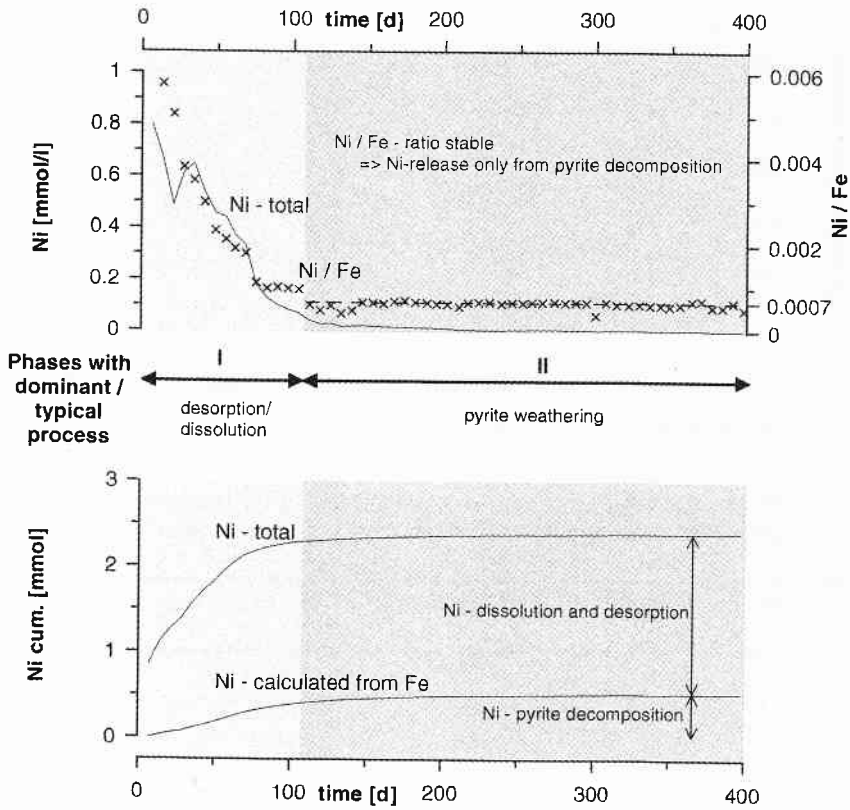


Figure 20.5: Ni-concentrations, Ni-Fe-ratio and cumulative Ni release over time.

total discharge. It amounts to 22% of total nickel. The remaining 78% is easily soluble or desorbable nickel.

The direct release of nickel from pyrite is of minor importance for the water quality. A larger proportion of easily mobilizable Ni is released to the seepage water due to the acidic geochemical environment caused by pyrite weathering. The pyrite decomposition is thus not the main source for nickel in this system, but the reason for the high concentrations. The investigation of the solid phase Ni content also shows the high mobility of nickel. At the end of the experiment, approx. 75% of the original solid phase nickel is leached from the sediment.

Cadmium shows leaching characteristics similar to nickel, yet, at a much lower concentration level. In Fig. 20.6 the different release curves and the cadmium-iron-ratio over the time are presented. The release and the discharge of cadmium are controlled by two processes. Similar to nickel, the highest cadmium concentrations occur at the beginning of the experiment. Almost 50% of the total cadmium is leached from the column from easily soluble phases or via desorption with the first effluent. With the identification

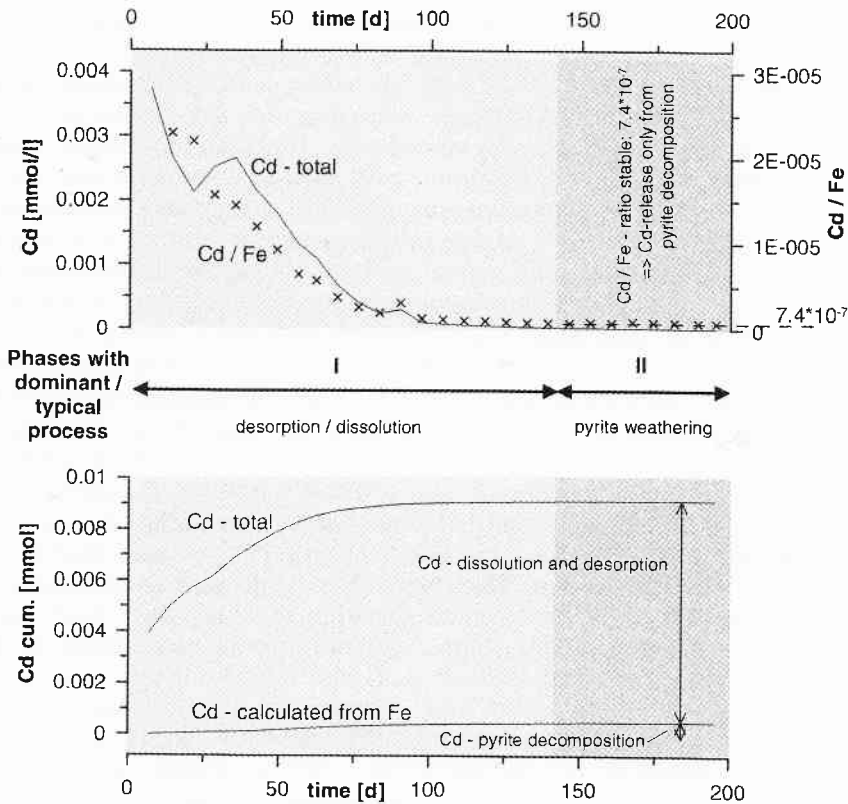


Figure 20.6: Cd-concentrations, Cd-Fe-ratio and cumulative Cd release over time.

of the processes the same problems occur, as in the case of nickel. Since the starting conditions in the pore water are unknown this fraction may not be defined more precisely. The first phase of the cadmium discharge is characterized by a very strong decrease of the concentrations with time indicating the limited quantity of this Cd source. The end of phase I is characterized by the fact that the concentrations become very low and the cadmium-iron-ratio reaches a stable value of  $7.4 \cdot 10^{-7}$ . PhreeqC calculations show that the major cadmium species are  $\text{Cd}^{2+}$ ,  $\text{CdSO}_4^0_{(\text{aq})}$  and  $\text{Cd}(\text{SO}_4)_2^{2-}$ . In the acid mine drainage solutions significant amounts of negatively charged sulfate complexes form with cadmium. These complexes could influence the leaching characteristics by anion sorption and therefore slow down the establishment of a stable cadmium-iron-ratio.

As in the case of nickel the stable ratio between Cd and Fe indicates the release and the discharge of cadmium associated with pyrite. In phase I this is a secondary process. In phase II it is the exclusive release process. The portion of the cadmium released from the pyrite decomposition amounts to 5.7 % (calculated from cadmium-iron-ratio and total iron release). Comparative

data for cadmium content within the investigated pyrites are not available. On the basis of discharges results a cadmium content in the pyrite of  $6.5 \cdot 10^{-5}$  wt%. For the contamination of the seepage water with cadmium its release from pyrite is of secondary importance. However, for the discharge of cadmium pyrite decomposition plays a crucial role. The high mobility is a result of the acid mine drainage environment. At higher seepage water pH Cd mobility would be limited by cation sorption. The solid phase investigations show that approximately 90% of the initial cadmium content was leached from the column. The final solid concentrations are higher in the lower part than in the rest of the column due to the formation of secondary minerals.

The mobility of lead is generally low and it shows a strong pH dependency (Fig. 20.7). In the initial phase of the experiment, there is a decrease of lead concentrations as a result of increased pH values caused by a sequence of buffering processes (Hecht and Kölling, 2002). During the experiment, only 4% of the total lead is leached from the column. Lead is an element of low mobility with a strong sorption tendency. It can be sorbed as cation noticeably below the point of zero charge. The slight rise in pH and the associated modification in the surface charge of a sorbent seem to be responsible for the decrease of discharges. Similar to nickel and cadmium, a large amount of lead (25%) is leached within the first days. Since pyrite dissolution is very small at this stage, lead must be released from another mineral or by desorption. Friedrich et al. (1999) found out that in the Neurather Sand Pb can be released from carbonates and silicates. This can explain the large release at the beginning (carbonate dissolution) and the pH-dependant release during the experiment (silicate weathering).

An exact balance of mobilization and fixing of lead within the entire experiment is not possible since there is little evidence in the effluent concentrations. The final solid concentrations point out that a portion of lead was displaced within the column. The concentrations in the lower part of the column are noticeably higher.

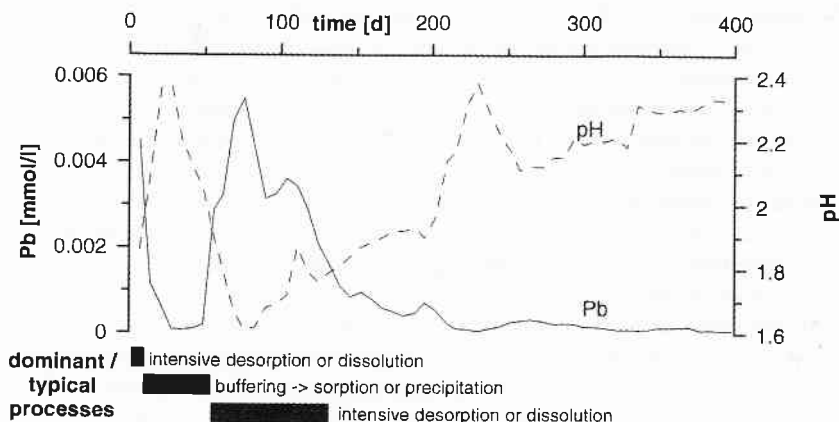


Figure 20.7: Pb concentrations and pH over time.

The distribution of lead species is determined by the high sulfate concentrations. The major species is uncharged lead sulfate. Other important species are  $\text{Pb}(\text{SO}_4)_2^{2-}$  and  $\text{Pb}^{2+}$ . At very low pH values  $\text{Pb}^{2+}$  becomes more important, since the availability of sulfate is limited by large portions of  $\text{HSO}_4^-$ . The species distributions do not give further information concerning the mobility of lead.

The mobility and the leaching characteristics of arsenic are directly coupled to the pyrite decomposition processes. For many mine waters pyrite can be seen as the only source for arsenic contamination (Williams 2001). From the cumulative releases and from the solid phase concentrations the content of arsenic in pyrite may be estimated at 0.06 wt%. Friedrich et al. (1999) found arsenic contents of up to 0.38 wt% for the pyrites of the Neurather Sand (detection limit 0.2 wt%). Contrary to the heavy metals, no release of arsenic from easily soluble phases or by desorption can be seen at the beginning of the experiment (see Fig. 20.3, starting point cumulative release As).

The primary source for arsenic is pyrite. The mass balance shows that only approximately 30 % of the released arsenic is leached from the column. Since the pyrite as primary source of arsenic is almost completely decomposed during the experiment, secondary processes causing a fixation of arsenic have to be postulated. The negative correlation of pH and arsenic

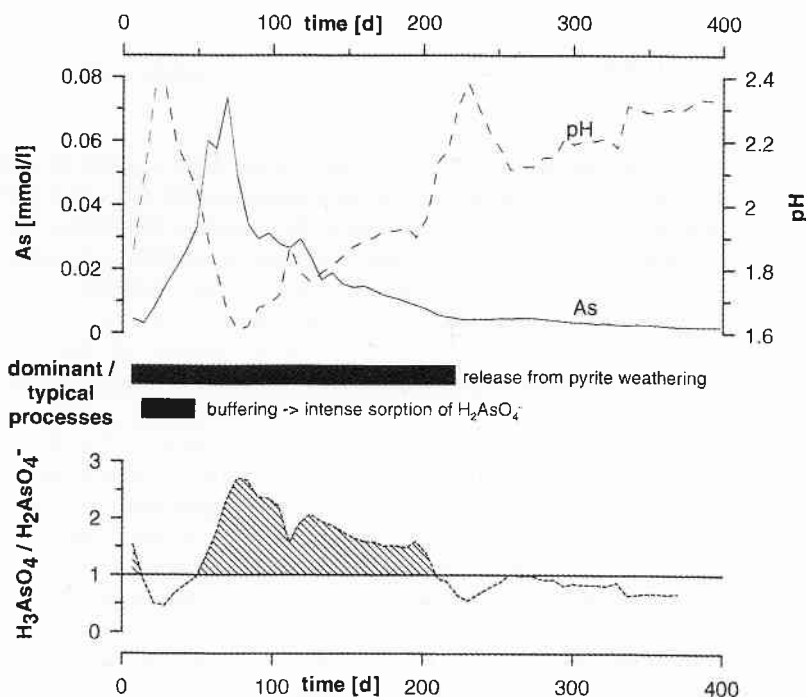


Figure 20.8: As concentrations, pH and ratio between  $\text{H}_3\text{AsO}_4$  and  $\text{H}_2\text{AsO}_4^-$  over time.

concentrations shows that the pH conditions are crucial for these processes (see Fig. 20.8). The pH affects the mobility of arsenic in two ways. The very low pH allows anion sorption since the point of zero charge of most potential sorbents is found at higher pH values (Appelo and Postma 1994). Due to this fact the sorption of arsenic is normally strong at low pH values. However, there is a very low pH range where arsenic behaves exactly opposite. At the given pH- $E_H$ -conditions the arsenic is almost totally present as  $H_3AsO_4^0$  or  $H_2AsO_4^-$ . The distribution between the charged and the uncharged species is pH dependent. As presented in Fig. 20.8 (bottom) the charged species  $H_2AsO_4^-$  is the dominant at higher pH (within tested solutions  $> \text{pH } 2.1$ ) (calculations with PhreeqC; Parkhurst 1995). This results in a stronger sorption at pH above 2.1 and thus decreased arsenic concentrations in solution.

Therefore, the pH controls the arsenic concentration in the seepage water also via species distribution. At the beginning of the experiment this dependency is dominated by the pH effect of the buffer reactions. After the 75<sup>th</sup> day the release of arsenic and the pH directly depend on pyrite decomposition. The clear decrease of the arsenic concentrations after approximately 220 days shows the end of pyrite decomposition and thus the end of main arsenic release.

## 20.5 Conclusions

In the experiment, the formation of acid mine drainage results in seepage waters with pH 1.6 to pH 2.4 and  $E_H$  values between 575 mV and 880 mV. The seepage water is characterized by very high mineralization. The dissolved concentrations of many elements are several orders of magnitude above appropriate limit values for drinking water. In the seepage water concentrations of up to 5500  $\mu\text{g/l}$  As, 420  $\mu\text{g/l}$  Cd, 47000  $\mu\text{g/l}$  Ni and 1000  $\mu\text{g/l}$  Pb are found. The sources and the leaching characteristics of the different elements are diverse. In most cases the pyrite decomposition plays a significant role:

Nickel is released to 78 % from easily soluble phases or by desorption. The remaining 22 % originates from pyrite weathering. Nickel has a high mobility under the redox conditions found in the experiment. 75 % of the total nickel is leached from the column material. 35 % of the total discharge takes place in the first week. The acidic conditions generated by pyrite weathering are responsible for nickel release and nickel mobility. Pyrite as source for nickel is of secondary importance.

The mobility of cadmium is still larger than the nickel mobility. Only 5 % of the initial cadmium content remains in the material. About 6 % of the released cadmium originates from pyrite weathering and to 94 % from easily



soluble phases and desorption processes. Almost 50 % of the total cadmium is leached in the first week of the experiment. The pH conditions generated by pyrite decomposition are crucial for the leaching characteristics of cadmium.

Lead is released and discharged at the beginning of the experiment from easily soluble phases (carbonates). This fraction represents 25 % of the total mobilizable lead. During the experiment only 5 % of the initial lead content is mobilized. The generally low mobility is pH dependent (dissolution of silicates). Pyrite decomposition is responsible for mobilization of a small proportion of lead when very low pH values are established.

In the investigated sediments, pyrite is the only source for arsenic. 100 % of the arsenic is released during pyrite decomposition. It is not completely leached from the column. After the experiment about 70 % of the total arsenic is still sorbed to the solid phase. Under the redox conditions found in the experiment, the sorption of arsenic becomes smaller with decreasing pH. Pyrite is the source of arsenic and controls the pH-dependent mobility of arsenic by its decomposition.

The species distributions of the elements are mainly determined by the high sulfate concentrations and the low pH. The investigations showed that the processes of pyrite decomposition influence the release and the behavior of the trace elements very strongly.

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