Sequential extraction procedure in columns. Part 1: Development and description of a new method

F. Wisotzky · N. Cremer

Abstract A sequential extraction procedure was carried out in columns using reagents that are known to be reliable from batch tests. The intention was to distinguish between different chemical forms of iron and heavy metals in samples from reduced porous aquifers, which demands anaerobic conditions for the extraction procedure and the determination of small amounts of reactive mineral phases in a quartz dominated sediment system. By means of the developed method, anaerobic conditions can be guaranteed in the columns, which could not be realized to full satisfaction in batch tests that were carried out in a glove box. In order to distinguish between the fractions that were water soluble, exchangeable, bound to carbonates and bound to hydroxides, different reagents were pumped through the sediments and sampled after passage of the columns. Sediment samples of 10 kg each were investigated in this way. The extraction steps were known to be complete when analyses revealed that no further major and trace elements were leached out of the columns. This approach enabled well-adjusted amounts of reagents to be used. By means of the sequential extraction procedure in columns the composition of even small amounts of reactive mineral phases can be determined successfully, which contributes to a deeper understanding of the hydrogeochemical processes in aquifers. In batch tests this accuracy cannot be reached because of the surplus of the extraction solution in relation to the amount of sediment (higher solution-sediment ratio).

Furthermore, larger samples are much more representative of the composition of the aquifers than smaller ones and the heterogeneity of the sediment does not limit the accuracy of the results as much as in batch tests. In addition, the technique of flushing sediment in a column is much more typical for the situation in an aquifer than suspending a few grams of a sample in the extracting reagents in batch extraction tests. In order to demonstrate the methodical improvements and field applications, the newly developed method was used to investigate the changing binding forms and mobility of iron and trace metals in samples from a lignite overburden dump, which are influenced by pyrite oxidation processes (acidification) followed by the addition of crushed limestone (neutralization) (see “Sequential extraction procedure in columns. Part 2: Application of a new method”).

Keywords Sequential extraction · binding forms · iron mobility · nickel · heavy metal mobility · aquifers · Germany

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Introduction

Sequential extraction procedures are used to distinguish between different binding forms of elements, particularly metals, in soils, sediments and solid matter in general. Based on these partitionings into specific fractions, an assessment of element mobility and environmental influences becomes possible, which cannot be concluded from total element concentrations.

First investigations aimed to determine the availability of microelements in soils as a factor controlling fertility (Jackson 1958). Later, the method was of growing importance for ecological research projects concerning heavy metal mobility in soils (Brümmer et al. 1986; Dües 1987; Zeien and Brümmer 1989), sewage sludge (Sposito et al. 1982) and fluvial deposits (Förstner and Patchineelam 1976; Förstner and Calmano 1982; Peula Lopez 1995; Von Lührte 1997). Latest applications of sequential chemical extractions are intended to determine the binding forms of metals in aquifer sediments in order to assess the heavy metal mobilizing potential of the deposits and to reveal the processes controlling heavy metal mobility in groundwater

(Böhler et al. 1995; Broers 1998; Wisotzky 2003; Cremer 2002).

Conceptually, the solid material can be partitioned into specific fractions, which can be extracted selectively by using appropriate reagents (Tessier et al. 1979). The following fractions are of major interest for the investigation of metal mobility: exchangeable, bound to carbonates, bound to hydroxides, bound to sulfides and residual. The common method of investigation is a batch test, in which a small amount of the dried sample is suspended in different extracting reagents one after another and shaken for a given time (Förstner and Patchineelam 1976; Tessier et al. 1979; Sposito et al. 1982 and others).

When investigating sediments of porous aquifers, batch tests involve some major disadvantages, which demand conceptual improvements. Firstly, aquifers are often characterized by anaerobic conditions. Therefore, it is essential to avoid contact of the samples with atmospheric oxygen to prevent sulfidic mineral phases and ferrous iron from being oxidized, which was already pointed out by Calmano and Förstner (1985). Tests, in which the extraction procedure was carried out in a glove box, did not solve the problem as low oxygen traces remained in the glove box atmosphere and caused a partial oxidation of the reduced phases. Secondly, the mineral phases in porous aquifer sediments are often dominated by quartz and feldspar, whereas the amount of more reactive mineral phases like carbonates, oxihydroxides or sulfides is relatively small. As the hydrochemical situation in an aquifer can be influenced substantially even by these small amounts of mineral phases being involved in hydrogeochemical reactions, the determination of the amount and composition of these reactive phases is very important. In a batch test a sediment sample is suspended in a large quantity of the reagent (typical sediment-solution ratio is 1:8 to 1:100). Most of the chemical is not needed for the extraction reaction and the large liquid-solid ratio leads to a dilution. As a consequence the detection limits of the elements that are extracted are relatively high and a quantification of the trace element contents of some reactive mineral phases might fail.

The objective of this paper is to show a new methodical approach which, by carrying out a sequential extraction in columns, involves the following improvements compared to batch tests:

- anaerobic conditions can be guaranteed during the experiments,
- the composition of very small amounts of reactive mineral phases can be determined (in the sediment samples that were investigated the trace metal contents of reactive mineral phases were successfully determined, although these phases could not even be detected with standard methods of investigation; see "Sequential extraction procedure in columns. Part 2: Application of a new method"),
- the flushing of several kilograms of sample material is quite representative of the composition of an aquifer, and
- in the extraction procedure, well-investigated reagents which are used in batch tests can be employed.

The aim of the second part ("Sequential extraction procedure in columns. Part 2: Application of a new method") is to present the results of an example for which the method was developed in order to confirm the advantages of the method and to illustrate some results that would not have been achieved without the sequential extraction procedure in columns.

Methods

Sampling methods and standard analytical procedures

The method was developed for lignite overburden samples of Miocene age from the Garzweiler open pit mine. Because of sediment aeration during the mining process, pyrite oxidation takes place. Before dumping, crushed limestone is added to the material, which has positive effects on the water quality, such as rising pH values of the acidified groundwater, as well as the limited mobility of iron, heavy metals and sulfate (Wisotzky and Kringel 1998; Wisotzky 2001). In the overburden dumps, the processes affecting the binding forms and mobility of iron are of major interest.

The sediment samples were taken from pilot scale containers of 10 m^3 volume that had been used to simulate the groundwater flow and quality in lignite overburden dumps with and without addition of crushed limestone under realistic conditions (Wisotzky 2001; for details see "Sequential extraction procedure in columns. Part 2: Application of a new method"). The column tests started immediately after sampling.

The total inorganic carbon content (TIC) was analyzed after addition of heated (90 °C) perchloric acid as carbon dioxide by infrared spectroscopy.

The pH value of the water samples was measured online with an electrode in a flow-through cell. In addition to the electrical conductivity, major ions of effluent samples after passage through the columns were analyzed by means of ion chromatography (DIONEX DX 500). Ferrous iron was determined using photometry (510 nm). Graphite furnace AAS (UNICAM 939 QZ) was used to determine the trace metal concentrations (nickel, cobalt, copper, lead, zinc, arsenic).

Sequential extraction procedure—fractions and reagents

The following fractions were analyzed using different reagents in the sequential extraction procedure in columns (Fig. 1).

Water-soluble fraction: Distilled water is used to mobilize water-soluble metals. Considering the batch tests, this procedure is equivalent to the German S4-test (DIN 38414-S4; Deutscher Normenausschuß 1984). In preparing the column experiments, nitrogen gas is bubbled through the distilled water reservoir to remove dissolved oxygen before

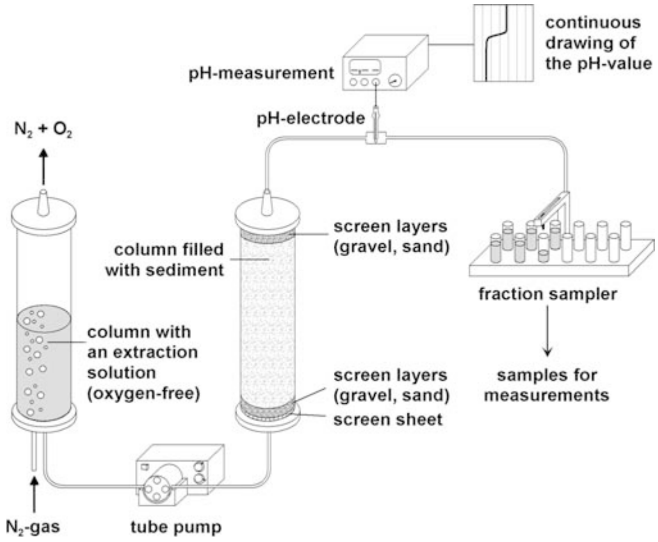

Fig. 1
Schematic illustration of the setup of the column experiments

passing the column that contains the investigated sediment samples (Fig. 1).

Exchangeable fraction: An ammonium chloride solution (0.1 m NH_4Cl; Dües 1987) is used to mobilize exchangeable cations. The ammonium ions are taken up by the exchangers and all other cations from the exchangers are released into the solution. The cation exchange capacity as well as the distribution of cations on the exchangers—including the heavy metal cations—can be calculated from the cation concentrations in the extract.

Bound to carbonates: Carbonate minerals are dissolved in an acid sodium acetate solution (1.0 m $NaCH_3COO$ adjusted to pH 5.0 with acetic acid (CH_3COOH); Tessier et al. 1979).

Bound to hydroxides: Amorphous and poorly crystalline hydroxidic mineral phases are extracted using an ammonium oxalate solution (0.2 m $(NH_4)_2C_2O_4$ adjusted to pH 3.0 with oxalic acid (0.2 m $C_2H_2O_4$); Förstner and Calmano 1982). The iron and manganese hydroxides are reduced to their ferrous respectively manganous forms under acid conditions at pH 3.0, which is described by the following equation for the example of iron:

$$C_2O_4^{2-}+Fe_2O_3+6H^+ \Rightarrow 2CO_2+2Fe^{2+}+3H_2O \qquad (1)$$

The complete sequence is illustrated schematically in Fig. 2, showing the four fractions and the reagents used for their extraction.

Sequential extraction procedure in columns—setup and realization of the experiments

Columns with a total length of 0.5 m and a diameter of 0.135 m were filled with sediments with a dry weight of about 10 kg. At the bottom and top of the columns screen layers were placed consisting of quartz sand and gravel (Fig. 1).

Before using the screen layer material, sand and gravel were cleaned with hydrochloric acid to remove all extractable iron and heavy metals aside from the complete dissolution of carbonate minerals. The oxygen-free extraction solutions were pumped through the columns with a tube pump. After passing the column the pH value was measured continuously before the extraction solution came into contact with atmospheric oxygen (Fig. 1). Samples were collected in a fraction sampler (100 ml each) and analyzed for major constituents as well as trace metals. In order to check the anaerobic conditions during the experiments, separate column tests were carried out with unoxidized pyrite-containing material. For this purpose sediment samples from a porous aquifer saturated with original groundwater from an exploration drilling were available.

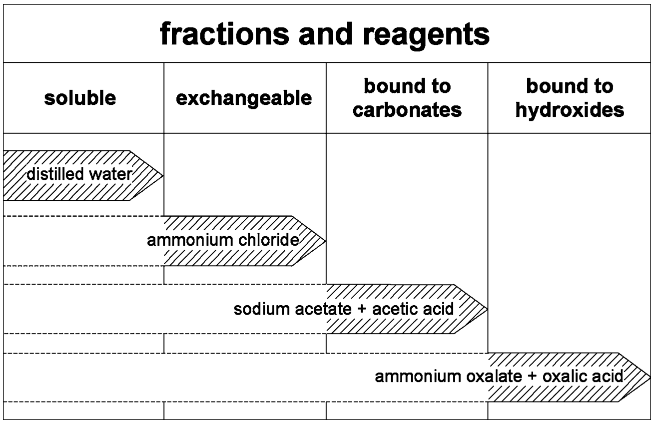

Fig. 2
Fractions and reagents in the extraction sequence

Results and discussion

With the infiltration of distilled water the pore water was flushed out of the column, which showed exactly the same composition as the groundwater. Due to the dilution with distilled water the element concentrations decreased afterwards as the development of the sulfate and chloride concentrations reveals (Fig. 3). If oxidation of the pyrite crystals had taken place, the concentrations of sulfate, which is a main product of pyrite oxidation, would have increased or at least decreased more slowly than the chloride concentrations. This phenomenon could not be observed (Fig. 3) and the anoxic conditions in the columns are verified this way.

After the extraction sequence the column was opened and aerated to stimulate bacterial oxidation under aerobic conditions. When the extraction sequence was repeated after the complete oxidation of the pyrite crystals, the sulfate concentrations reached 12,600 mg/l, which demonstrates the sulfate mobilizing potential of the sediment. For a certain classification of each sample after passing the columns, the electrical conductivity and the sodium and chloride concentration were measured and displayed against the exchanged volume (Fig. 4). The beginning of a new binding form fraction is marked by the breakthrough of a reagent and was identified by the changing electrical conductivity, sodium or chloride concentration.

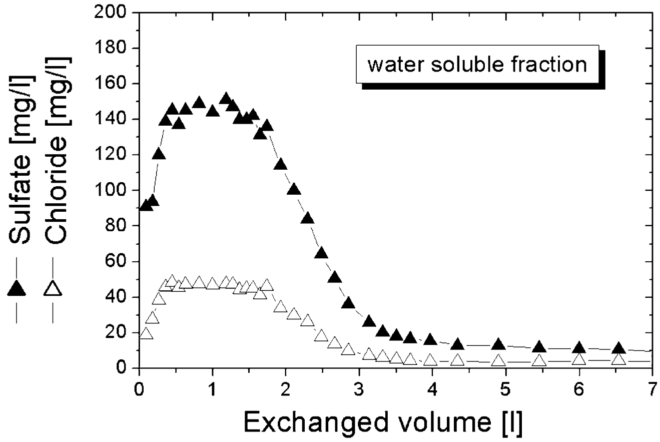

Fig. 3
Sulfate and chloride concentrations during the first step (water-soluble fraction) of a column experiment for testing the anaerobic conditions

An extraction step was known to be complete when analyses revealed that no further major and trace elements were leached (Fig. 5). At that point the reagent was changed to extract the next fraction, which means that the exchanged volume varied with the different samples. In this way, the amount of reagent was optimized to reach a sufficient sediment-solution ratio. As an example, the calcium, sulfate, iron and nickel concentrations in the effluent samples of a column experiment with sandy overburden material from lignite mining to which crushed limestone was added are discussed in detail (Fig. 5).

Due to the first infiltration of distilled water, the water-soluble fraction dissolves, which mainly consists of pyrite oxidation products in this example. After the flushing of about 2 l, which is the pore volume of the sediment in the column, a decrease in the electrical conductivity (Fig.4) and the iron concentrations (Fig. 5c) in the effluent of the column is observed. The calcium and sulfate concentrations nearly remain on a constant level in the first 6 l of exchanged volume (Fig. 5a,b) as a dissolution of secondarily formed gypsum takes place. Saturation calculations carried out with PHREEQC (Parkhurst 1995) reveal an equilibrium with regard to gypsum in this part of the experiment. The almost complete dissolution of the water soluble fraction is visible by a strong decrease of the electrical conductivity (Fig. 4) and the calcium, sulfate and iron concentrations as examples (Fig. 5a–c). The low iron and calcium concentrations after the flushing of about 13 l of exchanged volume mark the end of the extraction of the water-soluble fraction and the extraction solution was changed to ammonium chloride to determine the exchangeable fraction. However, this change of the extraction solution was a little bit too early with regard to calcium and sulfate.

The breakthrough of the ammonium chloride solution after flushing of about 15 l (13+2 l pore volume) was detected by increasing chloride concentrations and electrical conductivity (Fig. 4). The increasing ammonium concentration in the column leads to cation exchange in the column. This is visible by an increase in the dissolved calcium concentration up to 250 mg/l (Fig. 5a). This induced calcium peak marks the exchangeable calcium fraction of the sediment. Iron and nickel do not occur in the exchangeable fraction in measurable amounts (Fig. 5c, d). After the complete mobilization of cations from the exchangers of the sediment against ammonium from the extraction solution at about 18 l of exchanged volume (Mg, K, Na and Al measured but not displayed), the extraction solution was changed to sodium acetate with acetic acid.

The breakthrough of the sodium acetate solution is marked by a strong increase in sodium concentration and the measured electrical conductivity and the decrease in chloride concentration after about 20 l of exchanged volume of the extraction solutions (Fig. 4). The dissolution of iron carbonates from the sediment is visible by an increase in the dissolved iron concentration up to 300 mg/l (Fig. 5c). In the samples revealing the iron peak, rising calcium concentrations are also observed (Fig. 5a), which either

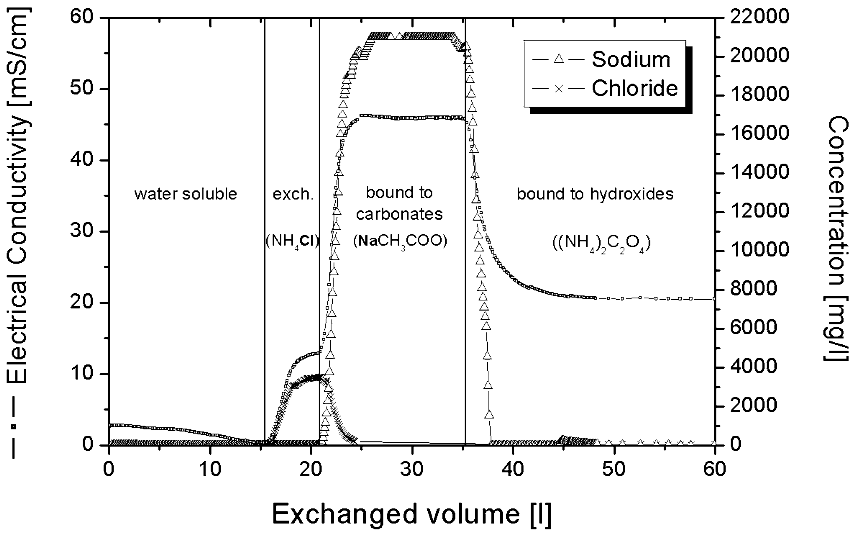

Fig. 4
Measured electrical conductivity as well as concentrations of sodium and chloride in column effluents to distinguish between different binding forms (water-soluble, exchangeable, bound to carbonates and hydroxides, subdivided by *vertical lines*), column material: lignite overburden with limestone addition (see "Sequential extraction procedure in columns. Part 2: Application of a new method")

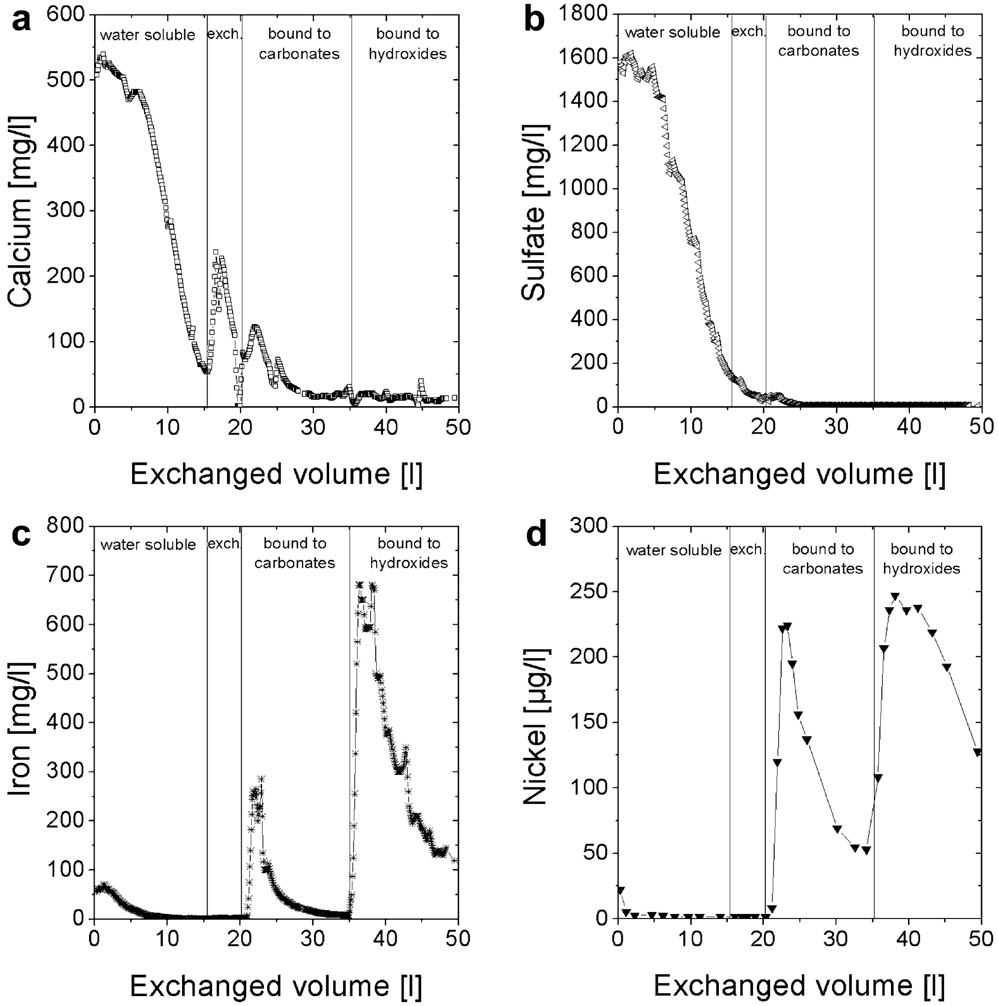

Fig. 5
Development of the **a** calcium, **b** sulfate, **c** iron and **d** nickel concentrations in the effluent samples after passage of the column as an example. The *area below the curves* represents the extracted element amount in each fraction

reveals the simultaneous dissolution of siderite and calcite or can give a hint at the existence of siderite/calcite solid solution. Nevertheless, the carbonate phases contain certain amounts of nickel (Fig. 5d) and other heavy metals (Co, Pb, Zn, measured but not displayed). From the data described above a total inorganic carbon content (TIC) of 0.004 wt% could be calculated. This amount cannot be detected using standard analytical procedures like infrared spectroscopy. In spite of this low inorganic carbon content, the following average carbonate composition could be determined as follows: $Ca_{0.516}Fe_{0.483}Ni_{0.001}CO_3$.

The high sodium concentration and electrical conductivity remained constant until the extraction solution was changed for the last time after about 33 l of exchanged volume of the extraction solutions (Fig. 4).

After passing the column, the mixture of ammonium oxalate and oxalic acid leads to a decrease in sodium concentration and measured electrical conductivity (Fig. 4). The breakthrough of this mixture at about 35 l of the volume is responsible for the sharp increase in dissolved iron concentration up to 700 mg/l in this fraction (bound to hydroxides; Fig. 5c). The observed iron peak occurs due to the dissolution of low crystalline iron oxihydroxide minerals from the column sediment also containing nickel (Fig. 5d) and other trace elements (As, Co, Cu, Pb, Zn). After the almost complete dissolution of these mineral phases, the extraction was stopped after about 70 l of exchanged volume in this example, which is not displayed completely for this general explanation.

The areas below the different segments of the concentration curves represent the total amounts of extractable substances (load) of the different fractions and are determined by integration.

A detailed description of the project for which the method was developed, as well as an interpretation of the results, are illustrated separately (“Sequential extraction procedure in columns. Part 2: Application of a new method”).

Conclusions

By carrying out sequential extractions in columns as a new methodical approach, anaerobic conditions can be guaranteed and the precision of the extraction procedure is improved. Compared to batch tests these advantages lead to a closer understanding of hydrogeochemical processes that are investigated and to a larger field of application for this new method.

As the columns represent closed systems, contact of the sediment samples in the columns with atmospheric oxygen does not take place and oxidation reactions of reduced mineral phases and reduced water constituents are prevented.

The large amounts of sediment (10 kg) that are extracted in the columns combined with well-adjusted volumes of the extraction solutions and an optimized sediment-solution ratio enable determination of the amounts and trace element contents of reactive mineral phases with high precision. So, the composition of some reactive phases like carbonate minerals could be determined even though standard mineralogical procedures failed to detect these phases.

The large investigated samples are representative for the composition of aquifers and the heterogeneity of the sediment does not limit the accuracy of the results as much as in batch tests. Furthermore, the technique of flushing sediment in a column is much more realistic and comparable to the process in the aquifer itself than suspending and shaking the samples.

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