Reduced sulphur compounds in sandy aquifers and their interactions with groundwater

W. KÖLLE
Stadtwerke Hannover AG, Hannover, FR Germany

O. STREBEL
Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, FR Germany

J. BÖTTCHER
Landesamt für Bodenforschung, Hannover, FR Germany

Abstract Reduced sulphur compounds participating in redox processes within aquifers are iron sulphides and native sulphur. The most important redox process is denitrification. Reaction products are gaseous nitrogen, sulphate, and ferrous iron. A complex system of kinetic interdependences, in which the activities of bacteria are involved, decides the extent of the oxidation of ferrous iron released from the iron sulphides. The reducing compounds — organic substances included — react sequentially according to their denitrification rate. Half-lives of the redox reactions range from several weeks to several decades. Trace components of sulphides may also be mobilized. Arsenic and nickel are of special interest.

INTRODUCTION

The knowledge of the quality and quantity of the reduced sulphur compounds and organic components of an aquifer material is frequently much more informative than any knowledge about the groundwater quality. Recently, much attention has been paid to components of the aquifer participating in redox processes with nitrate and oxygen. Reduced sulphur compounds play an important role in this context.

The knowledge of the stocks of these compounds is a prerequisite for the interpretation and prognosis of the quality changes in groundwater. This statement does not only refer to the main components of the water like nitrate, sulphate, and ferrous iron, but, in some cases, also to trace elements like arsenic or nickel. All of these components are essential quality parameters for drinking water and therefore of special importance.

IRON SULPHIDES

Reducing aquifers usually contain particles of organic substances like lignite, in
some cases in inconspicuous concentrations of less than 0.1%. However, lignite is a very slow reactant. As a consequence, minerals associated with lignite like iron sulphides usually play a dominant role with respect to the total turnover of redox processes.

Iron sulphides may occur as a component of the lignite itself but also independently as coatings on quartz particles and as crystals of metallic brightness. In some cases, pyrite can be observed as the matrix of petrified organisms.

Mineralogical examinations showed that the observable iron sulphide particles mainly consist of pyrite, marcasite, or coalesced combinations of pyrite and marcasite. The iron:sulphur ratio is 1:2.

Stoichiometry of the denitrification reactions

The denitrification by iron sulphides is mediated by bacteria (Kölle et al., 1983). The most important one is *Thiobacillus denitrificans* which oxidizes the sulphur component of the sulphides to sulphate. A second bacterium is able to oxidize the ferrous iron, released by the activity of the thiobacillus, to ferric iron with nitrate as the electron acceptor. The corresponding equations are the following:

\[ 14 \text{NO}_3^- + 5 \text{FeS}_2 + 4 \text{H}^+ = 7 \text{N}_2 + 10 \text{SO}_4^{2-} + 5 \text{Fe}^{2+} + 2 \text{H}_2\text{O} \quad (1) \]

\[ \text{NO}_3^- + 5 \text{Fe}^{2+} + 7 \text{H}_2\text{O} = 0.5 \text{N}_2 + 5 \text{FeOOH} + 9 \text{H}^+ \quad (2) \]

It is important that both bacteria (both reactions) compete for the available nitrate. When the nitrate is used up, the turnover of both reactions becomes zero. The concentration of ferrous iron at this point of the process is a function of the reaction rate of (2) \( (k_2) \) related to that of (1) \( (k_1) \). In addition, the equations show that the first reaction step consumes, and the second step produces hydrogen ions. Thus, equations (1) and (2) can be combined in such a way that the process is balanced with respect to hydrogen ions. The resulting equation (3) characterizes the situation in unbuffered aquifers, idealized with respect to possible external influences on the hydrogen ion balance. The presence of a sufficient amount of calcium carbonate within the aquifer favours reaction (2) because there is a sink for the hydrogen ions exceeding the balance. According to equation (4) the resulting groundwaters are approximately free from ferrous iron.

\[ 26 \text{NO}_3^- + 9 \text{FeS}_2 + 2 \text{H}_2\text{O} = 13 \text{N}_2 + 18 \text{SO}_4^{2-} + 4 \text{FeOOH} + 5 \text{Fe}^{2+} \quad (3) \]

\[ 3 \text{NO}_3^- + \text{FeS}_2 + \text{CaCO}_3 + \text{H}_2\text{O} = 1.5 \text{N}_2 + 2 \text{SO}_4^{2-} + \text{FeOOH} + \text{Ca}^{2+} + \text{HCO}_3^- \quad (4) \]

A scheme of these interdependences is presented in Fig. 1.
25 Reduced sulphur compounds in sandy aquifers

![Pattern of interdependences of denitrification reactions.](image)

Fig. 1 Pattern of interdependences of denitrification reactions.

It follows from these interdependences that the oxidation of ferrous iron according to reaction (2) is used for "back titration" of the system to a constant pH (in most cases between 6.1 and 6.6). Thus, the pH value is extremely constant, whereas the concentration of ferrous iron is extremely sensitive to external influences.

Stock of reactive sulphur compounds

Kölle et al. (1985) defined a sulphate formation capacity (SFC) of aquifers in kg sulphate per m$^3$ of sediment material. The SFC is based on the real turnover of iron sulphides during incubation experiments with sediment material, which is exposed to an aqueous nitrate solution. Thus, well crystallized sulphides of low reactivity are not included in the SFC results.

Additional information originates from the conventional analytic determination of the total sulphur of aquifer material. The results represent the "theoretical maximum SFC", as Strebel et al. (1985) pointed out. Figure 2 shows, as an example, the SFC-depth functions of the Fuhrberg basin near Hannover at three locations.

The difference between the SFC and the theoretical maximum SFC is due to sulphides of low reactivity. It is questionable if there are any sulphide components having a real long-term stability. Even if they oxidize in the presence of high concentrations of nitrate or even oxygen with a very low rate, they may be responsible for some essential water quality phenomena, especially the concentration of sulphate and traces of ferrous iron.

A very rough estimation for the Fuhrberg aquifer shows that the stock of reactive reduced sulphur compounds, based on results of SFC incubation experiments, is sufficient for a period of denitrification lasting several hundred years.

However, any conclusions from laboratory SFC data on the real behaviour of reduced sulphur compounds in the aquifer are uncertain. It is for example, at present impossible to describe the denitrification as a sequential process which is controlled by the actual reactivity of the available...
residual components. This situation is not adequate with respect to the general importance of long-term prognosis.

**Kinetic aspects**

Böttcher *et al.* (1985) estimated the kinetic parameters of the denitrification process in the Fuhrberg aquifer. It can be described as a first order reaction with a half-life of about two years. However, this is an actual result which is restricted to the present conditions existing in the Fuhrberg aquifer.

Many factors are of importance for denitrification kinetics, e.g. pore water velocity, solute transport conditions etc. Additionally, more detailed information about those properties of the stocks of reducing compounds which influence the kinetics should be available. Since iron sulphides are concerned, information is needed about their chemical and mineralogical identity, their particle size or surface: volume ratio, their crystal quality, and finally their concentration and distribution within the aquifer, which are accessible by prospecting activities.

It is important to realize that these kinetic aspects do not refer only to the process of working off a given stock of compounds by oxidation, but also to the kinetic competition of different reactions: even minor changes of the reaction rates may change the concentration of ferrous iron dramatically. Considerable effects are also to be supposed in the context of well deterioration.

**Chemical and mineralogical identity** It is important to distinguish between native sulphur and sulphidic components, as is pointed out later. Extraction of the aquifer samples with organic solvents and analysis of the extracts for sulphur is the usual method.

A magnetic separation covers pyrrhotite and magnetite, and sulphur
Reduced sulphur compounds in sandy aquifers

analysis of the magnetic components gives information about the pyrrhotite content. The decomposition of pyrrhotite by acids and analysis of the originating hydrogen sulphide is a classical method, based on the insolubility of pyrite and marcasite under the experimental conditions. However, according to the experience available to date pyrrhotite is of minor importance in most aquifers.

As a first approach to the problem, it seems to be adequate to operate with native sulphur on the one hand and the total minus native sulphur on the other hand. The latter criterion represents pyrite and marcasite with sufficient precision, according to the existing experience.

**Particle size** The denitrification by iron sulphides according to equation (1) is a surface reaction. Thus, it should be useful to know the reactive surface of iron sulphides per volume of the aquifer. Because of sulphide coatings on quartz particles and the occurrence of porous sulphide aggregates, results based on particle size distribution are questionable. As a consequence, we try to find specific surface reactions which give quantitative information about the surface area of the sulphides. Techniques of this kind are quite common for the characterization of adsorbents.

**Crystal quality** There are considerable differences in the quality of the crystal lattice of iron sulphides which may influence their chemical (biological) reactivity. This problem, as well as other detailed mineralogical characterizations should be investigated at least after solving the particle size problem.

**Deterioration of wells**

Denitrification by iron sulphides leads to nitrate concentrations of less than 0.1 mg l$^{-1}$ if the reaction time is sufficient. Groundwater containing ferrous iron from reaction (1) and intermediate nitrate concentrations of more than about 0.7 mg l$^{-1}$ should not be abstracted from its reaction milieu because reaction (2) is able to proceed still after abstraction until the nitrate is used up. The consequences are depositions of hydrous ferric oxide ("ochre formation") in wells and raw water pumps and pipes.

Measures resulting in a decrease of the nitrate input into the aquifer or in an increase of the residence time (available reaction time) that are necessary to successfully avoid deposition include: reducing of nitrate leaching from agricultural lands, increase of the distance between wells and areas with high nitrate input, shortening of the well filters and positioning them as deep as possible, and finally operation of the well at a low capacity.

**SULPHUR**

The previous sections of this paper neglected the additional occurrence of sulphate reduction which is possible in aquifers containing particulate organic
substance like lignite, if the reaction time is considerably longer — or the aquifer considerably deeper — than necessary for denitrification alone. Sulphate-reducing aquifers have been able to accumulate mineral stocks of a considerable complexity. The most interesting component is native sulphur.

Sulphur was discovered in aquifer material of a waterworks at Nordhorn. Some samples of this material revealed high SFC values but contained no sulphide phases detectable under a microscope. This was interpreted as the presence of sulphur particles of a few micrometres in diameter as they are stored by sulphur bacteria. Extraction of these samples with organic solvents confirmed this supposition. Organic substances, including hydrocarbons, were also extracted.

Native sulphur could be detected in the depth range from 15 to 70 m below surface with a maximum concentration of 0.75 g kg\(^{-1}\) at 21 m below surface. Iron sulphides occurred only below 32 m.

This aquifer should be used for the subterraneous water treatment for iron and manganese removal. This method implies a periodic change of the well operation; during an infiltration period, oxygen-containing water is introduced into the aquifer, and during an extraction period a groundwater free of iron and manganese can be obtained. The extraction: infiltration ratio is, in many cases, about ten. However, the change of participating volume of the aquifer from a reduced into an oxidized state makes it necessary to "burn out" the reducing components, previous to any subterraneous treatment activity. In the case of Nordhorn the influenced zone of the well is treated by infiltrating a sodium nitrate solution of about 200 mg l\(^{-1}\) nitrate. This procedure is more effective than the use of water with only about 9 mg l\(^{-1}\) of oxygen.

During this work interesting information about the kinetic behaviour of the different stocks of reducing compounds could be obtained under the conditions of the Nordhorn aquifer. The native sulphur denitrifies with a half-life of about 50 days. This rate is considerably higher than that of iron sulphides, which is probably an effect of the uniform distribution and the small particle size of the native sulphur and not of the chemical differences between sulphur and sulphides.

Table 1 represents an attempt to characterize the different stocks of the Nordhorn aquifer according to their kinetic behaviour. Nitrate is "harvesting" the different stocks sequentially according to the half-life of the denitrification reactions involved.

TRACE COMPONENTS

Natural minerals may contain impurities. In some cases the impurities play a more important role as a resource for industrial processes than the basis mineral. In the case of pyrite, nickel, cobalt, and arsenic are able to occupy positions in the crystal lattice of pyrite. Copper and zinc (and a series of other metals) contribute as separate mineral phases to the impurities of pyrite.

In groundwaters characterized by denitrification processes with iron
Reduced sulphur compounds in sandy aquifers

Table 1 Stocks of reducing compounds of the Nordhorn aquifer and their approximate half-lives of denitrification

<table>
<thead>
<tr>
<th>Stock of reducing substance</th>
<th>approximate half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native sulphur</td>
<td>weeks</td>
</tr>
<tr>
<td>Iron sulphides</td>
<td>years</td>
</tr>
<tr>
<td>Lignite</td>
<td>10–100 years</td>
</tr>
</tbody>
</table>

sulphides as reactants, nickel, cobalt, arsenic, and zinc were observed in some cases in remarkable concentrations. These groundwaters usually contain also ferrous iron. Thus, the trace components may occur in the finished drinking water or in the iron oxide precipitation of the treatment plant.

Koppers (1985) reported difficulties in the Netherlands originating from the arsenic content of iron oxide sludges of groundwater treatment plants. Above a maximum permissible concentration of 50 mg kg\(^{-1}\) (related to the dry residue) the sludge has to be considered as a chemical waste. The maximum concentration observed to date is 3100 mg kg\(^{-1}\), which may possibly be interpreted as an effect of a comparatively low iron concentration of the raw water. High concentrations in sludges above 1000 mg kg\(^{-1}\) have been stated also for cobalt, copper, and zinc. Nickel was obviously not analysed.

The advantage of the elimination of trace components from the water leads to the disadvantage of obtaining a chemical waste as a reaction product. About 50% of the Dutch waterworks are affected by this problem, especially with respect to arsenic.

Nickel is an element of a high mobility, or low tendency to be eliminated by adsorption on, or co-precipitation with, iron oxides. The European standard for drinking water of 50 \(\mu g\) l\(^{-1}\) can easily be exceeded, if minerals of the aquifer are releasing nickel.

To date, two treatment plants in the northern region of Germany are known to have some problems with nickel. However, the treatment plant of the waterworks of Fuhrberg is eliminating some nickel. It is interesting to compare (Table 2) the trace components of the Fuhrberg sludge with those of the Berkhof sludge, because these two plants are using practically the same aquifer but differ significantly in the treatment conditions, especially the pH

Table 2 Trace components of the Fuhrberg and the Berkhof sludge (mg component per kg iron, as Fe)

<table>
<thead>
<tr>
<th>Plant</th>
<th>pH</th>
<th>As</th>
<th>Se</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuhrberg</td>
<td>8.8</td>
<td>72</td>
<td>&lt; 1</td>
<td>225</td>
<td>740</td>
</tr>
<tr>
<td>Berkhof</td>
<td>7.3</td>
<td>144</td>
<td>1</td>
<td>&lt; 25</td>
<td>120</td>
</tr>
</tbody>
</table>
during iron removal. The analyses were carried out by the DVGW-Forschungsstelle at Karlsruhe with samples of December 1985. The results are related to the iron content of the sludge for eliminating a dilution effect caused by co-precipitated calcium carbonate in the Fuhrberg sludge. Further investigations should be directed to the pH influence on the mobilization of trace components from the aquifer and their immobilization during water treatment measures.

Acknowledgements It is gratefully acknowledged that part of these investigations has been supported by the Deutsche Forschungsgemeinschaft and part by the Ministerium für Forschung und Technologie.

REFERENCES


