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IN SITU TREATMENT OF ARSENIC CONTAMINATED GROUNDWATER

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ABSTRACT
Groundwater in a sand and gravel aquifer was contaminated by arsenic compounds. The extent and the As concentration of the polluted groundwater plume decreased from 1971 to 1975, whereas the content of free dissolved oxygen increased. High As concentrations (>1 mg/l) occured in groundwater with typical characteristics of a "reduced" water with negative Eh values and high concentrations of dissolved iron (up to 140 mg/l in 1971). When plotted into an As stability field diagram, the higher values (> 1 mg As/l) coincided with the fields of trivalent As species, whereas the lower values (<0.1 mg As/l) fitted to the fields of the pentavalent arsenic species. Therefore it was concluded that an improvement of the oxygen supply should accelerate the natural precipitation processes. By injection of 29,000 kg $KMnO_4$ into 17 wells and piezometers the soluble As (III) species were oxidized to As (V) species, which were precipitated as $FeAsO_4$ or $Mn_3(AsO_4)_2$ or co-precipitated with Mn- and Fe-hydroxides.

INTRODUCTION
The groundwater in the vicinity of a zinc ore smelter near Cologne, West-Germany, which operated from 1913-1971, was contaminated by arsenic compounds.They originated from the flue gas wash, which used sulphurous acid solution. Its effluent was treated with $Ca(OH)_2$ solution at pH >8 to precipitate As_2O_3 as $Ca_3(AsO_4)_2$. However due to the fairly high solubility of $Ca_3(AsO_4)_2$ traces of arsenic remained in solution and seeped from the cribs into the aquifer. The contaminated groundwater plume was detected in 1971 (Ref.1). Detailed studies and efforts for removing the dissolved As from groundwater followed in the interval 1971-1979.

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HYDROGEOLOGICAL AND HYDROGEOCHEMICAL CONDITIONS

The aquifer consists of Pleistocene sands and gravels with intercalated layers of silt, clay and coarse gravels. It is underlain at 18.5 - 27 m depths by silty fine sands of Oligocene age. The average hydraulic conductivity of the Pleistocene aquifer is $2.6.10^{-3}$ m/s (range $0.5.10^{-3}$-$3.7.10^{-3}$ m/s). For the underlying Oligocene clayey and silty fine sands an average value of 1.10^{-5} m/s is quoted (Ref.1). The groundwater flow direction and velocity is controlled by the water table in the river Rhine. At mean and low discharge it flows towards the river, however during floods river water infiltrates and groundwater flows for some time landwards. Nevertheless over the whole year a general, but retarded net groundwater inflow in the river occurs. The average flow velocity is 0.9 m/d (Ref.1), but higher flow velocities and even stagnant conditions are observed at times.

In the contaminated zone 41 piezometers of different lengths were installed, some of them as piezometer nests (2 nests with 4 piezometers, 2 nests with 3 piezometers and 11 nests with 2 piezometers). In addition five injection wells were drilled in 1976/77. Thus it was possible to investigate the spatial distribution of the contaminant.

Near the cribs the sediment grains were found to be coated by yellow and brown As containing precipitates (Ref.1). The As concentration in the sediments varied in horizontal and vertical direction. In a drill hole in the centre of the contaminated zone 10 to 170 mg As/kg sediment (average 78 mg/kg) were measured, with the highest values in the lower part of the Pleistocene aquifer. With help of selective extraction methods it could be shown that As was present in form of water soluble oxides, as sulphides insoluble in dilute acids and as compounds of the type FeAsS (arsenopyrite) poorly soluble in dilute acids. Realgar (AsS), a calcium arsenate ($CaAs_2O_6$, $CaAs_2O_7$) and gypsum (containing 50 mg As/kg) could be identified mineralogically. Besides these phases microcrystals and poorly crystallized As bearing substances were observed.

The contaminated groundwater plume was characterized by reducing conditions shown by elevated contents of dissolved ferrous iron (up to 140 mg Fe^{2+}/l in 1971), negative Eh and low pH values (Table 1). This reducing condition are presumable due to the oxidation of sulphurous to sulphuric compounds which in 1971 were present in concentrations up to 2010 mg/l.

In 1971 the As concentrations were as high as 56 mg/l at 20 m depth near the source of contamination, in contrast to a natural background of $<$0.01 mg/l. The contaminated groundwater plume diminished during the

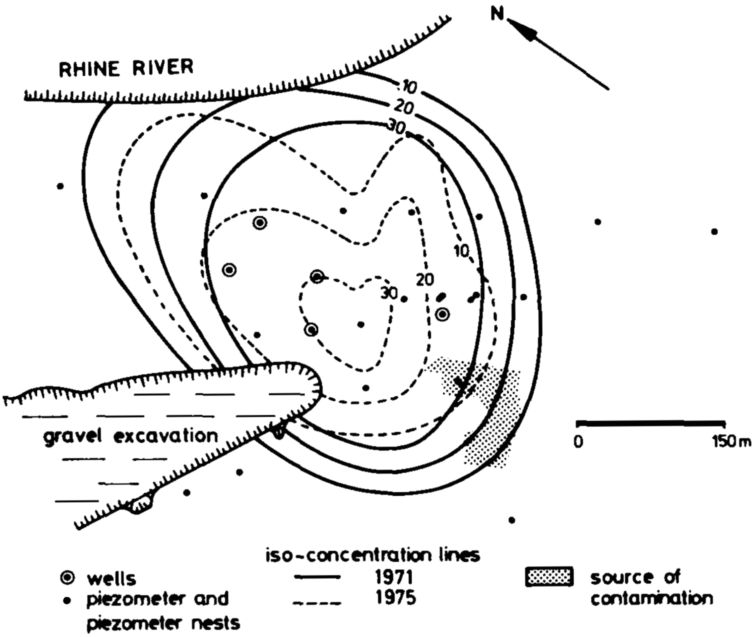

Fig. 1. As concentrations in the lower part of the aquifer

time interval 1971/1975, but the highest concentration, 26.4 mg/l, was still found in the same piezometer nest. In January 1975 Eh and pH measurements were performed together with simultaneous determination of dissolved arsenic. The observed pH-, Eh- and As-values were plotted on a stability field diagram (Ref.3). It turned out that the higher As contents ($>$1 mg As/l) fell into the $HAsO_{2aq}$ field, whereas the lower contents ($<$0.1 mg As/l) lie in the fields of the pentavalent arsenic species $H_2AsO_4^-$ and $HAsO_4^{2-}$. Water samples with As contents between 0.1 and 1 mg/l lie on or close to the boundary between trivalent and pentavalent As species. Therefore it was concluded that the dissolved As was present in a trivalent state and that the transfer into pentavalent species in presence of Ca^{2+}- and Fe^{2+}-ions would produce an appreciable precipitation of dissolved As. Another diagram of Hem (personal communication) including CO_2 and S species shows that at low Eh and pH values As sulphides are stable. Under oxidizing conditions the As sulphides will be oxidized to arsenate and sulphuric acid (1).

$$As_2S_3 + 8O_2 + 4H_2O \rightarrow 2HAsO_4^{2-} + 3H_2SO_4 \quad (1)$$

The free acids will react with dissolved or solid substances, e.g. calcium carbonate, calcium and iron II ions.

PROCEDURES AND RESULTS

The observation that during the interval 1971/1975 the As concentration and the extension of the contaminated plume were diminished, together with a shift of the pH and Eh to higher values led to the notion to accelerate this movement toward oxidizing conditions. Therefore various oxidizing chemicals were tried out (H_2O_2, NaOCl, $KMnO_4$). It could be shown that $KMnO_4$ is a strong oxidizing agent even in dilute solution, which oxidizes As (III) in acid and basic solution to As(V). For acid solutions its effect can be described by equation (2)

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O \quad (2)$$

and for basic solutions by equation (3)

$$MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4OH^- \quad (3)$$

In the contaminated groundwater plume acid and neutral pH conditions could be observed. Therefore both reactions may occur. The Mn^{2+} ions according to equation 2 may combine with the oxidized As species to form the fairly insoluble Mn II-arsenate $Mn_3(AsO_4)_2$ ($K_{SP} = 2.10^{-29}$) (Ref.5) or with Fe^{3+} ions to Fe III-arsenate ($FeAsO_4$) ($K_{SP} = 5.7.10^{-21}$) (Ref.2). Furthermore the As species may be coprecipitated with MnO_{2aq} according to equation 3 or with iron III hydroxides. Gulens et al. (Ref.4) indicated that As (V) and As (III) form complexes with Fe (III) in solution, with Fe (III) - As (III) complex being more soluble than the Fe (III)-As (V) complex. The consumption of H^+ (eqn.2) or production of OH^- (eqn.3) may shift the pH to a higher value.

After some laboratory experiments with sand filled lysimeters and some preliminary field experiments which proved that $KMnO_4$ is an effective, persistent oxidizing agent, it was decided to use a solution of about 2 g $KMnO_4$/l for the injection. This solution minimized the clogging effect close to the well screens which is due to the precipitation of iron III hydroxide and other substances. From December 1976 to May 1977 29.000 kg $KMnO_4$ were dissolved and injected into 17 wells and piezometers. The demand of $KMnO_4$ was calculated for each injection well using the measured average $KMnO_4$ demand of the water filled sediment of 0.472g $KMnO_4/m^3$. In the following time the injection water mixed with the contaminated groundwater due to dispersion in the aquifer, in which changing groundwater flow directions are typical.

TABLE 1:

pH, Eh, As-, Fe^{2+} contents and specific electrical conductance in the contaminated groundwater plume in 1971, 1975 and 1977.

	1971	1975	1977	1979
ph	3.1 - 7.0	4.8 - 7.0	5.5 - 7.8	5.8 - 8.2
Eh mV	-	-110 -+20	-100 -+440	-120 -+440
As mg/l	<0.01- 56	<0.01 - 26	<0.01 - 0.3	<0.01 - 5.6
As average mg/l	22.7	13.6	0.06	0.4
Fe^{2+} mg/l	0.2-140	<0.1 - 93.3	-	-
SO_4^{2-} mg/l	152-2010	80 -1670	-	-
Spec.electrical conductance $\mu S/cm$	-	440 -2300	600 -2250	650 -2150

The values vary according to the site and depth of the observation wells. The improvement of the groundwater quality is obvious, but as the negative Eh-values in 1977 and 1979 and the locally higher As concentrations (> 1 mg/l) in 1979 show no total mixing of contaminated water and injection water could be achieved up to now. Therefore the respective wells will be subject to new injections.

TABLE 2:

Supply of As into the river Rhine

Width of the contaminated plume	m	266
Thickness	m	20
Groundwater flow velocity	m/d	1
Groundwater discharge	m^3/d	5320
Average As concentration	g/m^3	0.06
As discharge	g/d	319.2
	g/s	$3.69.10^{-3}$
Rhine discharge (Emmerich) average	m^3/s	2330
Increase of As-concentration	g/m^3	$1.6.10^{-6}$

The As discharge, calculated for the data of 1977 (Table 2), is under the level of detection for the usual As measurement. It is about 0.01% of the up to date As discharge of the Rhine river (calculated for average discharge) and 0.3% of the natural background (Table 3, Ref.6).

Table 3:
Comparison of As discharge of the river Rhine (kg/a) and the As concentration (mg/l) (Ref. 6) with the As discharge from the contaminated groundwater plume.

		kg/a	g/s	mg/l
As discharge of the Rhine river at average discharge ($2330\ m^3/s$)	dissolved	375,000	11.89	$5.1.10^{-3}$
	suspended	500,000	15.85	$6.8.10^{-3}$
	total	875,000	27.74	$11.9.10^{-3}$
Natural background		34.000	1.08	$0.46.10^{-3}$
As discharge from Nievenheim		116.5	0.0037	$0.0016.10^{-3}$

CONCLUSIONS

The considerable reduction of the As concentration and the total amount of dissolved As species between 1971 and 1975 obviously occured without human contribution due to a gradual oxidation of trivalent to pentavalent As species and of ferrous to ferric iron species as oxygen was supplied by the seepage, the intermixture of oxygenated groundwater and gas exchange with the ground air. This oxidation favoured the precipitation of the fairly unsoluble $FeAsO_4$. This natural process was accelerated by the addition of $KMnO_4$ solution, which improved the removal of dissolved As by precipitation of $FeAsO_4$ and $Mn_3(AsO_4)_2$, by coprecipitation and adsorption of As on $Fe(OH)_3$ and $MnO_2\ nH_2O$

REFERENCES

1 K.-D.Balke, H. Kussmaul and G. Siebert, Z.deutsch.geol. Ges. (1973) 447-460, Hannover.

2 Chukhlantev, J.anal.Chim. 11 (1956) 529-535.

3 J.D. Hem, Geochim. Cosmochim Acta, 41 (1977) 527-538.

4 J. Gulens, D.R. Champ and R.E. Jackson, Chemical Modeling in Aqueous Systems, ACS Symp. Ser. 93 (1979) 81-95

5 L.Meites, Handbook of Analytical Chemistry, (1963) New York (McGraw-Hill).

6 R.D.Schuiling, Geologie en Mijnbouw, (1974) 123-197.