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FORMATION OF SECONDARY IRON MINERALS AND THEIR INFLUENCE ON THE MOBILITY OF
ARSENIC DURING THE FLOODING OF OPEN-CAST LIGNITE MINES

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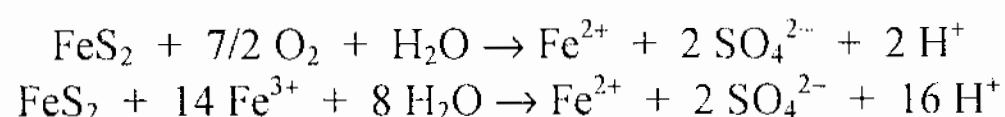
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ABSTRACT

The flooding of open cast lignite mines in Eastern Gemany raises the risk of widespread contamination of ground water due to the mobilization of oxidation products of the pyrites, which are common in the backfill. Samples from a research borehole in the shut-down open-cast Cospuden show distinct zones of immobilization and mobilization of iron and arsenic. After ten years the conveying bridge spoil was covered with an approximately 17 m thick stacker spoil dump. The upper 2-3 m of the older dump are a zone of reduced element mobility. Fe is immobilizied, e.g. as jarosite and arsenic is predominantly adsorbed on secondary minerals like ferrihydrite and/or schwertmannite. Beneath this upper zone follows a section with ongoing pyrite oxidation resulting in an enhanced mobility of iron and arsenic with the potential of ground water contamination during flooding of the open-cast.

INTRODUCTION

The open-cut mining of lignite in Eastern Germany produces the potential risk of ground water contaminations in post-mining periods. This is due to the pyrite content of up to 5 wt.% of the barren rocks. The drawdown of the ground water table during mining and the stacking of overburden dumps bring these pyrites in intensive contact with oxygen. The oxidation of pyrite by oxygen and/or iron(III) is a well established process (Lowson 1982, Moses and Herman 1991, Nicholson et al. 1988 Williamson and Rimstidt 1994), which can be expressed in the following overall reactions:

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$
$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$$

As a result, the pyrite oxidation produces acid, sulfate and iron - constituents, which could be released into the ground water during the flooding of former mining sites. However, there is also the possibility of stabilisation of the oxidation products in secondary minerals. The end-members of these secondary minerals are on the one hand Fe(II)-sulfates like melanterite and rozenite (Borek 1994) and on the other hand Fe(III)-oxyhydroxides/-oxides like goethite and hematite (Borek 1994, Schwertmann and Murad 1983, Nicholson et al. 1990). Besides them, intermediates like jarosite and especially schwertmannite (Bigham et al. 1990, 1996, Schwertmann et al. 1995)suggest a complete series of minerals with decreasing sulfur-content.

Furthermore, the pyrite oxidation releases not only the main constituents but also several trace elements, of which arsenic is a higly toxic and common one. As an isomorphic substituent for sulfur, arsenic can have concentrations of up to 3 wt% in hydrothermal pyrites (Arehardt 1993, Mumin et al. 1994). Belzile and Lebel (1986) and Belzile (1988) have reported of arsenic concentrations in sedimentary pyrites showing an As/Fe-ratio of up to 1:1000. Any evaluation of the potential of pyrite derived arsenic to contaminate ground water must be linked to the nature and stability of secondary iron minerals, as arsenic is strongly immobilized by sorption to these iron minerals (Dzombak and Morel 1990, Waychunas et al. 1993).

THE STUDY AREA

The former important open-cut coal mining in the region south of Leipzig in Eastern Germany (fig. 1) was reduced to only one vast open pit for the last few years. This open pit near the small village of Zwenkau is in production since 1924 and since 1930 the conveying bridge technology has been used. The mined areas were backfilled by the conveying bridge but not rehabilitated for a long period. A smaller site cut to the north is the pit of Cospuden (fig. 2), which was mined during the 1980s and has been rehabilitated in recent years. After ten years, the dumps of the conveying bridge were partly covered by a stacker spoil dump. Due to the mass deficit derived from the coal extraction, an open pit remains in the centre of Cospuden, which is now being flooded by ground water and surcharge from the drawdown in the area of active mining.

Research well Cospuden

A research well with core sampling was drilled 50 m down to the base of the backfill in Cospuden to investigate the influence of the spoiled materials in the ground water quality during the flooding. Drilling through 17.5 m of stacker spoil dump, the borehole reached the top of the conveying bridge dump. It is to be expected that the siltic clayey fine sands of the upper few meters of this older spoil are the zone of most extensive weathering due to the long lasting contact to air oxygen before they were covered by stacker spoil. Indeed a distinct zone of high jarosite-content of up to 10 wt.% was reported between 18 and 20 m depth (Pentinghaus et al. 1997).
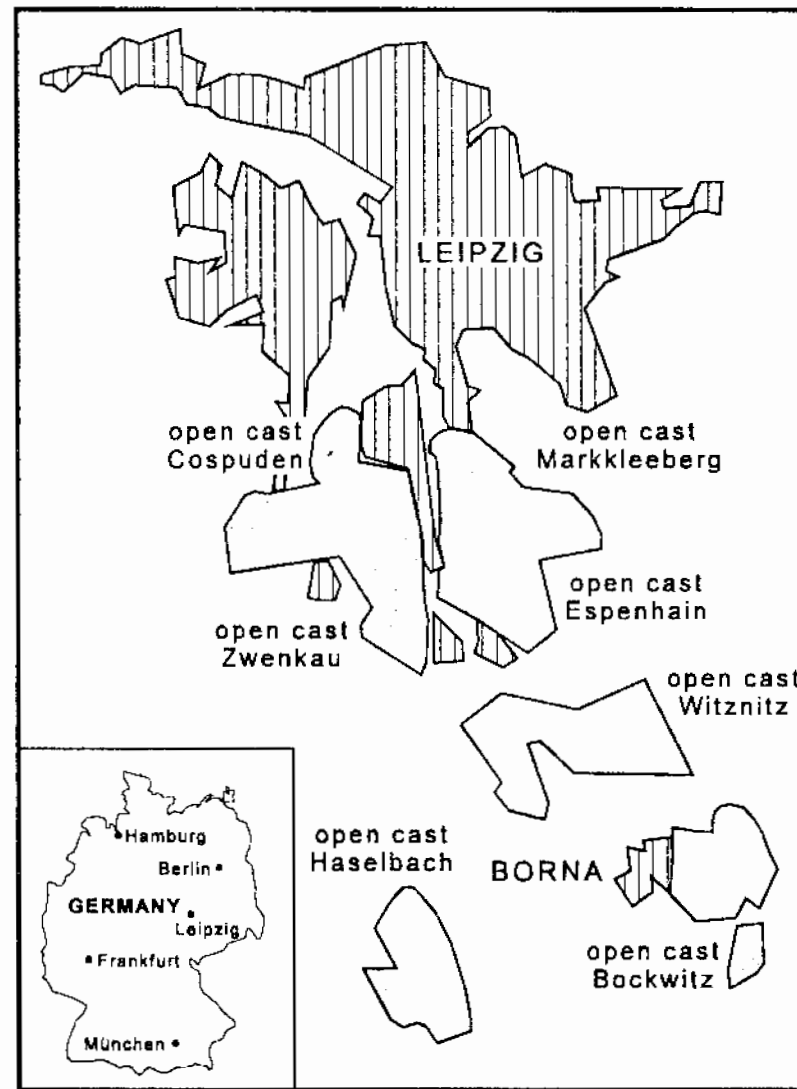
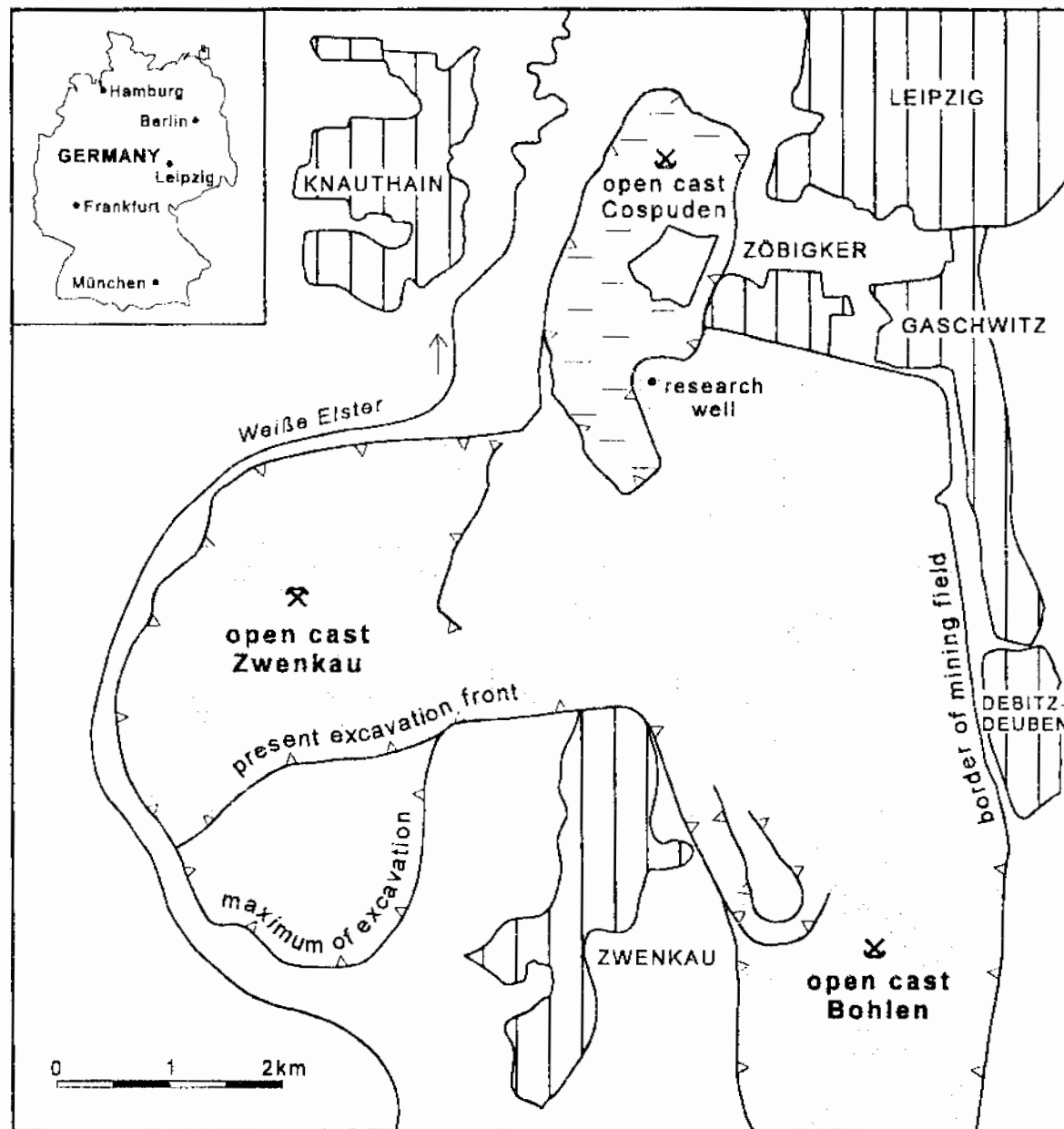Figure 1: Open-cast mining in the region of Leipzig (Eastern Germany).

Figure 2: Sketch map of the lignite mining field just south of Leipzig.

To clarify the mobility of iron and arsenic and/or the stability of secondary minerals in changing chemical environments, we used a sequential extraction scheme (Zeien & Brümmer 1989). Samples of the upper five meters of the conveying bridge spoil were sequentially extracted in a scheme characterized by a decreasing pH (from 7 down to 0) and a successively stronger extraction power of the reagents (tabl. 1). The samples were not dried prior to their extraction.

Table 1: Sequential extraction scheme used in this study (5g sample + 50 mL reagent each).

No.	reagent	Procedure	technically defined fraction
1.F	water	shake 30 min.	readily soluble
2.F	ammonium nitrate	shake 24 h	mobile
3.F	ammonium acetate	shake 24 h	easily successable
4.F	hydroxylamine-hydrochloride	shake 30 min.	adsorbed to Mn-oxyhydroxides
5.F	EDTA	shake 90 min.	organically bounded
6.F	oxalic buffer	shake 4 h in darkness	Fe-oxyhydroxides, low crystall.
7.F	oxalic buffer + ascorbic acid	90 min., T = 90 °C	Fe-oxyhydroxides, high crystall.
8.F	digestion	autoclave	residue

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RESULTS AND DISCUSSION

The total concentration of iron increases from the top of the conveying bridge spoil downwards from 15 g/kg up to 30 g/kg. The total arsenic concentrations show a more irregular pattern, with lower concentrations of 8 to 10 mg/kg in the upper 2-3 meters and higher concentrations between 15 and 29 mg/kg in the lower part of the sample core. These arsenic concentrations are not dramatic but well above the crustal background value of 1-2mg/kg (Woolson 1983) and reflect roughly a As/Fe-ratio similary to the findings of Belzile and Lebel (1986) and Belzile (1988).

The distribution of iron in different mineral phases of the spoil is mainly characterized by three fractions: iron readily soluble in water, iron oxyhydroxides and an acid soluble fraction (fig. 3).
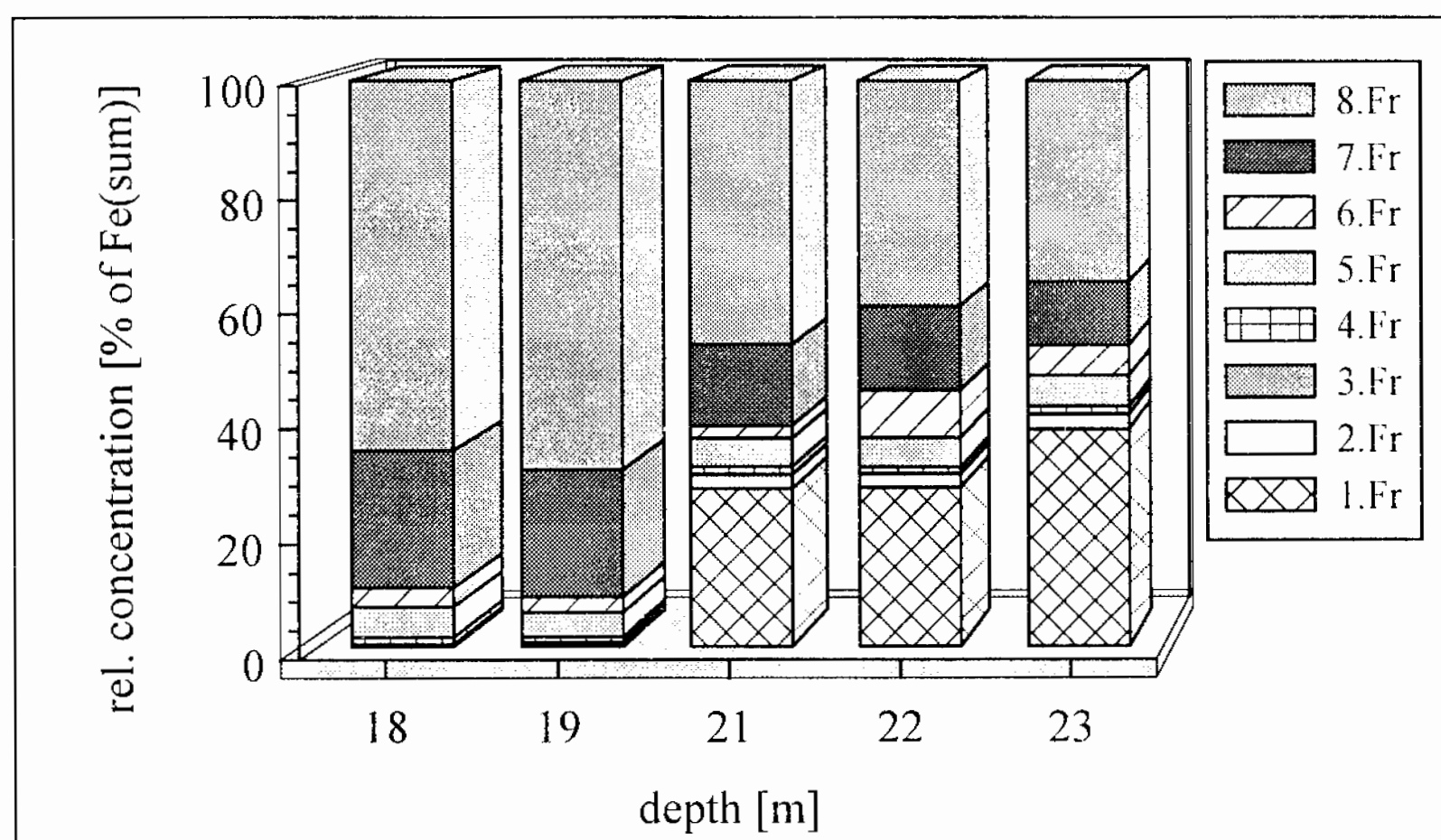

Figure 3: Distribution of iron in different fractions of samples from the drill core Cospuden.

In the upper 2-3 m of the conveying bridge spoil the water soluble Fe-fraction has only a small share of 0.5 % of the total concentration, which increases drastically down below 20 m borehole depth to values of 28 % to 38 % of Fe(sum). The oxyhydroxides have a share of 25-27 % in the upper and 14-22 % in the lower part. Remarkable is the shift between the two different oxyhydroxide fractions, e.g. the 6th and 7th one. The share of the 7th fraction, e.g. comprising goethite and/or hematite, is reduced from 22-24 % in the upper to less than 15 % in the lower part. Compared with this, the concentrations of less crystalline Fe-oxyhydroxides like ferrihydrite or schwertmannite, which are readily soluble in the 6th reagent (oxalic-buffer), are enhanced with increasing depth, although they occupy only a small share of the total iron concentrations.
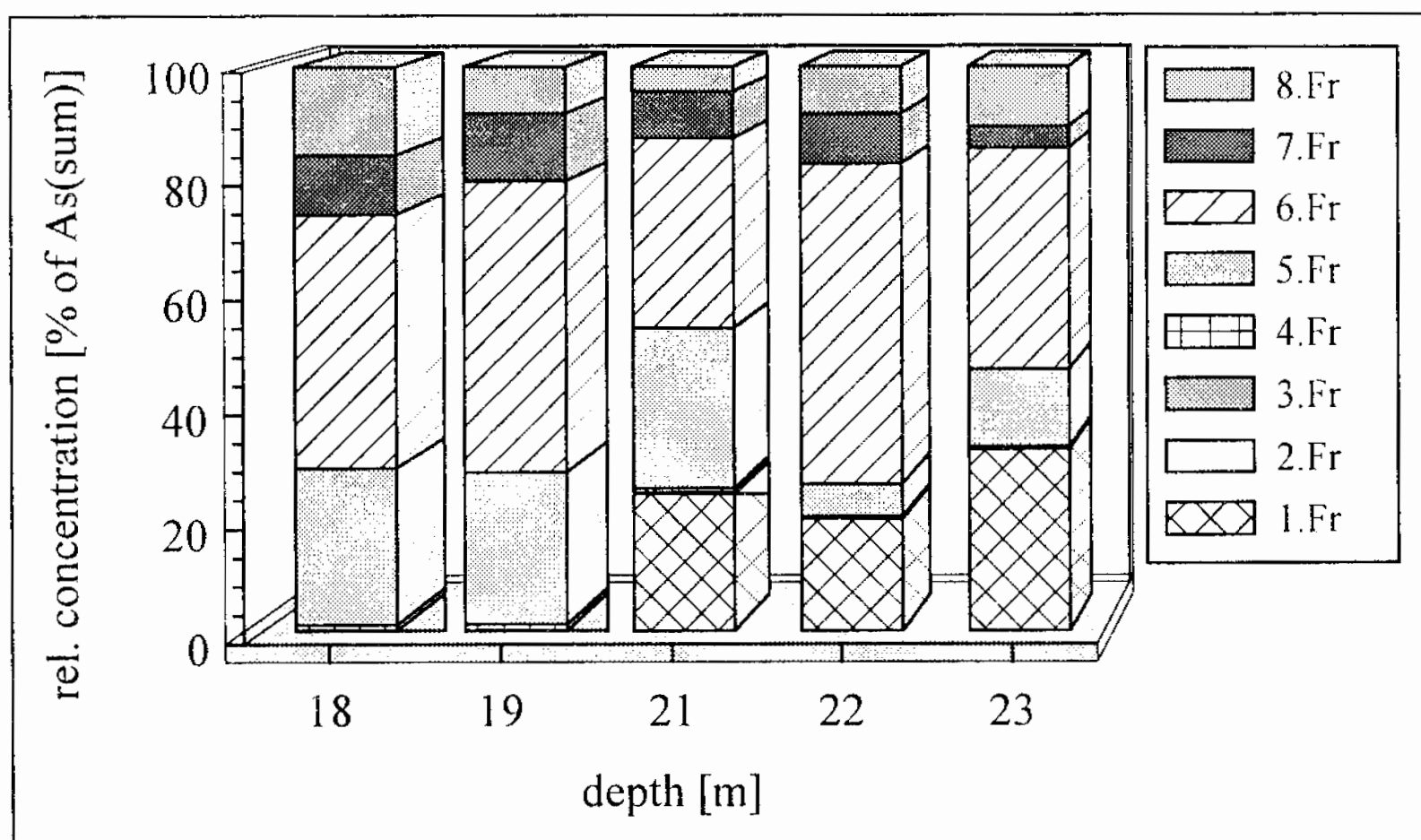
Figure 4: Distribution of arsenic in different fractions of samples from the drill core Cospuden.

The main fraction of iron is the acid soluble one. The residue of the extraction scheme comprises not only the silicate bounded iron, but also e.g. jarosite. This correspondes well to the observation of a high jarosite content in the upper two meters of the conveying bridge spoil (Pentinghaus et al. 1997). In these samples the 8th fraction has the highest share of the total Fe-concentrations, i.e. up to 68 %. With increasing depth, this share is noticeable reduced to values of around 40 %.

Arsenic (fig. 4) is preferentially fractionated into the organically bound fraction, into the 6th fraction adsorbed to iron oxyhydroxides of low crystallinity and, in three samples, into the water soluble fraction. Especially the last fraction shows a distinct depth pattern with low arsenic solubility in the upper samples, e.g. around 0.02 % of As(sum), and high shares of 20 - 30 % in the lower part of the core. The highest share of the total arsenic concentrations is in the 6th fraction with values of 34 to 56 %.

CONCLUSIONS

The drill core of the research well disclosed a distinct zoning in the conveying bridge spoil dump of Cospuden. The upper two to three meters are characterized by low solubility of arsenic and iron and a pronounced occurence of stable secondary iron minerals, e.g. jarosite. Below these upper few meters the solubility of both elements is strongly enhanced and the the most stable secondary iron minerals are decreased. With respect to the link of arsenic to the iron fractions, most important for the immobilisation of arsenic are secondary iron minerals like ferrihydrite and schwertmannite. Although they contribute only a small percentage to the total iron concentrations, they are highly important, due to their large specific surface and high adsorption capacity for oxyanions like arsenic.

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In summary, the fractionation pattern of iron and arsenic shows a cap zone in the top of the conveying bridge spoil,where elements are highly immobilized by stable secondary iron minerals. This zone could represent well oxidized material behind an inward migrating oxidation front. Beneath this zone follows a section with a high mobility of both elements, maybe representing a segment of ongoing pyrit oxidation and mobilisation of the constituents. In this lower part the former surface conditions of the dump seems to be conserved and there is still on the potential of releasing contaminants like arsenic into the upwelling ground water.

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