

ORIGINAL ARTICLES

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Sulfide oxidation—an environmental problem within colliery spoil dumps

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Abstract Because of the high degree of automation in the coal mining industry in the Ruhr area, Germany, about 1 metric ton of crushed rock/colliery spoil is brought to the surface for every metric ton of coal. Most of the colliery spoil disposed of must be dumped. These colliery spoil dumps are anthropogenic geological sediment bodies, which have a characteristic “facies” resulting from geological, technical, and economical factors connected with the formation of the dumps. The relation between the facies of the dumps and these factors, for example, is exemplified with the pyrite content within the colliery spoil. Pyrite content within the dumps is dependent both on the conditions during sedimentation and (early) diagenesis and the techniques used for mining and processing. Thus, this “geologic-technical” facies of the dumps controls the weathering processes on and in dumps. These human-induced processes are mainly responsible for the environmental impact on soil and groundwater. Oxidation of pyrite as well as alteration of pyrite under anoxic conditions yields dissolution of carbonates, accompanied by gypsum formation, by acid attack and strong acidification takes place.

Key words Sulfide oxidation — Colliery-Spoil dumps

Introduction

In the Ruhr area of Germany, Upper Carboniferous coal is mined. With the development of hard-coal mining from shallow-depth workings in the 13th century to contemporary, highly mechanized actual underground mining, the proportion of colliery spoil (*Berge*) in the run-of-mine production increased steadily. With actual mining, clay-, silt-

and sandstones from the roof, from dirt bands in the seams, and from the floors of the seams are brought to the surface. Smaller amounts of colliery spoil come from shaft sinking and from development headings. Colliery spoils actually account for up to 50 mass % of the run-of-mine production. From the 50 million tons of colliery spoils mined annually, only small portions are utilized or stowed underground. The largest portion, an average of 36 million tonnes per year, has to be dumped. In the early period of underground mining cone-shaped dumps were tipped by conveyors immediately adjacent to the mine. In the early 1950s dumps were given a plateau shape in order to make better use of ground surface and to prevent spontaneous combustion. Currently, dumps are shaped according to landscaping criteria with the intention of making them harmonize with their surroundings.

Weathering of the colliery spoil mined from Upper Carboniferous strata causes a breakdown of the coarse spoil particles. The effectiveness of weathering mechanisms is related to the petrography of the spoils (Wiggering 1984; Kerth 1988; Kerth and Wiggering 1990). Within a few years of being dumped, the spoils acidify due to iron disulfide (pyrite) oxidation. The pH of the solid colliery spoil drops from about 8 to about 3.

Composition of colliery spoil

Petrographically, the spoil consists of sand- and clay/siltstones, together with small amounts of coal, pyrite and siderite concretions. Minor amounts of underground building materials (concrete, slag, steel parts, polyurethane foam etc.) are also present. Fresh spoil consists of illite, chlorite, and kaolinite, quartz, small amounts of feldspar, siderite, ankerite, calcite, sulfides (mainly pyrite), and chlorides. Additives used for coal processing such as magnetite are frequently present.

The mineralogical composition of the clay minerals of the colliery spoils is dependent on the depositional lithofacies of the Carboniferous clay/siltstones and sandstones.

From the detrital clays, kaolinite is concentrated in the finer grained sediments relative to the amounts of illite. The chlorite and interstratified illite-smectite undergoes diagenetic modification (Teichmüller 1962; Esch 1962). The fresh, unweathered colliery spoils investigated in this study are dominated by illite, chlorite, and kaolinite (Wiggering 1987). Only a few vermiculites and illite-smectites have been retained by the rock material.

Weathering of dumped colliery spoil

For studying weathering of colliery spoils of the Ruhr area, spoil profiles of differing age have been sampled and analyzed and weathering experiments under controlled laboratory conditions have been carried out. The investigations show that the initial process during weathering is the dissolution and leaching out of the chlorides with rainwater. In the weathering experiments, an almost instantaneous leaching out of chlorides can be observed (Kerth 1988).

Mechanical weathering produces small particles and so enhances the weathering processes by exposing the spoils to oxygen and water. The dominant weathering process is the bacterially catalyzed oxidation of pyrite. Within a few years time of being dumped, the iron disulfides are completely oxidized in the upper meter or so of the spoil profiles investigated (Fig. 1) (after Kerth and Wiggering 1990)).

In a first weathering stage with pH values buffered by carbonates at about 7, the acid generated by iron disulfide oxidation is neutralized by the carbonates present in the spoil. By acid attack, even the less acid-soluble siderite is dissolved. Iron hydroxides, gypsum, and thenardite are formed (Wiggering 1984; Kerth 1988). The latter results from exchange of calcium and sodium at the Na-saturated cation exchange sites of the spoil (Kerth 1988). Concrete particles in the spoil are attacked and ettringite is formed. Through the action of rainwater, gypsum and thenardite are partly leached out of the spoils

A second weathering stage starts when all carbonates are dissolved by the acid (Fig. 1). The pH rapidly drops to values of about 3. The presence of jarosite ($\text{KFe}_3(\text{OH})_6[\text{SO}_4]_2$), together with kaolinite and silica, is responsible for buffering pH at this value (Miller 1979). Jarosite is a product of iron disulfide weathering at acid conditions (Brown 1971).

Buffering mechanisms clearly can be shown if pH values of colliery spoils of different ages are plotted according to their abundance (Fig. 2). Distinct maxima occur at pH values of about 7 and 3. Between 6.5 and 3.5 no buffering systems exist in colliery spoil, thus leading to a fast drop of pH from near neutral to strongly acid conditions when all carbonates are dissolved.

In weathering experiments, some spoils show a rapid drop of pH of leachates from 7 to about 3 within one year of investigation, a result that also illustrates the lack of buffering systems between pH 6.5 and 3.5 (Kerth 1988).

If neutralizing materials are added to weathered spoil,

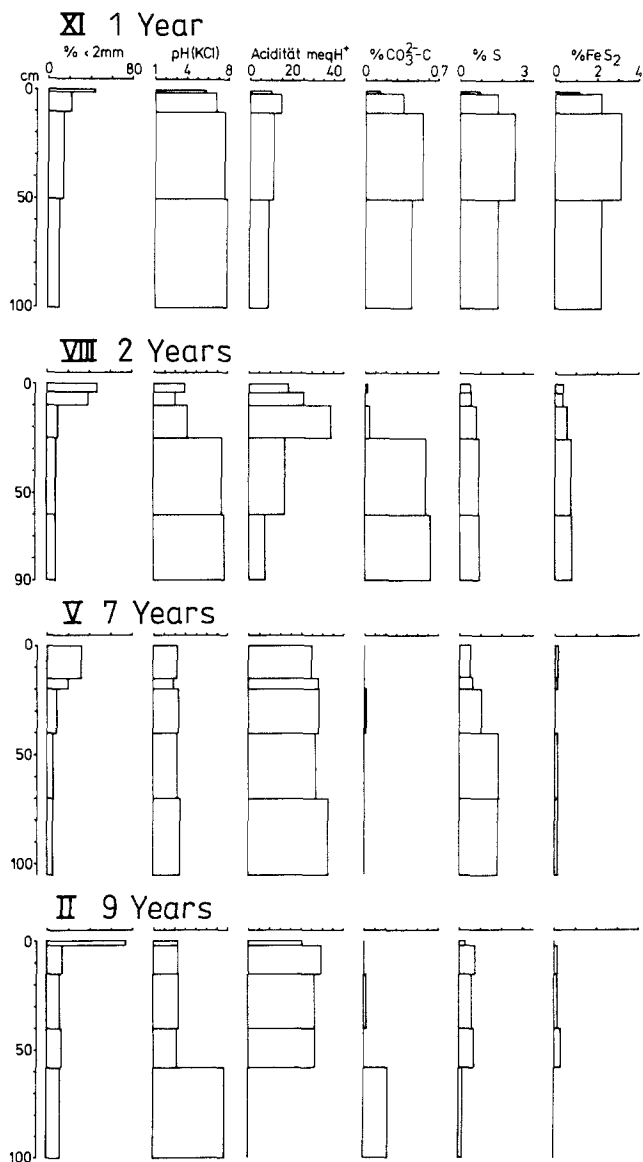


Fig. 1. Progress of pyrite oxidation and geochemical changes (pH measured in 1 N KCl) of the solid colliery spoil due to the pyrite oxidation on dumps of different age (after Kerth and Wiggering 1990)

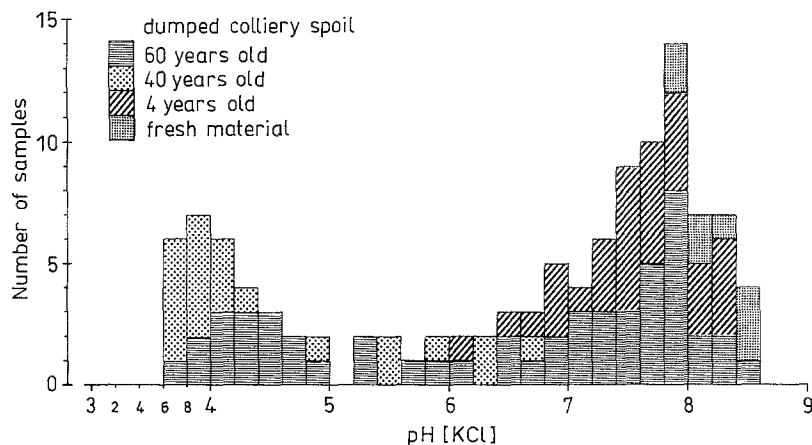
jarosite becomes unstable and dissolves. The jarosite iron is precipitated as iron oxyhydroxide. Since the precipitation of iron oxyhydroxides leads to the formation of free acidity, jarosite stores the acidity formed by iron disulfide weathering (Van Breemen 1973, Kerth 1988).

Thus, although the iron disulfides are oxidized within a few years, the acidity of spoil remains high due to the presence of jarosite.

The strong acidification of the spoils is generally followed by a chemical degradation, leading to a progressive decomposition of clay minerals (Wiggering 1984, 1986, 1987):

1. After a fast physical splitting of the colliery spoil during initial weathering, these processes slow down and chemical attack on the clay minerals predominates. During initial weathering, "open" illites

Fig. 2. Buffering systems shown by plotting pH values (pH measured in 1 N KCl) of colliery spoil of differing age against their abundance



(smectite–illites) with montmorillonite behavior occur (3 to 4-year-old dumps).

2. During weathering there is a continuous transition between well-crystallized illite, mixed layers built on illite layers, and montmorillonitic interlayers. Heat labile, unstable chlorites occur in colliery spoil with low pH (5 to 30-year-old dumps).
3. In strongly weathered, old colliery spoils (40 to 70-year-old dumps), smectites and/or randomly mixed layers composed of montmorillonite and illite layers occur. The smectites are interpreted to be illite-derived smectites.

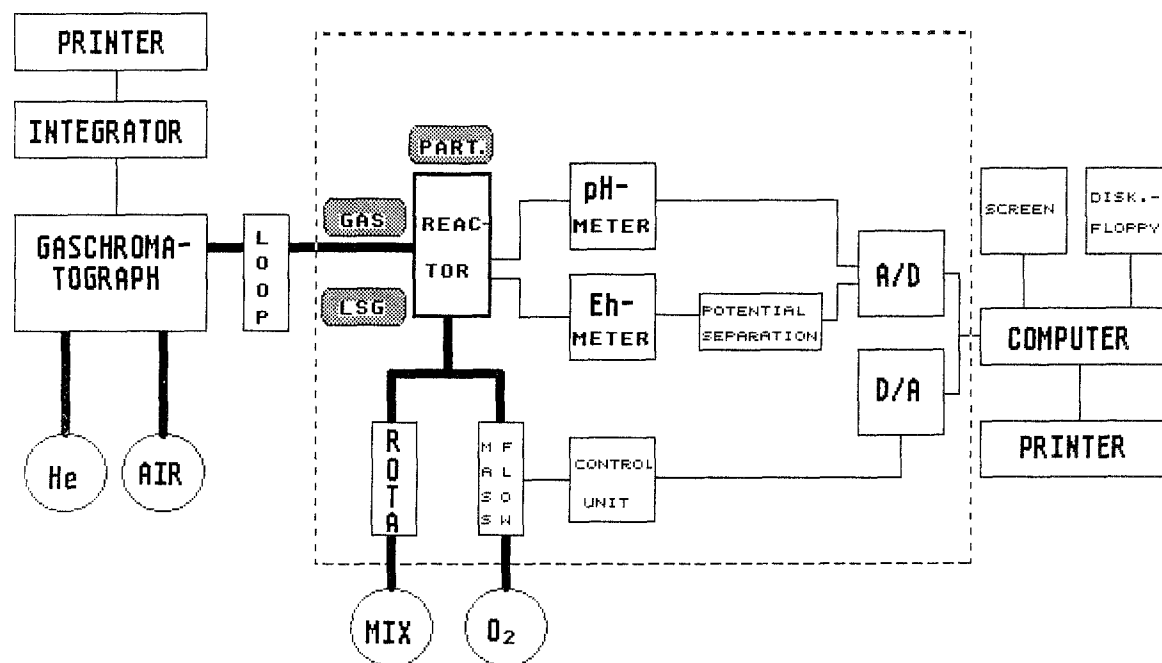
we can accommodate up to five reactors to carry out experiments simultaneously under different conditions. The reactors (Fig. 4) are manufactured of Duran glass. The gas mixtures are supplied through glass frits. Two apertures closed off with silicon stoppers permit sampling of gas, solutions, and/or suspensions. Solid weathering products are removed from the reactors without air contamination. The samples are prepared for further analysis in an N_2 atmosphere. Eh and pH are recorded continuously, and the data are transferred to a PC by an analog-to-digital converter. Gas is supplied through a special piping system controlled by a rotameter. An N_2 (68 mass %)- CO_2 (31 mass %)- H_2 (1 mass %) synthetic anoxic atmosphere was passed as “standard atmosphere” continuously through the sample-containing reactor at a constant rate of 2 l/h while the pyrite samples were submerged under water. Oxygen was purged separately by mass flowmeters, regulated by another control unit.

To avoid the effect of microbiological encroachment, the reactors, the samples, and the double-distilled water were sterilized by exposure to a pressure of 2 bar and a

Weathering experiments: Technical procedure

A special apparatus was designed for the experiments (Fig. 3). In the field surrounded with dashed lines in this scheme

Fig. 3. Sketch of the weathering apparatus



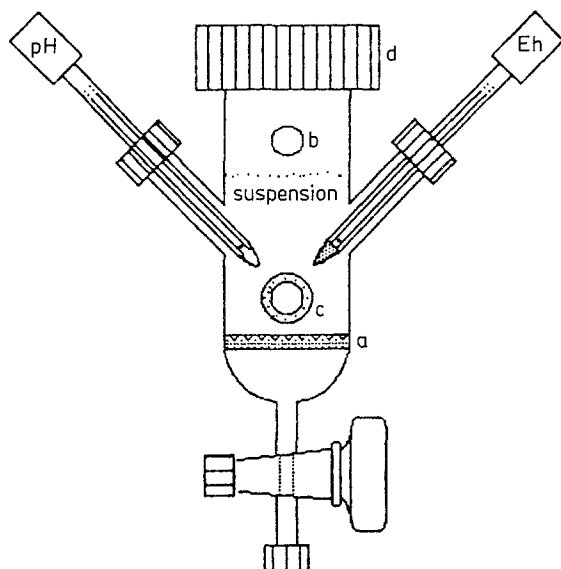
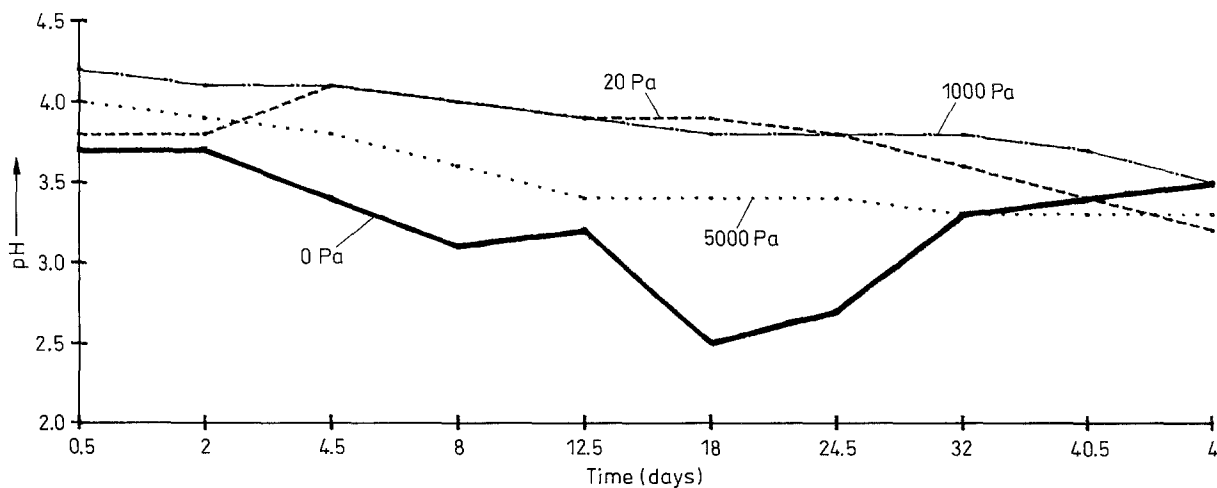


Fig. 4. Sketch of a weathering reactor equipped with pH and Eh electrodes (a = glass frit, b = aperture for sampling gas, c = aperture for sampling solutions and suspensions, d = aperture to remove solid particles)

temperature of 120°C in an autoclave. Subsequently, the water was stripped of oxygen by N₂ percolation. The electrodes were sterilized in 90% ethanol before use in the apparatus.

To minimize the noncalculable parameters, distilled water was used during the experiments reported here. Under "realistic" conditions the properties of modern rainwater, in terms of pH, redox potential, temperature, etc., and their changes with time should be taken into account. Preliminary tests using rainwater showed that the course of the experiments should not be very different from the experiments reported here, but the preliminary test also showed that the pyrite oxidation is more effective and somewhat faster using distilled water. Furthermore, the experiments reported here only can show the very first trend of pyrite alteration under anoxic and oxic conditions.

Fig. 5. Change in pH during the pyrite weathering experiments



Pyrite grains of 0.2–0.6 mm diameter from the colliery spoil were selected for the experiments; 35 mg of pyrite and 30 ml double-distilled, sterilized, N₂-purged water were drawn into each reactor; 2 ml of the sample covering solution were removed during each sampling after $x^2/2$ ($\frac{1}{2}$, 2, 4 $\frac{1}{2}$, 8, 12 $\frac{1}{2}$...) days. To avoid oxygen contamination, the samples were preserved in an N₂ atmosphere. Analysis of dissolved elements was conducted by an atomic absorption spectrophotometry (AAS) graphite furnace technique. At the end of the experiments, the solutions of each reactor were analyzed by ion chromatography, and the weathering residues by microprobe. The surfaces of the residues were investigated by scanning electron microscopy.

Dissolution/precipitation of pyrite

Theoretical considerations

The pH and Eh diagrams of the system Fe–S–O–H (e.g., Brookins 1988) show the stabilities of the iron sulfur species. Even when the sulfur activity is greatly reduced, a small stability field of pyrite still exists over a wide range of pH. With increasing Eh, pyrite becomes unstable.

The mechanism of pyrite dissolution in water is discussed by Moses and others (1987). The S₂²⁻ ion is fully spin-paired, whereas reactions with a paramagnetic molecule such as O₂ would be spin-restricted. O₂ must be chemisorbed on the subaqueous pyrite surface and thus be activated to a diamagnetic electronic configuration. This process is impeded kinetically. The probability of pyrite dissolution grows with increasing oxygen supply in the atmosphere. S₂²⁻ could be oxidized to S₀, S₂O₃²⁻, S₄O₆²⁻ (McKibben and Barnes 1986) and SO₄²⁻.



Without O₂, sulfur could be dissolved through the disproportionation of S₂²⁻ to S₀ and S²⁻. The iron concentration in the water limits the dissolution of pyrite.

Under the simulated atmosphere, the Fe²⁺ concentra-

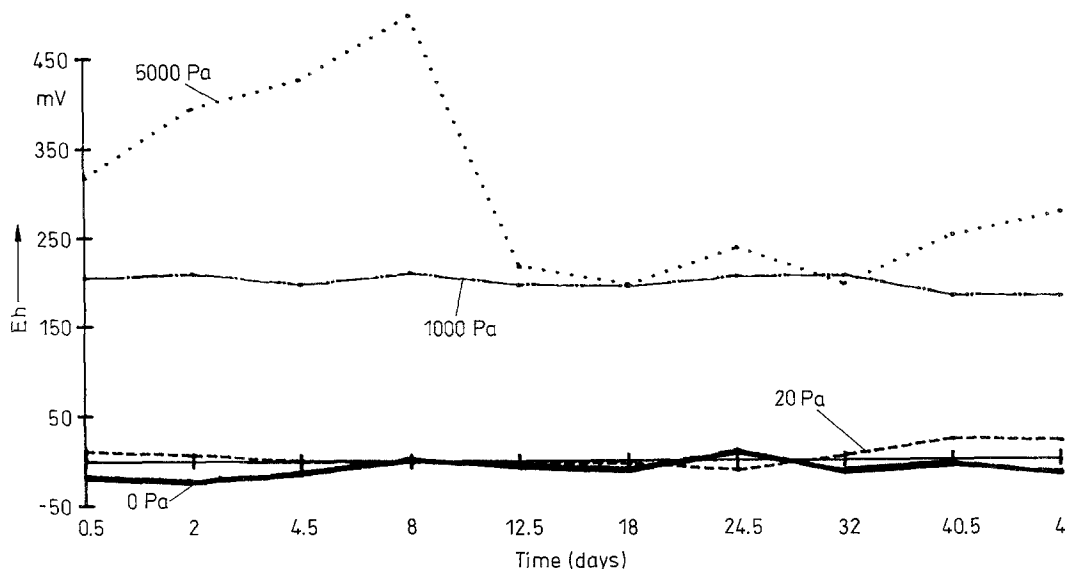


Fig. 6. Eh measurements during the pyrite weathering experiments with different oxygen partial pressures

tion is limited by the most insoluble components. With a S_2 concentration of 1.23×10^{-14} mol/l, the limiting value of Fe^{2+} is approximately 1 ppm, according to the solubility product of FeS .

Experimental results

During the experiments, the pH dropped from an initial 4.5–4 to about 3.4, irrespective of the different atmospheres. There were strong variations during the experiments with the anoxic $N_2-CO_2-H_2$ supply, while the curve is relatively regular when O_2 was supplied (Fig. 5). The redox potential (Eh) varied in a significantly wide range only at P_{O_2} 5000 Pa (Fig. 6). The redox potentials show a direct dependence on P_{O_2} (Fig. 7).

The solution covering the sample did not change color during the experiments; however, black, brownish, and yellow precipitates appeared in the glass frits of the reactors. At P_{O_2} 5000 Pa, yellowish precipitates were identified as sulfur. Ion chromatographic analyses showed that there

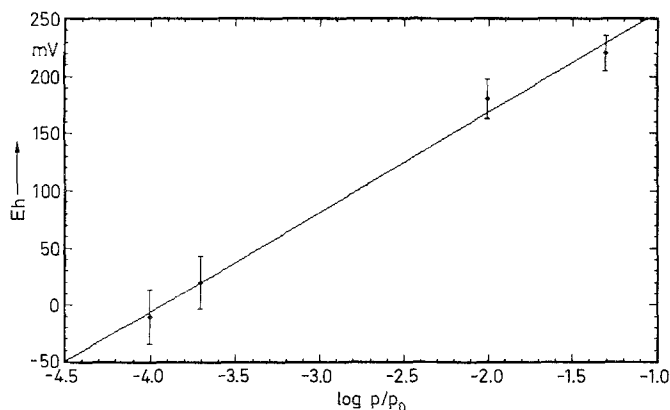


Fig. 7. Change in redox potential (Eh) due to P_{O_2}

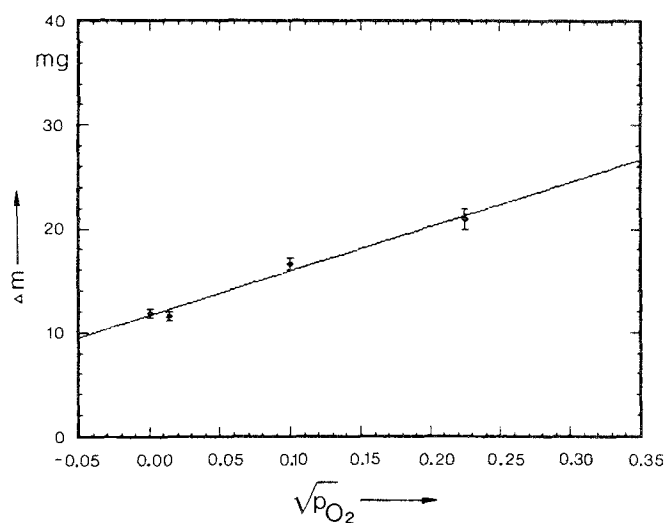


Fig. 8. Mass loss (Δm) of pyrite after 45 days weathering as a function of P_{O_2}

Table 1. SO_4^{2-} concentration in solution covering pyrite after finishing experiments

P_{O_2} (Pa)	SO_4^{2-} (ppm)
0	12
20	12
1000	17
5000	50

were no or only minor amounts of SO_3^{2-} , $S_2O_3^{2-}$ in the solutions covering the sample. The SO_4^{2-} concentrations increased with increasing P_{O_2} (Table 1).

At the end of the weathering experiments, the weathering residues showed leaching channels into the crystals, apparently resulting from selective dissolution of individual zones within the crystals. Table 2 shows the dissolution rate of Fe from the pyrites against reaction time and oxygen supply. A calculation of the kinetic constant of pyrite dissolution is not possible. But the ratio $\Delta[Fe]/\Delta t$ shows

Table 2. Concentration of Fe (ppb) and [Fe]/*t* ratio in solutions covering pyrites during experiments with different P_{O₂}

Duration of experiments (days)	Fe [ppb] ($\Delta[\text{Fe}]/\Delta t$)			
	P _{O₂} 0 Pa	P _{O₂} 20 Pa	P _{O₂} 1000 Pa	P _{O₂} 5000 Pa
0	0	0	0	0
0.5	232 (+464)	2087 (+4174)	140 (+280)	405 (+810)
2	4250 (+2678)	32 (-1369)	2720 (+1720)	115 (-913)
4.5	185 (-1626)	220 (+75)	2655 (-26)	140 (+10)
8	4015 (+1094)	450 (+65)	147 (-716)	3705 (+1018)
12.5	250 (-835)	37 (-92)	187 (+9)	152 (-790)
18	137 (-20)	27 (-2)	152 (-6)	155 (+1)
24.5	335 (+30)	195 (+25)	122 (-5)	115 (-6)
32	2152 (+242)	2335 (+285)	1815 (+225)	172 (+8)
40.5	170 (-232)	302 (-239)	717 (-129)	422 (+29)
45	175 (+1)	185 (-26)	217 (-111)	435 (+3)

Table 3. Mass loss (Δm) of pyrites after 45 days of weathering

P _{O₂} (Pa)	Δm (g)
0	0.01198
20	0.01160
1000	0.01664
5000	0.02106

a time dependence (Table 2). The function is comparable with a deaden vibration.

A mass balance calculation shows that pyrite dissolved under all atmospheric conditions used in the experiments (Table 3). According to McKibben and Barnes (1986), the dissolution of pyrite in the presence of oxygen is a function of P_{O₂}. The correlation coefficient of $r = 0.9915$ calculated from the results here supports this conclusion. Even under anoxic conditions, the dissolution of pyrite is strong, but only half of that with a P_{O₂} of 5000 Pa. This may explain pyrite alteration and the resulting acidification also in sealed colliery spoils without oxygen access. The relative accumulation of pyrite in the colliery spoils through mining processes is critical.

Environmental impacts caused by pyrite oxidation on colliery spoil dumps

Coal mining waste heaps are anthropogeological bodies, which have a characteristic "facies" resulting from geological, technical, and economic factors connected with the formation of the heaps. The relation between the facies of the dumps and these factors can be exemplified by the sulfide content (foremost pyrite) within the colliery spoil. The facies of the heap controls the anthropogenically induced geological processes on and in dumps. Thus, weathering of colliery spoil dumps is strongly influenced by the changes in material parameters produced by mining, processing, and dumping. The dominant weathering process is the oxidation of the sulfides, resulting in a strong acidification after dissolution of the carbonates by acid attack.

Leachates analyzed from coal mining waste lysimeters

allow the definition of three different phases of weathering (Schmidt and Schöpel 1986): (1) leaching of salts leads to highly mineralized NaCl-rich waters; (2) NaHCO₃ and Na₂SO₄ leachates are formed due to the process of sulfide oxidation; and (3) acidic leachates rich in heavy metals may result after exhaustion of the acid-buffering capacity of the waste rocks. The leachate components percolate through the unsaturated soil horizons underneath the dumps and get into the groundwater. Thus, risks of contamination of drinking water wells exist due to the specific hydrogeological conditions. Therefore, effective planning and control measures such as measurements of piezometric height and computer-aided assessment, chemical analysis of groundwater quality, and groundwater models are necessary (Rathke and Schröder 1991).

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