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EXPLANATION OF HYDROCHEMICAL PROCESSES BY GAS ISOTOPIC AND FIBRE OPTIC TEMPERATURE MEASUREMENTS IN LIGNITE MINING DUMPS SOUTH OF LEIPZIG, GERMANY

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INTRODUCTION

Parts of central and eastern Germany contain large opencast mining areas where in 1989 as much as 37 million tons of coal was extracted. However, the economic developments in the wake of German unification resulted in the volume of mining activity being significantly reduced. Expensive reclamation workings have been necessary since this time.

In our paper we present two of the environmental observation techniques used for investigations based in the area south of the city of Leipzig, where the first reclamation activities were begun. Most of the disused opencast pits are now being flooded, and so the hydrochemical interactions between the resulting pit lakes and the mining dumps are of particular interest.

AREA OF INVESTIGATION

The mining area south of Leipzig is located in the River Elster basin. The pre-Tertiary underground was quarried by tectonic movements during the Alpidic epoch. Depending on their structural position, the pre-Tertiary layers comprise both mesozoic sediments and riphaic hard rocks. Slow epirogenic movements initialised coal seam genesis during the Eocene epoch (Figure 1). Directly south of the city of Leipzig, a complex of three opencast pits exploited a double seam. One of these former opencast mines is the pit remaining at the village of Cospuden, which was closed down in 1992 and is currently being flooded. The mining lake has a maximum depth of about 40 m, and it will have an area of some 4 km^2. The volume of the lake will be around 180 million m^3. The flooding process is boosted by additional groundwater from other coal mines (64.000 m^3/d) and will be complete in the year 2000.

QUATERNARY	GRAVELS, SANDS	10m
marine sediments	various carbonate content	
TERTIARY-OLIGOCENE	SILT, SAND	35m
terestrial-limnic sediments	pyrite content to 8%	
	SILT, SAND	
	SEAM IV	
TERTIARY-EOCENE	SAND	20m
	SEAM II	
	SAND	

Figure 1. Schematic geological profile.

MEASURING FIELD

The area under investigation is a 2 km² section of a large dump connected to the dump massif of another former opencast pit to the south. This dump is vertically subdivided into the conveyer bridge dump below and the spreader dump on top. The spreader dump contains a mixture of the sediments occurring between the two seams and also a Quaternary substratum. The conveyer bridge dump contains the Oligocene substratum above the seams (marine and limnic sands and silts) with varying content of carboniferous and sulphide fossils and minerals. In addition, the conveyer bridge dump was exposed to the atmosphere for a long time before being covered by the spreader dump substratum. These facts are important for understanding the chemical reactions inside the dump massif. The dumps thickness is about 50 m, while its average surface is about 113 m above sea level.

The recent lake water level of about 105 m above sea level (April, 1999) causes a pressure gradient towards the unsaturated parts of the dump massif. The water's penetration of the dump can now be observed by geoelectric or electromagnetic field measurements. However, gauging the initial water distribution within dumps is very difficult. The research programme is chiefly focusing on long-term hydrochemical reactions in the dump. Two special multilevel gauge wells, 4 gauge wells, 4 temperature measurement systems, several gas sampling stations at various depths and some geophysical investigation profiles have been set up on the dump (Figure 2). Additional lance techniques were used to set upmonitoring systems.

Particularly the formation of sulphuric acid in the dump massif due to contact between water and products of pyrite oxidation could affect the lake water's quality once hydrodynamic equilibrium has been established. As the formation of alkalinity or acidification in such dumps is very complex, our investigations only take into account the following basic oxidation reactions:

Pyrite:

$$FeS_2 + 3\ O_2 + H_2O \longrightarrow Fe_2^{+} + 2\ SO_4^{2-} + 2\ H^+ + 1448\ \text{kJ/mol}\ (1)$$

Organic carbon:

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O + 2822\ \text{kJ/mol}\ (2)$$

Figure 2. Map of the area.

The acidification process caused by the generation of sulphates will certainly affect and change the mineral composition in the dump body and also the groundwater quality.

Both temperature phenomena and CO_2 genesis can be related to acidic activities inside the dump massif. Yet we also need to know the dump's mineral contents. Drilling and sampling activities followed by very complex analysis are commonly used to describe hydrochemical reactions inside dumps. Here, however, we only consider the possibilities for such investigations by recording thermal effects and taking gas samples with subsequent gas isotopic analysis.

TEMPERATURE MONITORING

For investigating the thermal condition of a subsurface in conjunction with chemical processes a Soil Groundwater Monitoring system (SGM - System) was extended with a distributed fibre - optic temperature measurement system (DTS - system) and installed on the dump of the remaining pit. Thus it was possible to determine the vertical temperature distribution of the soil body and to take depth - orientated water examinations without a further disturbance on the subsurface through the monitoring process after the system was installed.

Measurement principle

The basic principle of the scattering mechanism needs a microscopic reflection of the effects. Coherent laser light enters the fibre and is transmitted through the fibre. In case of no impact on the fibre from the outside there is no change of light intensity in the fibre. The impact on the fibre changes its microscopic properties and loss of the laser light occurs on the output of the fibre. This loss is caused by light scattering effects in the fibre because of the impact on the fibre from the outside. Scattering is mostly applied to molecules result from the characteristic behaviour of molecules with regard to their possible energetic states. Every molecule shows specific, discrete rotational and vibrational energy levels. If a laser photon hits the electron cover, the electrons move to a state of higher energy and the energy gap is increasing. When the laser impulse is over, the electron moves back to its former energy state by transmitting the received energy in form of light in all directions. Only the light, which is emitted in an angle which is smaller than the angle of total reflection, can be carried through the fibre core and its frequency and wave shifting is determined.

Installation of the DTS-System in Cospuden dump

Two installation techniques were used for installing a distributed temperature sensing measurement. At first the fibre cable was installed at the outer diameter of the borehole casing. A second method for installing the fibre cable inside the dump uses lance technique. Both techniques have been facilitated at the Cospuden site.

Measurement results

The results derived from the fibre optic distributed temperature sensing (Figure 3) are then compared with those of an one - dimensional vertical heat transport model. The separation of soil influencing temperature processes from the natural temperature distribution inside the borehole of the SGM - System was conducted using the following idea. Variations in temperature distribution in the subsurface are caused through:

- temperature variations at the surface through vertical heat penetration,
- internal heat production sources,
- heat transport through groundwater flow and
- heat transport from the dump side surface.

The vertical penetration of heat from the surface into an unsaturated subsurface (A) can be described by a vertical one - dimensional heat transfer model.

If it would be possible to determine the vertical distribution of temperature in the subsurface with a high spatial resolution and high accuracy and without any impact on the subsurface through the monitoring process, the comparison of the data obtained and the data of such a model would enable the possibility to determine the location and quantity of the sum of (B) + (C) + (D) (Figure 4).

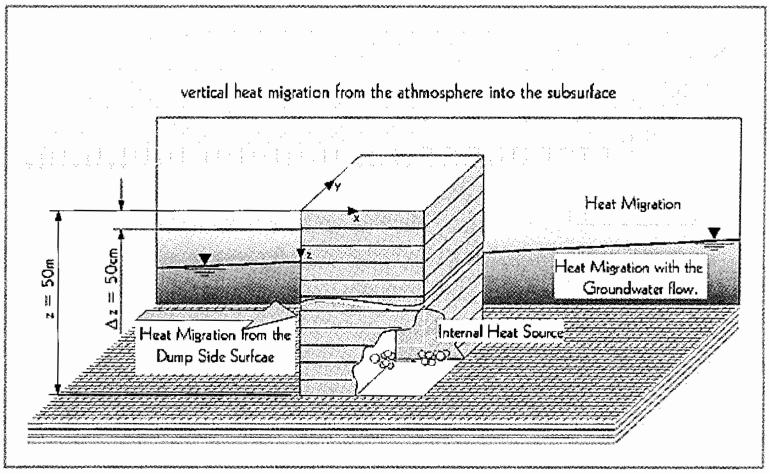

Figure 4. Shares of heat balance.

Section 1 reaches up to a depth of about 5 m. Here the temperature changes are mainly caused formed by seasonal thermal changes at the surface and the heat processes are caused by vertical heat penetration from the surface of the dump into the subsurface. Section 2 starts at a depth of about 5 m and reaches up to a depth of 12 m. Here the function of the temperature vertical distribution shows a significant increase in temperature. Section 3 starts at the depth of 12 m and reaches down to the bottom of the installed measurement.

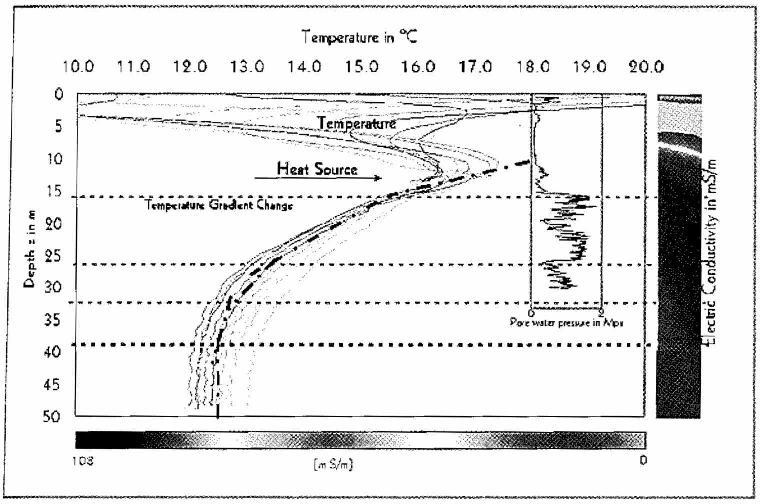

Figure 3. Temperature distribution versus depth (February 1995 – July 1996).

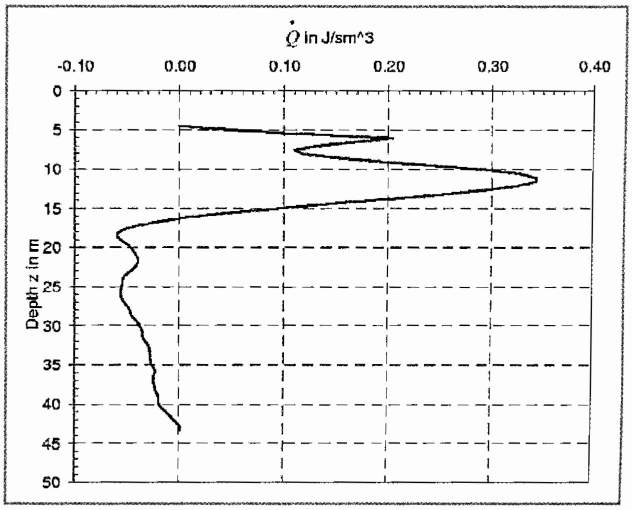

Figure 5. Heat production rate in J/(s x m^3).

COMPUTATION RESULTS

The computation algorithm for computing the heat production was presented in (Schreck et al., 1998). The computed result is shown in Figure 5. Basically it was found, that a heat production within a depth of 5 - 17 m is taking place. The maximum in heat production can be found at a depth of 11 m. The inner minimum between of 7 m and 9 m results from special deposits of riversands without high content of pyrite and organic carbon. This zone is also described by less density by radiometric borehole measurement.

It has been discussed (Ritchie et al., 1991) that convection of air in the horizontal direction within the unsaturated layer of a waste dump provides a significant source of heat. Heat conductivity depends on the thermal conductivity of each phase, the structure of the solid matrix, the contact resistance and for gas convection at an unsaturated subsurface on the ratio of the mean free path and the average linear pore dimension (Kaviany, 1995). This result was later backed up by chemical investigations of the chemical condition in the subsurface, whereas different contents of organic carbon supplied the information about the reason of the heat production (Table 1).

INVESTIGATIONS OF GASES

The evolution of carbon dioxide from dump material of the Rhine coalfield has been reported in the literature (Wisotzky, 1994). Due to the composition of the dump material used for the batch experiments, it was concluded that this carbon dioxide results from the decomposition of carbonates with sulphuric acid formed by pyrite oxidation. As the levels of carbonates and pyrite in the overburden sediments in the Central German region are higher than in the Rhine coalfield, the formation of carbon dioxide ought also to be more intensive. Initial investigations of the soil atmosphere at a depth of 1 m yielded carbon dioxide contents of about 8%.

Depth (m)	Sulphide (Mass %) SGM	Organic carbon (Mass %) SGM	Organic carbon (Mass %) CML
2	0.49	9.19	
6	0.14	2.26	
10			9.1
12	0.47	8.68	
14	0.78	14.73	0.7
16	0.62	12.87	
17	0.07	1.68	5.1
18	0.15	1.01	10.8
20	0.43	0.90	
24	0.90	0.81	
27	0.60	0.55	
28	0.68	0.82	
48	0.87	1.15	

Table 1. Sulphide and organic carbon with respect to depth.

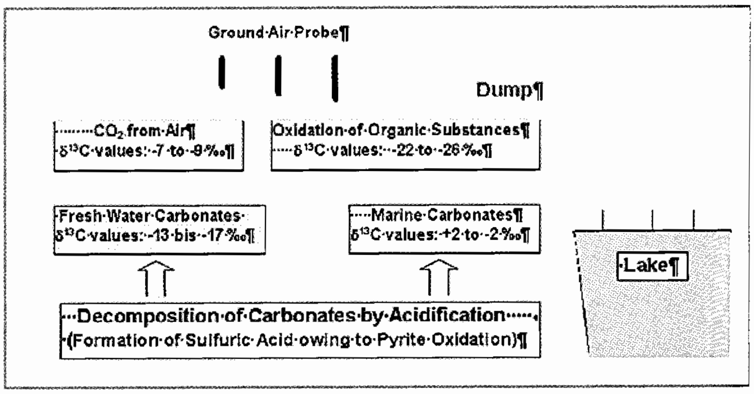

Figure 6. Possible sources of carbon dioxide in lignite mining dumps.

Possible sources for the carbon dioxide in addition to the decomposition of carbonates are schematically shown in Figure 6.

By analysing the carbon isotope ratios in terms of $\sigma^{13}C$ values, we can distinguish between different sources of carbon dioxide. From the literature (Rösler et al., 1977) it is known that not only marine carbonates occur in this mining area, but also altered carbonates formed by the dissolution of marine carbonates by meteoric waters rich in carbon dioxide and re-precipitation. Such formations are local features. To find out whether such carbonates are present in our area of investigation, we took some samples from borehole RCO15 and determined the contents of the carbon species and their isotopic compositions. The results are plotted in Figures 7 and 8.

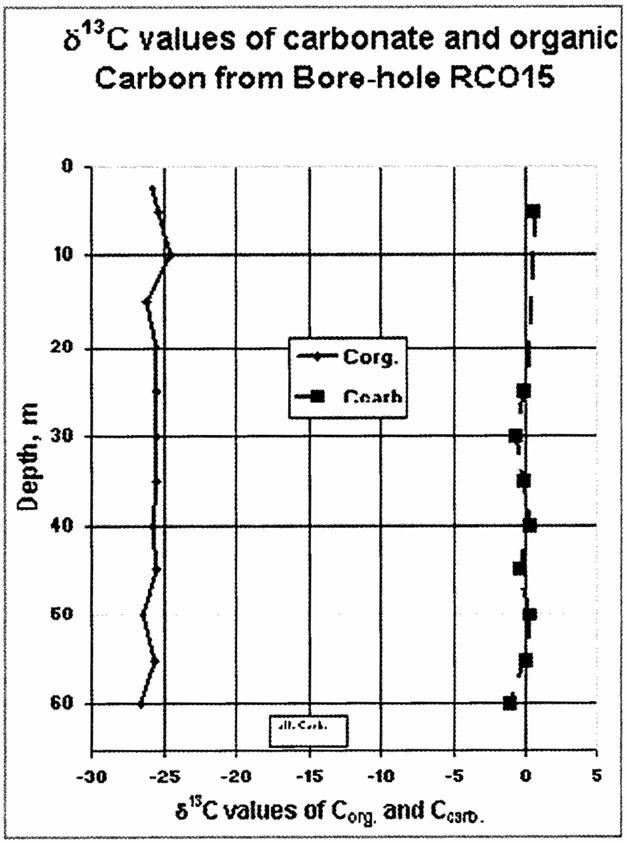

Figure 7. σ^{13} values of carbonate and organic carbon from borehole RCO15.

Figure 7 shows that no altered carbonates are present. Within their range marked by an arrow, no samples were found. The σ^{13}C values of the marine carbonates and the organic carbon are scattered around the typical means for these materials.

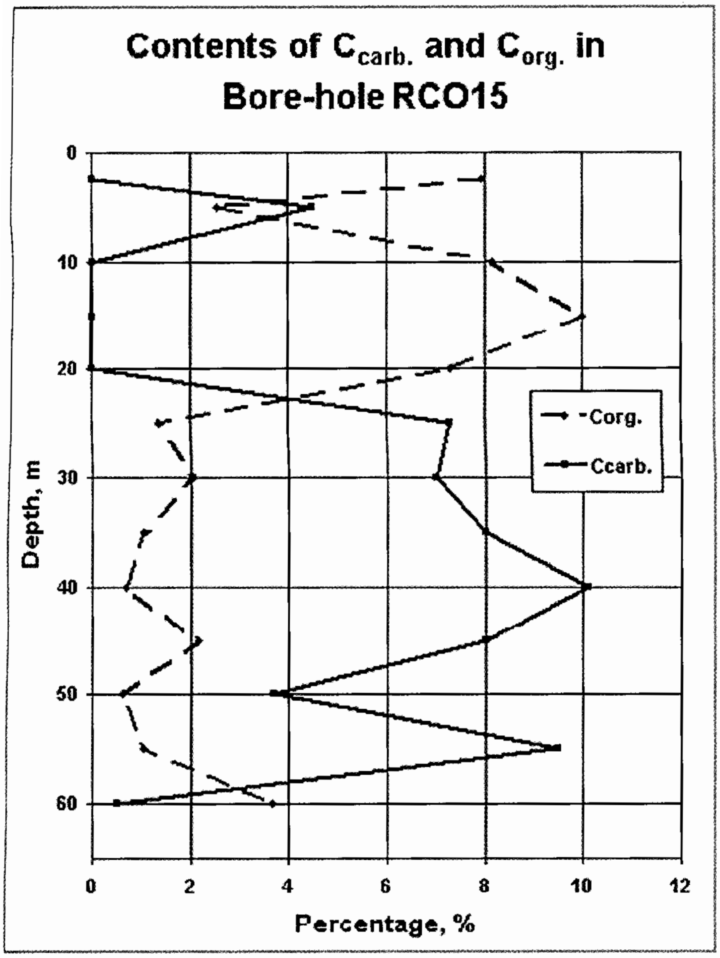

Figure 8. Contents of $C_{Org.}$ and $C_{Carb.}$ in borehole RCO15.

The contents of organic carbon and marine carbonates vary differently with depth, possibly indicating the dump structure (Figure 8). The total amounts represent a large reservoir for carbondioxide formation.

SAMPLING AND ANALYTICAL PROCEDURE

Some of the probes were installed at various depth (1, 2, 5, and 10 metres) near the location SGM. Other probes were distributed over the dump. During the measuring period, the dump around the probes was unsaturated and the groundwater level was far deeper. More recently, stationary probes have been installed to study different types of dump materials. In two cases we measured profiles along an inclination starting from the surface of the lake. For this purpose we used mobile probes only installed for individual sampling. Gas composition was determined by gas chromatography. The isotope ratio mass spectrometry (IRMS) of carbon requires pure carbon dioxide. Therefore the gas mixtures have to be separated and the components of interest individually prepared for isotope analysis. We used a gas chromatographic method combined with trapping and combustion lines. The results are given in the usual σ-notation vs. The international PDB standard. To examine the dump material, samples were taken at regular distances from the core of borehole RCO15. Determination of the carbonate content was performed with a pressure bomb (decomposition of carbonates with hydrochloric acid), while for that of organic carbon we used an elementary analyser after removing the carbonate. For isotope analysis, we used purified carbon dioxide yielded by the decomposition of the carbonates with 100\% phosphoric acid (McCrea-Method), as well as the combustion of the organic carbon with oxygen.

RESULTS OF SOIL ATMOSPHERE INVESTIGATIONS

The four probes near the SGM (multilevel) indicate the carbon dioxide content to increase with depth (Table 2).

The corresponding nitrogen and oxygen plus argon contents decrease. Due to some local particularities, the probe at a depth of 2 m displays specific behaviour. Despite the various chemical compositions, the isotopic composition of the carbon dioxide remains very uniform. In view of the isotopic composition of the organic material in the dump, this is not surprising. This indicates that the source of the carbon dioxide found is the oxidation of the disperse humic substances. These findings are confirmed by the results from the recently installed borehole 2 and probe Z. The influence of isotopic heavy carbon dioxide originating from carbonate decomposition can be seen in profile 1 (Table 3). Near the water surface, sulphuric acid resulting from pyrite oxidation is mobilised and reacts with any carbonates present. The results are σ^{13} values of around -17.5 ppm a mixing value between light organic and heavy inorganic carbon.

Probe I (Table 2) is located on an island recently formed due to the rapidly rising water level of the lake. The σ^{13}C value of the CO_2 indicates the strong influence of carbonates. In the case of profile 2 the heavier σ^{13} values around 40 metres are not caused by the influence of carbon dioxide from carbonates, but by methanogenesis under reducing conditions. This is proved by gas analysis (methane content more than 1\%) and the negative σ^{13} values of the methane found. For reasons of balance the coexisting carbon dioxide has less negative σ^{13} values than the source material. The reason for this evidence may be a floating body of water due to a local clay layer. These facts underline that only the combination of gas analysis and isotope ratio measurements provide a solid foundation for accurate interpretation.

Depth	Samples	Percentages (vol. %)				$\sigma^{13}C_{CO2}$, (ppm)
		Ar + O_2	N_2	CO_2	CH_4	
Location borehole 1 (SGM)						
1	6	2.60 + 0.70	87.79 + 0.95	9.60 + 1.23	Tr.	-24.2 + 0.6
2	4	4.80 + 1.00	84.35 + 1.79	10.38 + 2.15	Tr.	-24.0 + 1.4
5	4	2.36 + 1.00	80.96 + 1.03	16.70 + 2.00	Tr.	-24.6 + 0.7
10	4	1.38 + 0.08	76.78 + 0.82	21.38 + 0.70	Tr.	-24.3 + 0.3
Location borehole 2 (C-ML)						
8	2	3.93 + 2.17	84.60 + 1.46	11.20 + 0.44	Tr.	-23.8 + 1.0
Probe Z						
10	3	3.81 + 2.47	82.51 + 2.63	13.68 + 0.18	Tr.	-22.7 + 0.3
Probe I						
10	3	2.81 + 2.81	84.85 + 2.65	9.95 + 0.80	Tr.	-11.1 + 0.3

Table 2. Results from soil atmosphere of stationary probes.

Profile 1 (26th June, 1996)						
5m	1.45	78.36	20.18	Tr.	-17.1	
10m	5.29	81.09	13.61	Tr.	-17.1	
Profile 2 (22nd August, 1996)						
10m	9.94	76.58	13.35	0.12	-23.8	
20m	3.14	69.67	26.92	0.26	-23.7	
30m	0.86	44.97	50.76	3.40	-23.5	-50.0
40m	1.34	66.38	29.98	2.29	-19.6	-44.5
50m	1.96	47.69	46.15	4.19	-21.7	-53.1
60m	7.66	71.94	19.90	0.49	-21.7	

Table 3. Results from soil atmosphere of two profiles.

CONCLUSIONS

A new approach for monitoring hydro-chemical processes in the subsurface is facilitated. The subsurface is widely monitored using fibre-optic temperature sensing. Thus chemically active zones are pre-selected by their thermal effects. Further chemical investigations are then carried out at these pre-selected boreholes at pre-selected depth. Thus the efficiency of long-term monitoring of hydro-chemical processes can be enhanced.

Both temperature measurements and soil atmosphere investigations are suitable tools to describe chemical reactions in dump bodies. Temperature measurements (especially via the permanently installed DTS technique) are the best way of carrying out long-term observations at chosen locations. To find the most "active" locations in a dump area, screening by gas sampling combined with isotopic analyses should be performed. The significant environmentally related processes in dump massifs are the generation of sulphuric acid and the genesis of carbon dioxide. Moreover, mineral conversion may also affect the mechanical stability inside the dump.

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