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Fe(0)/Lignitic Coal: An Efficient and Mechanically Stable Reactive Material for Purification of Water Containing Heavy Metals, Radionuclides, and Nitroaromatics

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Mine water in the former uranium mine of Königstein (Saxony, Germany) contains high concentrations of acid, sulfate, iron, aluminum, various heavy metals, radionuclides, and nitroaromatics. Research has been conducted for several years to establish the extent to which reduction of pollutant concentrations can be positively influenced and accelerated by storage of reactive materials in mine cavities. Investigations were made at different scales to test and select materials with respect to maximum fixation of contaminants (underground column tests) to examine hydraulic effects (underground large-scale column tests) and to optimize material properties (laboratory tests). The investigations have shown that a mixture of Fe chips and lignitic coal is capable of efficiently cleaning acid and contaminant-containing mine water. The examined material is easily available and compatible with the environment. A large-scale application of such a reactive barrier is being considered for mine water treatment in the future and is deemed to be a reasonable conception for a safety component after conclusion of the flooding.

1. Introduction

Contaminant sources in groundwater typically cause long-term release of contaminants at relatively low concentration levels. This is due to generally low release rates and slow groundwater flow. Particularly in regard to this long-term phenomenon intense research was undertaken to identify low-energy and, to the extent possible, low-maintenance passive processes.

A viable concept which has been put into practice at a number of sites is the use of reactive barriers downstream from the contaminant source(s). Technically, this is often implemented in the form of reactive walls. Feasibility of this approach is exemplified by a great number of applications which take the site-specific hydraulic and hydrochemical conditions into account (*1, 2*).

Since the early 1990s, zerovalent iron (Fe(0)) has been successfully used to immobilize metals in contaminated groundwater. Mixtures of Fe(0) and organic substances have proved to be extraordinarily efficient in this regard. Such mixtures promote several processes of contaminant fixation such as pH buffering and sulfate reduction (and, consequently, metal sulfide precipitation) as well as sorption and coprecipitation reactions (*3–5*). Laboratory and field tests using standard reactive materials to purify in some cases acid mine waters have shown permanent retardation of toxic and radioactive substances (*6–9*). During these tests, organic carbon was added to Fe(0) in the form of relatively soft, easily degradable materials such as compost, peat, forestry waste, and the like.

Remediation of former mining sites offers a great variety of potential applications for such passive processes. As current knowledge suggests, contaminant release from mines, dumps, and tailing ponds into ground and surface water may continue for a long time. Experience of the past few decades shows that conventional water purification techniques (pump and treat) are unsuitable in the long run because of high operational costs and the need to dispose of treatment residues.

Remediation of the former Königstein uranium mine (FR of Germany, Free State of Saxony) has to exclude long-term release of heavy metals, radionuclides, and nitroaromatics into the aquifer at reasonable cost (*10*). One possible approach is to bring contaminated effluent or mine water into contact with reactive materials either in a geochemical barrier in situ or in a suitable reactor. Unlike the standard reactive wall, an in situ geochemical barrier can be built within the discharge stream by backfilling of underground mine workings. Selection of appropriate material shall ensure long-term cleaning of low-contaminated effluent water after mine abandonment.

2. General Site Conditions

Remediation of the Königstein uranium mine near Dresden has to consider the location in a ecological sensitive and highly populated area. Mining started in the 1960s with approximately 19 000 t U produced till 1990. The ore body is located in the fourth sandstone aquifer, the deepest of four hydraulic isolated aquifers in a cretaceous basin. Between the fourth and third aquifer a 10–30 m thick aquitard is located, which is perforated by natural faults and man-made connections due to mining activities. The third aquifer is an important water reservoir for the Dresden region and of high environmental and economical significance. The uranium was extracted from the fourth sandstone aquifer, using initially conventional mining methods and between 1984 and 1990 an underground in situ leaching (ISL) method using sulfuric acid. The in situ leaching was performed on sandstone blocks with volumes of 100 000 to 1 000 000 m^3. During the in situ leaching period altogether 130 000 t of sulfuric acid (residual product of blasting agent production containing nitroaromatics) were applied within the deposit (*10*).

Placing reactive materials into open underground mine workings has to take site-specific conditions into account: i.e., hydraulic situation, contaminant spectrum, hydrochemical environment, and mine engineering aspects. Persistent water permeability is an essential condition for the long-term efficiency of an underground geochemical barrier. In addition, the material must have a suitable mechanical stability to ensure continued permeability despite dissolution processes and precipitation of reaction products.

For use in the sulfuric acid water in the Königstein mine (Table 1), materials which are effective in hydrochemical terms are those which lead to a sustainable change in the

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TABLE 1. Mean Chemical Composition of Sulfuric Acidic Mine Waters in the Königstein Mine

		mine water 1	mine water 2	precision (μg/L)	S_{rel} (%)
pH		2.0	3.0	abs. 0.1	
Eh	mV	600	550	abs. 1 mV	
EC	mS/cm	11	3	10 (μS/cm)	5
Na	mg/L	95	51	200	5
K	mg/L	5	17	100	5
Ca	mg/L	133	244	100	5
Mg	mg/L	29	20	100	5
Mn	mg/L	12	5	0.15	10
Al	mg/L	272	66	0.25	10
Fe total	mg/L	2160	289	10	10
Fe(II)	mg/L	1900	283	10	10
Fe(III)	mg/L	260	3	10	10
Cl	mg/L	103	53	100	10
SO_4	mg/L	7040	1721	1000	10
As	mg/L	3.52	0.207	2	5
Pb	mg/L	0.20	<0.05	10	10
Cu	mg/L	2.5	0.042	20	5
Ni	mg/L	5.1	1.07	20	5
Zn	mg/L	107	22.2	100	5
Sr	mg/L	1.5	1.35	0.1	5
Co	mg/L	2.6	0.29	20	5
Cr	mg/L	0.95	0.08	10	10
Cd	mg/L	0.65	0.10	2	10
Ba	mg/L	0.05	0.027	0.1	10
Mo	mg/L	0.43	0.013	20	5
U	mg/L	68	12	0.1	10
Ra	mBq/L	12000	2500	10	10
Σ nitroaromatics[a]	μg/L	60	2.3	0.5	20

[a] Nitrobenzene, nitrotoluenes, dinitrotoluenes, and trinitrotoluene.

water milieu in terms of rising pH and decreasing Eh values and which have good sorption properties. The main focus in material selection was on the efficient coverage of the full range of contaminants including heavy metals, arsenic, aluminum, and radionuclides as well as nitroaromatics.

Reactions in the geochemical barrier should result in permanent fixation of the relevant contaminants and must avoid negative side-effects. Over and above that, the materials chosen have to secure safe handling underground and should be available at low cost.

3. Methods and Results

With these basic conditions in mind, investigations were made at different scales: (1) test and selection of materials with respect to maximum fixation of contaminants (underground column tests) (*11*) and (2) examination of hydraulic effects (underground large-scale column tests) and optimization of material properties (laboratory tests).

3.1. Test and Selection of Suitable Reactive Materials. Because of the prevailing general conditions, use of metallic iron is a preferred option for the Königstein mine. Reaction of the heavily acid mine water with Fe(0) causes an increase in pH and the creation of reducing conditions (*12*). Once generated, these environmental conditions facilitate or support precipitation and the higher sorption of heavy metals. A number of other potentially efficient materials have also been tested with a view of examining combined effects: hard coal and lignitic coal, organic residues, barite-containing materials, fine grained lignite coal ash, and limestone (Table 2).

Performance of these materials was studied in vertical column tests using original mine water. Tests were carried out in an underground test arrangement in the Königstein mine at a depth of 300 m. The PVC columns had a diameter of 30 cm, and the filling level was between 30 and approximately 60 cm. Flow in the columns was from bottom to top, i.e., under saturated conditions. At the end of the column, a gastight tube led the percolate to a measuring cell where, just like in the mine water feeder, temperature, conductivity, pH, and redox potential were measured. Sampling and analyzing were conducted at regular intervals. Reaction gases were taken up by separate collector lines (Figure 1).

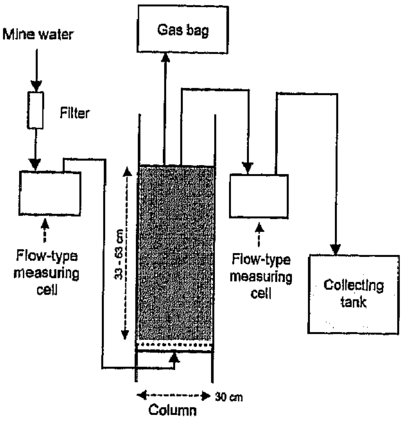

FIGURE 1. Schematic setup of a vertical column in the underground testing facility.

The percolating solution (mine water 1, Table 1) was taken directly from a mine section that had been flooded for experimental purposes. This mine water was heavily acidic (pH 2) and showed a nearly constant chemical composition for the test period of about 1 year. The flow rates were adapted to the hydraulic conditions prevailing in the mine after the flooding, although identical flow rates could not be achieved in each column due to different characteristics of the materials. Residence times were between 2 and 5 days, and the pore volumes exchanged between 20 and 50 times. One column with washed gravel was included in the test series as a blind test.

To take into account inflow conditions over the test period mass balances of input and output were calculated for each column and for mine water components of interest. Figure 4 shows the fixed uranium masses in consideration of the particular input volumes and concentrations. So in dependency of percolated mine water volume fixed portions of contaminant input are given as sum of the fixed masses of the collected and periodically analyzed percolate. Analytical errors of the individual values will partly be compensated over time. Main quality control for sampling and analyzing is the blind test with the gravel column RM 5 which shows practically even balances. Table 3 gives the calculated values after a test period of about 1 year for all reactive materials and substances. Precision of these values depends on specific chemical substance properties and has to take into consideration the specific conditions of an underground test site in a mine. Deviation from the expected zero value is about 5% for most elements in the gravel column. The balance for the siderophilic elements As, Mo, and Cr is disturbed by partial coprecipitation with iron hydroxides in the collecting tanks. Because of minor outflow loads of the columns with the reactive materials deviations here will be lower, however.

In contrast to the other materials checked, with reactivity partially being limited by precipitation and aggregation effects, elementary iron had the expected contaminant-fixing effect on the mine water in all tests. A relatively high reaction capacity can be expected with iron because none of the tests showed any exhaustion of reactivity after about 1 year of performance. Significant differences have been found in the efficiency of scrap, iron chips, and mixtures with iron chips.

TABLE 2. Survey and Characteristics of the Reactive Materials Used in the Vertical Columns

column	material filled in column
RM 1	crushed iron scrap (rough-sized, ~10 cm) from the Königstein mine
RM 2	iron chips from lathe operation in the metal-working industry (low-alloy steels, chip lengths 1–10 cm)
RM 3	iron chips[a] + hard coal (Ruhr-carbonian, grain size 5–30 mm, ash 4 %)
RM 4	iron chips[a] + lignitic coal 1 (Central Germany, grain size 2.5–20 mm, ash 10 %)
RM 5	gravel, washed (grain size 2–4 mm)
RM 6	iron chips[a] + brewer grains
RM 7	iron chips[a] + material containing barium sulfate ($BaSO_4$, coke, ash, gravel, grain size 1–10 mm)
RM 8	gravel + fine grained lignitic coal fly ash (grain size < 1 mm)
RM 9	crushed limestone rock (grain size 4–8 mm)

column RM	material 1	mass (kg)	material 2	mass (kg)	vol (L)	porosity (%)	pore vol (L)
RM 1	Fe-scrap	40.5			24.9	78	19.4
RM 2	iron chips	17.0			37.8	94	35.5
RM 3	iron chips	18.0	hard coal	18	40.3	68	27.4
RM 4	iron chips	12.0	lignitic coal 1	12	29.5	59	17.4
RM 5	gravel	50.0			31.9	44	14.0
RM 6	iron chips	9.0	Brewer grains	9	29.2	70	20.4
RM 7	iron chips	13.0	$BaSO_4$ mat.	13	25.5	69	17.6
RM 8	gravel	40.0	fly ash	2.04	24.1	40	9.6
RM 9	limestone	42.5			26.6	44	11.7

[a] Like in column 2.

TABLE 3. Fixed (Positive Values) and Mobilized Portions (Negative Values) in Relation to the Input Contaminant Loads[a]

		Fe-scrap	Fe-chips	Fe + hard coal	Fe + lignitic coal 1	gravel	Fe + Brewer grains	Fe + $BaSO_4$	ash + gravel	limestone
column		RM 1	RM 2	RM 3	RM 4	RM 5	RM 6	RM 7	RM 8	RM 9
As	%	74	91	97	99	25	64	97	36	92
Pb	%	68	87	87	87	0	86	87	24	63
Cu	%	68	100	100	100	2	94	100	12	37
Ni	%	6	1	1	68	4	4	0	5	4
Zn	%	1	0	4	81	1	9	−28	4	2
Co	%	−3	−4	−4	40	1	−6	−28	−1	−7
Cr	%	28	67	76	54	15	−66	79	20	37
Cd	%	9	21	31	99	−4	26	97	4	13
Mo	%	87	100	100	99	28	85	100	41	98
U	%	41	52	66	96	−2	50	68	6	38
Ra	%	−20	−28	−45	67	−2	−54	90	37	11
Al	%	6	30	66	83	−5	9	61	−7	58
SO_4	%	0	1	1	3	−2	1	6	3	19
Σ nitroaromatics[b]	%	83	99	99	98	46	97	100	59	47

[a] Vertical columns, mine water 1, test period: 12 months. [b] Nitrobenzene, nitrotoluenes, dinitrotoluenes, and trinitrotoluene.

TABLE 4. Chemical Composition of the Components in the Mixture of Metallic Iron and Lignitic Coals

		lignitic coal (1) Central German	lignitic coal (2) Rheinbraun	Fe-chips
particle size	mm	2.5–20	10–40	10–100
Fe_2O_3	%	1.4	0.38	
Fe(0)	%			97
MnO	%	<0.05	<0.05	<0.05
TOC	%	47.5	60.2	
Zn	ppm	47	55	245
Ni	ppm	4.9	3.8	1960
Cr	ppm	31	14	19000
V	ppm			
Mo	ppm	<3	<3	16000

Whereas most calculated values of mobile and evidently nonfixed elements lie in the blind test accuracy-range of ±5%, the radium data need some more explanation in particular. High negative values and therefore mobilization of radium occurs with reactive materials, which show relevant fixation rates for uranium and thorium but offer no fixation process for radium. Thus radioactive decay of fixed thorium isotopes causes release of radium isotopes (predominantly Ra-224 and Ra-223). Only reactive materials with specific fixation properties for radium-like column RM 5 (precipitation by barium sulfate) or RM 4 (sorption) are able to retain the primary radium input and the additional decay products.

The mixtures with iron chips turned out to be the most efficient. The efficiency of metallic iron thus can be increased by additives. The combination of iron chips with lignitic coal practically fixes almost all potential contaminants. Table 4 gives the chemical composition for these reactive materials used in different test series. Also the relatively mobile elements U, Co, Zn, and Ni are given a clearly better fixation than with the other materials investigated. In the columns filled with iron, generation of H_2 gas continued until the end of the test. After completion of the test the columns were opened, and the reactive materials were examined. The most efficient material mixture, i.e., iron chips and lignitic coal, showed the following features: (1) The mechanical grain structure remained almost unchanged (no signs of squeeze or decomposition of the lignitic coal, no aggregate formation, only small portions of fine grained sediment). (2) Lower Fe-(0)-content (29%) at the inflow side of the column as compared to the outflow end (50%, initial value)—therefore

TABLE 5. Contaminant Accumulation in the Reactive Mixture of Iron Chips–Lignitic Coal after Completion of the Column Tests[a]

			original	column length (cm)						
			mixture	5	20	40	50	100	150	200
column RM 4	Zn	ppm	150	3880	13100	9300				
column RM 4	U	ppm	<0.2	10690	12690	4150				
column RM 4	As	ppm	80	1155	910	230				
column RM 11	Zn	ppm	150	3970			1260	978	726	276
column RM 11	U	ppm	<0.2	3300			2090	895	330	130
column RM 11	As	ppm	80	182			110	91	72	81

[a] Column 4: water solid ratio = 119 L/kg, mine water 1; column 11: water solid ratio = 48 L/kg, mine water 2.

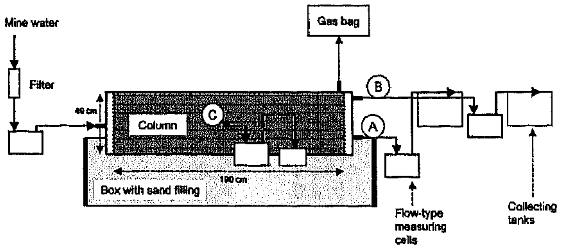

FIGURE 2. Setup of components in the horizontal column test arrangement (RM 11) for underground use.

only a minor part of iron stock was used up after the test period of 1 year. (3) Higher concentrations of contaminants at the inflow side of the column than at the outflow side. Long time percolation with high uranium and zinc concentrations (mine water 1, see Table 1) causes shifting of the maximum loads into the middle of the column and relatively high accumulation even at the outflow end (column RM 4, Table 5 and Figure 5). So the fixation limit may have been almost reached. However, fixation rates of uranium show only a minor decrease (cf. Figure 4). Column RM 11 percolated with mine water 2, and, therefore, the lower contaminant input is far away from a uranium and zinc breakthrough. This applies accordingly to arsenic (Table 5), lead, and cadmium in both tests.

3.2. Hydraulic Effects and Materials Properties. The results of the first test series for a mixture of iron chips and lignitic coal meet most of the criteria for an overall depletion of contaminants in the mine water. Further tests examined the hydraulic and geochemical behavior of a horizontal flow simulating the conditions in underground galleries. Another aim was optimization of material properties of the mixture and a quantitative analysis of H_2 generation to provide conclusions for the technological circumstances in large-scale implementation of such techniques in a mine.

3.2.1. Underground Test of Hydraulic and Geochemical Behavior with Horizontal Flow. The main focus was the efficiency of the favorite material mixture under realistic flow conditions. The basic conditions (underground test site, residence time, mixing ratio of reactive materials) largely corresponded to the vertical-column flow test RM 4 in order to obtain data comparable to this long-term test. The incoming mine water (Table 1, mine water 2) however contained considerably lower acid and metal concentrations so examining efficiency at lower contamination levels at a later flooding stage.

To simulate the situation in a horizontal mine gallery, a 2 m long horizontal column (inner diameter 48.8 cm, PVC) was used. A filter plate was installed on the feed end to provide a homogeneous incoming flow. With an effective length of 189.5 cm, the filling capacity is 354 L. To enable control of spatial differentiation of the processes in the column, sampling facilities were installed in the middle of the column (C) as well as at two different levels at the outlet end ("close to the floor" (A) and "close to the roof" (B)) (Figure 2). The expected gas emissions were taken up by gas bags via an escape opening. Continuous measuring cells were employed to quantify the in-situ parameters.

The filling material was a mix of Fe chips and lignitic coal. The Fe chips correspond to those of the tests in Table 2. The lignitic coal (Rheinbraun AG, open-cast mine Hambach) was screened to a size of 1–4 cm. The materials were homogenized at a mass ratio of 1:1 and placed manually into the column.

The weighed portions of material (wet weight basis) and physical parameters in the horizontal column filled with Fe chips–lignitic coal were as follows: material mixture of Fe chips (105 kg) and lignitic coal (105 kg); volume of mixture (326 L); porosity of mixture (68%); and pore volume (221 L). The mine water passed through a solid-matter filter and a measuring cell (in-situ determination of input parameters) before filling the column. Corresponding to a residence time of 2–4 days, the flow rate was adjusted to approximately 40 mL/min.

This test simulated the following various flow scenarios: phase 1 (3 months), discharge of the percolate at the column bottom (outlet A); phase 2 (2.5 months), discharge of the percolate at the column roof (outlet B); and phase 3 (2 months), discharge of the percolate at both outlets (A and B).

The following water–solid ratios were achieved in each case: phase 1, 19.2 L/kg; phase 2, 35.7 L/kg; and phase 3, 47.7 L/kg.

3.2.2. Optimization of Materials Properties (Laboratory Tests). Optimization of materials properties took place in specifically designed laboratory equipment facilitating exact monitoring of the test conditions. To determine the factors relevant for contaminant fixation, variations were made in the lignitic coal, the iron, and the residence time inside the column.

Furthermore, it was necessary to determine the reliability of easily workable downscale tests compared to an upscale test, which is practicable only under underground conditions because of the required mine water quantities.

The test arrangement for the small scaled laboratory tests (Figure 3) corresponded to that of the underground test RM 11 (Figure 2). Mine water 2 (Table 1) was used as water input. The vessels used in the experiment were horizontal glass columns, 32.5 cm in length with an inner diameter of 10 cm (≘volume 2.55 L). The environmental parameters pH and redox potential were determined directly in the reaction chamber. A pump controlled adjustment of a constant flow. The gases generated in the process were collected via a tap on the top side of the column.

The materials tested in the experiments were two types of iron and two types of lignitic coal. Table 6 shows the fundamental test parameters. The porosities and bulk densities of the experimental mixture S 1 are in perfect agreement with the test data of the underground test in the upscale (2 m) column. Characteristics of both types of coal are given in Table 7. Percolation period was of up to 7 months.

TABLE 6. Material Characteristics and Physical Parameters in the Horizontal Laboratory Columns Filled with Metallic Iron and Lignitic Coal

column	material 1 iron	mass (kg)	material 2 lignitic coal	mass (kg)	vol (L)	porosity (%)	pore vol in column (L)
S 1	Fe chips	0.67	(2) Rheinbraun	0.67	2.55	68	1.72
S 2	crushed iron sheets	1.06	(2) Rheinbraun	1.07	2.55	55	1.40
S 3	Fe chips	0.74	(1) Central German	0.74	2.55	67	1.71

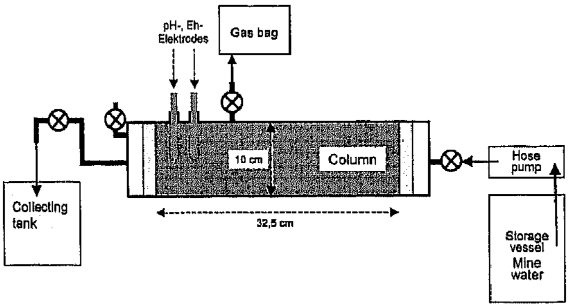

FIGURE 3. Setup of components in the laboratory test arrangement.

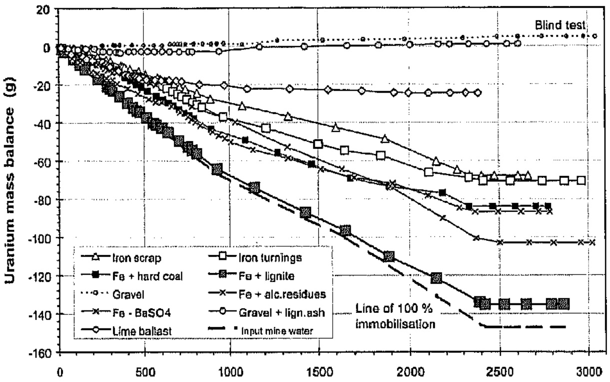

FIGURE 4. Uranium mass balance of mine water input and output of vertical columns filled with different reactive materials.

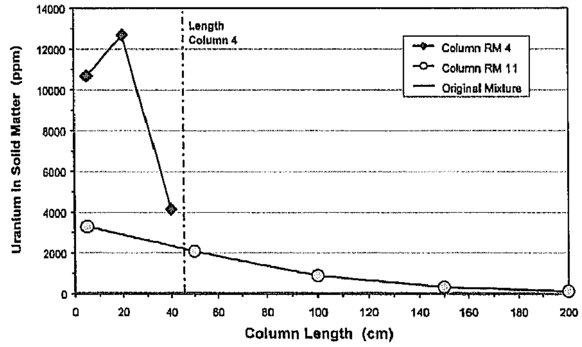

FIGURE 5. Uranium content in the reactive mixture of iron chips–lignitic coal after completion of the column tests (column 4: water solid ratio = 119 L/kg, mine water 1; column 11: water solid ratio = 48 L/kg, mine water 2).

TABLE 7. Characteristics of the Tested Lignitic Coals[a]

lignitic coal	ash (%)	sulfur (%)	CEC (mval/100 g)	pH after 1 h	pH after 200 h
(1) Central German	10	2.4	5.9	5.0	4.2
(2) Rheinbraun	4	0.4	15.9	6.2	4.2

[a] CEC was determined as effective CEC with the original pH in a not buffered solution.

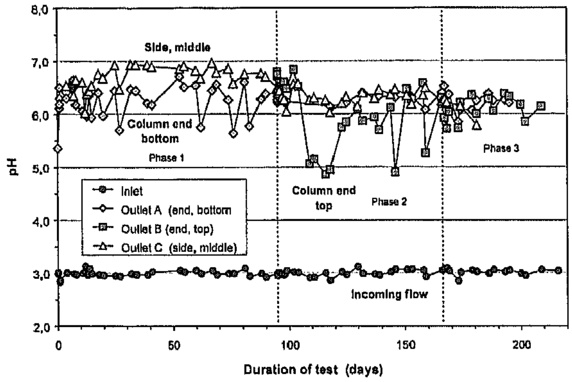

FIGURE 6. Development of the pH values in the incoming flow and the three measuring points of the horizontal column RM 11 filled with iron chips and Rhine lignitic coal.

4. Comparative Evaluation of the Iron–Lignitic Coal Reactive Material

In total five experiments were carried out at three different scales with the mixture of metallic iron and lignitic coal. A comparative evaluation considers not only the absolute values for substance fixation to assess the materials properties but also the reproducibility of the results and the sensitivity to the general conditions.

4.1. Influencing Conditions. Due to the lower acid content (pH 3) mine water 2 was buffered to pH 6–7 in the upscale column RM 11. The pH values give no evidence of different material conversions at the various flow scenarios (Figure 6). With the upper outlet opened, the buffer effects were slightly lower, which may be an indication of a preferred top flow. In phase C (both outlets open) there was a pH-adjustment of these two flow paths. The water taken as a sample through outlet C in the middle of the column showed evidence of intense contact with the reactive material.

Electric conductivity in the mine water decreased during the test period, which directly affected the discharge flow. Despite the dissolution of iron, there was an overall decrease of dissolved salt contents along the flowpath through the column (Figure 7). However, the development of the redox potentials (Figure 8) shows a clear relationship with the flow scenarios. After a short initial phase the Eh values at the bottom outlet A were definitely lower than those at the top outlet B later on.

Under these general conditions at the lower contamination level the efficacy of the mixture is decisively better than in the vertical column test RM 4 (section 3.1). There is no indication of any decrease in reaction rates of the iron or the lignitic coal (Table 8).

The additional small scale experiments with mixture variants of metallic iron and lignitic coal endorsed the good contaminant fixing properties. Of the two types of lignitic coal examined, the Central German coal (see Table 4) achieved better results in contaminant fixation. The differences, however, were only slight so that with a given mechanical stability the type of lignitic coal is less important than the optimum grain size. However consistent results of the diversified scaled tests prove a minor influence of flow properties within the chosen particle sizes.

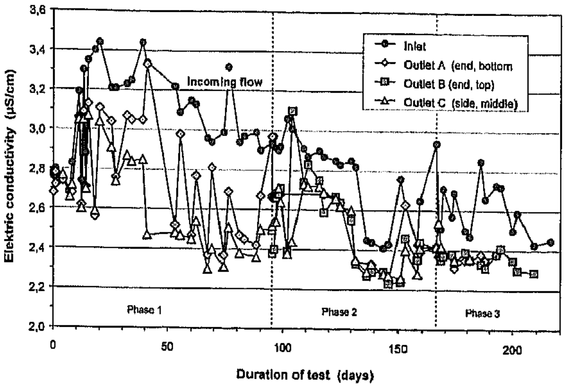

FIGURE 7. Development of electric conductivity in the incoming flow and the three measuring points of the horizontal column RM 11 filled with iron chips and Rhine lignitic coal.

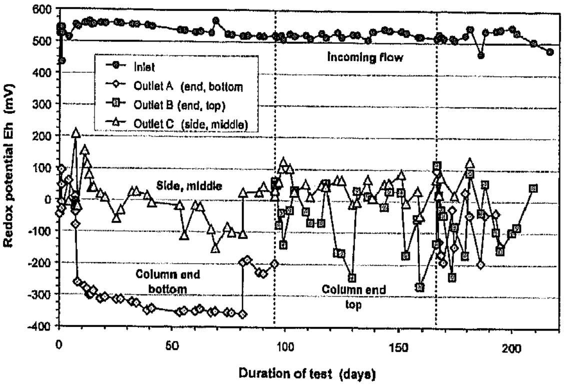

FIGURE 8. Development of the redox potential in the incoming flow and the three measuring points of the horizontal column RM 11 filled with iron chips and Rhine lignitic coal.

The iron chips used as reactive material yielded good results and are preferable to the iron scrap. Corrosion of the coarse-crushed iron scrap resulted in lower material reaction with the acid as compared to the chips and thus produced lower buffering effects. For the sake of releasing a minimum of contaminants from the reactive material itself, the steel should be low-alloy steel and not zinc-coated.

It was found that horizontal flow through the reactive material did not lead to notable losses in efficiency. What matters primarily is a sufficiently long residence time. The experiments carried out so far show for the mine waters examined contact times of >2 days as essential for an obvious decrease in the stock of the dissolved contaminants.

The three test series with approximately 2, 20, and 200 kg of reactive material in the vessels (corresponding to a factor of approximately 10) did not reveal any results from which a scaling effect could be concluded. Therefore it was possible to demonstrate the reproducibility of the effective processes from laboratory scale to semitechnical scale. Similar results can be expected for a large-scale application (here: discharge from mine or suitable reactor).

4.2. Efficiency. The fixing rates for substances from the input mine water vary, depending on the reactive mixtures and in terms of the specifics of the elements. Table 9 shows the fixed contaminant portions for the four reactive iron chips–lignitic coal systems examined. These fixed portions of the supplied contaminant loads were determined by accumulation up to a water–solid ratio of 22 L/kg. The water–solid ratio represents the best benchmark for comparison of results, and all these tests were performed up to at least this value.

TABLE 8. Mean Values of the Chemical Composition of the Waters at the Three Measuring Points of the Horizontal Column RM 11[a]

		outlet A	outlet B	outlet C
pH		6.1	5.7	6.5
Eh	mV	−227	−57	−201
Lf	mS/cm	2.7	2.5	2.5
Fe ges	mg/L	459	421	339
Na	mg/L	74	50	99
K	mg/L	18	17	20
Ca	mg/L	240	242	226
Mg	mg/L	37	27	71
Mn	mg/L	7.0	7.4	6.0
Al	mg/L	0.5	3.2	0.1
Cl	mg/L	56	53	61
SO_4	mg/L	1665	1509	1528
HCO_3	mg/L	12	19	33
U	mg/L	0.3	0.8	0.0
Co	mg/L	0.22	0.064	0.015
Cr	mg/L	0.015	0.007	0.009
Cd	mg/L	0.004	0.004	<0.001
As	mg/L	<0.02	<0.02	<0.02
Pb	mg/L	<0.05	<0.05	<0.05
Cu	mg/L	0.002	0.002	<0.001
Zn	mg/L	7.06	2.08	0.21
Ni	mg/L	0.64	0.13	0.02
Mo	mg/L	<0.005	<0.005	<0.005
Ra	mBq/L	1940	2270	nb
Σ nitroaromatics[b]	µg/L	<0.5	<0.5	<0.5

[a] Iron chips + Rhine lignitic coal. [b] Nitrotoluenes, dinitrotoluenes, and trinitrotoluene.

TABLE 9. Efficiency (Fixed Portions of the Input Contaminant Loads) of the Iron Chips–Lignitic Coal Mixtures for Selected Contaminants

test	S 1	RM 11	RM 4	S 3	mean value across all tests and mixtures
As	100.0	100.0	99.3	100.0	99.8
Cd	98.2	98.8	98.8	99.0	98.7
U	99.6	96.9	97.2	100.0	98.4
Al	99.8	99.0	90.5	99.8	97.3
Cu	90.2	97.2	99.8	90.1	94.3
Cr	79.7	86.5	91.5	83.1	85.2
Zn	80.1	72.5	78.8	97.5	82.2
Ni	28.1	35.0	70.8	89.1	55.8
Co	39.5	37.6	40.8	89.9	51.9
total efficiency across all elements	79.5	80.4	85.3	94.3	

Many contaminants especially As, U (reduction), Al (hydroxide precipitation), and Cd are retained almost completely by the iron–lignitic coal mixtures. Under the highly reducing environment precipitation can be attributed to the reduction of, in this regard, sensitive contaminants. For uranium the formation of uraninite (UO_2) can be expected. Similar redox sensitive components in mine water are arsenic and chromium for example. Aluminum, sulfur, and uranium were found to be dominating components in precipitation products on the surface of iron chips (scanning electron microscopy). So formation of aluminum hydroxide will provide both coprecipitation and secondary sorption capacities. In addition these processes are superimposed by the sorption properties of the lignitic coal.

After an initial phase, also the mobile elements zinc, nickel, and cobalt are almost completely fixed under stable test conditions. This can be attributed to the efficiency of sulfate reduction.

Considering the whole range of elements, the mixture of iron chips with lignite coal (S 1, RM 11, RM 4, S 3) obtains mean values of 80% to 94% of fixed contaminants. Using finer grained Central German coal is even more efficient for the acid, highly mineralized mine water in column RM 4 (85%) than the coarser Rhine lignitic coal for the less mineralized mine water (RM 11 and S 1; 80% efficiency in both cases). The use of iron sheet, however, recorded remarkably lower fixations and even releases of zinc and cobalt.

The tests carried out for 1 year with mine water of pH 2 (Table 1, mine water 1) allow an extrapolation of adequate retaining properties for at least 10 years for water with a contaminant potential 10 times lower (Table 1, mine water 2). A subsequent flow of uncontaminated groundwater through column RM 4 for a period of 3 months did not reveal any release of metals already fixed (Figure 4). Tests with the iron–lignitic coal mixture showed neither a significant decrease in fixing of the relevant contaminants nor in iron reactivity due to the formation of reaction products or iron surfaces rendered inert.

Sulfate reduction in the reactive mixture is indicated by black finely dispersed ferric sulfide deposits at the discharge end of the laboratory glass columns. The fixation of almost 100% of zinc in column S 3 and with stable flow later on in RM 11 has to be attributed to a sulfidic precipitation as well. After completion of the test, sulfate-reducing bacteria were identified in column S 3. These observations confirm that the environmental conditions and nutrients provided by the lignitic coal and metallic iron in the mine water environment facilitate the efficient propagation of sulfate-reducing bacteria. Thus precipitation of metals with a usually higher mobility can be expected in very large quantities.

4.3. Gas Generation. In the first test series (columns RM 1–9), a temporary generation of gas due to the acidic waters was clearly identified in all columns filled with metallic iron. As expected, this gas largely consisted of hydrogen. Since a sufficient quantification was not possible, both the laboratory columns and the 2 m column RM 11 operated underground were provided with gas escapes and gas bags to collect the reaction gases.

Due to the moderate pH value of mine water 2 (pH 3), gas generation in column RM 11 was much lower than in RM 4. Apart from traces of oxygen and carbon dioxide (both < 10 L), 172 L of hydrogen and 133 L of nitrogen were released during the test period (water–solid ratio 48 L/kg = 10.4 m^3 of mine water percolated). This correlates with a low gas generation of 0.03 L gas/1 L mine water.

For evaluation of data conclusiveness and to identify possible measuring errors, appraisals for processes and reaction rates contributing to the generation of hydrogen were worked out for column RM 11. Since the mine water used contained almost no dissolved Fe(III), dissolution of metallic iron is caused predominantly by reaction with the acid content:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2(g)$$

From the almost complete buffering of the acid content in the mine water (from pH 3 to about pH 6), a cumulative hydrogen generation of 27 mol can be calculated. Another appraised value can be taken from iron release. Over the test period (till a final water–solid ratio of 48 L/kg), the amount of ~1.3 kg of iron (iron input–iron output) was dissolved (which is ~1.2% of the iron in the column). Assuming iron corrosion to be the only acid consuming process this iron dissolution corresponds to a hydrogen generation of 46 mol. This means that approximately 30 mol of hydrogen is assumed to be generated in the column, which is equivalent to an average of 3 mg of hydrogen per liter of mine water (Figure 9).

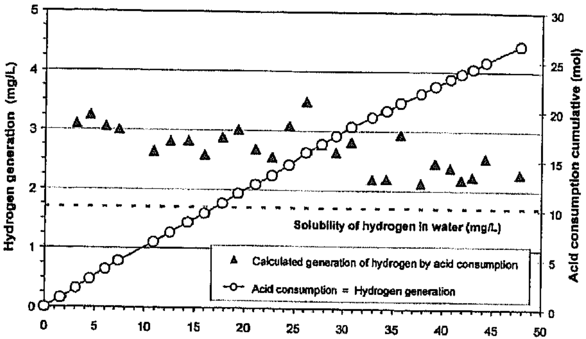

FIGURE 9. Generation of hydrogen in column RM 11 calculated from acid consumption.

The collected 172 L of hydrogen gas correspond to a hydrogen quantity of 7 mol H_2 or 14 mol H at a standard volume of 24.46 L/mol (at 25 °C). This amount of hydrogen represents 47% of the total hydrogen generated. Consequently, 16 mol (=53%) dissolved in water must have been discharged from the reaction system. These values coincide with the theoretical solubility of hydrogen in water (~2 mL of H_2 in 100 g at 20 °C correspond to approximately 1.7 mg of hydrogen/L). This means that in case the percolate is saturated with dissolved hydrogen gas, 17 mol of hydrogen (=55% of the generated hydrogen) can be discharged from the column along with the percolate under atmospheric pressure. This corresponds to the theoretical hydrogen production with mine water of pH 3.2. This could be confirmed by no gas generation in additional laboratory tests with iron chips and the lignitic coals 1 and 2 with mine water at pH 3.2.

The examinations of gas can be interpreted as follows: (1) When leaving the reaction chamber, the mine water is saturated with hydrogen gas. (2) Of the amount of hydrogen of 0.0026 mol/L generated at the mine water pH (approximately pH 3), approximately 50% can be dissolved in the mine water. (3) Approximately 50% of the hydrogen generated escape as gas phase. (4) With a mine water pH of 3.2—given identical buffer reactions—the total amount of hydrogen generated can be dissolved in water with no formation of hydrogen gas.

5. Outlook

The investigations have shown that the results obtained in laboratory experiments and semitechnical underground tests are reproducible and to a large extent transferable to real underground conditions. Mixtures of Fe chips and lignitic coal are capable of efficiently cleaning acid and contaminant-containing mine water in a reactive downstream barrier. The examined material is easily available and compatible with the environment. Hydrogen gas production is controlled particularly by mine water pH and can be minimized corresponding with the expected future mine water quality. A large-scale application of such a barrier is being considered for mine water treatment in the future and is deemed to be promising in the light of the present results.

In the period of 2002/2003 pilot tests are planned to be carried out under realistic conditions and to work out applicable technologies. They aim to provide the basis for technological developments for applications in underground cavities (galleries or built geochemical barriers) and in fixed-bed reactors. Apart from the treatment of mine waters, possible applications are envisaged for other waters polluted with heavy metals, natural radionuclides, and nitroaromatics.

Literature Cited

(1) Dahmke, A. Texte und Berichte zur Altlastenbearbeitung, Landesamt für Umweltschutz Baden-Württemberg, Karlsruhe, 1997.

(2) Teutsch, G.; Schüth, C.; Melzer, R. Altlastenforum Baden-Württemberg e. V., E. Schweizerbartsche Verlagsbuchhandlung, Stuttgart, 1999.

(3) Blowes, D. W.; Ptacek, C. J. Third International Conference on Groundwater Quality Research, Dallas, TX, Jun 21–24, 1992.

(4) Blowes, D. W.; Ptacek, C. J. U.S. Patent No. 5,362,394, 1994.

(5) Blowes, D. W.; Ptacek, C. J.; Jambor, J. L. *Environ. Sci. Technol.* **1997**, *31*, 3348–3357.

(6) Benner, S. G.; Blowes, D. W.; Ptacek, C. J. *Ground Water Monit. Rem.* **1997**, XVII (4), 99–107.

(7) Blowes, D. W.; Ptacek, C. J.; Benner, S. G.; McRea, C. W. T.; Bennett, T. A.; Puls, R. W. *J. Contam. Hydrol.* **2000**, *45*, 123–137.

(8) Neitzel, P. L.; Schneider, P.; Zaddach, V.; Hurst, S. Proc. Zur Jahrestagung der Fachgruppe Wasserchemie der Gesellschaft Deutscher Chemiker e. V., Weimar, 2000.

(9) Smyth, D. J. A.; Blowes, D. W.; Benner, S. G.; Hulshof, A. M. Presented at Tailings and Mine Waste '01, Colorado State University, Fort Collins, CO Jan 15–19, 2001.

(10) Schreyer, J. *Geowissenschaften* **1996**, *14*(11), 452–457.

(11) Klinger, C.; Jenk, U.; Schreyer, J. *Proceedings 7th International Mine Water Association Congress, Mine Water and the Environment*, September 11–15, 2000, Katowice – Ustron, Poland, Published by The Int. Mine Water Association and Uniwersytet Slaski (Poland).

(12) Fiedor, J. N.; Bostick, W. D.; Jarabeck, R. J.; Farrell, J. *Environ. Sci. Technol.* **1998**, *32*(10), 1466–1743.

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