SUMMARY

Wide variation of redox conditions, mineralization, and chemistry of ground and surface water, physical and mechanical properties of matter, distribution of organic matter and its altering properties are the cause for a large diversity of geochemical barriers. According to Russian scientist A.I. Perelman, a **geochemical barrier** represents a zone where intensity of element migration is decreased sharply causing accumulation of elements. In natural environments, geochemical barriers form chemistry of different soil horizons, sediments and ore deposits.

Industrial centers are often associated with a combination of contamination sources (wastewater, areas polluted with waste products, sumps, etc.). This concentrated pollution results in local technogenic geochemical anomalies that negatively influence the environment. The formation of such anomalies is often the result of technogenic migration of pollutants with water flows. Numerous methods have been developed to curb negative effects of the pollution.

One of such methods is the usage of artificial geochemical barriers. Successful experience of their application allowed formulating principles of strategic approach to environmental protection based on acceleration of natural transformation of pollutants into non-migratory forms or purposeful pollutant accumulation within a confined area in the lithosphere, i.e. construction of geochemical barriers.

There are different types of geochemical barriers used in environmental protection (Figure 1). Different materials have been utilized in their construction depending on the targets of protection and economic efficiency (Figure 2).

The book presents author’s experience of practical application of geochemical barriers in environmental protection in Russia. The areas of application include refinement of wastewater from suspended particles, neutralization of acid mine water and flows from mine heaps, reduction of sulphate content in service water and sulphate aggressiveness of underground water, and biochemical mitigation of oil pollution. Natural or other materials, e.g., alkaline waste, have been used in construction of artificial geochemical barriers. Such methods allow avoiding building expensive cleaning facilities.

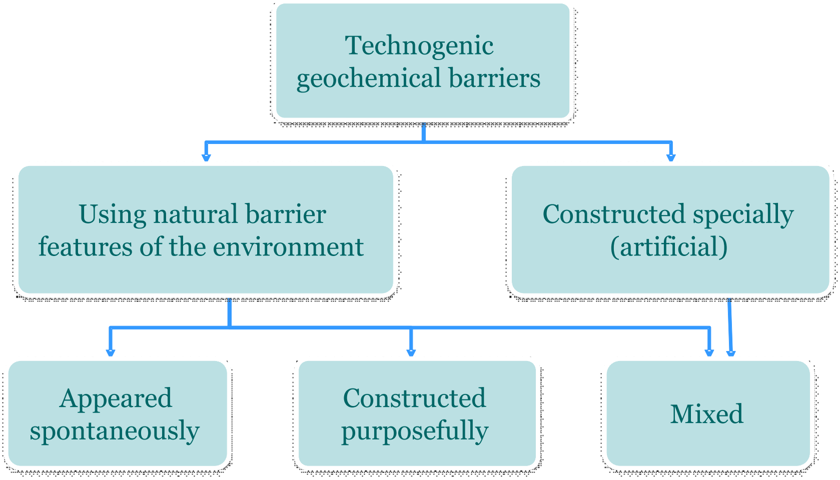

Figure 1. Types of technogenic geochemical barriers used in environmental protection

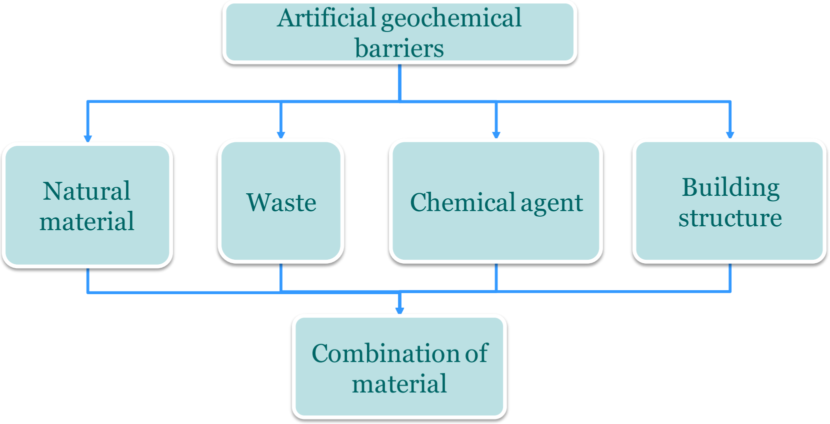

Figure 2. Construction materials used in artificial geochemical barriers

PLACER MINING

Environment consequences of placer mining.

The Vishera river basin (Northern Urals) where the diamond placers are mined is composed of the Riphean, Vendian, Ordovician, Silurian, Devonian, Carboniferous, and Permian deposits. This region contains both ancient and recent karst deposits, including karsted carbonate seamy rocks of the Silurian, Devonian, Carboniferous and Lower Permian of the total thickness reaching 4,000 m. Diamond deposits buried in the erosion-and-karst depressions are associated with the overlapping suballuvial and subfluvioglacial karst.

The depressions consist of the deposits of sandstone, quartzitic sandstone, quartz, flint, limestone, and dolomite. Sand portion in the deposits of the erosion-and-karst depressions is presented mainly by the light fractions of quartz, calcite, dolomite, phosphates, and feldspars. The heavy fraction content varies from 0,1 to 4,2%. Its composition includes hydrogoethite, magnetite, hematite, siderite, manganese oxides, phosphates, leucoxene, zircon, tourmaline, rutile, ilmenite, chrome-spinellids, anatase, garnets, epidote, pyroxenes, amphiboles, moissanite, and fluorite. Terrigenous material of the depression deposits consists primarily of clay minerals with the following main components: kaolinite, hydromica, montmorillonite, and chlorite.

The region has ground water of alluvial and eluvial-deluvial deposits; karst water of the Visean-Artinskian, Fransian-Tournasian, and Ordovician-Silurian carbonate aquiferous complexes; and fissure-ground and fissure-stratal water of the Devonian, Ordovician-Silurian, and Asselian-Artinskian terrigenous aquiferous complexes. The first two aquiferous complexes are hydraulically communicating through the karsted rocks.

The diamond deposits are mined by the dredge and hydromechanical methods with four dredges and one seasonal concentrating mill (SCM). The dredges and SCM extract a portion of the heavy fraction containing diamonds. The rubbly-pebbly and sandy-argillaceous fractions are dumped into the rivers and form the heaps several meters high. The rivers are dammed up to maintain the required water level for the floating dredges.

Construction of the dams and settling ponds, organization of the circulating water supply system, operation of the hydraulic units result in the change of the hydrodynamic regime of the surface and subsurface water. Higher level of subsurface water causes underflooding and swamping of the territories.

Dams create the subsurface water hydrostatic head that drives polluted river water into the groundwater. Leakages from the SCM settling ponds contaminate the groundwater too. The dredge operations change not only the riverbed profile but also the granulometric composition of the bottomset beds and in some karsted areas of river valleys, this activates the flow of the surface and groundwater into the underlying aquifers. Higher heads of water reservoirs enhance this phenomenon. Surface and groundwater become contaminated by roiling and extraction of the ground components in the course of technological operations.

Unstable minerals in the heaps are prone to intensive weathering as they come under changed physical and chemical conditions. The products of interaction between the rock heaps and surface water and atmospheric precipitation infiltrate into the subsurface water.

The pulp of the dredges and SCM has increased iron content (up to 3,55 mg/l which is 12 times greater than the maximum permissible concentration(MPC). The rivers in this region also have increased content of sulphates, chlorides, nitrates, nitrites, calcium, sodium, potassium, ammonium, silicon, and iron.

The dredge heaps in small rivers of the valleys have high content of iron (up to 9,9) (from iron-bearing minerals in the heaps), nitrites (up to 1,6), and ammonium (up to 11 mg/kg). Maximum contamination of the bottomset beds with iron (up to 10,4 mg/kg) can be seen along the rivers near the operating dredges decreasing downstream.

High concentrations of iron, nitrites, ammonium, and sulphates are observed in the subsurface water influenced by placer mining. In some samples, the concentration of nitrites, ammonium, and iron, are 2,5, 6, and 35 times greater than the MPC, respectively. The content of sulphates is 10 times greater than the background values. In the course of placer diamond mining, the surface water is most severely contaminated with suspended matter. Data analysis have shown that suspended matter concentration in the Rassolnaja river downstream of the operating dredge zone varies from 0,2 up to 12 g/l (i.e., tens and even hundreds times over the background values), depending upon the amount of precipitations.

Removal of suspended matter from the drainage water

To decrease concentration of the suspended matter in the river water, the authors propose to create filters made of the dredge heap rocks in the river bed (Figure 3). The experimental work has shown that, depending upon the filtration path length, the concentration of suspended matter could be decreased by as much as a factor of one hundred.

The use of filters constructed from the dredge heaps to clean the river water of suspended matter have proved highly efficient at a low cost of construction. According to some data, iron concentration could be decreased in this case too.

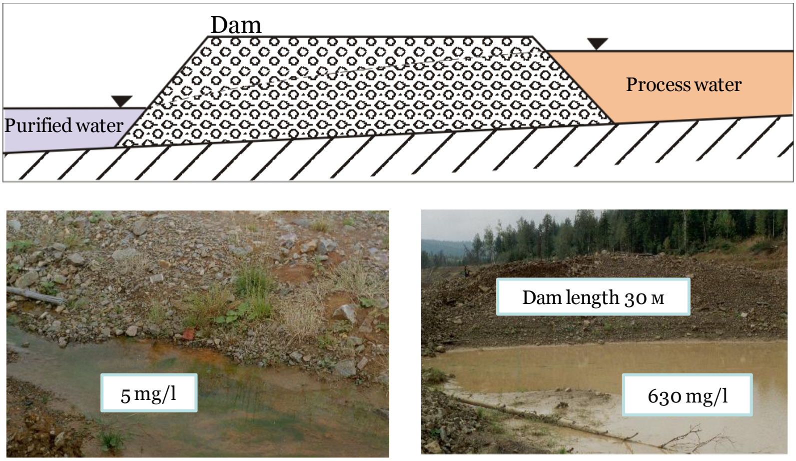

Figure 3. Purification of process water by removing suspended particles

COAL MINING

The geology in the Kizel Coal Basin, West Urals, Russia, is largely Carboniferous. The recent cessation of mining in the area and subsequent water table rebound have caused serious environmental problems. After mine closures, geochemical interaction between acid mine water and the surrounding geology has resulted in high concentrations of iron, aluminum, and trace metals in the tributaries of the Kama and Chusovaya rivers. The coal horizons in the Kizel Coal Basin differ from other basins in the region as they contain high levels of sulphur (mainly as a pyrite) (5.8%) and ash (21.5%) (Kler et al., 1988).

The mine water chemistry is largely dependent on the levels of sulphur, carbonate, and trace elements found within the carboniferous strata. A concentration of more than 4% pyrite results in high acidity (pH=2-3) and a sulfide chemistry. Total Dissolved Solid (TDS) concentrations of the sulfide (Fe-Al, Na-Ca) water of the Kizel Coal Basin was 2.5-19 g/l and levels higher than this value reached during the exploitation. The lead, copper, zinc, silver, nickel, cobalt, and other trace elements content in the acid mine water are elevated in comparison with ambient groundwater (Maximovich and Gorbunova 1990)

During the exploitation of the basin, mine waters were released to the surface without any prior purification or treatment. Before mine waters entered the river network, natural levels of the hydrochemical facies HCO_3-Ca-Na (TDS of 90-150 mg/l) were circumneutral. After the discharge, the SO_4-Fe-Al TDS ranged from 640 to 6000 mg/l, sulphate concentration - from 1000 to 3700, iron – from 70 to 900, and aluminum – from 11 to 160 mg/l at pH 2.5-2.9 (Maximovich et al., 1995).

Mine closures occurred during the 1990s but this did not resolve the environmental problems. Despite acid mine waters no longer being pumped to the surface, 12 disused mine adits started to discharge water to the surface once groundwater rose to its natural level.

The total average annual flow for the River Kos’va is 2500 m^3/hour. This is several times less than during mining activity. However, the TDS of discharge increased greatly – in some cases, in excess of 25 g/l. The ferrous iron content increased sharply too - up to 5 g/l. Discharge water entered 19 rivers, 15 of which are the sources of water for people in the area.

In the more polluted river sections, accumulation of several tones of man-made bottom deposits were found. This accumulation includes amorphous iron and aluminum hydroxides with high concentration of Mn, Cu, Ni, Zn, Pb and other elements. These bottom deposits are washed downstream to the Kama and Chusovaya Rivers, where they become a secondary source of water pollution.

Since the 1980s, the author has actively worked on the problem of purification of acid mine water and spoil heap drainage to find a method for removing harmful elements using artificial geochemical barriers with industrial waste as a reagent.

Acid mine water purification using alkaline waste products

At the end of the 1980s, alkaline waste products (so-called “white seas”) from the Bereznikovsky Soda Factory were tested as a reagent for neutralization of acid discharge. The neutralization technique was developed by Maximovich et al. (2000) (Figure 4). Alkaline waste products consist of 70-80% calcite ($CaCO_3$) with pH of 9-12. The average contents of 38 determined elements do not exceed MPC in soils (Table 1). There were no harmful organic compounds. The volume of waste suitable as a reagent for neutralization of acid mine water without any treatment exceeds 1 mln m^3.

When acid discharge reacts with alkaline waste, pH increases due to reaction with carbonate and hydroxide of calcium.

This in turn decreases the concentrations of Fe, Al, Mn, Co, Zn, Cu, Ni, Pb, Cd, Ti, and other elements resulting in the purification of water.

A pilot field experiment was conducted on “The 40 Years of October” adit, where water discharge varied from 180-220 m^3/hour in summer to 300-400 m^3/hour during the flood period. Mineralization ranged from 4000-600 mg/l to 800-900 mg/l with pH of 2,6-2,9. The concentrations of some elements exceed MPC: Fe – by 400, Al – by 46, SO_4^2 – by 1,3, Be – by 52,8, Mn – by 36,9, Ni – by 2,5, Cd – by 1,9, Co – by 1,6, Ba – by 1,5, and Ti – by 1,2 times.

In this experiment, the pH of the discharge increased from 2.6-2.9 to 7 resulting in a decrease in the concentration of iron from 30-40 mg/l to 0,2-0,3 mg/l. The content of Al, Be, Li, Ni, Cd, Co, and Ti does not exceed MPC (Figure 5).

Table 1. Average data for the alkaline waste products from the Bereznikovsky Soda Factory, mg/kg

N of sample	Depth, m	pH	Ni	Co	Cr	Mn	V	Sc	Ye	Cu	Zn	Pb	Ba	Sr		Zr	Y	La	Li	Nb
1	0		7	3	10	500	10	3	-	20	70	10	5	500	-	50	20	15	15	-
3	0	8,8	10	5	30	700	10	-	-	15	50	4	200	500	<1	30	40	-	-	-
2	1,6	11,8	9	4	30	500	10	3	-	18	-	7	300	400	1	30	30	-	-	7
5	0	8,7	7	3	18	1000	10	3	-	15	-	7	200	400	-	20	40	-	-	-
4	1,0	11,8	6	3	15	400	10	-	-	10	-	30	200	300	1,5	20	30	-	-	7
8	0	9 ,9	6	3	30	700	10	-	-	10	-	7	200	300	1	20	40	-	-	-
7	1,0	11,4	9	3	30	700	10	-	-	10	-	70	200	300	1	50	40	-	-	-
6	3,5	11,8	10	3	40	1500	10	3	-	20	50	180	200	400	1	20	40	-	-	7
11	0	9,2	7	3	30	1000	10	-	-	10	-	20	200	300	-	20	40	-	-	-
10	1,5	11,5	9	3	50	1000	10	3	-	20	-	180	200	300	15	20	50	-	-	-
9	4,0	1,6	9	3	70	1000	10	4	-	18	-	180	1500	500	1	30	50	-	-	-
12	0	2,3	5	-	15	1000	10	3	-	18	-	15	200	200	1	20	15	-	-	-
13	2,5	12,4	7	3	30	700	10	3	1	18	-	100	200	200	1,5	40	18	-	-	-
14	3,5	12,4	9	3	30	900	10	3	-	20	50	150	200	300	1	40	18	-	-	-
MPC			50	50	100	1500	150			55	100	32								

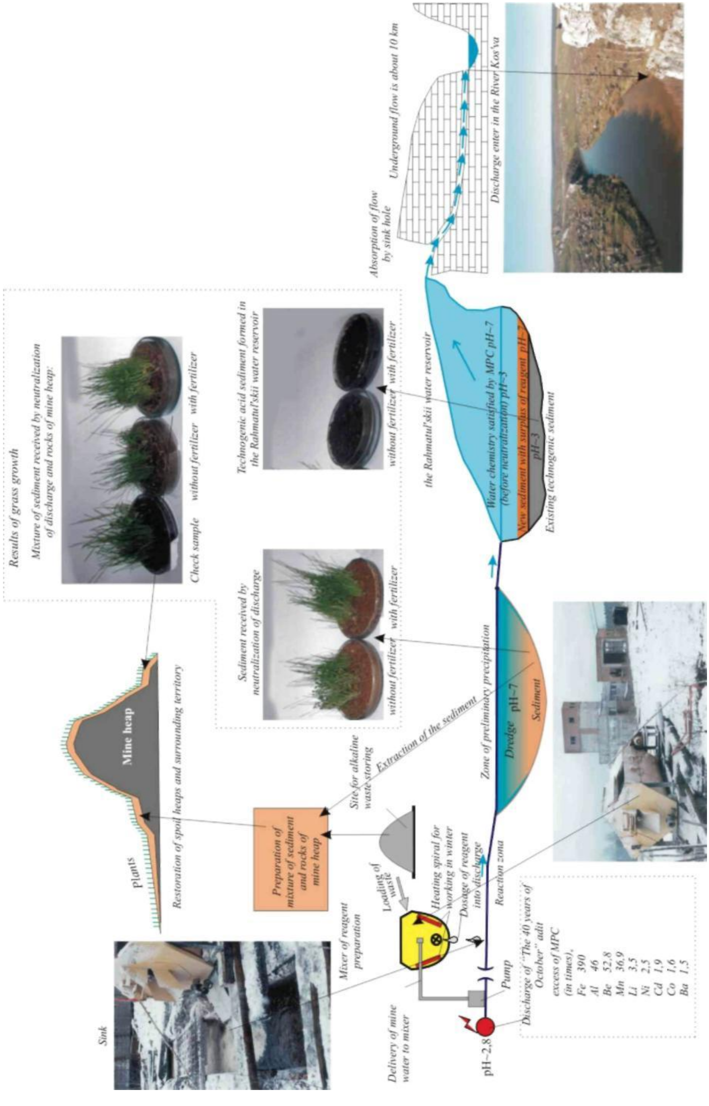

Figure 4. Technological schema of improving environment of the Kizel Coal Basin by alkaline waste products from the Bereznikovsky Soda Factory

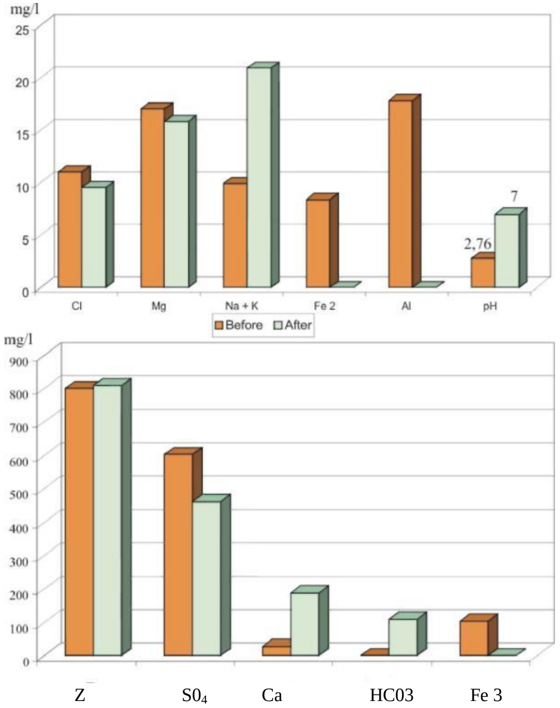

Figure 5. Chemistry of water from “The 40 Years of October” adit before and after neutralization of discharge

As a result of neutralization, the sediment becomes a mixture of iron and gypsum hydroxide and carbonate calcium with a neutral pH. Mobile forms of Fe, Al, Mn, Pb and other elements were not found (Table 2). Sediment is overgrowing with perennial grasses (timothy, fescue, couch-grass, and alfalfa) in the same way as the control soil plot.

The pilot field experiment demonstrated the prospect for the use of geochemical barriers to solve environmental problems. Additionally, this mine water purification technology helps to resolve the serious problem of the disposal of alkaline waste products.

Purification of acid rock drainage

Storage of coal mine waste in Kizel Basin causes intensive pollution of the underground water. In the areas of mine heaps, the groundwater of upper water-bearing horizon have low pH values, heightened salinity, and also high content of sulphates, iron, aluminium, and heavy metals.

Artificial alkaline barrier can be used for normalization of the underground water composition in the areas of Kizel Basin. The limestone mining waste widespread in the surrounding area may serve as a reagent.

Before the field experiment, observed iron and sulphates content in groundwater reached 5,3 g/l and 19,7 g/l, respectively. Mineralization and pH varied from 17 to 28 g/l and 1,7 to 2,1, respectively.

The groundwater purification trench with clay aquiclude, 1,0-2,0 m in depth, was filled up with limestone (Figure 6).

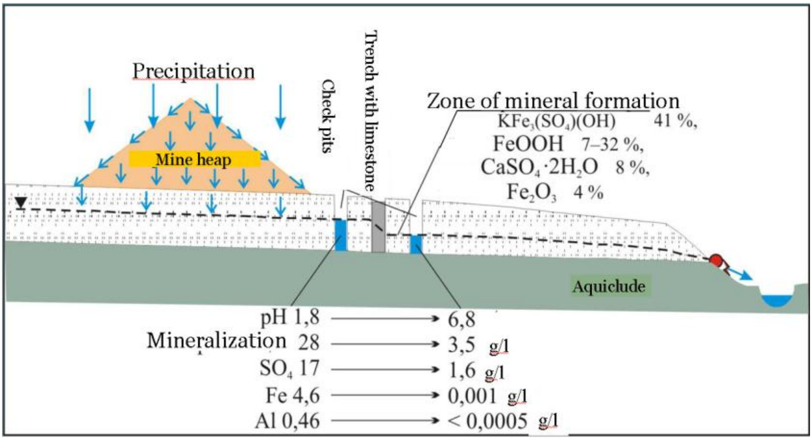

Figure 6. Schema of the field experiment on purification of acid rock drainage

At the end of the experiment, pH increased from 1,8 to 6,8 and was stable during the further years of monitoring research. The groundwater chemistry became close to natural – SO_4- CO_3-Ca hydrochemical facies. Mineralization decreased considerably from 28 to 3,5 g/l, and the content of main pollutants decreased too.

Table. 2. Chemistry of sediments before and after neutralization of discharges, mg/kg

Sample	pH	Ni	Co	Cr	Mn	V	Sc	Cu	Zn	Pb	Ag	Mo	Ba	Sr	Be	Zr	Y	Nb
Total content																		
1 (before)	2,92	30	9	150	100	150	1,5	100	100	30	0,2	2	300	150	10	300	60	30
2 (after)	7,22	70	30	90	1500	40	9	100	500	90	0,2	3	300	180	10	100	90	15
	Was not determined	40	18	100	1000	30	7	90	400	90	0,1	1,5	300	150	9	100	70	10
MPC		50	50	100	1500	150		55	100	32								
Mobile forms																		
1 (before)	2,92	0,81	0,81	0,08	27,1	0,03	0,02	27,1	27,1	0,04	-	0,005	0,8	0,8	0,108	0,14	0,4	0,03
2 (after)	7,22	0,02	-	<0,06	-	<0,06	-	<0,06	0,3	-	-	0,009	1,8	0,6	0,006	0,24	<0,06	0,05

X-ray structural analysis of loam in the contact zone showed goethite 7-32 %, jarosite – up to 41 %, gypsum – up to 8 %, and hematite – up to 4 %. The sludge from the process filled in the pore space, which decreased filtration by cementing the ground. This, in turn, changed the deformation behavior of loam. The deformation modulus determined through compressive tests increased by two and more times.

Reduction of sulphate content in industrial water of Coal Basin (East Siberia)

High sulphates content reaching 1200 mg/l prevented the use of industrial water collected in large reserves on Holboldzhinsky coal opencast mine in Buryatia (arid zone) for watering. A special technological scheme was developed to reduce the sulphate content using barium compounds (Figure 7). In these experiments, the sulphates content decreased to 440 mg/l (at MPC of 500 mg/l). The content of other components did not exceed permissible values.

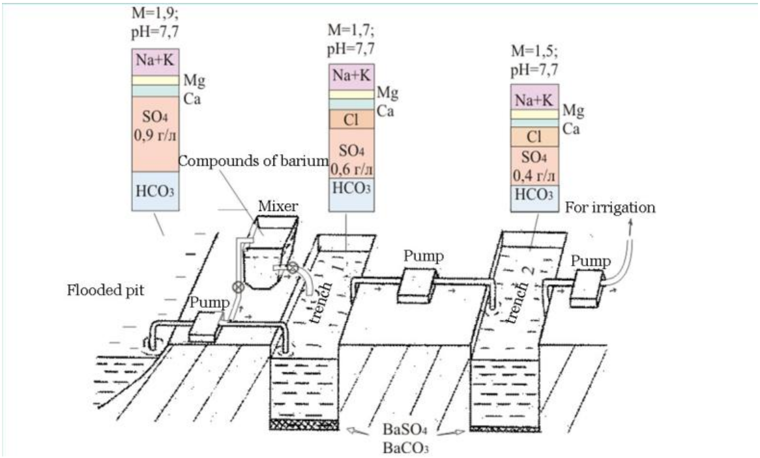

Figure 7. Reduction of sulphates content in industrial water of Holboldzhinsky coal opencast mine using barium compounds

Oil industry

Removal of oil spills

Oil spills from pipelines accidents represent an essential threat to the environment. After the Surgut-Polotsk oil pipeline rupture in Perm Krai, a method of using a multi-component sorbent has been developed to mitigate the impact of such accidents. As was shown in laboratory experiments, this sorbent (created from absorbite waste products) is capable of capturing water-emulsified crude oil removing it from the surface water thus decreasing the oil’s volume. Some sorbent components form sorbing layer at the bottom after its deposition. This layer works as a precoat filter for underground water filtration. The floating component of sorbent can then be removed from the water surface. Sorbent is not toxic and can be incinerated after usage.

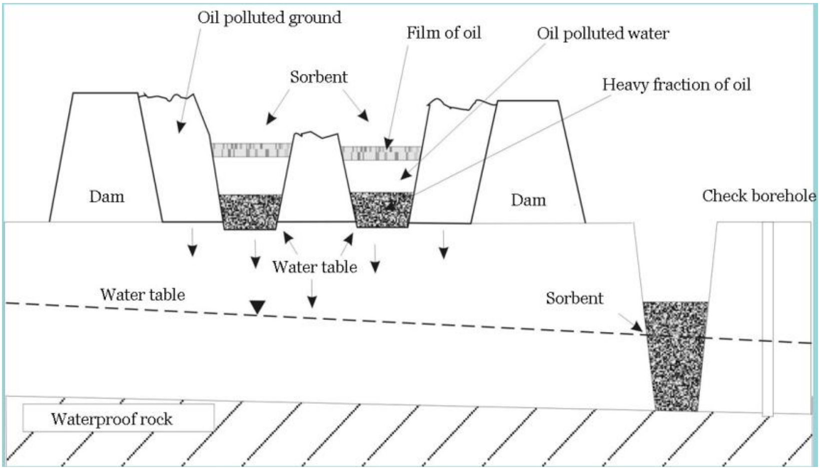

Figure 8. Schematic representation of removing oil pollution using sorbents

Oil pollution control in ground- and surface water at oil fields.

In some cases in order to achieve environmental protection, it may be necessary to destroy geochemical barriers. Such barriers may be destroied by microorganisms that are capable of destructing petroleum substances. Field experiments conducted by the authors at the Polaznenskoe oil deposit showed promising results of this scientific direction.

The hydrosphere at oil deposits in places with highly karstified surface is vulnerable to pollution. Contaminated groundwater is discharged to water reservoirs and causes a significant pollution of water reservoirs and adjacent areas. At the Polaznenskoe oil deposit, oil lenses were formed at the groundwater surface during its half-a-century development. These lenses continue to contaminate water of the Kama water reservoir.

Geological and hydro-geological data suggests that oil discharge to the coast is related to the long-term operation of this oil deposit. The intense karstification of the area appears to be one of the principal natural factors that enhances the impact of the oil pollution source at the surface of fracture-karst water.

Borehole testing of the oil lens indicated similar water levels in the Kama water reservoir and boreholes drilled 50-400 m far from the shore, as well as their close hydraulic relationship due to a high level of rock karstification. The groundwater in the boreholes had sulfate-hydrocarbonate-calcium mineralization in the range of 2,2 to 3,0 g/1.

Two methods of pollution control in the Kama water reservoir were used. These methods involved pumping oil from the lens surface using special technique and oil biodegradation using natural microbial activation (figure 9).

The groundwater provides a habitat for prokaryotic and eukaryotic microorganisms alike, but bacteria are the most abundant. Nowadays, groundwater microbes are systematically studied. A great number of subsurface environmental factors can influence microbial activity and, therefore, transformation of pollutants. These factors are temperature, pH, redox potential, availability of electron acceptors, salinity and hydrostatic pressure, porosity of the aquifer's rocks, chemical recalcitrance and solubility, chemical and physical adsorption and desorption on rock particles, etc. A large variety of different microorganisms was isolated and characterized for varying habitats of different geographic regions and subsurface depths. The number of bacteria was about 10^6-10^7 per gram in the vadose zone and some shallow-water table aquifers.

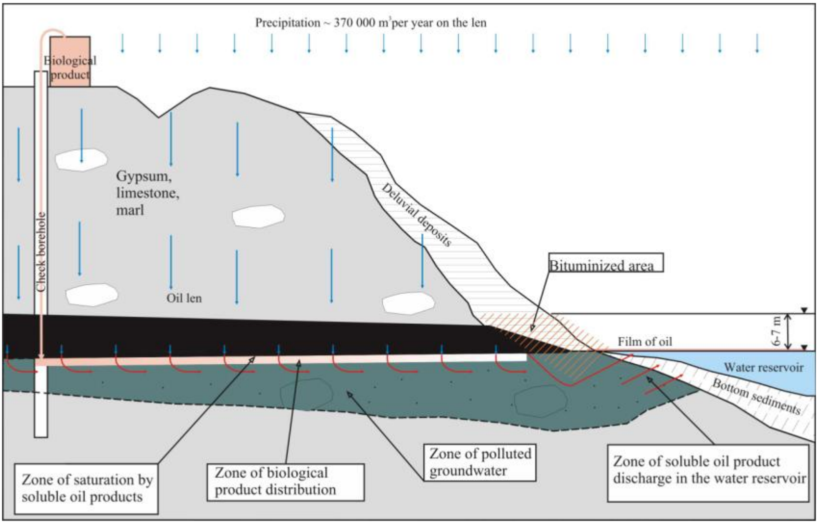

Figure 9. Schema of groundwater treatment by biological product

Although groundwater is more difficult to be contaminated than surface water, its reclamation is much more complicated. Improved analytical capability revealed widespread presence of toxic waste chemicals in the oil deposit groundwater.

The most common pollutants of groundwater are hydrocarbons and heterocyclic compounds of oil and oil-products. There are two main biotechnological methods of oil polluted natural habitats remediation: (1) stimulation of natural microbial hydrocarbon-oxidizing populations by addining nutrients (especially nitrogen and phosphorus) and (2) introduction of active hydrocarbon-oxidizing bacteria (and nutrients) into polluted environments.

In this study, we attempted to combine these approaches to achieve the cleaning up of oil-polluted karstic aquifer. This work had the following several stages:

- isolation of active hydrocarbon-oxidizing bacteria from karstic groundwater and identification of their oil degrading potential;

- development of a bacterial preparation based on isolated aboriginal hydrocarbon-oxidizing bacteria for remediation of oil polluted groundwater;
- stimulation of hydrocarbon-oxidizing microflora of the aquifer by inorganic nutrients; and
- introduction of the developed bacterial preparation into the aquifer to achieve complete oil removal.

The introduction of actively metabolizing hydrocarbon-oxidizing bacteria into polluted environments is especially important in the regions of cold and temperate climate, where a warm season is short.

Laboratory and field research showed that, due to groundwater microbial metabolism, the content of n-alkylic compounds in oil decreased by a factor of four. At the same time in control samples, the decrease of these substances did not exceed 20%. Karstic groundwater contained active hydrocarbon-oxidizing bacteria that can be used in bacterial preparation for cleaning oil-polluted aquifers.

METALLURGY

The impact of sludge settling on the environment.

The Pashiya concrete-metallurgic enterprise is located in the Perm Krai. The disposal of gas-purification wastes in unequipped settler has lasted for many years, and has resulted at pollution of groundwater and the Pashiika River with toxic compounds. The research conducted by the authors targeted both the composition and scales of the pollution and measures of environment protection to reduce negative effect of the sludge settler on aquifers and surface waters.

Bauxite and coke, and metallic cut are the raw materials for smelting titanic cast iron. These materials are charged into a blast furnace, where heating, melting, and smelting the metal occurs. The technology of collection of gas-purification wastes from smelting the metal first captures the coarse particles on the blast-furnace catchers (blast-furnace dust). Then, the fine dust enters into the system of pipelines where gases undergo hydraulic purification. The wastewater with ash particles (the pulp) is accumulated in settling reservoirs located at the enterprise site. This water contains 5% of solids. The pulp is clarified in the settling reservoirs and it runs through the process several times until the reservoirs are filled with solids, thus making impossible utilization of clarified water. During the processes of water transfer and the contact of solution with new portions of highly dispersed and chemically active ash repeated many times, the concentrations of soluble compounds in the liquid phase, including harmful and toxic compounds, increase and reach very high levels at the end of the cycle. Content of solid phase is up to 10 %.

According to a bulk chemical analysis of (Table 3), mineralization of the pulp liquid phase is (34-42 g/1) and it is alkaline (pH 8,9-9,4). Hydrocarbonate (up to 18,2 g/1), carbonate (up to 5,2 g/1), and chloride (up to 7,8 g/1) are the predominant anions. The content of calcium and magnesium are low while the content of sodium and potassium are significant (up to 14 g/l). The dry residual obtained in the experiments exceeded that calculated from the bulk chemical analysis by 10,2 g/1. This indicates that the pulp contains high amounts of components not detectable by a bulk chemical analysis.

Atomic absorption spectrophotometers AAS-3, Hitachi Z-8000, and Perkin-Elmer were used to determine trace components of the pulp. Some samples were analyzed with an inductively coupled plasma (ICP) spectrometry instrument.

The analyses showed that the pulp became more concentrated towards the end of the accumulation cycle in the intermediate settler. The concentrations of nearly all heavy metals in the end pulp exceeded the MPCs: 240-fold for cadmium, 1120-fold for lead, 330-fold for zinc, 16-fold for nickel, 3-30-fold for copper, 15-fold for iron, twice for manganese, molybdenum and titanium, 10-fold for boron, and 60-fold for lithium. The concentrations of arsenic, vanadium, selenium and beryllium were within the MPCs (Tabl. 4 and 5).

The concentrations of elements in the pulp varied greatly, some times by 2-3 orders of magnitude, depending upon the raw materials composition, accumulation during recirculation of water, and changes in the technological regime.

Values of oxygen chemical intake were determined to estimate the bulk amount of organic matter in the waste. The intake ranged from 820 to 960 mg O/l, thus indicating the presence of organic matter in significant amounts. Paraffin hydrocarbons of high fractions, aromatic hydrocarbons, and their oxidized products (poliphenoles) were detected among the organic compounds. The dissolved organic compounds formed stable complexes with heavy metals in alkaline medium.

Both composition of solid phase of the pulp and migration properties of its components was studied using atomic-emission spectral analysis. Various samples of ash, including those treated with water and 0,5 N HCl, were analyzed.

Characteristics of raw materials used in smelting cast iron were also studied. Bauxite was undoubtedly the source of highly toxic beryllium that migrated to the ash in sizable amounts.

The mobile components of the liquid phase are not at equilibrium with the solid phase. The concentrations of a number of elements vary in the presence of the solid phase in the pulp.

The pulp is removed from a detention reservoir to the sludge settler, which is located near the watershed between the Vizhaya and Pashiika rivers. The spread of pollution is largely controlled by the properties of geological-hydrogeological environment within the area of disposal.

Figure 10 presents a schematic representation of the geological-hydrogeological section of the area. The bedrock is the Upper Devonian fissured karst limestone with a ragged roof surface Limestone that exceeds 100 in thickness. The Upper Devonian sediments are overlapped by a suite of the Neogenic-Quatcrnary deluvial, alluvial, and limnic sediments which are presented by clay and loams with rubble, pebbles and boulders. The thickness of the cover sediments approaches 20-30 m near the watershed.

The main aquifer lies within fissured and karsted limestone of the Upper Devonian. The most permeable zone is located in the upper part of the suite. Water permeability of rocks is small due to a sharp decrease in occurrence of fissures and karst cavities decay rapidly downwards. Fissure-karst waters are in direct hydraulic relation with the Pashiika River, and in most cases have discharged.

The fissure-karst aquifer falls towards the Pashiika River and in the streamwise direction. The inclination corresponds to the fall of valley bottom and is about 0,01. The water discharges to the Pa-

Table 3. Composition of major components in the liquid phase of the pulp (mg/l).

Sample	CO_3^-	HCO_3^-	Cl^-	SO_4^-	Ca^{++}	Mg^{++}	Na^+	K^+	Mineralization	pH
1	5161	18183	3630	1201	271	6	13413		41865	8,9
2	4200	7015	7810	284	25	137	3700	10998	34169	9,4

Table 4. Heavy metals concentrations (mg/l) in the liquid phase of the waste (atomic absorption spectrometry).

Sample	***pH***	***Cd***	***Pb***	***Zn***	***Cu***	***Mn***	***Ni***	***Fe***	***Co***	***Mo***	***As***	***V***	***Se***	***Be***
P_1VIII	9,40	0,243	11,95	994,0	3.7	0,19	1,56	4,52	0.74	2,03	10,1	0,38	2,65	4,53
P_1	9,65	0,132	8,42	330,0	33.0									
P_1XII	9.15	0,107	4,00	465,0	0,3									
MAL		0,001	0,01	0,3	1.0	0,1	0,1	0.3	1,0	0,1	0,05	0,1	0,01	0,0002

Table 5. Elements concentrations in the P-1CM2 pulp (ICP spectrometry)..

Element	***Al***	***Ba***	***Ca***	***Cd***	***Cr***	***Cu***	***Mg***	***Mn***	***Mo***	***Ni***	***Pb***	***Sr***	***Ti***
Concentration	0,6893	0,0129	6.2	0.0263	<0,005	2,393	15,3	0,0717	0,1734	0,4371	4,542	0,0942	0,2228
MAL	0.2	0,1	-	0,001	0.05	1.0		0,1	0,25	0,1	0,05	7.0	0,1
Element	***V***	***Zn***	***Zr***	***Co***	***Fe***	***K***	***B***	***Na***	***Li***	***Be***	***P***	***As***	***Se***
Concentration	0,1041	460.3	0.0873	0,0614	0.8752	3891	5,727	1475	2,028	<0.005	1.017	0.005	0,008
MAL	0,1	5,0		0.1	0.3		0,1		0,03	0,0002		0.05	0.01

Note: As and Se are determined by atomic absorption spectroscopy (mg/l) shiika river through alluvial deposits and wells.

The wastes of the Pashiya concrete-metallurgic enterprise are disposed into old abandoned quarry. The bottoms of this old quarry corresponds to a practically stripped roof of the fissured bedrock covered in some places with clay deposits rangin 0.5-2 m in thickness. In some places, the Devonian limestone outcrops to the bottom of the quarries. A tectonic fault runs along the western edge of the quarry thus causing limestone be more fissured and permeable at this zones. These features make the groundwater open to the pollutants coming from the surface in the waste disposal area.

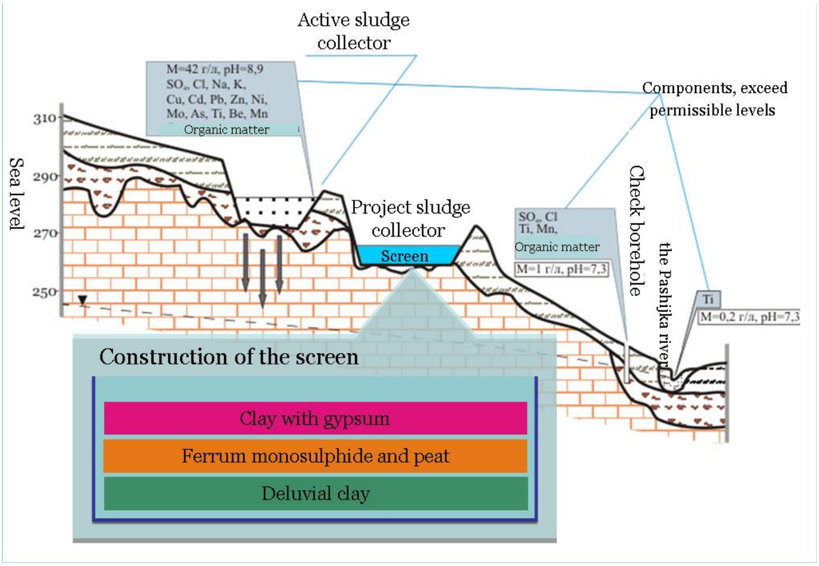

Figure 10. Geological-hydrogeological structure of the area and a complex screen for groundwater protection at sludge sites

The liquid phase of the pulp infiltrates the bedrock and pollutes the fissure-karst aquifer. The impact of the sludge settler on the groundwater was investigated in the zone of fissure-karst water discharge to the Pashiika River. Four observation boreholes and two springs discharging from bedrock limestone were sampled to determine hydro-chemical properties. Mineralization of the groundwater in the zone of the settler impact is 0,6-1,0 g/1 which exceeds background mineralization 6-10-fold. The concentrations of sulfates and chlorides are 3 and 90 times greater than the background concentrations, respectively, which is indicative of pollution. The concentrations of some trace elements are also higher: 1,0-1,7 mg/1 of titanium, 0,2-0,3 mg/1 of manganese, 0,2 mg/1 of copper, 0,5-0,7 mg/1 of zinc, and 2,9-3,4 mg/1 of strontium. The contents of manganese and titanium are 1,5-3,4 and 10-17 greater than the MPC. The content of organic substances in the polluted groundwater calculated from oxygen chemical intake was 50-59 mg/l, twice exceeding standard values and 5 times higher than the values of the nearby not polluted spring.

Despite a multi-fold dilution, the discharge of the groundwater to the Pashiika River changes its chemistry. The chemical composition of the river water was determined with temperature measurements done prior to sampling. This allowed distinguishing sites of a relatively concentrated groundwater discharge where hydrochemical samples were collected. The content of the most trace elements released by the settler exceeds the background levels at the discharge site and downstream. However, only titanium exceeds the MPC. The concentration of titanium ranges 0,10-0,13 mg/1, which is 10-13 times higher than the background level, and 1,3 times higher than the MPC. The value of chemical oxygen demand (COD), compared to the background level, was more than twice at the discharge site and downstream, and averaged 17,5 mg O/l, which is slightly higher the maximum allowable limit. The content of organic substances calculated from COD comprised 13 mg/1.

Design of a complex screen for groundwater protection at the sludge sites

Construction of an artificial screen at the bottom of the sludge settler was considered to protect the underground and surface water from the pollution at the discharge sit. The screen was designed with sufficient capacity to absorb pollutants in the infiltrate. Potential pollutants identified through the analyses of the ground and surface water included Cu, Cd, Pb, Zn, Ni, Mo, As, Ti, and Be. The concentrations of these elements in the liquid discharge significantly exceeded the MPCs (Table 6).

Table 6. Sorption capacity of clay in relation to Cd, Zn, Cu, and Pb estimated from the experiments with a model solution (clay to solution proportion of 1:200).

Cd			**Zn**			**Cu**			**Pb**		
Initial concentration	Residu. concentration	N, mg/g	Initial concentration	Residu. concentration	N, mg/g	Initial concentration	Residu. concentration	N, mg/g	Initial concentration	Residu. concentration	N, mg/g
12,6	1,3	2,1	25,6	5,6	4,0	27,0	6,7	4,1	17,1	0,0	>3
37,0	4,2	6,6	51,5	20,0	6,3	53,0	22,7	6,1	41,3	0,0	>8
74,7	16,8	11,5	103,0	61,0	8,4	110,5	70,0	8,1	84,8	6,8	6,8

The material for the screen was chosen from the experiments to study properties of local clay subsoils, different natural and artificial reagents, and their combinations.

The counter-filtration sorption screen may be constructed using deluvial clay. Sufficient deposits of this clay have been prospected in the area of the sludge settler. This is highly dispersive clay: clay (less than 0,001 mm) and fine-dust (0,005-0,001 mm) particles comprise 20% and 22,9%, respectively. The clay mineral composition was studied by X-ray structural, silicate and carbonate chemical. According to X-ray analysis, the most dispersed clay fraction consists of hydromica - 2,8 %, kaolinite - 2,5%, microcline - 3,1 %, mixed-layer minerals - 10,2 %, and quartz - 80%. Albite, chlorite, and goethite are present in minor amounts. The clay is characterized by a significant hypergenic alteration of alumino-silicate material, especially clay minerals. The alteration is expressed in poor crystallinity, high dispersion, partial amorphization, and as a consequence, very low degree of structural perfection. Mixed-layer minerals (the products of leaching of hydromicas and destruction of chlorite) predominate in the clay fraction. Their formation relates to refining and leaching of hydromicas and to destruction of chlorite. Therefore, their composition is not uniform and predominated swelling layers may alternate with mica-like and chlorite. Goethite and small amount of structureless iron oxides are also the products of destruction and oxidation of chlorite.

The sorption potential of the clay was evaluated through experiments and analysis of available published data. Sorption properties of the clay were studied using model solutions of sulfate salts of Cd, Zn, Cu, and Pb (the main pollutants). The weighted rubbed clay sample was placed into a flask with a measured volume of the solution at a specified concentration level. The residual concentration in the solution was determined in 24 hours after solution-clay interaction. The sorption capacity of clay (N) was estimated from the difference in the contents of the metals before and after the experiment. It appeared that the clay capacity to absorp heavy metals is satisfactory.

However, the experiments with the liquid phase of the discharge under both static and dynamic conditions did not show any positive effect. There was practically no significant absorption of Pb, Zn, Cu, and Cd by the clay. High mineralization of the discharge liquid phase and large amount of dissolved organic substances prevented constructing the screen from the clay only, primarily due to formation of organic-metal complexes that impedes absorption of metals by the clay.

This fact dictated performing a number of static experimental runs on heavy metals removal from the solution with controlled amounts of chemical and mineral agents, specifically, gypsum, peat, gel of humic acid, superphosphate, lime, slag, pyrite tailings (FeS), sodium sulfide, iron sulfate, active carbon, and their combinations. Attempts were made to decompose organic complexes with ultraviolet radiation, aeration, and oxidation by such strong oxidizers as hydrogen peroxide, potassium persulfate, and manganese dioxide. Static tests showed positive results on immobilization of heavy metal complexes by active carbon (absorption of copper complexes by 80%, lead - by 77%, zinc – by 58%, and cadmium – by 30%) and iron monosulfide (absorption of Cu by 80-90%, Pb - by 70-80%, Zn - by nearly 100%, and Cd - by 20-30%). These experiments demonstrated that ferric clay, iron monosulfide FeS (pyrite tailings) and active carbon could be the main screen components.

Such screen however is not capable of completely solving the problem of groundwater protection from oxianions of As, Se, V, Mo, Ti, Be, and, in part, Zn, if concentration of salts in the pulp and its alkalinity are high. Peat may be used as a good absorbent for oxianions. Experiments showed that FeS powder possesses good element capturing properties controlled by different from absorption mechanism of fixing metals to sulfides during FeS dissolution. Reaction properties of FeS surface may improve under filtration conditions, if accumulation of hydroxides of Fe (II) on the surface with is prevented. Peat humates are good dissolution reagents for iron. Therefore, it was decided to abandon the usage of active carbon and fix metals with FeS at a reaction barrier directly to poorly soluble sulfides.

The dynamic experimental runs considered projected filtration load onto the bottom of the sludge settler in the location of the future screen. The experiments showed that a number of main pollutants, i.e., Zn, Cu, Pb, Cd, and As, are immobilized nearly completely down to concentration levels not exceeding MPCs. The immobilization dynamics differs principally from that of sorption and corresponds to the reaction of FeS dissolution under alkaline reduction conditions. Concentrations in filtrate are generally minimal in first samples, if sorption entrapment runs. The effective entrapment of metals and their fixing to sulfides proceeds on the screen of this type after partial dissolution of FeS and reaching the stationary concentration of S_2 ion, that is similar to the equilibrium one. It is important in such process to provide for a long time of exploitation of sludge settler the reaction accessibility of FeS surface to progressive filtrate portions. Peat serves the function. Peat humatcs are rather soluble under alkaline conditions and provide not only for iron dissolution in amounts 0,5-1 mg-cquiv./l (correspondingly, 0,5-1 mg-equiv./l of HS and S_2 ions) but also for preservation reducing conditions within the screen. These conditions inhibit oxidation of Fe (II) to Fe (III) and sulfide sulfur. Stability of sulfides in peats under anaerobic conditions is well known. Even such phases as troilite (FeS), hydrotroilite (FeS-nH_2O) and pyrite (FeS_2), which are susceptible to oxidation, are common minerals in peats under preserved reducing conditions.

The results of investigations have shown, that chemical fixing of the most toxicants at the screen-barrier is known to be provided by dissolution of FeS, that lasts for hundreds of years. This is true for both degradation of the FeS layer and repeated dissolution of pollutants. The process acts with rates of mass-output, which control concentrations of toxicants on background levels during infiltration of precipitation through the layer of not preserved sludge.

Iron behavior deserves special attention. The artificial geochemical barrier of the composition discussed above does not prevent iron from migrating down to the groundwater. Nevertheless, ferritization of limestone under infiltration of bog peat waters, which contain iron humates, is a common event. Formation of authigenic screen only requires a change from reduction conditions peat bogs to conditions to their sufficient aeration. Percolative karsted limestone under the sludge settler provides for oxidation conditions. These conditions guarantee oxidation of dissolved Fe (II) and transition of positively charged (under carbonate equilibrium in limestone) colloid formations of $Fe(OH)_3$ to a non-migratory state when they are occluded on a negatively charged surface of enleached limestone. Amorphous sediments of $Fe(OH)_3$ that are formed serve the powerful additional absorbent for Hg, oxianions of As, Se, Ti, V, Mo, and anion hydroxide complexes of Be and Zn.

The authors, in cooperation with the Laboratory for Geo-Environment Protection (Moscow State University, Moscow, Russia), developed a complex multilayer screen capable of decreasing pollution of underground water (Figure 10). The recommended screen includes three layers:

- The bottom clay layer is at least 20 cm in thickness. The layer has to be leveled, compacted by rolling and finished to a true horizontal upper surface. This layer may be constructed from the local deluvial clay, the sufficient resources of which exist in the vicinity. Special attention should be paid to the layer integrity.
- The intermediate layer of the screen, which acts the main interceptor of the pollutants from the liquid phase, is constructed from the mixture of FeS and peat in proportion 13 tons of FeS per 3 tons of peat. The thickness of 10 cm is sufficient for the layer. It is necessary to use FeS or pyritc tailings with a minimal amount of metallic iron and prevalence of the fraction less than 0,1 mm. The second component is mesotrophic decomposed top peat of bog-lake origin. The components have to be thoroughly mixed before placing and compacting by rolling.
- The upper layer consists of gypsum clays with the addition of gypsum (up to 10-15%), 10 cm in thickness. The layer has to be compacted and finished to a true horizontal upper surface.

The upper (10 cm) and the bottom (20 cm) layers in the screen structure reduce and spread filtration load over the entire area of the sludge settler and preserve anaerobic reductive conditions of the intermediate layer (FeS^+ peat, 10 cm). The smaller thickness of the upper clay layer provides for filtration retardation of solutions inside the FeS^+ peat layer. This facilitates the spread of the liquid phase over the peat, which conserves air-dry across the extensive continuous area of the sludge settler, even if the discharge is confined to a single location.

Introduction of 10-15% gypsum or gypsum clays into the upper cover layer should decrease alkalinity of the filtered phase. According to the results of static experiments this allows to lower the pulp pH down to 7,4-7,5 and facilitate formation of calcium carbonate, i.e., to transfer a significant portion of carbonates in the liquid phase to solids. Lowering pH down to neutral values will facilitate hydrolysis and sedimentation of heavy metal oxianions.

Thus, the research performed by the authors confirmed high efficiency of recommended protective screen for the whole time of its planned exploitation in relation to pollutants present in the discharge. Construction and exploitation of the sludge settler with the protective screen at its bottom requires organization of a network of observation boreholes and hydrometric points for monitoring the underground and surface water.

Construction

The problem of strong sulphate aggressiveness in relation to concrete.

Underground engineering structures are to some extent always subject to chemical and physical-chemical attacks of the environment. Aggressive underground water or soils cause strength reduction or even failure of structures. In construction, concrete structures are most frequently subject to the influence of sulphate and acid corrosive media.

Corrosive media may be both of natural and technogenic origin, the latter being a result of production activities (spillage, leakage, artificial soils) (Maximovich, Gorbunova 1990). Technogenic corrosive media are formed as a result of changes in the hydrodynamic and geochemical parameters of natural media, for example, in the cases of saline soil underflooding, pyrite oxidation, etc. (Rethati 1981; Hawkins, Pinches 1989). Microbiological processes can also be of a certain effect (Boch 1984). The protection of underground structures is mainly restricted to the enhancement of their chemical resistance by some methods: addition of special ingredients to concrete, enhancement of its density, application of waterproofing compounds on concrete surfaces. These methods are described in Russian regulatory documents. Sometime it may be necessary to replace the corrosive soil or lower the underground water. All these methods increase the operating cost of construction considerably. Most of the methods can not be used at operating facilities.

The experience of combating corrosive media shows that it is necessary to find new approaches to this problem considering economic and technological costs. One of such methods is the method of geochemical mitigation of corrosive media.

Strong sulphate aggressiveness of ground water associated with rocks in coal mine dumps

This approach was used by the authors at one of the sites of the Industrial Association METANOL in Gubakha (Perm Krai, Russia). The site is located on a slope of the river Kosaya (the Kama River basin) in the west zone of folding of the Urals. There, the aleurolite and coaly-clay shale of Carbon are overlaid with eluvial clay containing gruss and quartz aleurolite debris 0.5-17.0 m thick. The clay is overlaid with deluvial clay 2.0-16.0 m thick containing inclusions of quartz sand and aleurolite debris and gruss.

During grading and formation of the embankment, rocks from coal mine dumps of Kizel Coal deposit were used in addition to the soil moved within the site. The soils from the dumps contained high concentrations of sulfur in various compounds with concentrations reaching 8,7 %. A considerable amount of sulfur was in the form of water-soluble compounds. The results of aqueous extract analysis showed that the content of sulfates could be as high as hundreds of grams per kilogram of soil. Weathering of the rocks on the surface caused pH of water that is in contact with the rocks to drop to 1.0-3.0.

As a result of underflooding of the back-fill soils concrete-corrosive water emerges at elevations above the levels of lower foundation surfaces. The observations conducted starting from 1984 showed that sulfate corrosiveness of the water has increased. In some zones, the content of sulfates has increased to 4.1 g/1, which is way over the MPC. The composition of the underground water is as follows (in g/1): 0.22 HC1, 2.57 SO_4, 0.115 Cl, 0.414 Ca, 0.04 Mg, and 0.80 Na+K. The water pH is 6.6 to 7.9. Laboratory analysis suggests that chemical composition of the water is the result of its interaction with mine dump waste rocks. The interaction with clay soil and inclusions of carbonate debris results in relatively high values of pH. Stripping away the foundations and conducting of corrosion-proofing work at an operating continuous cycle manufacturing complex is practically impossible. The lowering of water level and soil replacement under are often unacceptable or too expensive.

Protection of foundation from aggressiveness

The experience gained in the reduction of sulfate and acid corrosiveness of the environment is relatively small. Few studies have investigated the possibility of using ash resulting from coal burning as an additive to soils to neutralize their acidity and to precipitate deleterious components. Positive results have been obtained from the use of alkaline additives such as lime, limestone and trona (Sandereggen. Donovan 1984). Some investigators propose various additives to suppress microbiological oxidation of sulfides in soils to curb sulfate corrosiveness (Evangelon et al. 1985). However, these processes are difficult to control.

For the precipitation of sulfates the authors have offered to use soluble barium compounds.

$$SO_4 + Ba = BaSO_4 \text{ (barite)}$$

This reaction is practically instantaneous and does not depend on medium pH. It is feasible to use barium hydroxide and barium chloride as the reagents. Barium chloride is highly soluble in water, so concentrated solutions can be used. The solubility of barium hydroxide is one order of magnitude lower than that of barium chloride but its use neutralizes the acid reaction of the medium and no extra components have to be added to the underground water.

$$Ba(OH)_2 + H_2SO_4 = BaSO_4 + 2H_2O$$

The resulting barite is relatively stable under exogenic conditions and practically does not decompose under weathering. It is not toxic, is used in drilling muds, and may be used as concrete filler.

In nature, the processes of barite formation are rather widespread. The understanding of these processes is important in the development of methods aimed to combat corrosive sulfate water. There are several processes of barite formation: mixing of waters carrying separately barium ions and SO_4 ions; reaction of solutions containing barium ions with sulfate rocks; reaction of solution containing sulfate ions with barium-containing rocks; and oxidation of solutions containing Ba and S ions. In underground water occurring at small depths, barium ions are rare because this water always contains some quantity of sulfates.

The major barite deposits were formed in hydrothermal conditions. In the hypergenesis zone of the coastal areas of seas, barite occurs in the form of nodules in clay and sand deposits. Barite modules can also occur in the oozes of recent sediments. Barite is formed as a result of chemical erosion of rocks. Sulfuric acid, which is the product of sulfide oxidation, reacts with barium ions and forms barite. With the other minerals evacuated, the so-called barite sypuchkas are formed replacing the ore bodies.

Three kinds of soil with different sulfur contents taken on the site were studied in the laboratory to determine if barium compounds can be used for the neutralization of corrosive media and to define their optimal concentrations. Barium chloride and hydroxide solutions of various concentrations and distilled water were filtered through the soil samples placed in special devices. The filtered solutions were analyzed for the content of sulfate ions and pH. A total of 29 series of experiments were performed. When distilled water was flittered through the soil, 19 % to 62 % of the total sulfur content passed into solution.

Also, the amount of barium salts required to precipitate sulfate ions was experimentally determined. It appeared that soil may precipitate up to 97% of mobile sulfur from the infiltrating solutions.

The experiments were carried out at two sites. At the first site where the underground water was of medium sulfate corrosiveness, two holes with a diameter of 60 mm were drilled; 30 kg of barium chloride ($BaCl_2 \cdot 8H_2O$) and 10 l of demineralized water were poured into each holes. The composition of the underground water was analyzed in the well located in underground water downstream direction. A day after the beginning of the experiments, the content of sulfates in the well decreased to zero. Shortly, sulfate corrosiveness and chlorine ions content increase in two holes was observed. Barium ion also appeared. Forteen days after, there were no Ba ions found in the water and the content of chlorine ions and mineralization were close to the their original values; the content of sulfates was 0,55 g/1. At a later time, the content of sulfates and mineralization was steadily decreasing (Figure 11). By the end of the fourth month of the observations, the concentration of sulfate ions was 0,18 g/1, i.e. the water became non-corrosive relative to concrete and its sulfate-calcium composition transitioned to the chloride-calcium. During the whole period of the observations, the content of chlorides was far less than in the water classified as salt corrosive.

At the second experimental site, two trenches to bury the reagent were dug and four observation holes were drilled in underground water downstream direction (Figure 11). The results of water extracts analyses showed that the content of sulfates in the soils varied within the range of 1,05-7,43 g/kg. The soils, in accordance with Russian regulatory standards, were classified as corrosive. The content of sulfates in the underground water this location before the experiments was 1,09-1,52 g/1 and mineralization ranged from 2.81 to 3,422 g/1.

The experiments on the decrease of sulfates corrosiveness were performed in several stages. At the first stage, 45 kg of barium chloride ($BaCl_2 \cdot 8H_20$) were buried in the trench. Chemical analyses showed that in all the observation wells, the content of sulfate ions decreased. By the end of the fourth month of the observations, their concentration did not exceed 0,36 g/1. The content of chlorides varied from 0,01 to 1,08 g/1 and mineralization decreased to 1,50-2,48 g/1 (Figure 11). The concentration of sulfates varied greatly due to their transport from the zone of aeration by atmospheric precipitation. There was a direct relationship between the amount of atmospheric precipitation and the content of SO_4, but during the whole period of the observations, their amount tended to decrease. At the second stage, barium hydroxide ($Ba(OH)_2 \cdot 8H_2O$) was used to neutralize the corrosiveness of the medium. A year and a half after the beginning of the experiment, 60 kg of the reagent was buried in the second trench. The average content of sulfates decreased to 0,04 g/1 and was. Water mineralization also decreased and was 0,39 to 1,40 g/1 by the final stage of the observations (Figure 11).

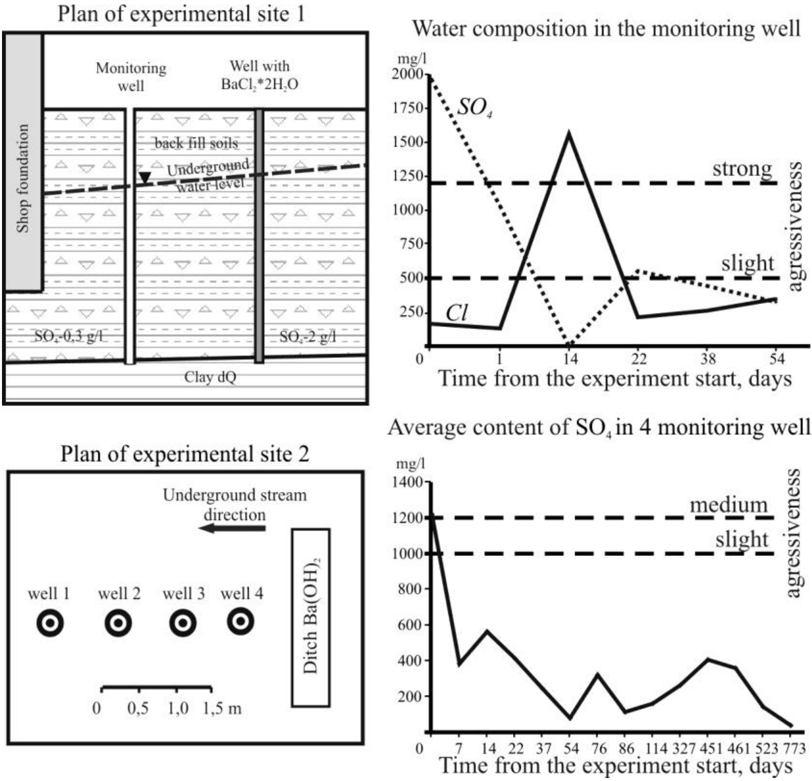

Figure 11. Decrease of underground water sulphate aggressiveness by barium compounds

These experiments demonstrated that the medium to strong corrosive underground water at the site became non-corrosive relative to concrete. The content of chlorides and pH were normal during the entire period of the observations. Reagent introduction considerably changed the geochemical activity of the soils. Analyses of the water extracts showed that the content of soluble salts in the soil of site 2 decreased by a factor of 2,5 and was 2,69 g/kg by the end of observations; the contents of sulfides decreased by a factor of 3 and was 1,30 g/kg. The content of soluble salts at a distance of 1 m from the trench with the reagent, did not exceed 0,07 g/kg; hydrocarbonate and calcium ions prevailed in the water extracts. To achieve a positive effect, 29 kg of barium chloride, or 22 kg of barium chloride, or 22 kg of barium hydroxide was required per a cubic meter of soil. Those values were close to the results of the calculations based on the laboratory analyses.

The treatment of soils with soluble barium compounds caused changes in the mineral composition and properties. Yellow sediment was found at the bottom of the trench filled with barium hydroxide. Roentgenometric analyses showed that the sediment contains 24 % of barite, 15 % of calcite, 30 % of witherite, and 30 % of quartz gypsum. The soil in the walls and in the lower part of the trench was cemented and difficult for cracking with a pinch.

To determine the composition of the precipitate separating from the underground water due to the reaction with barium salts, water was sampled from the hole at the first located of the site. The water had the following composition (in g/1): 0,23 HCO_3, 4,08 SO_4, 0,07 Cl, 0,37 Ca, 0,04 Mg, 1,51 Na+K, and 0,02 Fe*** with the total mineral content of 6,31 at pH 5,65. An excess of barium hydroxide or barium chloride was added to the water. The resulting precipitate was collected and subject to X-ray structural analyses. In the case of barium chloride, 99 % of the precipitate was barite and in the case of barium hydrochloride, the precipitate consisted of barite (72 %) and witherite.

It is known that if a solution contains sulfate ions, there is an exchange reaction because the solubility of barite is much lower than that of witherite (Bisehberg, Plummer 1986):

$$BaCO_3 + SO_4 = BaSO_4 + CO_3.$$

This should be considered as a positive factor because if sulfate ions penetrate into the soil under the treatment they precipitate in accordance with the above reaction. The formation of barite and witherite and the reaction of the alkaline component with the soil result in a considerable increase in its strength. The filling of the pores decreases the water permeability of the soil. These additional effects represent other positive factors decreasing soil permeability to water and the intensity of water exchange. This in turn diminishes the impact of corrosive water on concrete structures, increases soil strength, and enhances the reliability of structures foundations. The use of barium chloride and barium hydroxide does not cause negative changes in the composition of the underground water. In holes adjacent to the source, barium ions are found only during the first moments after the start of the treatment. In the case of barium chloride, the concentration of chlorine ions increases only at the initial stage, but its content is always lower than the MPC. No increase in pH was observed when barium hydroxide was used. Barium ions are not corrosive for concrete.

Depending on the actual geological conditions and the features of structures, various ways of application of the new method are possible. If the underground water occurs at the small depths, trenches that are upstream of the structure to be protected may be used to introduce the reagents into the soil. If the underground water occurs at the great depths, the reagents can be injected. If there is a possibility that corrosive media may be present, the reagents can be introduced into the soil in the course of construction. Thus, the experiments performed showed that these non-traditional approaches can be successfully used to combat media corrosive to structures.

The experiments also indicated that actual conditions of the natural environment and the availability and properties of materials considered for creation of geochemical barriers should be carefully evaluated when used in the models and computational methods in the assessment of pollutants migration.

The mitigation methods developed by the authors, allow avoiding building expensive protection structures by realizing features of the natural environment. The use of the geochemical barriers discussed in this book can considerably lower the cost of construction while providing effective protection from an array of different pollutants in many fields of industrial activity.