Solid Waste: Assessment, Monitoring and Remediation
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III.6

Mining waste

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III.6.1. Introduction

III.6.1.1. Mining waste sources and amounts

Mining waste is the high-volume material that originates from the processes of excavation, dressing and further physical and chemical processing of wide range of metalliferous and non-metalliferous minerals by opencast and deep shaft methods. It comprises overburden, run-of-mine rock as well as discard, slurry and tailings from the preparation/beneficiation or extraction plants. Wastes from mineral excavation both under US Resource Conservation and Recovery Act (RCRA, 1976 with further amendments) and EU regulations pursuant to Article 1 (a) of Council Directive 75/442/EEC (1975) on waste and article 1(4) of Directive 91/689/EEC (1991) on hazardous waste is considered non-hazardous, though many aspects related to its safe disposal and use with respect to the environmental behavior and impact are applicable also to hazardous waste. Some types of wastes from physical and chemical processing of minerals are classified as hazardous in the European list of wastes (Commission Decisions 2000/532/EC and 2001/118/EC). These wastes comprise: acid generating tailings from processing of sulfide ore (code 01 03 04*); other tailings containing dangerous substances (code 01 03 05*); other wastes containing dangerous substances from physical and chemical processing of metalliferous (code 01 03 07*) and non-metalliferous minerals (code 01 04 07*), as well as drilling muds and other drilling wastes containing oil (code 01 05 05*) and dangerous substances (code 01 05 06*). The kind of mining waste and its share in the total waste stream in the different countries highly depend on their natural resources, economic value of a mineral and market demand, and therefore ranges from almost none to the predominant proportion. Unfortunately, due to the scarce statistical data, the information on the mining waste generated and disposed is not available for countries with the highest mining output, such as China, the USA, India, Australia, Russian Federation and South Africa.

Mining activities (excluding coal) in over 130,000 of non-coal mines concentrated largely in nine western states of the USA are estimated to produce between 1000 and 2000 million tons (Mt) of mining waste annually. These activities include extraction and beneficiation of metallic ores, phosphate, uranium and oil shale, and are reported to be responsible for polluting over 3400 mile (i.e. over 5470 km) of streams and over 440,000 acre (i.e. over 178,000 km^2) of land. About 70 of these sites are on the National

Priority List for Superfund remediation (Wilmoth, 2000). The total non-coal mine waste lying in dumps was estimated in 1985 at 50,000 Mt, of this 33% being tailings, 17% dump/heap leach wastes and mine water and 50% surface and underground wastes (1985 Report to Congress, after Wilmoth, 2000).

According to published incomplete data (not including the USA and 10 other countries), among 19 of the 30 OECD member states (OECD, 1997, 1999), Canada held the dominant position in the amount of mining waste generated annually (~65.4% of the total); 23 member states of OECD – Europe produced 402.4 Mt, which was about 25%, while 15 EU member states generated 19.0% of the total OECD production covered by statistics (see Chapter I, Table I.2.1).

According to EUROSTAT (2001), 15 EU member states, 3 associated countries and 11 candidates to the EU generated in 1995–1999, a total of 420.9 Mt of mining/quarrying waste. The biggest mining waste generators were the UK (28.0%), Germany (16.1%), Sweden (15.2%), Poland (11.8%) and Romania (11.4%).

The proportion of mining waste in the total waste stream in these countries differs considerably. In Poland, waste from mineral excavation comprised 36.5 and 35.3% of the total annual waste generation, and 44.0 and 39.8% of waste lying in dumps in 2000 and 2001, respectively, that reflects a decline of coal mining activity (Central Statistical Office, 2001, 2002). Waste from physical and chemical processing of metalliferous minerals, mainly copper tailings, comprised 24.1% of the total annual waste generation and 28.2% of lying waste, which constituted 59.4% of the total annual waste generation and 68.0% of waste lying in dumps (Central Statistical Office, 2002). In Spain, mining waste accounted for about 31%, in UK 17.5% (29.8% in 1999 after EUROSTAT, 2001) and in France 12.5% (Chapter I, Table I.2.1). In some EU countries, mining activity generates a substantial part of the waste stream, e.g. in Sweden (~53.4%) (OECD, 1999). The major demerit of both OECD and EUROSTAT statistical data is their incompleteness that causes significant divergence of these sources (see e.g. data for the UK).

The character of mining waste and their share of total waste stream in different countries and regions worldwide are determined by the mineral resources and the part, which mineral excavation constitutes in their economies.

Nowadays, Western Europe (EU-15 and associated countries) in general plays a modest role in the world mineral mining, producing scarcely from 1 to 8% of metalliferous ores and 2.3% of hard coal. Of 1872 identified mining sites in the EU, only 917 are reported to be still active, of which 740 sites produce industrial minerals, 119 coal, 45 non-ferrous metals and 13 ferrous metals (BGRM, 2001). It still occupies a leading place in mercury supply (Spain) and lignite excavation (Germany), and retains an important position in salt (Germany, Finland, UK, the Netherlands, Spain), potash (Greece) and sulfur mining (Germany, France, Finland and other EU Members) (Table III.6.1) (Coakley et al., 2002; Gurmendi et al., 2002; Kuo et al., 2002a,b). Western Europe continues to be a major world processor, fabricator and consumer of minerals, whereas Central Eurasia, mainly Russian Federation, Ukraine and Kazakhstan, remains one of the major world supplier of most mineral commodities (Kuo et al., 2002a,b). The leading positions in terms of the share of world output are held by Asia and the Pacific region, in particular China and Indonesia, and America (the USA, Canada and several Latin American countries), which are endowed with a great diversity and richness of mineral resources of all kinds (Gurmendi et al., 2002; Kuo et al., 2002b). Africa ranks first or second in terms of world mining of

Table III.6.1. World mining output of principal non-metalliferous and metalliferous minerals in 2000 (after Coakley et al., 2002; Gurmendi et al., 2002; Kuo et al., 2002a,b).

Mineral	Region or country														
	Thousand tons unless otherwise specified								Percentage of world total (%)						
	EU (+associates)	Europe and Central Eurasia	China	Asia and the Pacific	USA	Latin America and Canada	Africa	Total, world	EU (+associates)	Europe and Central Eurasia	China	Asia and the Pacific	USA	Latin America and Canada	Africa
Non-metalliferous minerals															
Hard coal	83,970 (84,300)	530,854	880,000	1,620,000	896,150	136,814	228,900	3,621,000	2.3 (2.3)	15	24	45	25	3	5
Lignite	243,651 (243,651)	565,098			77,600			857,000	28 (28)	66			9		
Salt	42,056 (42,360)	57,437	31,280	61,900	45,600	36,859		214,000	20 (20)	27	15	29	21	18	
Phosphate	700 (700)	13,501			38,600	3,189 (P_2O_5)	38,000	133,000	1 (1)	10			29	7	29
Sulfur (100%)	5,970 (6,088)	16,168			10,300	12,857		57,200	10 (11)	28			18	22	
Potash, K_2O	4,852 (4,852)	12,368			1,300			25,400	19 (19)	49			5		
Metalliferous minerals and ores (mining/metal production, in terms of pure ingredient)															
Iron ore	NA	NA	224,000	474,000	63,095	287,756	48,900	1,060,000	NA	NA	21	45	6	27	5
Pig iron			131,030	278,000	47,878			567,000			23	49	8		
Bauxite	1,991 (1,991)	11,673	9,000	72,000	NA	35,340	15,500	135,000	1 (1)	9	7	53	NA	26	11
Alumina	5,050 (5,050)	11,714	4,330	22,630	4,780			49,300	10 (10)	24	9	46	10		
Chromite	–						7,480	14,400							52
Copper	189 (189)	1,912	590	2,867	1,470	6,324	465	13,300	1 (1)	14	4	22	11	48	4
Zinc	672 (672)	1,339	1,710	3,560	829	2,597	260	8,730	8 (8)	15	20	41	9	30	3
Lead	235 (235)	417	570	1,377	468	600	177	3,100	8 (8)	13	18	44	15	19	6
Nickel			51	460	–	393		1,230	NA	NA	4	37	–	32	
Tin (t)	1,203 (1,203)	6,203	97,000	171,000	–	97,000		238,000	1 (1)	3	41	72	–	41	
Tungsten W (t)	2,350 (2,350)	5,850	37,000	38,000				45,200	6 (6)	16	82	84			
Cobalt (t)							14,000	33,300							42
Silver (t)	477 (477)	3,107			1,860	8,107		18,300	3 (3)	17			10	45	
Gold (t)	0.019632 (0.019632)	285.303	178	780	353	528	605	2,550	1 (1)	11	7	31	14	21	24
Mercury (t)	545 (545)	895	200	200	NA			1,350	40	66	12	12	NA		
Diamonds (th. carats)	–	23,200					61,700	118,000	–	20					52

NA, not available; –, zero.

diamonds, chromite, cobalt, gold, manganese, phosphate rock, bauxite and uranium; the highest diversity of mineral commodities is being mined in South Africa (Coakley et al., 2002). The world mining output of principal non-metalliferous and metalliferous minerals in 2000 is summarized in Table III.6.1.

The predominant place in the world supply of minerals with respect to the mined amounts is held by coal of all grades; hard coal (bituminous coal and anthracite) comprises 81% and lignite 19% of the total world coal output. Metalliferous ore mining is dominated by iron ore and bauxite production. Other mineral commodities that comprise a wide variety of industrial minerals, and ferrous and non-ferrous metal ores are mined in substantially smaller amounts with respect to the total world balance (Table III.6.1). The scale of a mined mineral output, besides the methods of excavation and processing, to a great extent determines the amount of waste generation.

The major high-volume waste-generating mining activity in many countries worldwide is coal mining. Coal plays an integral role in the economy of many countries, and thus constitutes a substantial part of the global stream of mining waste.

III.6.1.2. Coal mining waste

Known coal reserves are spread over almost 100 countries and estimated to last over 200 years. In contrast, proven oil and gas reserves are equivalent to around 40 and 60 years, respectively, and are concentrated in the Middle East and the former Soviet Union area. The total global hard coal production has shown almost 50% growth over the past 25 years (WCI, 2002b). A further increase in coal consumption, though unevenly distributed, by an average of nearby 1.9% per year up to 2010 is expected to fulfill a substantial part of the total world energy demand (Fig. III.6.1). In OECD Europe, coal use for power generation is forecast to decrease by 0.6–0.8% per year, while in North America an annual increase by 1.6% is anticipated. Unlike the stagnating or decreasing coal market in OECD Europe, for ASEAN countries the growth of coal use for power generation is expected to increase most dramatically by over 9% a year, and 2.8% for the rest of the developing economies including India and China. The growth of hard coal consumption in some developed economies, such as the USA, Australia and Japan, where increasingly competitive electricity markets favor low-cost power, is also projected. The expanding Asian coal market brings extensive opportunities for exporters of thermal coal, in particular for China, Australia, Indonesia and Latin America. The annual growth rate of Chinese thermal coal exports by 2010 is anticipated to be the highest (6.4–11.4%), while the largest coal exporter Australia, and emerging coal suppliers Indonesia and Latin America are likely to reach annual growth rates in the range 1.1–3.6%. The growth in the global consumption of coking coal by 2010 is estimated at 1.1% per year that is linked to increases in iron and steel production in Asia (WCI, 2002a).

Currently, the top three major coal producers are China, USA and India, which in 2001 covered 66.7% of the world's supply. Other 10 countries mined from 6.7 to 0.21% of world total hard coal output. Germany is the world's largest brown coal/lignite producing country (Table III.6.2). In OECD Europe, the biggest hard coal producer is Poland, where underground mining is concentrated in the Upper Silesia coal basin (USCB). In 1980–1985, the total coal output was 192–193 Mt (Central Statistical Office, 1996), falling down by 2001 to 104 Mt/a (WCI, 2002b). Further decrease of coal production below

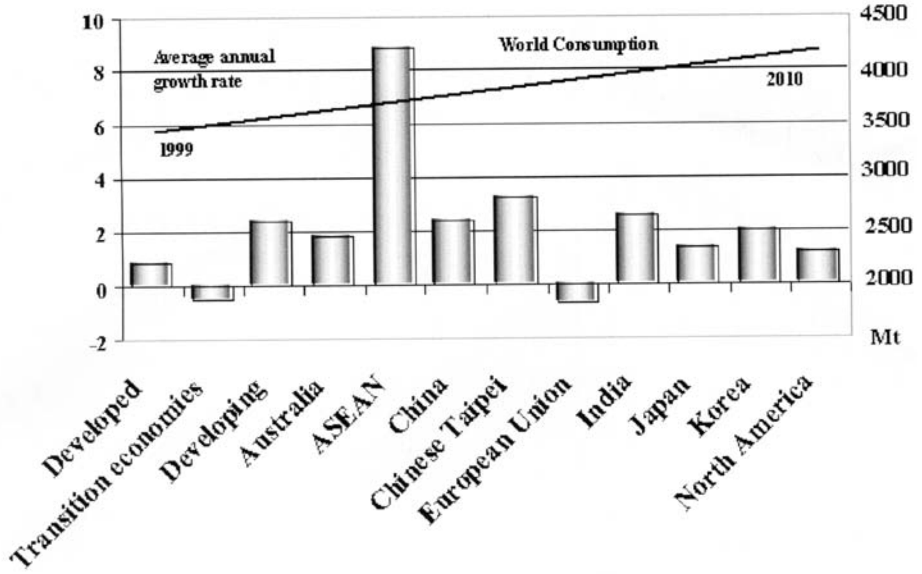

Figure III.6.1. Prospects for world hard coal consumption to 2010 (after WCI, 2002a; ABARE, 2002).

100 Mt/a will occur in 2003, reflecting general trends in coal consumption in OECD Europe that showed a dramatic decline of 95% (from 19.5 to 10% of global hard coal consumption) in two decades, 1981–2001. Coal consumption in North America remained stable (22–25%), while Asia-Pacific region showed continuous dynamic growth (from 34 to 52.5%). In 2000, 39.1% of total world electricity generation and almost 70% of total global steel production was dependent on coal, which confirms the importance of coal in total world primary energy consumption (WCI, 2002b).

The amount and characteristics of coal mining waste highly depends upon the local geological conditions and the methods of mining. As a result of mechanization of the mining, as well as of coal preparation process, the proportion of waste rock compared to the saleable coal produced accounts for some 30–50% (Glover, 1978). Annual world generation of hard coal mining wastes can be estimated roughly to be 1200–1400 Mt in 1995, and approximate amounts of wastes already lying in dumps throughout the coalfields of different countries account for 3000 Mt in the USA, 2000 Mt in the UK, 1200 Mt in China, 1000 Mt in South Africa, 600 Mt in Japan and 200 Mt in France (Skarżyńska, 1995a). In Poland, the waste/saleable coal ratio in 2001 was as high as 0.39; total hard coal mining waste generation accounted for 38.4 Mt, while 668.5 Mt were deposited in dumps in the USCB area (Central Statistical Office, 2002).

Considerable amount of coal mining waste deposited at the big central dumping sites or smaller colliery tips has been reused, predominantly in civil engineering. To underline beneficial properties of coal mining wastes and the commercial applicability in civil engineering, the term "minestone" for this material has been introduced by British Coal's Minestone Services, and since 1990 has been increasingly used by civil engineers involved in its reuse. By far, the biggest application for mining waste is as

Table III.6.2. Coal production and major producers in 1998, 2000 and 2001 (after Gurmendi et al., 2002; Kuo et al., 2000a; WCI, 1999, 2001, 2002b).

Producer	Hard coal						Producer	Lignite					
	Mt			% of total				Mt			% of total		
	1998	2000	2001	1998	2000	2001		1998	2000[a]	2001	1998	2000[a]	2001
World total	3,656	3,639	3,834	100			World total	895	857	903	100		
China	1,236	1,171	1,294	33.8	32.2	33.8	Germany		168		~20.0	19.6	
USA	936	899	945	25.6	24.7	24.6	Russia		84			9.8	
India[b]	303	310	312.5	8.3	8.5	8.2	USA		78			9.1	
Australia	219	238	257	5.6	6.5	6.7	Greece		62			7.2	
S. Africa	223	225	224.5	6.1	6.2	5.9	Poland		59			6.9	
Russia	149	169	168	4.1	4.6	4.4	Czech R.		51			6.0	
Poland	117	102	104	3.2	2.8	2.7							
Indonesia[b]	61.2	79	92.5	1.7	2.2								
Ukraine	74	81	82	2.0	2.2	2.2							
Kazakhstan	67	71	73	1.8	2.0	1.9							
Canada		69[c]			1.9								
Columbia[b]	33.8	38.1[c]		0.92	1.04								
Venezuela[b]	6.8	7.8[c]		0.18	0.21								

[a] Data for lignite production after Kuo et al., 2000a.

[b] Countries showing significant growth of coal production since the early 1980s.

[c] Data for coal, all grades after Gurmendi et al., 2002.

fill and earthworks material: (i) for restoration of mining subsidence areas in close proximity to mines and filling disused open pits and quarries, land leveling and elimination of surface irregularities on building sites; (ii) filling of disused canals and docks; (iii) mine backfilling; (iv) reclamation of municipal waste disposal sites (landfills). Another vast area of coal mining waste utilization is application as construction material in hydraulic and road engineering structures: river, road and railway embankments, dams, harbor constructions, quays, etc. Minor amounts of mining waste is used as raw material for manufacturing construction materials and mineral recovery (British Coal; Skarżyńska, 1995b).

In Poland, the reuse of carboniferous waste rock in 2001 accounted for 91% of its annual generation (Central Statistical Office, 2002). In 1995–1996, it was applied mainly at the surface for reclamation of land disturbed by mining (87.9%) with the remaining 12.1% being disposed off underground (State Inspectorate of Environment Protection, 1997). In 2000–2002, considerable amount of coal mining waste was used for road engineering and construction of river embankments. Application at the surface, besides undisputable economical and technical benefits, results in an extension of exposure to atmospheric conditions and development of the exposed surface of material, vulnerable to interaction with the environment, generally known as weathering processes. This leads to the considerable transformations of waste properties and chemical composition of pore solutions within the waste layer.

Coal mining waste is thus an abundant, high-volume waste worldwide, usually concentrated in the relatively small, but thickly populated coal mining areas, which brings about complex environmental problems, not always adequately recognized and managed.

Since coal mining is a source of the bulk amount of mine waste in Poland and also in the world as a whole, this chapter focuses on characterization of this waste with regard to its environmental impact. Environmental behavior of this material has been exemplified in the evaluation of pollution potential of coal mining waste generated and disposed in the USCB (Poland), on the background of the environmental issues in other coalfields of the world.

Simultaneously, it addresses the general aspects of leaching behavior of other groups of sulfidic wastes from metal ore mining that despite different origins, display a substantial similarity in geochemistry, major mechanisms of pollutant loads generation, release and transport to ground and surface waters (Lawrence, 1994; Ritchoe, 1994; Munroe and McLemore, 1999; Munroe et al., 2000).

III.6.2. Waste composition and properties

III.6.2.1. Waste sources and kinds

In general, coal mining waste comprise: (i) run-of-mine waste (usually dry rocks discharged directly from the mine workings, of particle size 0–500 mm); (ii) coarse-grained washery discard (wet solids of 10–250 mm discharged from dense medium separation); (iii) fine-grained discard (wet solids of 0.5–30 mm discarded from jigs); (iv) slurry, reject, tailings (solids <1 mm from flotation process).

III.6.2.2. Lithological characteristics

Petrographically, coal mining waste consists of argillaceous and arenaceous rocks, represented mainly by mudstone, siltstone and sandstone with admixture of coal and coal shale.

The properties of freshly wrought waste largely depend on the regional variability and stratigraphic position of mined coal seams. In the USCB, they belong to the Westphalian A–D and the Namurian A–C series of the carboniferous formation. The proportion of run-of-mine and different kinds of washery discards in waste is also of considerable importance. In coal mining waste (known also as "spoil" or "minestone"), the predominant lithological type of rock is usually mudstone, which ranges from <50 to $>80\%$ of the total. Due to changeable petrographical composition of carboniferous strata, run-of-mine waste has a variable petrographical, mineralogical and chemical composition. The characteristic feature of run-of-mine is the frequent occurrence of just one type of rock, i.e. mudstone, siltstone or sandstone in the subsequent portions of output. The material is usually resistant to particle size degradation due to wetting and a low content of coal shale. Washery discards display much higher stability of composition, increasing with the decrease of the particle size. Along with the decrease of particle size of spoil, sandstone and siltstone contents also decrease, while the proportion of coal shale substantially grows. Average lithological/petrographical characteristics of waste disposed is a resultant of the lithology of mined seams determined by their location within the carboniferous sequence and the proportion of different waste kinds in the discarded output.

III.6.2.3. Mineralogical composition

Mineralogical composition of the waste material is determined by the presence or dominance of the particular lithological types of carboniferous rocks, which is, in most cases, mudstone. The major components of waste are thus clay minerals, quartz and coal. Clay minerals are predominantly those with non-swelling lattices: kaolinite/illite and minor amounts of chlorite. In rare cases, mixed swelling illite/montmorillonite structures also occur. Abundant component of mudstone is quartz (up to about 20%) and coal (up to several percent). In siltstone, quartz content is higher (up to 30%), while clay and coal proportions are distinctly lower than in mudstone; coarse-grained quartz is the major component of sandstone. Minor, but common components of coal mining wastes are feldspar, mica and plagioclase. All lithological rock types contain minor amounts of iron disulfide FeS_2 (mainly pyrite, more rarely marcasite) and carbonate minerals: calcite $CaCO_3$, dolomite $Ca,Mg(CO_3)_2$, siderite $FeCO_3$ and anchorite $Ca(Mg,Fe)(CO_3)_2$ in different proportions and concentrations. The lowest pyrite content is contained in sandstone, the highest in coal shale, as the main pyrite carrier in carboniferous rocks is coal. Sulfides of other metals also occur in trace amounts, e.g. chalcopyrite $CuFeS_2$ (in shale), sphalerite ZnS and galena PbS_2 (in shale and sandstone). Different trace metals are also ubiquitous admixtures in iron sulfide (Twardowska, 1981; Twardowska et al., 1988).

These minerals are commonly occurring in all mining waste, while presence, proportions and kinds of sulfide and carbonate minerals determine its pollution potential.

III.6.2.4. Chemical composition

The chemical composition of coal mining waste is a resultant of its lithological and mineralogical composition (Table III.6.3). Broad constituents' lithological/mineralogical composition and concentration range in the fresh wrought spoil reflect heterogeneity of rocks, both spatial and vertical, along the carboniferous profile, as well as the generic structure of waste. At the same time, comparison of data from different coalfields and countries, presented in the comprehensive overview by Skarżyńska (1995a,b), displays similarity of the component contents, though their overlapping within a wide range does not show the specificity of the particular materials with respect to critical factors and their interrelations, controlling the environmental behavior. In general, the trace element contents in coal and coal mining waste are within the range of mean, up to maximum concentrations occurring in the surface soils (Kabata-Pendias, 2001) (Table III.6.4). These elements are being released during the pyrite decomposition; therefore their migration to the groundwater with infiltration water determines the risk to the environment. In sulfidic metal ores, concentrations of metals in waste rock are determined by the metals and accessory elements extracted, and the efficiency of metal extraction.

Leaching of trace elements from coal mining waste was reported by different authors in late 1970s/early 1980s (Wewerka et al., 1976a,b; Palmer, 1978; Krothe et al., 1980; Twardowska, 1981), and registered directly by authors in pore solutions, leachate and groundwater in lysimetric and field studies, as will be presented further.

III.6.2.5. Environmental impact

The environmental burden of coal mining dumps, caused by obvious factors, such as development of an anthropogenic landscape, land deformation, problems with establishment of vegetation, self-ignitability and atmospheric pollution, has been known for a long time. Spontaneous combustion of waste dumps is being now effectively controlled by substantial reduction of coal content in spoil and air permeability of disposed material due to improvement of coal preparation, dump reshaping and compaction of waste in thin layers. At the same time, the pollution potential of coal mining wastes to the aquatic environment, though already recognized by specialists, is still not thoroughly understood by decision-makers and civil engineers dealing with waste management, since, hidden from view as it is, few realize how seriously the water resources can be compromised. Despite the knowledge of pollution potential formation processes and controlling factors suggesting a specific approach to the evaluation of coal mining waste pollution potential (e.g. Caruccio, 1975, 1978; Palmer, 1978; Twardowska, 1981; Twardowska et al., 1988, 1990; Hutchinson and Ellison, 1992), as well as a general evidence on the time-delayed, long-term adverse environmental impact of coal mining waste (e.g. Glover, 1978; Nutting, 1987; Szczepańska and Twardowska, 1987; Sleeman, 1990; Twardowska and Szczepańska, 1990; Hutchinson and Ellison, 1992), there is still a common practice of evaluation of the pollution potential of these wastes on the basis of a simplified batch leach testing of fresh wrought material (e.g. Cañibano et al., 1990), while the long-term environmental impact of sulfide-bearing non-coal mining wastes has been recognized and considered since a long time (Durkin and Hermann, 1996).

Table III.6.3. Chemical composition of coal mining wastes from the USCB, Poland (%, dry weight).

Constituent	Run-of-mine waste 0–500 mm	Washery discards from		Slurry, tailings (<2 mm)
		DLS[a] (20–200 mm)	Jigs (20–0 mm)	
Min–max concentration range				
LOI	2.40–42.47	8.13–52.88	17.04–68.02	23.24–62.51
SiO_2	32.81–89.36	22.08–61.07	25.79–58.39	11.30–37.79
$Al_2O_3 + TiO_2$	3.46–28.97	12.79–28.09	12.98–26.50	5.80–21.85
Fe_2O_3	1.18–9.77	1.40–13.88	2.19–11.80	3.10–28.64
CaO	0.00–3.75	0.00–4.48	0.38–4.40	0.78–11.95
MgO	0.00–3.32	0.11–5.70	0.47–3.30	1.17–4.96
$Na_2O + K_2O$	1.26–5.14	0.05–3.62	0.37–3.23	0.77–2.55
MnO	0.01–0.21	0.65[b]	0.03–0.19	
S_t	0.03–2.93	−3.91 (5.29[c])	0.22–4.17	0.32–7.71 (21.60[b])
CO_2	0.00–5.26	0.00–7.16	5.84[b]	1.66–12.70
C	0.48–25.65	0.38–31.69	8.09–43.47	7.98–50.65
Mean concentration range				
LOI	6.89–18.16	11.31–35.54	22.93–37.18	29.36–45.60
SiO_2	51.19–74.84	42.13–56.94	31.61–56.77	21.83–33.10
$Al_2O_3 + TiO_2$	10.16–26.26	18.00–25.32	13.09–25.80	9.92–18.00
Fe_2O_3	2.07–6.65	2.94–9.49	2.19–11.80	4.54–19.41
CaO	0.32–1.16	0.50–3.31	0.38–2.89	1.35–9.38
MgO	0.68–1.88	1.09–3.60	0.83–3.09	1.58–4.79
$Na_2O + K_2O$	1.57–4.05	0.42–3.70	0.85–3.38	1.44–2.09
MnO	0.05–0.10	0.03–0.29	0.05–0.13	
S_t	0.16–0.71	3.00[b]	0.33–3.09	0.48–5.58 (12.98[c])
CO_2	0.31–1.64	0.24–4.60	0.17–5.52	1.68–11.00
C	3.84–9.80	3.93–18.88	10.58–26.94	11.49–35.42

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[a] DLS – dense liquid separator.

[b] Single available value.

[c] Single outlier value.

Table III.6.4. Concentrations of trace elements in coal and coal mining waste (mg/kg).

Trace element (mg kg^{-1})	USCB, Poland		The Netherlands	Soils of the world[a]	
	Coal mining waste, seams 100–700	Pyrites, coal seams 618–625	Coal[b]	Min–max	Average
As	3.5–4.3	0.02–0.63	3.7	<0.1–66.5	4.4–8.5
B			43	<1–210	22–45
Ba			158	10–1,500	330–520
Be	<0.10–0.40		3.3		
Br			5.4		
Cd			0.10	0.01–2.7	0.37–0.62
Ce			17		
Co	4.2–115	0.01–0.21 (10.18[b])	5.8	0.1–70	5.5–12
Cr	12–21		14.4	1–1,100	47–83
Cs			1.0		
Cu	4.6–190.5	0.10–0.24	16.6	1–140	13–24
Eu			0.4		
F	11–75		80	<10–1,194	130–550
Ga	8–9				
Ge	<5		2.0		
Hf			1.2		
Hg			0.16	0.008–1.11	0.05–0.1
I			2.2	<0.1–10.8	1.7–3.4
La			7.6		
Mn	14–42		4	7–9,200	270–525
Mo	<2	0.88–1.12	3.0	0.1–7.4	1.3–2.8
Ni	7–60	0.00–0.16	11	0.2–450	13–34
Pb	11–44.7		8.5	1.5–176	22–28
Rb			9.2		
Sb			0.8		
Sc			3.3	0.8–30	5–10
Se		0.00–0.17	2.2	0.005–1.9	0.25–0.38
Sm			1.8		
Sr			107	5–1,000	87–210
Th			2.9		
Tl			1.0		
U			1.5		
V	52–60		29	6.3–500	67–115
W			1.0		
Zn	17.6–525		24	3.5–770	45–100
Zr	6–8				

[a] Kabata-Pendias (2001).

[b] Meij and Schaftenaar (1994).

III.6.3. Pollution potential of mining waste to the aquatic environment

III.6.3.1. Factors determining leaching behavior of waste

Pollution potential to the aquatic environment from coal mining and other mine waste disposed in tips or used in civil engineering works is determined by several basic factors: (i) content of soluble compounds (chlorides and sulfates) in fresh wrought rock material; (ii) content and reactivity of iron disulfide FeS_2 (pyrite, marcasite) and other sulfides, chemically unstable under atmospheric conditions; (iii) buffering capacity of Ca, Mn-carbonates and aluminosilicates; (iv) occurrence and availability of trace elements in the waste matrix and the vadose zone beneath a waste layer; (v) water balance, hydraulic conductivity and air penetration to the waste layer.

While soluble compounds in fresh wrought waste (chlorides and sulfates) determine the initial pollution potential of the material, the total life cycle pollution potential of waste, its extent, duration and character are dictated by the dynamics of generation, release and migration of qualitatively and quantitatively new loads of pollutants generated from the decomposition of geochemically unstable constituents, of which iron disulfide FeS_2 is a critical one. Complex physical and biogeochemical transformations in time that mining waste rocks undergo as a result of exposure to the atmospheric conditions, are known as weathering processes and comprise: (i) physical particle size degradation in rock material due to cyclic wetting–drying, freezing–thawing; (ii) chemical or biochemical decomposition of sulfide minerals with consecutive interaction of reaction products with other constituents of wastes, formation of secondary minerals, release, migration and transport of newly formed constituents within the waste layer and in to the dump bedrock, and interaction of leachate with the compounds of the vadose zone.

III.6.3.2. Pollution potential of fresh wrought waste

Soluble compounds in the fresh wrought waste discharged from the USCB occur in relatively low concentrations, usually from 0.1 to 0.5% wt, rarely >1% wt, and comprise mainly chlorides ranging from 0.001 to about 0.1% wt balanced by sodium ions, and minor amounts of sulfates. Chlorides occur predominantly in pore solution. Their content in mining waste is a function of chloride salinity of mine water and porosity of the rock material, which confirms that chloride content in carboniferous strata is a consequence of filling pore voids with water occurring in the strata. In the USCB, the chloride salinity of mine water of the carboniferous sequence is highly variable and shows both regional and vertical hydrogeochemical zonality (general increase with depth), while chloride concentration in rock material (C_{Cl}, mg/100 g) can be derived from an equation (Herzig et al., 1986; Twardowska et al., 1988; Szczepańska and Twardowska, 1999) showing good conformity with the direct measurements:

$$C_{\mathrm{Cl}} = 3.6889 c_{\mathrm{Cl}}^{0.621} W \qquad \text{(III.6.1)}$$

where c_{Cl} is the chloride salinity of ambient mine water, g/l and W the natural moisture content of a rock, %.

Beside chlorides, soluble compounds in fresh wrought material comprise sulfates. Their concentration in rock is generally low (from 0 to 3–5% of the total sulfur content S_t), while the pH is neutral up to weakly or moderately alkaline, within the stability field of the majority of trace elements. Therefore, the pollution potential of fresh wrought waste is relatively low, though it cannot be neglected due to specificity of constituents' migration in the anthropogenic and natural vadose zone under the conditions of waste disposal in dumps or use for civil engineering constructions (that will be discussed further).

III.6.3.3. ***Long-term pollution potential of mining waste***

III.6.3.3.1. Acid generation potential

III.6.3.3.1.1. Mechanism and kinetics of acid generation

Long-term pollution potential of mining waste results from the oxidation of the thermodynamically instable sulfide minerals (predominantly iron disulphide FeS_2: pyrite, occasionally marcasite and minor amounts of other sulfides) in waste rocks extracted from underground anoxic environment and exposed to air and water on the surface. This process may result in the formation of an acidic and sulfate-rich solution that has the potential to mobilize toxic trace metals both from waste and any material or the vadose zone matrix of the bedrock. The mechanism of iron sulfide oxidation is generally recognized as a multi-stage process involving direct abiotic pyrite oxidation from the reaction with oxygen and water, indirect reaction with ferric iron and biochemical oxidation by bacteria *Thiobacillus ferrooxidans*. The mechanism of reaction as a three-stage process proceeding both abiotically and by direct bacterial oxidation was presented by Kleinmann et al. (1981):

1. $$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (III.6.2)$$

2. $$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+ \qquad (III.6.3)$$

3. $$2Fe^{2+} + O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \qquad (III.6.4)$$

4. $$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (III.6.5)$$

Stage I: Reaction 1 – both mechanisms, Reaction 2 – abiotic; gradually slowing down. Chemical conditions: $pH > 4.5$; high SO_4^{2-}, low Fe^{2+} and acidity.

Stage II: Reaction 1 – both mechanisms, Reaction 2 – bacterial oxidation. Chemical conditions: pH 2.5–4.5, high SO_4^{2-} and acidity, increasing Fe_t, low Fe^{3+}/Fe^{2+}.

Stage III: Reaction 3 – totally bacterial oxidation, Reaction 4 – rate determined by Reaction 3. Chemical conditions: $pH < 2.5$, high SO_4^{2-}, acidity, high Fe_t and Fe^{3+}/Fe^{2+}.

Various aspects of the process have been discussed in a vast number of publications. A comprehensive review of the state of the art concerning acid-forming processes in sulfide-bearing rocks is presented by Hutchinson and Ellison (1992). The intensity of sulfide decomposition, which is typically a surface process, and the resultant acid and sulfate generation capacity depends on the pyrite content, specific surface of pyrite grains and availability of reagents, i.e. oxygen and water that also plays the role of transport means for the generated reaction products.

It has been shown by Caruccio (1978), Caruccio and Geidel (1981) and Caruccio et al. (1983) that the sulfide oxidation and acid generation is a direct function of the mineralogical and textural mode of the sulfide, which determines the specific exposed surface area. Low-crystalline metacolloidal and framboidal forms show particularly high reactivity.

Physical weathering or mechanical crushing of the rock material also facilitates sulfide oxidation due to the increase of physical accessibility. In turn, the secondary mineral formation in the reactions (gypsum, jarosite, melanterite, copiapite, etc.) may cause coating of mineral surface and thus decrease its availability to reagents.

It should be added that the extensive sulfide oxidation occurs predominantly under the vadose zone conditions, while in a water-logged material the intensity of the process is very low due to the lack of oxygen accessibility.

In general, duration and extent of sulfide oxidation is determined by the reaction kinetics (sulfide reactivity) that can be expressed in terms of half-life of sulfide ($t_{1/2}$ days) or intensity of acidity or sulfate generation vs sulfide content in rock material expressed as a first-order kinetic equation (Caruccio, 1975):

$$(C_S)_t = (C_S)_0 \exp(-kt) \qquad \text{(III.6.6)}$$

where $(C_S)_t$ is the residual sulfide content in waste (mg/100 g) after a period of time t (days), $(C_S)_0$ the initial sulfide content in waste material (mg/100 g) and $k = \ln 2 \cdot t_{1/2}^{-1}$ the kinetic constant (days^{-1}).

III.6.3.3.2. Acid generation potential of coal mining waste

III.6.3.3.2.1. Sulfide abundance

Total sulfur content S_t of coal mining waste from the USCB ranges from 0.01 to above 10% wt, the mean value being as low as about 1% wt. The dominating form is sulfide sulfur, mainly pyritic S_p, comprising 85–95% S_t. In the carboniferous strata of USCB, the organic sulfur content is negligible (in some world coalfields and mining areas, e.g. in the majority of those in India, organic sulfur is abundant or prevails). The main sulfur-bearing rock is coal. In the USCB, sulfur concentrations in coal display spatial zonality, and generally increase in SW to NE direction, showing the highest concentrations in the shallow seams of 100 and 200 group (Westphalian C, D series), while the mean S_t content in coals from two-thirds of all mines is below 1% (Szczepańska and Twardowska, 1999). A similar tendency is shown in the wrought waste material also. In conformity with coal content, the highest sulfur concentrations occur in coal shale, lesser in mudstone. Distinctly, the poorest in sulfide is sandstone. During the coal preparation process, due to the difference of the specific gravity of coal and pyrite, considerable amounts of FeS_2 pass to waste, enriching particularly the finer-grained material (Table III.6.3). In general, though, sulfur content in the averaged waste material does not exceed 1%, occurring most frequently in the form of pyrite, occasionally marcasite.

III.6.3.3.2.2. Textural forms of sulfides in waste rock from the USCB

Grain size of crystals ranges from micrometers to several millimeters, present separately or in aggregates of size ranging from several tens of μm (mainly in shale) to about 3 mm. Practically in all rock material, the advanced process of sulfide crystallization or re-crystallization is observed. The crystallization of sulfides is the most advanced in sandstone, weaker in coal, the weakest in shale, where the finest microcrystalline aggregates were preponderant.

With respect to the primary and secondary sulfide deposits, three major FeS_2 generations were identified.

- Syndiagenetic: the oldest one, represented by ball, framboidal, more seldom striped, impregnating, metacolloidal and microcrystalline textures.
- Anadiagenetic: younger generation represented mainly by organogenic, but also stripe/lenticular and pseudo-vein forms.
- Catadiagenetic: the youngest generation, where sulfide grains occur in pocket or vein forms and crystal aggregates.

Generally, in the older stratigraphic rock formations, the proportion of crystalline forms increases, while metacolloidal and framboidal sulfides decrease, though no distinct spatial regularities were found. Sulfide abundance, availability to water and air and the extent of the specific surface development are the critical factors for the acid generation potential of waste material.

Taking into account substantial differentiation of textural modes of sulfides in different types of waste and rock position along the carboniferous sequence, different ranges of pyrite reactivity of wastes from different seams could also have been anticipated.

III.6.3.3.2.3. Sulfide reactivity

The half-life of sulfide in rock along the Upper Silesia carboniferous sequence, $t_{1/2}$, was found to range within the wide limits: from 29.11 to 10,502 days, following a log-normal distribution. The mean half-period was estimated to be $t_{1/2} = 588.2$ days, and the sulfate generation rate per mass unit of rock R_{SO4} was 20.8 g/t d (Fig. III.6.2A and B) at full accessibility of oxygen and moisture to the pyrite surface (Witczak and Postawa, 1993). Under natural conditions, though, in coarse-grained and compacted material disposed at the dumps, the process is substantially slower.

Sulfide reactivity shows clear dependence on the rock lithostratigraphic position (Fig. III.6.3). Observations confirmed the highest reactivity of syndiagenetic framboidal, microcrystalline and organogenic forms and resistance of catadiagenetic vein and aggregate forms. Sulfides occurring in coal and mudstone display the highest decomposition rate, while sulfides present in sandstones are the most resistant to decomposition. Corrosion of sulfides is being developed in microfissures and along the borders of aggregates. The factors stimulating reactivity appeared to be the occurrence of microfissures, textural type of sulfides and structural type of sulfide mineralization.

III.6.3.3.3. Buffering capacity of coal mining waste

III.6.3.3.3.1. Principal components of buffering

The pollution potential of coal mining waste and other mining waste, besides acid generation due to sulfide oxidation, depends also on the buffering capacity of the material. The principal acid-consuming processes are: (I) reaction with calcium and magnesium carbonate minerals: calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$ (siderite $FeCO_3$ has no neutralizing properties) and (II) reaction with aluminosilicates, involving two mechanisms: (i) cation exchange capacity of clay minerals (most abundant in waste kaolinite,

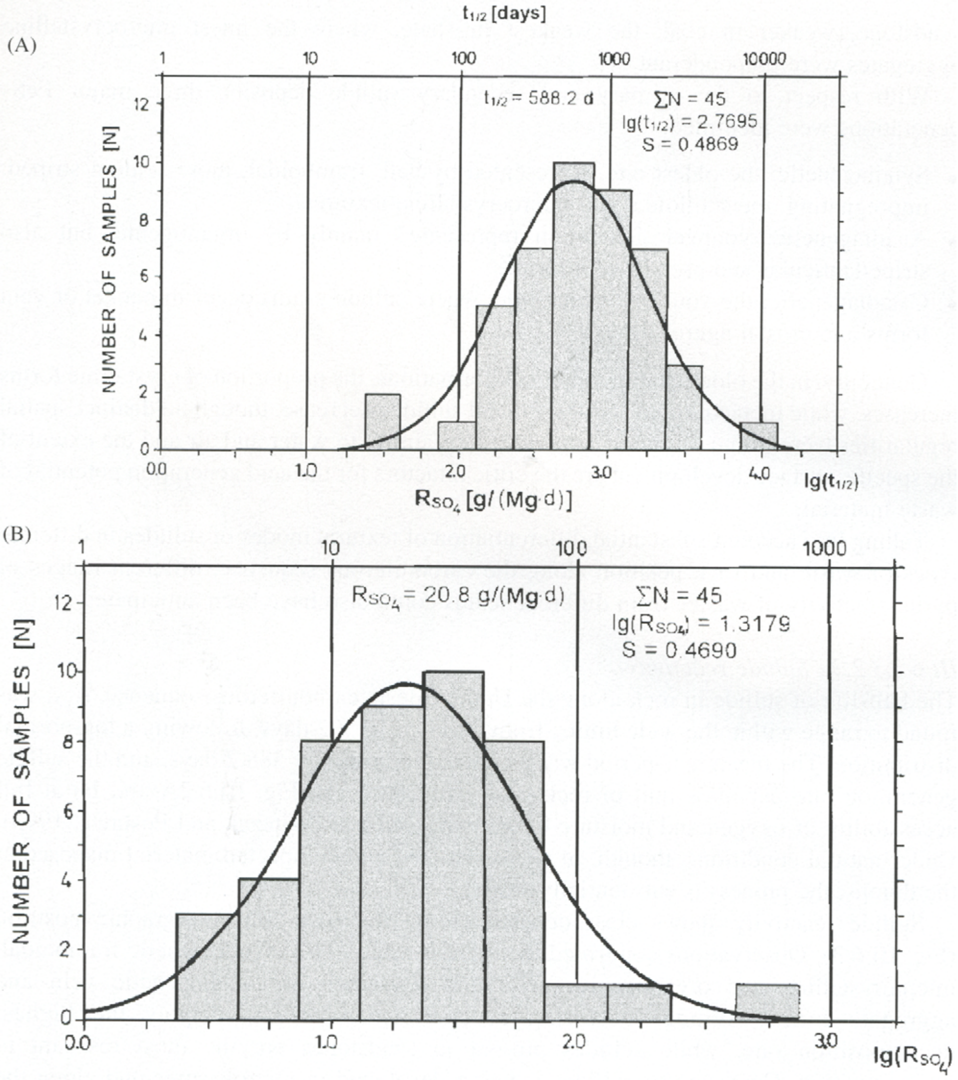


Figure III.6.2. (A) Distribution of sulfide half-life values for rocks of the Upper Silesia carboniferous sequence (Poland). (B) Distribution of sulfate generation rates in the rocks of the Upper Silesia carboniferous sequence (Poland).

illite, chlorite) and mica; (ii) dissolution of aluminosilicates and silicates (e.g. feldspars) with formation of Al-rich clay minerals or hydrolysis in solution of aluminum ion released from the lattice of clay minerals, congruently limited by dissolution of kaolinite (Palmer, 1978; Hutchinson and Ellison, 1992).

Just Ca^{2+}- and Mg^{2+}-carbonate buffering and the cation exchange in clay minerals have the neutralizing effect (pH ≈ 7.0, dependent on the pCO_2). Coal mining waste is rather poorly buffered in the range pH 5.0–3.5, while high acid consumption at

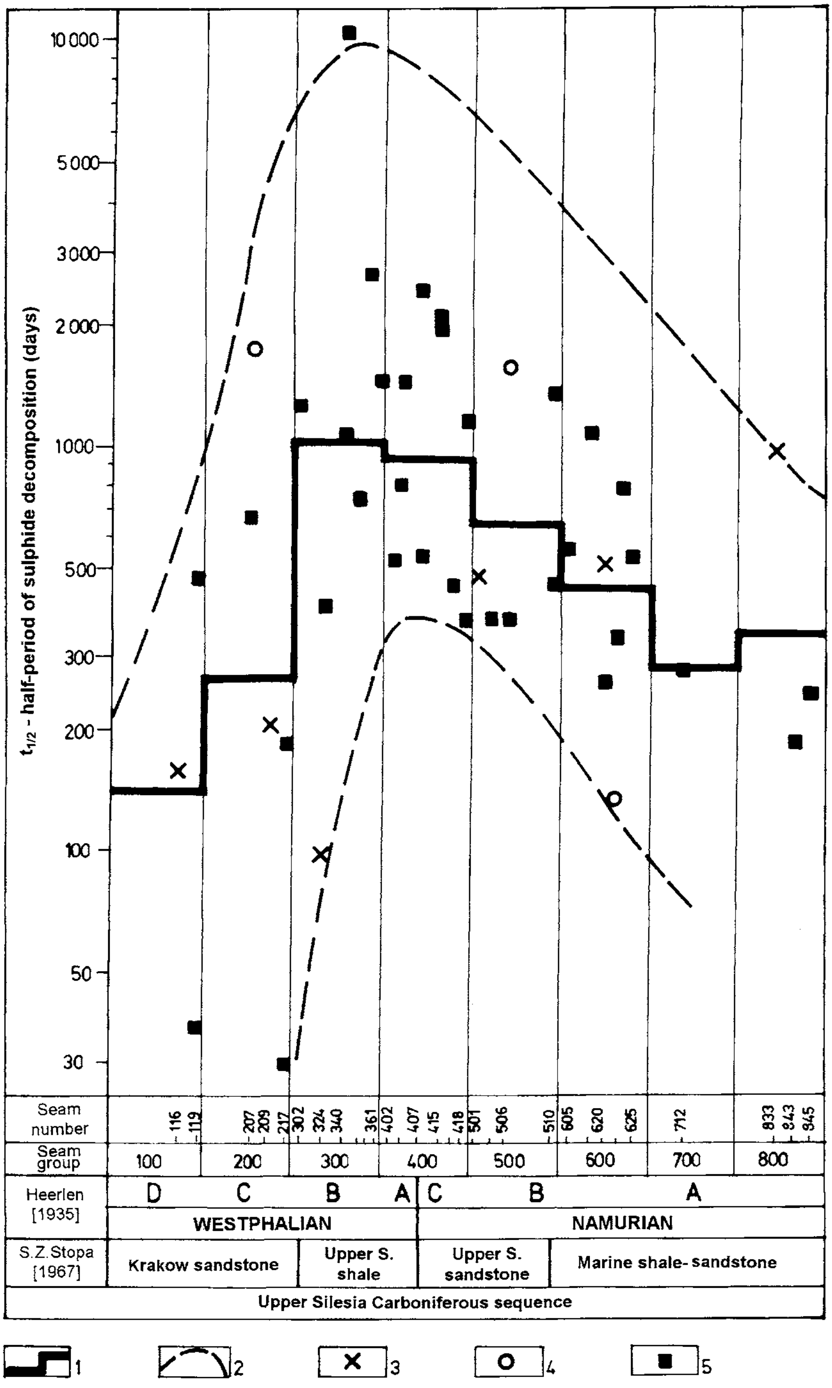


Figure III.6.3. Variability of sulfide half-life values along the Upper Silesia carboniferous sequence. 1, Estimated values of $t_{1/2}$ for seams of Upper Silesia carboniferous sequence; 2, range of $t_{1/2}$ variance; 3, mudstone; 4, sandstone; 5, coal.

the dissolution of aluminosilicates occurs at low pH range 2.5–2.8 (Palmer, 1978; Hutchinson and Ellison, 1992). From the environmental safety reasons, buffering at pH values close to neutral, which are within the stability fields of trace elements, is of particular importance.

III.6.3.3.3.2. Buffering capacity and mechanism

The main part of buffering capacity comprises calcium and magnesium carbonates (calcite and dolomite). Exchangeable ions are also of considerable importance.

Though clay minerals are abundant compounds of coal mining waste, the preponderance of minerals with non-expanding lattices in the carboniferous sequence of the USCB (kaolinite, illite, accessory chlorite) results in the relatively low cation exchange capacity of fresh wrought rock material ($CEC_t = 47-113$ eq/Mg) ranging within the mean values specific for kaolinite. Composition of exchangeable ions distinctly depends upon the chloride salinity of ambient mine waters. Downwards in the carboniferous profile, the proportion of Na^+ ion in sorption sites grows (up to 43–72%) in parallel with the increase of mine water and rock salinity. This leads to the conclusion that sodium ions were introduced onto the exchange surfaces through cation exchange with mine waters. The rest of the exchangeable places are occupied by Ca^{2+} and Mg^{2+} ions. The proportion of exchangeable ions in the total buffering capacity (C_{buf}) ranges from 7 to 40%.

In general, in buffered Ca,Mg-carbonate-rich material of low NaCl salinity, the role of cation exchange capacity of the material in acid buffering is minor (Figs. III.6.4I and III.6.5I), while in Na-saline and low-buffered rocks, cation exchange processes are of considerable importance. In buffered material, the effect of buffering through ion exchange results in displacing alkali in exchange surfaces for Ca^{2+} and Mg^{2+} ions, and thus in mainly qualitative changes of CEC_t (Figs. III.6.4II and III.6.5II). In low-buffered rock, further decrease of Ca^{2+} displaced by H_3O^+ ions, increase of the Mg^{2+} proportion and decline of the total sorption capacity CEC_t occurs (Figs. III.6.4III, III.6.5III and III.6.6). In deeper layers of the dump, these processes are time-delayed with respect to the surface layer (Figs. III.6.4–III.6.6). The H_3O^+ ions in low-buffered rock may further displace Al^{3+} ions from the lattice, enriching pore solution. The pH of a solution is then determined by the hydrolysis reaction of aluminum ions (at the level $\leq$pH 5), limited by the dissolution of kaolinite and reaction with aluminosilicate minerals (feldspar) at low pH <3.5, affecting the composition of the pore solution.

Buffering of acidification potential by Ca^{2+}- and Mg^{2+}-carbonates in the coal mining waste dumps occurs by two different mechanisms, dictated by the heterogeneity of the rock material. This buffering of acidification results from the occurrence of acid-generating and buffering minerals in different microenvironments and makes their direct interaction difficult. (i) The acid generation and equilibrium-limited process of carbonate dissolution occur independently in pore solutions of separate microenvironments; protons and carbonate ions migrate to water infiltrating through voids of the dump where neutralization of acidity occurs. (ii) Decomposition of carbonates results from its direct interaction with acid loads and transfer of Ca^{2+} and Mg^{2+} ions to infiltrating solution.

The process of carbonate dissolution is determined by the equilibria constraints, mineralogical form, extent of crystallization and abundance in the rock matrix. Carbonate minerals are ubiquitous components in the seams of the Upper Silesia carboniferous sequence and occur in the form of a binder or a component of the binding agent in

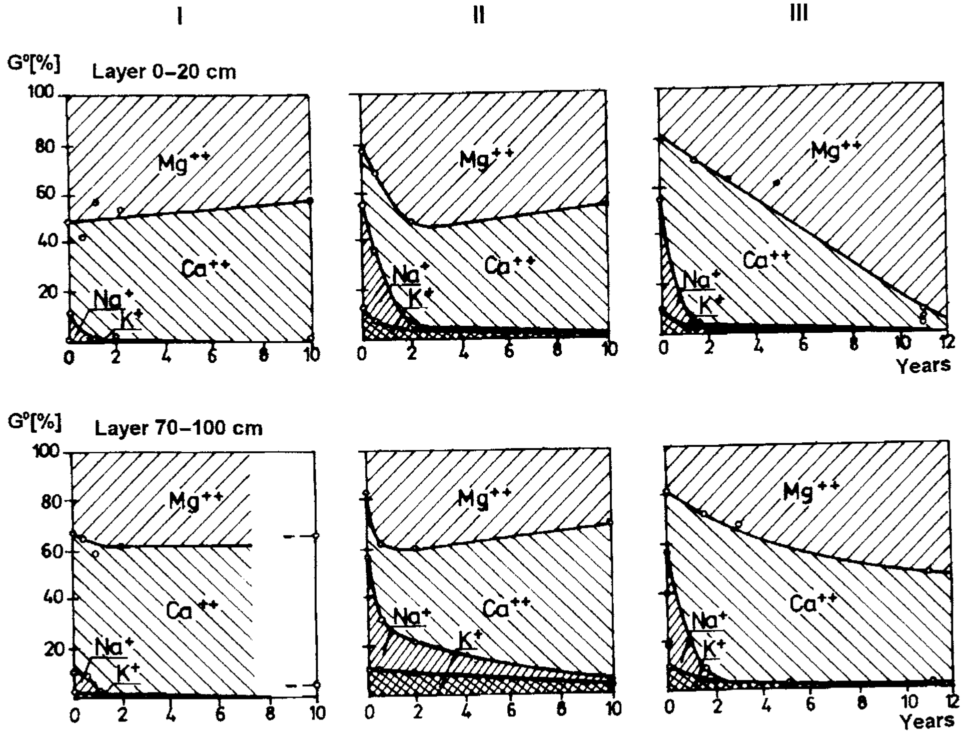


Figure III.6.4. Qualitative transformations of exchangeable ion composition in disposed coal mining waste of different buffering capacity and chloride salinity vs period of dumping. (I) Buffered waste from Siersza mine ($\xi = 2.5$) of a low chloride salinity (0.95–1.96 eq Cl/t), Siersza-Misiury dump; (II) buffered waste from Pawlowice mine ($\xi = 3.3$) of a high chloride salinity (28 eq Cl/t), Przezchlebie dump; (III) low-buffered waste from Szczyglowice mine ($\xi = 0.60–0.70$) of a mean chloride salinity (15.0 eq Cl/t), Smolnica dump.

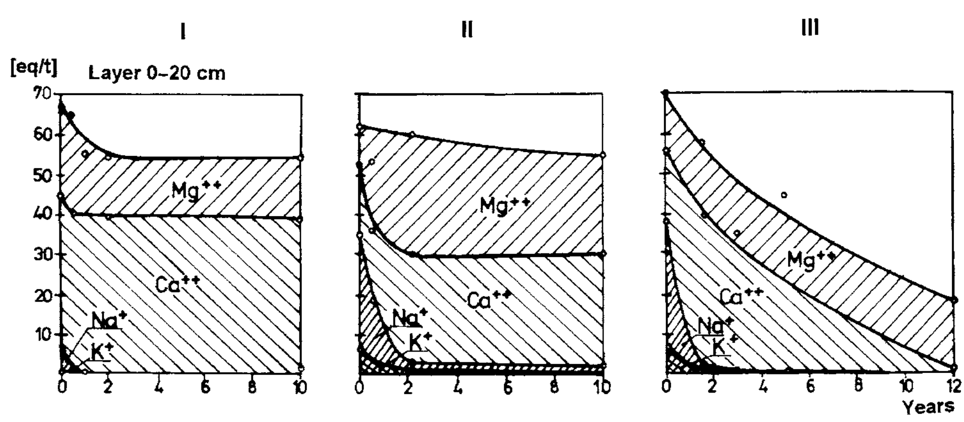


Figure III.6.5. Quantitative and qualitative changes of cation exchange capacity of disposed coal mining waste of different buffering capacity and chloride salinity vs period of dumping. Descriptions as in Figure III.6.4.

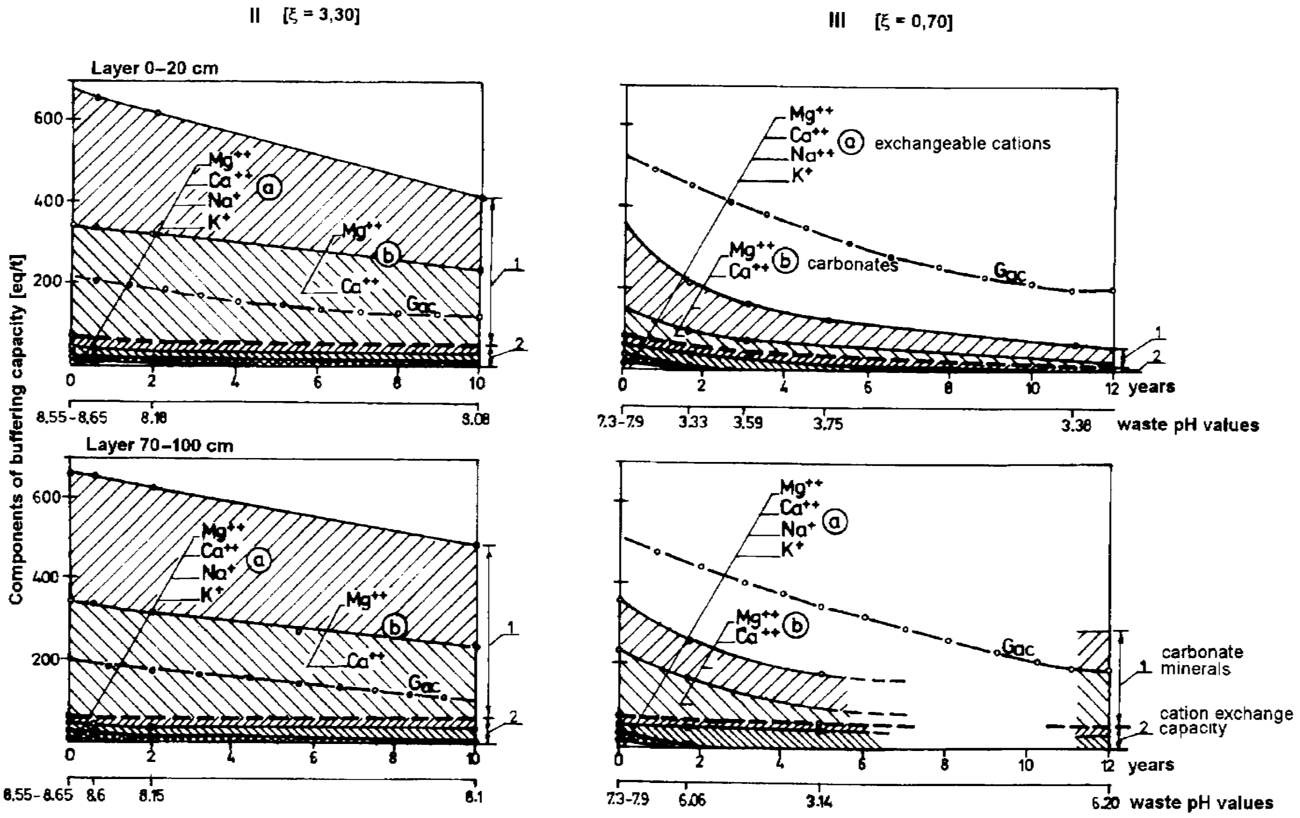


Figure III.6.6. Changes of buffering capacity of buffered (II) and low-buffered (III) coal mining waste disposed at a dump vs period of dumping. Descriptions as in Figure III.6.4.

sandstone, aggregates in mudstones and coal, as well as veins, impregnations and pockets in coal seams. In some parts of a seam, carbonates occur in a disseminated, fine- or microcrystalline form. As both the direct and indirect buffering by carbonates is a surface process, the specific surface of carbonates is an important factor in the process efficiency. No clear regularity in abundance and mineralogical forms of carbonate occurrence along the profile of the USCB carboniferous series has been observed. This hinders the accurate prognosis of the buffering capacity of the waste rock material on the basis of the stratigraphic position of a mined seam.

Due to the domination of the indirect buffering mechanism by means of the dissolution of the carbonate minerals, the acidification of low-buffered material deposited at the dump depends on the length of a dry period. Maximum acid load in the rock occurs at the end of a dry period, when acid generation proceeds, but is not released due to the declining infiltration or lack of flushing. The total load of the generated acid is therefore proportional to the duration of the dry periods, while dissolution of buffering carbonates is limited by equilibria constrains (Garrels and Christ, 1965; Pačes, 1983; Brookins, 1988). This statement has been thoroughly confirmed by field results (Vimmerstedt and Struthers, 1968; Morth et al., 1972; Twardowska, 1981; Twardowska et al., 1988; Olyphant et al., 1991) and column studies (Geidel and Caruccio, 1977; Geidel, 1979; Twardowska, 1981), when maximum acidification of rock and leachate from the coal mining waste dump was observed after long dry periods. In case of the permanent leaching/flushing, the acidification often does not occur even in low-buffered material. A particular vulnerability of a rock material to acidification in the top layer of the dump (Neumann-Malkau, 1993), besides other factors such as permeability to air, is due to the more frequent water deficiency than in deeper layers. This results in lower availability of dissolved carbonates at the same acid generation rate.

The secondary products forming as a result of buffering reactions within the matrix are mainly gypsum appearing commonly as precipitate on the rock particles in the mining waste dumps of USCB and iron hydroxide (Twardowska, 1981, 1986). Other identified secondary minerals are jarosite, melanterite, copiapite, halotrichite (Caruccio, 1978; Hutchinson and Ellison, 1992). Possible coating effect of precipitates is assumed to have stronger effect on shielding buffering minerals than on acid generating process (Hutchinson and Ellison, 1992).

Taking into consideration that the pollution potential of mining wastes largely depends on susceptibility to acidification, which commonly is a time-delayed process, the evaluation of acid generation potential of wastes is of particular importance. Due to inconsistency of stoichiometric proportions and actual interaction of minerals in a heterogeneous matrix, buffering potential $\xi = C_{\text{buf}}/C_{\text{ac-t}}$ of rock material and resistance to acidification has been evaluated as the ratio of total buffering capacity C_{buf} (or neutralization potential (NP)), assessed as the total cation exchange capacity and calcium/magnesium carbonates content, to the total acid-generation potential $C_{\text{ac-t}}$ (or acidification potential (AP)) in terms of the total sulfur in real systems under field conditions, both values converted to common equivalent units (Twardowska, 1981, 1990; Twardowska et al., 1988) (Fig. III.6.5). Use of total sulfur content instead of the more exact sulfide sulfur assures more conservative estimation of the potential for acidification. Acidification of the material does not require the consumption of all carbonate minerals, which are usually still present in substantial amounts in the acid rock. The prerequisite of a satisfactory buffering effect is the balanced dissolution of carbonates, able to neutralize generated acid loads. Due to the different kinetics of these two processes and heterogeneity of the material, buffering minerals should occur in the matrix much in excess compared to sulfides, and their specific surface at the solid–liquid interface should be adequately high. On the basis of the long-term observations and generalization of a large number of cases, mining waste has been defined by the authors with respect to the buffering potential within three-range limits (Twardowska et al., 1988; Twardowska, 1990).

(I) $\xi = C_{\mathrm{buf}}/C_{\mathrm{ac\text{-}t}} \geq 2.4$: buffered waste, no acidification will occur in the life-cycle of a dump;

(II) $\xi = C_{\mathrm{buf}}/C_{\mathrm{ac\text{-}t}} \leq 1.5$: low-buffered waste, susceptible to acidification; threshold of acidification to start was evaluated for $\xi \leq 0.6$;

(III) $\xi = C_{\mathrm{buf}}/C_{\mathrm{ac\text{-}t}} > 1.5 < 2.4$: weakly buffered waste, acidification may occur (possibly acid generating waste).

Very close to the evaluation proposed earlier by authors is the method by Smith and Barton-Bridges (1991). In general, it consists of a three-stage procedure; the first stage is the same, but with a higher degree of conservatism with respect to the estimation of potential for acidification.

(I) $\xi = C_{\mathrm{buf}}/C_{\mathrm{ac\text{-}t}} \geq 3.0$: buffered, non-acid generating waste. If $\xi = C_{\mathrm{buf}}/C_{\mathrm{ac\text{-}t}} < 3.0$, then the material should be tested with respect to $C_{\mathrm{ac\text{-}s}}$ (sulfide sulfur). If

(II) $\xi = C_{\mathrm{buf}}/C_{\mathrm{ac\text{-}s}} \geq 3.0$: buffered, non-acid generating waste. If $\xi = C_{\mathrm{buf}}/C_{\mathrm{ac\text{-}s}} < 3.0$:

(III) Perform a kinetic test using the humidity cell or column/lysimeter and a leach test. Determine all mobile/mobilizable species (leachable plus potential products of acid generation).

Hutchinson and Ellison (1992) present several short static test techniques for evaluation of AP (or C_{ac}) and NP (or C_{buf}), along with their summary evaluation. The tests include the BC research initial test, the Sobek test, the modified Sobek test, the alkaline production method, the hydrogen peroxide test and net acid production. All of them except the last two are based on the total sulfur and sulfur-bearing forms' analysis for AP evaluation, and acid titration of sample to evaluate NP (the same approach has also been used independently by the authors) and give comparable results. Hydrogen peroxide tests were not recommended as non-reliable. Reliability of acid rock drainage (ARD) testing, besides proper selection of test methods, require careful sampling and representative sample preparation techniques (Broughton and Robertson, 1992; US EPA, 1994).

III.6.3.4. Geophysical parameters critical for the pollution potential from mining waste dumps

III.6.3.4.1. Air penetration

Intensive sulfide oxidation can occur entirely under the vadose zone conditions, which are predominant within mining waste dumps. Inundation of the waste layer causes inhibition of the reaction due to the decrease of oxygen in water at pyrite surfaces by more than an order of magnitude; diffusion or convection transport in water-saturated pores cannot supply enough oxygen, while less than 10% of air content in pore atmosphere is sufficient for sulfide oxidation to proceed (Good, 1970; Morth et al., 1972; Frost, 1979; Twardowska, 1981; Twardowska et al., 1988). Due to the lack of analytical data, some authors previously assumed that in a well-compacted waste, the permeability to air is effectively nil and evaluated air penetration depth for the range 0.1–0.25 m to a maximum of about 4 m (Good, 1970; Glover, 1978). The contemporary approach considers air penetration measurements as an essential factor in evaluation of environmental behavior of sulfidic waste rock dumps (Helgen et al., 2000; Hockley et al., 2000).

Results of our own studies conducted at compacted coal mining dumps of different ages (7–15 years old) displayed the presence of oxygen in the full profiles 10–12 m thick of the vadose zone of both high and low hydraulic conductivity ($k = 10^{-2}-10^{-6}$ cm/s, i.e. $10^{2}-10^{-2}$ m/d). The gas composition of the pore atmosphere is typical for an oxic environment in the full profile ($O_2 = 12.78-20.54\%$ vol, lack of CO and H_2S) and proves active oxidation of sulfide and coal (consistency of O_2 diminution and CO_2 increase, relatively high CO_2 values, up to 1.7–4.48 vol%, occurrence of CH_4 and C_2H_6, mode of respiration index distribution). Distinct corrosion of all textural forms of sulfides, in particular framboidal, metacolloidal, micro- and fine-crystalline forms and the occurrence of secondary products of sulfide decomposition (gypsum, goethite and iron oxyhydroxides) confirmed the occurrence of oxidation processes and water infiltration in the whole profile of the investigated dumps. The most susceptible to oxidation appeared to be sulfides in coal shale and coal; the most resistant are sulfides in carbonatic rocks.

III.6.3.4.2. Conditions determining water flow in the waste dump and transport of the released contaminants to groundwater and surface waters

III.6.3.4.2.1. Hydraulic conductivity

Hydraulic conductivity of coal mining wastes deposited in dumps or used in civil engineering constructions depends on a number of factors, the most essential are particle size distribution, susceptibility and character of weathering decomposition (effect of drying–wetting, freezing–thawing, chemical processes of salt leaching, pyrite oxidation and secondary reactions) and technical conditions of waste dump construction (layer formation and compaction).

In general, as results from the waste generic structure, more than 75% of coal mining waste in the USCB represents coarse, massive granular material of grain size ranging from 30 to 500 mm. Rock material from marine shale/sandstone and brackish sandstone series of Namurian A–C is resistant to the physical weathering breakdown. Upwards the carboniferous sequence susceptibility to weathering grows, up to the maximum values in the youngest sandstone Westphalian C–D formations.

Hydraulic conductivity for surface layer of the tips where the typical coarse-grained coal mining wastes are disposed ranged from 10^{-7} to 10^{-1} cm/s ($10^{-3}-10^{3}$ m/d), reflecting the effect of lithological type and position in the carboniferous sequence, which determine rock susceptibility to weathering. Physical weathering disintegration of waste rock material is the strongest in the first months or year of exposure to atmospheric conditions, while further disintegration proceeds very slowly. The conditions of water infiltration through the dump thus undergo fast stabilization. In the majority of profiles, the decrease of hydraulic conductivity in the top layer of several tens of cm, up to 1.0 m thick is observed. This confirms a limited thickness of the physical weathering zone as proven by other authors (Sullivan and Sobek, 1982).

Mechanical compaction causes reduction of hydraulic conductivity up to four orders of magnitude compared to a fresh wrought waste in a layer of about 20 cm thick, but never less than $k = 10^{-7}$ cm/s (10^{-3} m/d), in many cases not less than 10^{-3} cm/s, i.e. 10^{-1} m/d (rocks from the oldest strata). Therefore, compacted dumps in the USCB are either fairly permeable or at least semi-permeable to water. The pattern of hydraulic conductivity in two characteristic coal mining waste dumps in the USCB of different susceptibilities of the rock material to self-sealing is presented in Figure III.6.7A and B.

The relevant values for loose and compacted mining waste from the various coalfields of the world (Czech Republic, Germany, Spain, UK and the USA) quoted by Skarżyńska (1995a) showed similar permeability range as rocks from the USCB, i.e. from 10^{-1} to 10^{-4} cm/s (10^3–10^{-1} m/d) for loose coarse material and 10^{-3}–10^{-5} cm/s (10–10^{-1} m/d) for the compacted layer, with the exception of some mining waste from UK coalfields, which are generally less permeable both in the loose (10^{-2}–10^{-6} cm/s, i.e. 10^2–10^{-2} m/d) and compacted state (10^{-2}–10^{-9} cm/s, i.e. 10^2–10^{-5} m/d).

III.6.3.4.2.2. Moisture content in the vadose zone of the dump

Water occurring in granular waste material in a dump represents several categories. The total volume of voids in rock and spaces between rock particles delimits the maximum amount of water in material in a saturated state (w_t). Part of it is physically bound by molecular forces (sorption water w_m), and held by capillary forces or suspended on the local interlayers of low permeability (retention capacity w_r). Water ($w_n - w_r$) determined by the natural moisture content w_n in excess with respect to w_r forms an infiltration stream w_i, which percolates downward through the waste layer under the vadose zone conditions due to gravitational forces and transports contaminants released from solid rock matrix out of the dump. In the initial stage, part of the infiltrating stream fills up the retention capacity of the consecutive waste layers, provided a dry or semi-dry material is disposed. Retained water, being a function of the specific surface of the rock, forms an environment for equilibria–non-equilibria processes at the liquid–solid phase interface, controlling the released contaminant load. An amount of free water percolating through the waste layer depends on the waste properties determining a hydraulic conductivity, atmospheric conditions (precipitation), and water balance of the dump.

III.6.3.4.2.3. Total moisture content of the vadose zone in the coal mining waste dump

A sufficiently thick waste layer forming the anthropogenic vadose and saturated zones, can be divided into three specific parts with different conditions of water flow and moisture content (Fig. III.6.8):

- upper surface zone, up to about 1.0 m thick, of unsteady water flow, depending upon the atmospheric conditions (precipitation, evaporation and evapotranspiration);
- dump body, of a relatively stable moisture content, proportional to average infiltration rate;
- bottom part at the border of the vadose and saturated zones, where moisture content increases up to the complete saturation (w_t) in the capillary suction zone or at the water table border.

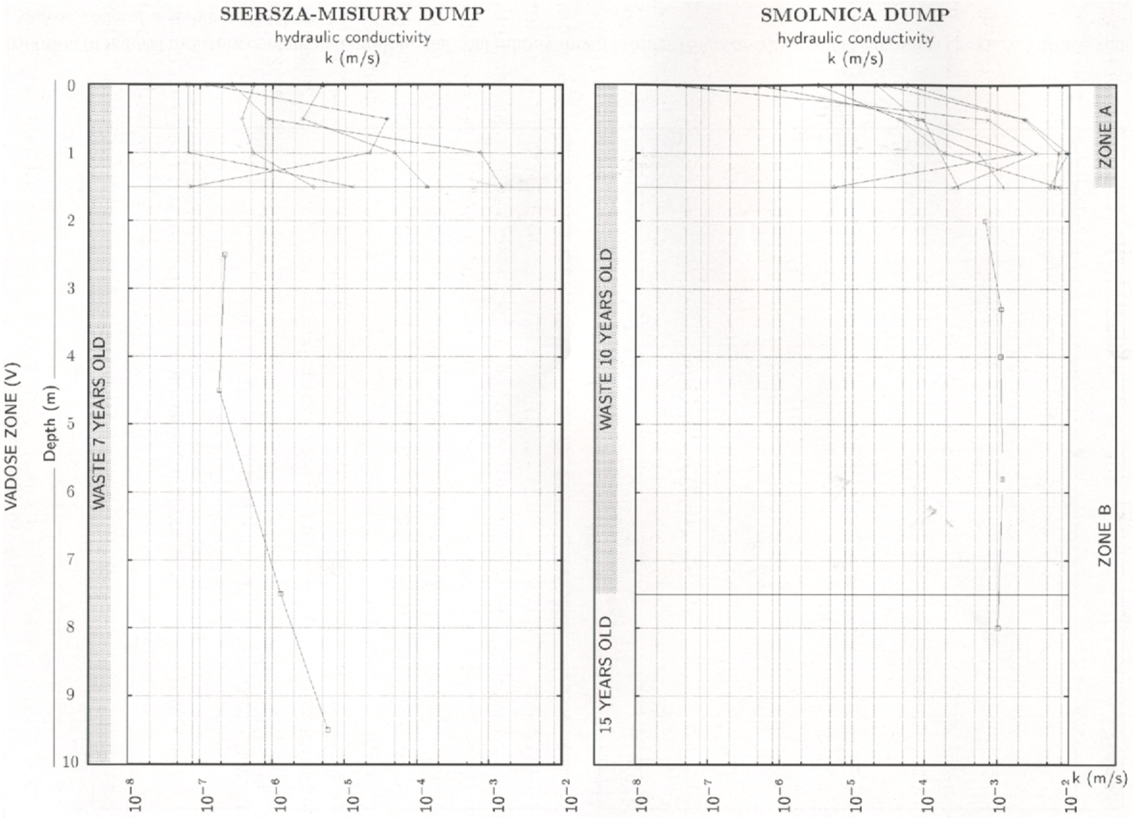


Figure III.6.7. Hydraulic conductivity of waste rock material in the coal mining dump (Siersza-Misiury and Smolnica sites). A, Surface vadose zone of unsteady hydraulic conductivity; B, vadose zone of a stable hydraulic conductivity.

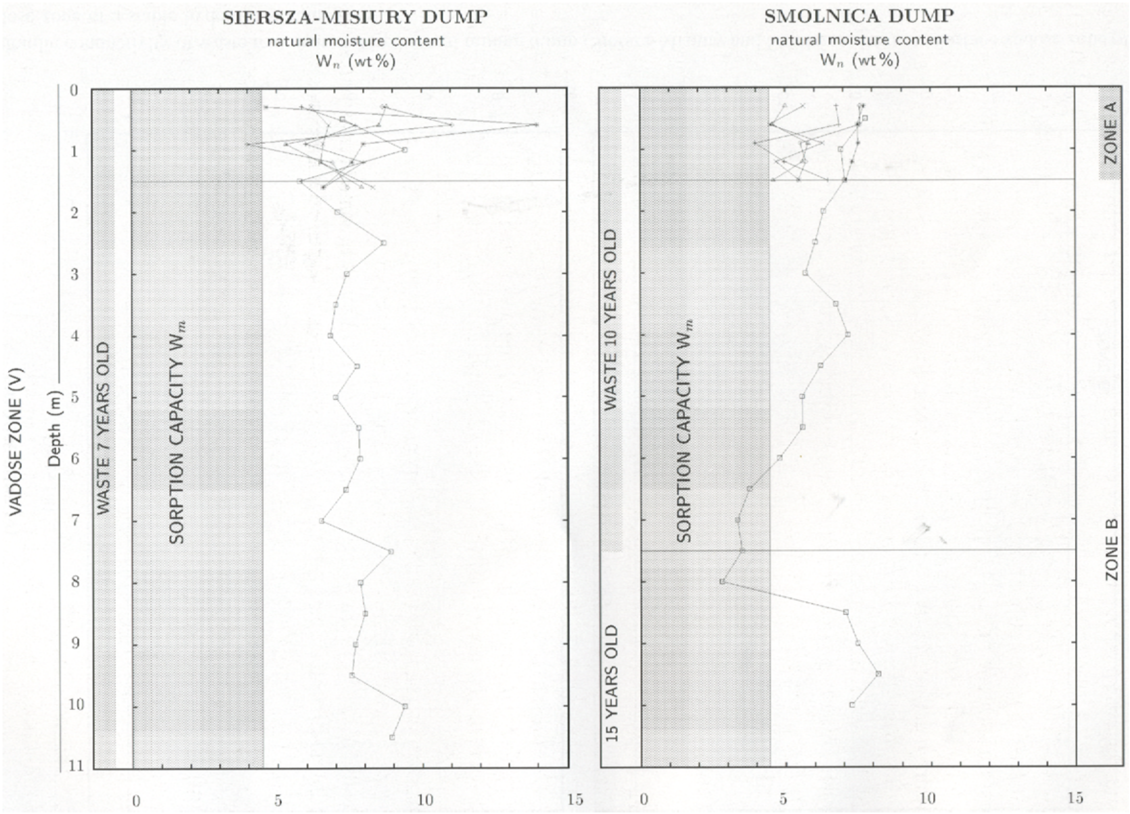


Figure III.6.8. Distribution of natural moisture content values along the coal mining dump profiles (Siersza-Misiury and Smolnica sites). A, Surface vadose zone of unsteady moisture content; B, vadose zone of a stable water flow.

The total free water not bound by molecular forces ($w_n - w_m$) takes part in water percolation through the dump. Also the retained, looser bound water is gradually exchanged.

The stability of moisture content in the dump body largely depends upon the uniformity of grain size distribution. In coarse, granular shales from the Namurian C series (e.g. Smolnica site, Fig. III.6.8A), the decrease of moisture content with the increase of grain size vs depth was observed, while in easily disintegrating rock material from the Westphalian C–D series (e.g. Siersza-Misiury site, Fig. III.6.8B) the natural moisture content in dump body was uniform.

The moisture content profiles for different dumps fills pore spaces in the mean range from 25 to 50%. Moisture content values range from several to more than 10% wt, and are considerably above the w_m values estimated for 2.29 to 4.64% wt. The difference determines the proportion of infiltration water stream in the dump.

The available data on moisture content in the coal mining dumps in the different coalfields worldwide are very close to those evaluated for the USCB and range from 2 to 15% wt; only for coalfields of the UK, the reported moisture content values are higher, up to 28% wt (Skarżyńska, 1995a).

III.6.3.4.3. Water balance of coal mining waste dumps

III.6.3.4.3.1. Elements of a waste dump water balance

The basic elements of water balance that is one of the decisive factors in the assessment of pollution potential from a dump are: (i) surface runoff; (ii) evapotranspiration; (iii) infiltration. The infiltration rate is crucial for transport of contaminants from the dump. Runoff waters also participate in contaminants leaching and transport to receiving waters, but to a considerably lower extent (Swift, 1982; Vipulanandan and Krizek, 1983; Trouart and Knight, 1985).

For evaluation of the water balance of typical coal mining waste dumps, experimental studies on two typical dumps (Smolnica and Siersza-Misiury sites) were conducted. Surface runoff (in the 5 cm thick surface layer) was evaluated by simulating precipitation of different intensities in experimental plots on the top and slopes of a bare and a grassed dump surface, using F method of sprinkling (Ven Te Chow, 1964).

Infiltration and evaporation assessment was based on lysimetric studies (Fig. III.6.9). Lysimeters of an effective height (1.5 m), adequate to the thickness of the surface active zone, were filled with representative coal mining waste from the USCB of different ages and exposed to natural atmospheric conditions (experiment began at the end of 1984 and was continued for more than a decade) (Fig. III.6.10).

III.6.3.4.3.2. Surface runoff

The rate of the surface runoff depends on a number of factors, the most essential being ground slope, hydraulic conductivity of the material and its change due to weathering, intensity and duration of the rainfall, the antecedent moisture content in the surface layer, extent of a surface retention (dumps) and subsurface flow (Atkinson, 1977), as well as vegetative cover.

At the flat surface of the dumps having small ground slopes, in particular of those constructed of permeable waste, at a low precipitation intensity (such as 0.026 mm/min,

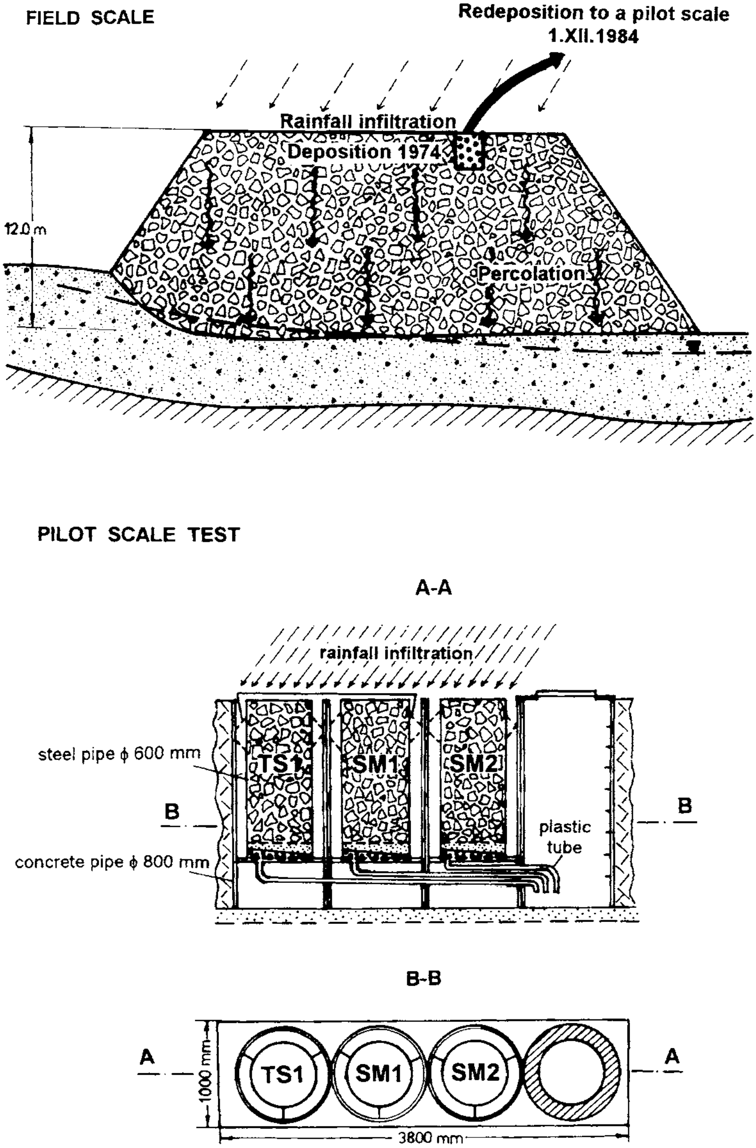


Figure III.6.9. Scheme of the long-term lysimetric studies (1984–1996) of water balance, kinetics of sulfide decomposition and contaminant leaching in the surface vadose zone layer 1.5 m thick of coal mining waste dumps. Lysimeter fill: TS1, 7 year old waste of $w_n = 7.5\%$ wt from Siersza-Misiury dump; SM1, fresh wrought waste; SM2, 10 year old waste from the Smolnica dump.

a mean annual intensity in the Upper Silesia area) surface runoff is effectively nil. During storms, runoff comprises 50–60% of the total precipitation. Following the nomogram to determine storm runoff coefficients (NCB, 1982), a similar one was constructed for the approximate evaluation of a mean annual runoff for permeable and low-permeable mining

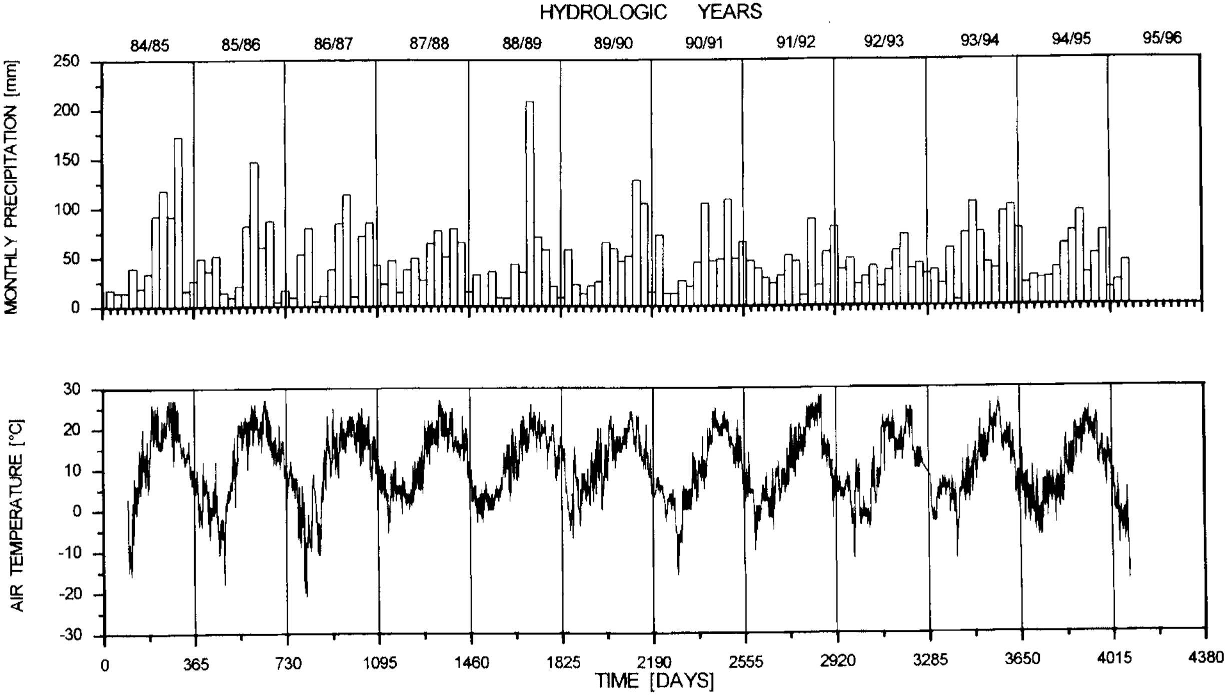


Figure III.6.10. Atmospheric precipitation and air temperatures at the lysimetric site during study (hydrologic years 1984–1996).

waste (Fig. III.6.11). The obtained values account for 5–15% of the mean annual precipitation, i.e. much less than for storms. In case of environmental impact assessment, the safety coefficient should be, though negative, greater than used for the design of the drainage system. Field observations also confirm low values of runoff in the coal mining waste dumps.

Hutchinson and Ellison (1992), following the Soil Conservation Service methodology (USDA, 1972), constructed a more detailed approximate rainfall–runoff relationship, though it was not validated experimentally.

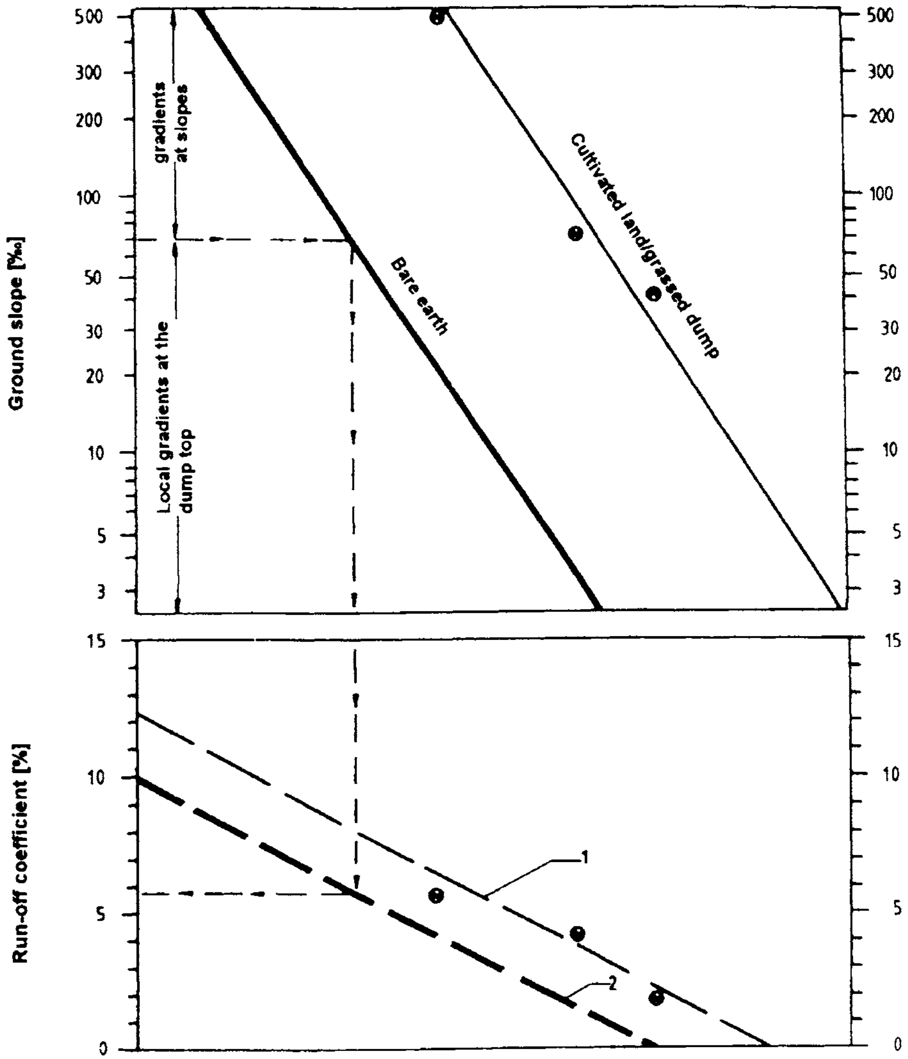


Figure III.6.11. Nomogram to estimate mean annual runoff coefficients for coal mining waste dumps (percent of the annual precipitation sum) for: (1) a revegetated dump; (2) the bare dump surface.

III.6.3.4.3.3. Infiltration and evaporation

Water balance derived from lysimetric studies shows a high rate of infiltration with respect to evaporation from the bare non-compacted surface. The rate of evaporation for both permeable and low-permeable materials was as high as 39–45% of precipitation in the case of a low runoff, or of precipitation of less runoff. The infiltration rate for flat top surfaces of the waste dump, simulated by lysimetric studies, comprise 55–61% of the total precipitation (Fig. III.6.12).

III.6.3.4.3.4. Water exchange rate in a dump

Due to the heterogeneity and granularity of rock material, as well as to physiochemical changes in the properties of waste resulting from weathering processes, conditions of water flow within the dump are complex. During the vertical flow of percolating water, both retardation of flow resulting from either retention capacity (capillary bound water) or formation of zones with low permeability, or voids of privileged flow within the dump can occur.

Water exchange rate and liquid/solid (L/S) ratio during water percolation under the vadose zone conditions are crucial for a correct evaluation of contaminant loads and concentrations in leachate. The common practice of using very high proportions of water in leach laboratory tests (L/S ratio) leads to deriving too optimistic conclusions concerning leaching behavior of coal mining waste. Actually, under the vadose zone conditions, the amount of percolating water is low compared to the mass of deposited rock. At a mean moisture content ranging from several to $>10\%$ wt, and average natural moisture content accounting for about 6% wt, the stream of percolating water will account for 6% wt, i.e. about 9.5% vol. This is equivalent to a column of water about 1.9 m high in a waste layer 20 m high. At the mean annual precipitation in the USCB area accounting for 700 mm/a and infiltration rate for the Upper Silesia coalfield area of 420 mm/a (0.42 m), a single water exchange in the waste dump 20 m high will last for about 5 years. This rough estimation shows that the process of contaminant leaching and transport to groundwater can be a long-term process, in addition retarded by a number of factors, e.g. filling up the retention capacity of a dump.

In the environmental evaluation and monitoring of coal mining dumps and engineering constructions built of mining waste, their long-term effects should be therefore strongly considered.

III.6.4. Environmental behavior of disposed mining waste

III.6.4.1. Testing methods

The above conclusion, along with the double nature of the pollution potential of sulfidic mining waste rock, suggests the necessity of applying testing methods specific for this kind of material and its exposure to environmental conditions. As most of the processes determining the loads and concentrations of pollutants occur within the mining dump, which forms an anthropogenic vadose zone, the testing methods were focused on either direct observation of the processes of contaminants' generation, release and transport along the profiles of the existing dumps and engineering constructions (Twardowska, 1981; Twardowska et al., 1988; Szczepańska and Twardowska, 1999; Helgen et al., 2000;

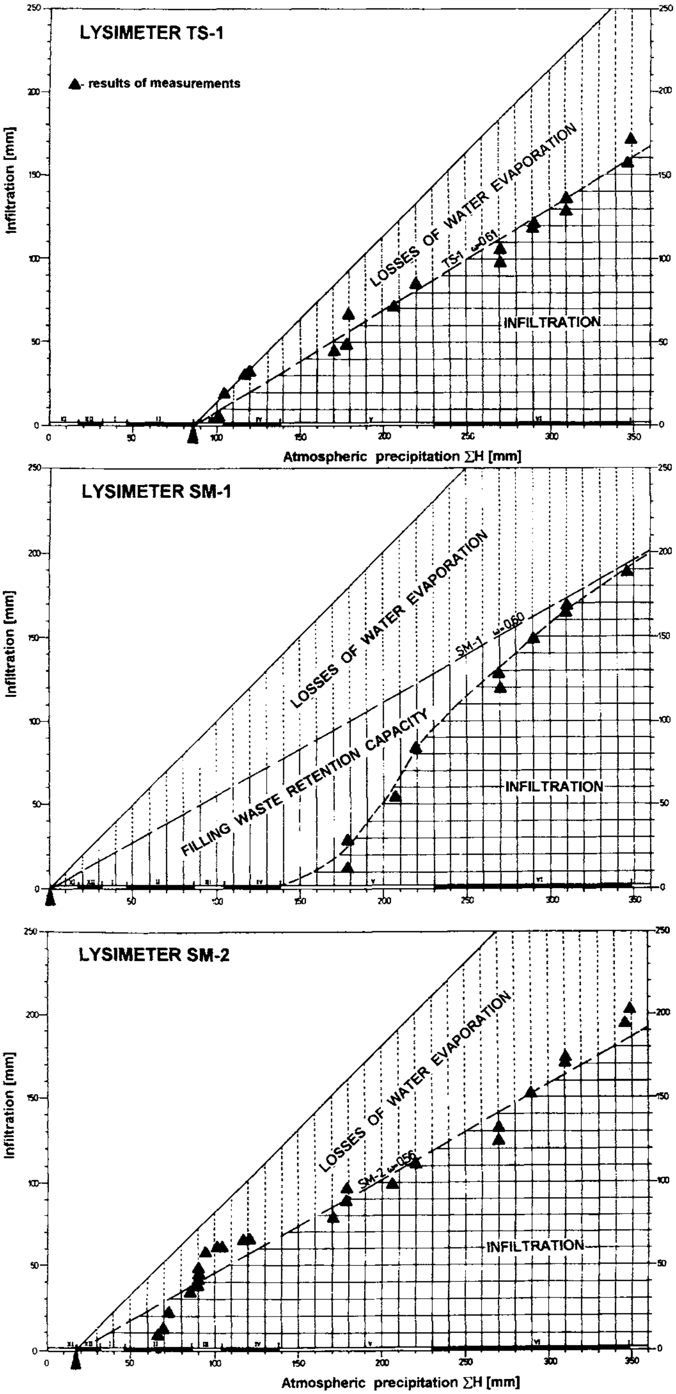


Figure III.6.12. Infiltration vs evaporation in the surface coal mining waste layer 1.5 m thick in 12 years' hydrologic cycle (lysimetric studies).

Hockley et al., 2000) or simulation of the real conditions in the geochemical kinetic tests. The concept behind the development of kinetic tests or anthropogenic vadose zone monitoring is to elucidate the mechanisms and kinetics of formation of contaminant loads in order to correctly predict, and subsequently attenuate, the chemical constituents leached from the rock matrix or the bedrock before the recoverable groundwater resources become degraded. The tasks of geochemical kinetic tests are to provide data on the oxidation rate, retardation period for onset of acidification (lag time), metal release and loading in the leachate from waste. A comprehensive review of geochemical kinetic tests and vadose zone monitoring methods with respect to mining wastes are presented in a fundamental publication by Hutchinson and Ellison (1992). The columns and humidity cells reported by Environment Australia (1997) are those most frequently used laboratory-based techniques; column tests being considered more representative for simulating field conditions. Humidity cells have been developed by the mining industry for testing overburden materials in opencast mines. The duration of a standard testing procedure for this technique is 8–10 weeks or more, which is considered to be enough for evaluation of a lag period for an overburden (Environment Australia, 1997). The lag period for the mining waste from the USCB lasts for several years. Therefore, this technique cannot be used directly for acid generation assessment. The authors modified it successfully for assessment of kinetics of sulfide oxidation measured as sulfate production and release.

The further development of the testing methods based on the simulation of time-dependent changes that occur in waste, leads to the integrated and unified, and at the same time waste-, use- and site-specific "tailor-made" approach to evaluation of leaching behavior of various solid waste materials (Eighmy and van der Sloot, 1994; Quevauviller et al., 1996). Apart from the variety of methods and protocols, the basic scheme used by the authors, which comprises characterization of waste materials and long-term tests that can be conducted for a period of months or even years, are discussed below.

For obtaining correct qualitative and quantitative information, the applied geochemical kinetic testing methods were focused on providing procedures close to the actual conditions of the environmental exposure. In particular:

(i) For evaluation of the dynamics of soluble constituents' leaching occurring in a fresh wrought material, a sequence of 10 columns ϕ 0.4 m, $H_{\mathrm{ef}} = 2.0$ m, filled with fresh wrought coal mining waste of a natural grain size was used. Distilled water of pH 6.5, equivalent to the pH value of rain water in the area, was added to the first column in portions corresponding to the mean annual daily precipitation in rainy periods, and the leachate was consecutively directed to the subsequent columns, simulating the total actual dump thickness of 20 m.

(ii) Sulfide decomposition kinetics, generation and release of contaminants, along with the water balance of the surface vadose zone layer of the typical coal mining wastes deposited in dumps were studied in the lysimetric investigation described above (Fig. III.6.9) for 12 years.

(iii) The role of *T. ferrooxidans* in pyrite decomposition at the colliery dumps was estimated on the basis of active cell number in the surface layers of different dumps up to a depth of 100 cm below the surface.

(iv) Transformations of chemical composition of pore solution along the dump vadose/saturated zone profile vs water exchange rate have been studied on core samples of a natural moisture content taken along the dump profiles of the age defined from the dump construction scheme. Pore solution has been extracted from the rock by a pressure method under nitrogen and analyzed for metals using ICP-OES. The method is routinely used by the authors in different cases and environmental impact assessment studies, from which come examples of different situations, presented in the chapter.

(v) Transformations of groundwater chemical composition in the saturated zone in the vicinity of a coal mining dump have been studied during the routine local monitoring programs and exemplified by the data from 1994–2002 for the network of 28 monitoring wells in the Smolnica site.

III.6.4.2. Time-dependent transformations of chemical composition of pore solution and leachate from mining waste

Environmental behavior of sulfidic mining waste disposed in dumps displays two major phases of macro- and trace elements leaching of different dynamics dictated by the constituents leached and controlling factors specific for the process.

- *Phase I*: Leaching of soluble constituents available in the fresh wrought mining waste, mainly chlorides and sulfates. The process is controlled by the hydrology of the dump, and availability and vertical redistribution of soluble constituents.
- *Phase II*: Leaching of soluble constituents generated from the sulfide decomposition. The controlling factors are kinetics of sulfide decomposition and buffering capacity of the material.

III.6.4.2.1. Phase I: leaching of primary soluble constituents from fresh wrought mining waste

In this phase, the major constituents leached from the dump are macro-compounds, such as chlorides predominantly balanced by Na^+ ions and sulfate, generally occurring in fresh wrought rock in amounts not exceeding some 5% of the total sulfur content, and balanced by Ca^{2+}, Mg^{2+} and Na^+. In general, disposed material shows a deficiency of moisture content with respect to the retention capacity, while the amount of percolating water depends on the water balance of a dump under the vadose zone conditions. In the leaching of soluble constituents during the gravitational flow of percolating water from atmospheric precipitation through a mining waste layer, two stages can be distinguished.

1. Initial stage of unstable flow, when the deficient retention capacity of the material is gradually filled up by the subsequent portions of percolating water.
2. Phase of a stable flow, when water percolates through the whole waste layer; the beginning of this stage is indicated by the appearance of leachate from the dump toe.

Chlorides and the sodium ions balancing them, occurring predominantly in the primary pore solution of the rock and unconstrained by equilibria limitations, readily migrate with infiltration water filling up deficient retention capacity of consecutive dump layers by subsequent portions of infiltrating precipitation water. It results in the vertical redistribution of chloride content along the dump profile, showing a decrease in the upper part of the profile, and higher concentrations in consecutive layers, increasing downwards proportionally to the deficiency of the retention capacity (Fig. III.6.13). Due to high dynamics of chloride migration, a single water exchange in a particular layer is generally enough to reduce chloride content to the permissible level (MCL), therefore the time required to reach this level is controlled by the single water exchange rate within the dump. Considering the time required for thorough exchange in a dump several meters thick, in a short time after waste disposal the chloride content in pore water will be negligible in the uppermost layers of a dump, whereas the concentrations of this ion in leachate at the dump toe within several years after its appearance will be many times higher than in the original pore solution of mined rock. Its concentration in leachate will be proportional to the thickness of the layer and the retention capacity deficit and water exchange rate in the layer.

Chloride concentrations in actual pore solutions of dumps constructed of mining waste of elevated chloride salinity show the specific pattern described above, which reflects the shifting of maximum concentrations from the top in a freshly constructed layer downward in older dumps and a gradual decrease up to a uniform low residual concentration in dumps, in which the thorough pore water exchange has already been completed (Fig. III.6.14).

The pattern of a vertical redistribution of sulfate in the pore solution of the vadose zone of a dump in the initial stage, when primary sulfate load in rock matrix exceeds sulfate generation, strongly depends upon the balancing cation. In the rock of a moderate up to high NaCl salinity, where the bulk of the cation exchange capacity of clay minerals is occupied by Na^+ ions balancing released sulfate, the leaching behavior is similar to that of chlorides. To summarize, for chloride-bearing waste, the leachate quality will be controlled by the released primary load of sodium chlorides and sulfates. In materials of low chloride salinity, the sulfate concentration along the vertical profile of the waste layer is controlled by the geochemical constraints (equilibrium with gypsum and carbonate

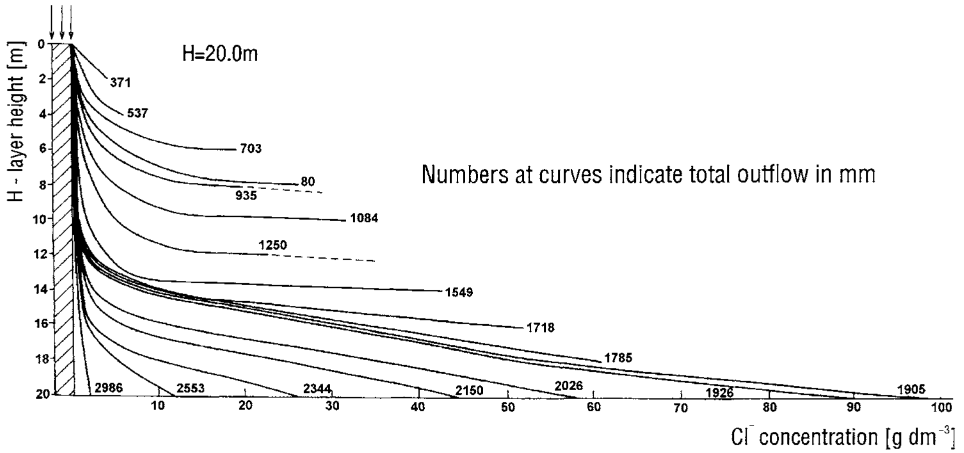


Figure III.6.13. Chloride redistribution along the vertical profile of fresh wrought minestone layer 20 m thick. Column leach experiments.

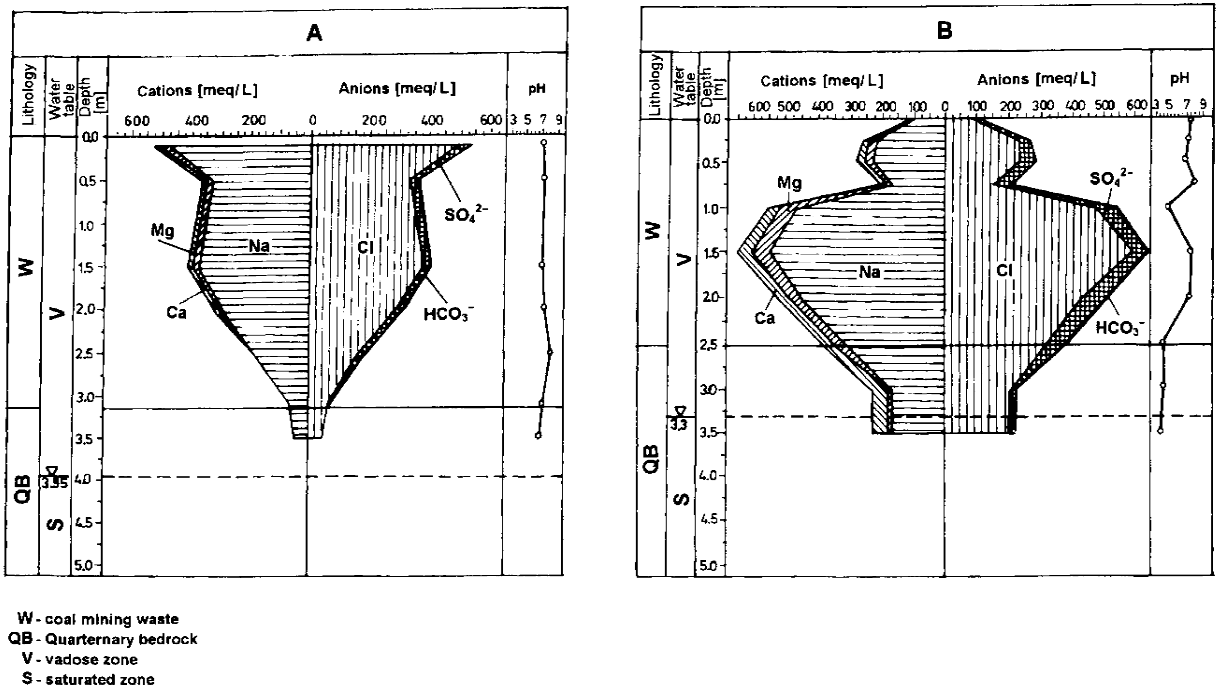


Figure III.6.14. Pattern of chloride redistribution along the vertical profiles of coal mining dumps vs waste age. (A) Freshly disposed waste; (B) weathered waste.

equilibria). The time of a single water exchange in a waste layer 1.5 m thick, estimated for the mean natural humidity of a surface waste layer (7% wt) and infiltration rate of 400 l/m^2 a, is 157–183 days, i.e. about a half-year period after the filling is required to satisfy the water retention capacity.

At the initial stage of leaching, the buffering capacity of carboniferous rock material is sufficient for neutralization of relatively low loads of acidity: the pH value of leachate is generally neutral or slightly or even moderately alkaline within the stability field of trace elements occurring in the matrix of carboniferous rock or the bedrock of a dump. Therefore, no elevated release of toxic trace elements occurs. Nevertheless, due to the concentration of high volumes of this waste in a relatively limited area, and the leaching pattern of macro-constituents showing downward vertical redistribution, the deep deterioration of groundwater quality in the vicinity of a coal mining dump by the extensive release of macro-components already occurs in the initial stage of the dump construction.

III.6.4.2.2. Phase II: leaching of soluble constituents generated from sulfide decomposition

III.6.4.2.2.1. Controlling factors

The environmental behavior of coal mine wastes at this stage is controlled mainly by the sulfide decomposition and is a resultant of two opposite processes: acid load generation being a function of sulfide content and its reactivity and the buffering of acid loads at $pH \approx 7.0$ determined by the content and availability of calcium and magnesium carbonates. The long-term lysimetric experiments (Fig. III.6.9, Table III.6.5), along with results of the direct field studies in mining waste dumping sites confirmed sulfide decomposition to be a first-order process described by Equation (III.6.6). In the changeable hydrological and temperature conditions in subsequent years, the half-period of sulfate decomposition was invariably stable for each of the three kinds of waste and ranged from 328 days (about 1 year) for a buffered 7 year old material from Westphalian C series TS1 to 1440 days (about 4 years) and 1037 days (about 3 years) for non-buffered fresh wrought material from Namurian C series SM1 (Fig. III.6.15, Table III.6.5).

The comparative analysis of laboratory and long-term lysimetric experiments leads to several conclusions, the most important of them are: (i) The kinetics of sulfide decomposition appeared to be stable for a particular rock material, but are distinctly higher for 10–12 years old acidic material than 0–12 years old alkaline rock from the same site. This suggests changes in the prevailing mechanisms of pyritic sulfide oxidation, e.g. from the stage I slower abiotic process at $pH > 4.5$ to the stage II reactions at pH 2.5–4.5 with much faster process catalyzed primarily by the activity of *T. ferrooxidans* (Kleinmann et al., 1981); the growth of *T. ferrooxidans* in the surface layer up to a depth of 100 cm in different coal mining dumps proved that the number of bacteria in waste (maximum 10^5 cells/g) is not large enough to significantly affect pyrite oxidation (Fig. III.6.16), though its catalytic effect in Reaction 2 according to Kleinmann et al. (1981) should not be neglected (Twardowska, 1986, 1987). In carbonate-depleted rock, bacterial activity can play a more important role (Environment Australia, 1997). (ii) Sulfide reactivity is determined by the location of the rock in the lithological profile of the carboniferous sequence (and thus mainly by the textural types of sulfides) (Fig. III.6.2); data obtained

Table III.6.5. Long-term lysimetric studies on water balance, kinetics of sulfide oxidation and constituent leaching in the natural 12 years' hydrologic cycle (1984–1996).

Lysimeter	Series	Waste age t_0 (years)	Initial sulfur content S[a] in waste (%)			Concentration range of major hydrochemical parameters			Reactive sulfide half-life $t_{1/2}$ (days)	Reactive sulfide 99% decomposition time t_{99} (years)
			S_t	S_S	$S_{S(r)}$	pH	γ_{25} (μS/cm)	SO_4 mg/l		
TS1	Westphalian C	7	1.72	1.48	0.062	6.8–8.5	900–55,000	372–3,461	328	6
SM1	Namurian C	0	0.90	0.81	0.087	6.4–9.1	770–22,500	332–7,967	1,440	26
SM2		10			0.140	2.6–6.3	530–6,400	298–6,153	1,037	19

[a] S_t, total sulfur; S_S, sulfide sulfur; $S_{S(r)}$, reactive sulfide sulfur.

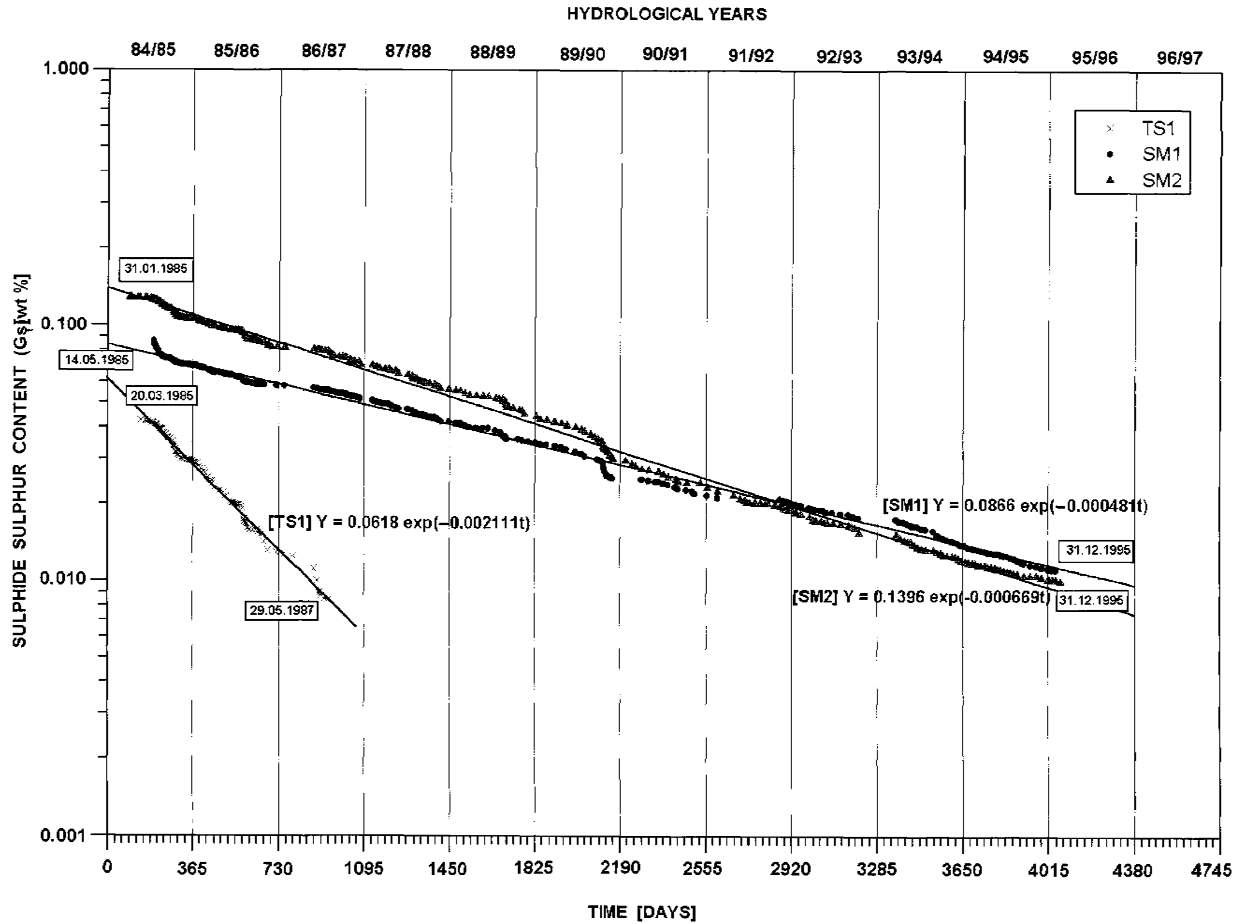


Figure III.6.15. Kinetics of sulfide decomposition in surface coal mining waste layer 1.5 m thick. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1994–1996). Description as in Figure III.6.9.

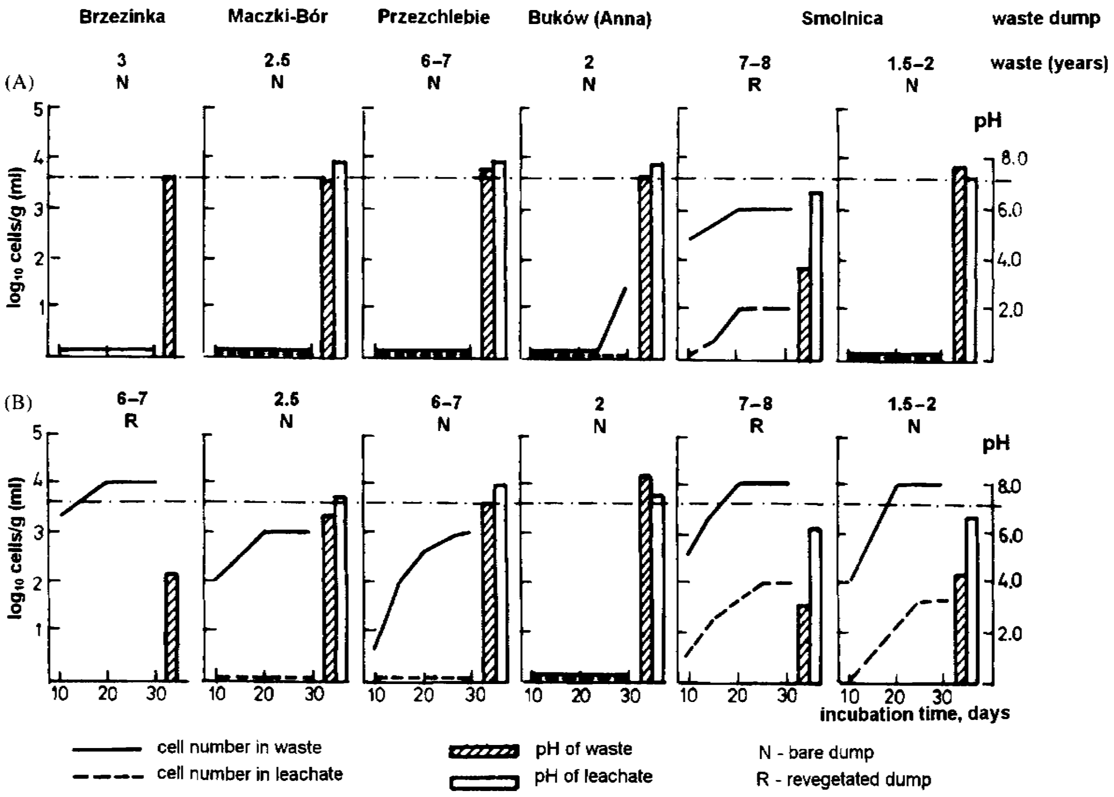


Figure III.6.16. Growth of *T. ferrooxidans* in the surface vadose zone layer of coal mining dumps. (A) Summer period; (B) autumn period.

from the lysimetric studies show good qualitative correlation with the laboratory experiments. The half-period of pyritic sulfide decomposition, estimated from laboratory kinetic tests, is though distinctly shorter than in the lysimetric studies; for the fresh wrought rock SM, it appeared to be 45–52%, for TS, even 80% shorter than that obtained from the lysimetric experiments due to optimum exposure of pyrite to air and moisture. (iii) Values of the initial load of sulfide undergoing oxidation, derived from the results of the long-term dynamic experiments and described by the first-order Reaction (6), appeared to be much lower than the total load of sulfides in the fresh wrought material and comprised: 11.0% (SM1), 17.7% (SM2) and 4.2% (TS1) of S_s (Table III.6.5). It results from the surface character of sulfide oxidation and proves that just part of the pyrite is available to the oxidation and release processes.

III.6.4.2.2.2. Macro-components release and chemical transformations of pore solutions

The composition of leachate from waste rock material in this stage follows the pattern defined by the dynamics of sulfide oxidation generating acidity and sulfates, as well as by the buffering capacity of rock. The beginning of the phase II of leaching starts after a single water exchange in the waste layer. After this period, primary soluble compounds (chlorides and sodium-balanced sulfates) are practically removed from the rock matrix. The macro-components' leaching is controlled by the sulfide decomposition – sulfate/acidity generation and release process. Therefore major anions in the leachate become sulfates (Fig. III.6.17) and balancing cations, mainly Ca^{2+} (Fig. III.6.18) and Mg^{2+} ions are in proportion, showing that the buffering mineral is dolomite. The succession of the dry periods when the acidity/sulfate loads are generated and stored within the material, and wet periods when the leaching of generated loads from the material by the percolating infiltration water prevails, result in observed fluctuations of sulfate concentrations in leachate from the surface layer, which reflect the fluctuations of precipitation (Fig. III.6.10).

The alkaline reaction of leachate reflects the heterogeneity of the disposed rock, which causes the acidification of low-buffered waste SM to start after different periods of exposure, generally after about 10–12 years of disposal. This moment illustrates leachate from 10 year old waste (SM2). In 10 year old waste (SM2), the depletion of buffering capacity below the critical level resulted in a sharp drop of pH from 6.5 to <3.0 and acidification of material to a deep level (Fig. III.6.19), with a simultaneous increase of sulfate concentrations in leachate from about 500 to above 6000 mg SO_4/l due to intensification of pyritic sulfide oxidation and dissolution of gypsum under conditions of the lack of equilibria limitations. In the next 10 years of exposure, the concentrations of sulfates in leachate had more than a twofold increase in concentration as a result of leaching from the fresh wrought rock, and just in the last 2 years was the concentration brought close to that in the input water due to the gradual depletion of sulfides (Fig. III.6.17). The general pattern of sulfate release shows a gradually declining tendency in 12 years period, due to the depletion of the exposed sulfide load (Fig. III.6.17, Table III.6.5). In the acidic conditions (SM2), an increase of pH during the long-term leaching cycle was observed (Fig. III.6.19), in parallel with an increase of Ca^{2+} (Fig. III.6.18) and an elevated occurrence of Al^{3+} and SiO_2 in leachate, which is specific for the transformations that were proceeding. In this stage, the major buffering compounds are aluminosilicates: kaolinite

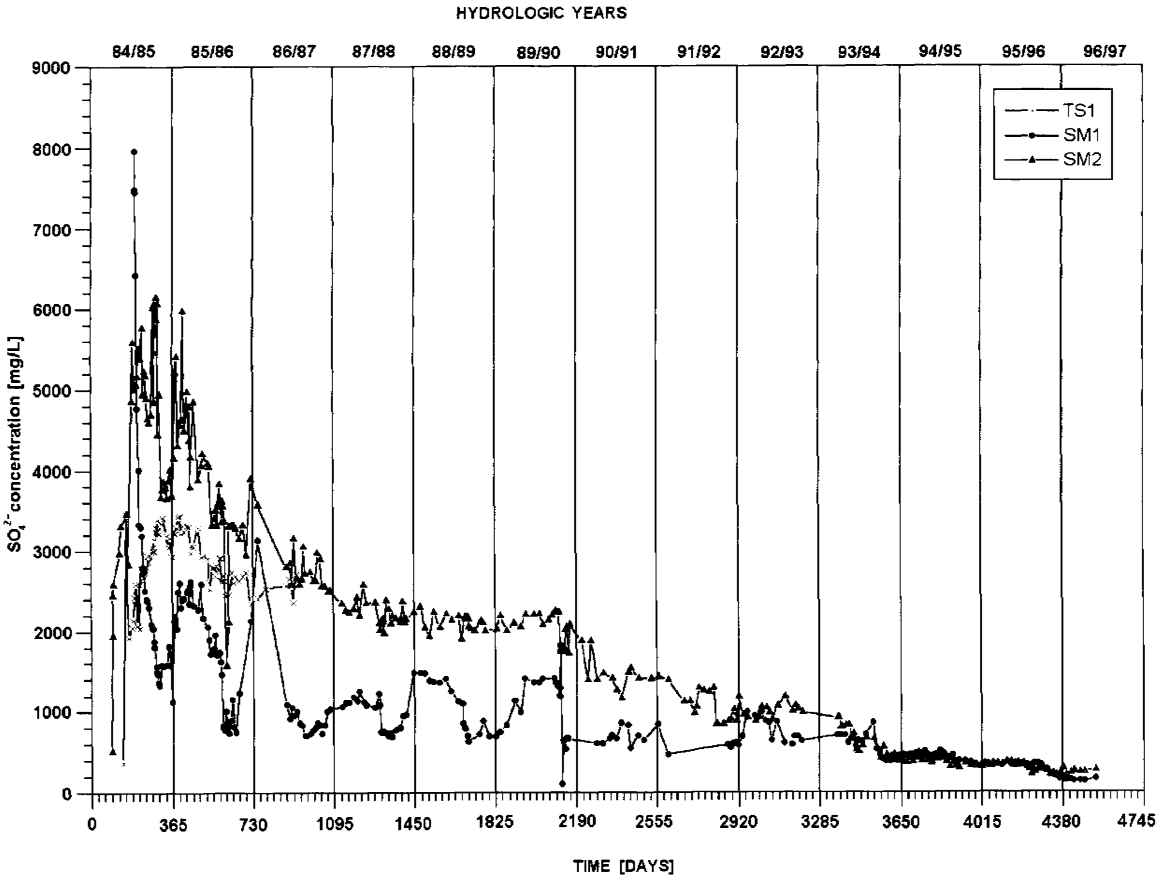


Figure III.6.17. Sulfate leaching from the surface coal mining waste layer 1.5 m thick of different buffering capacity. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1984–1996).

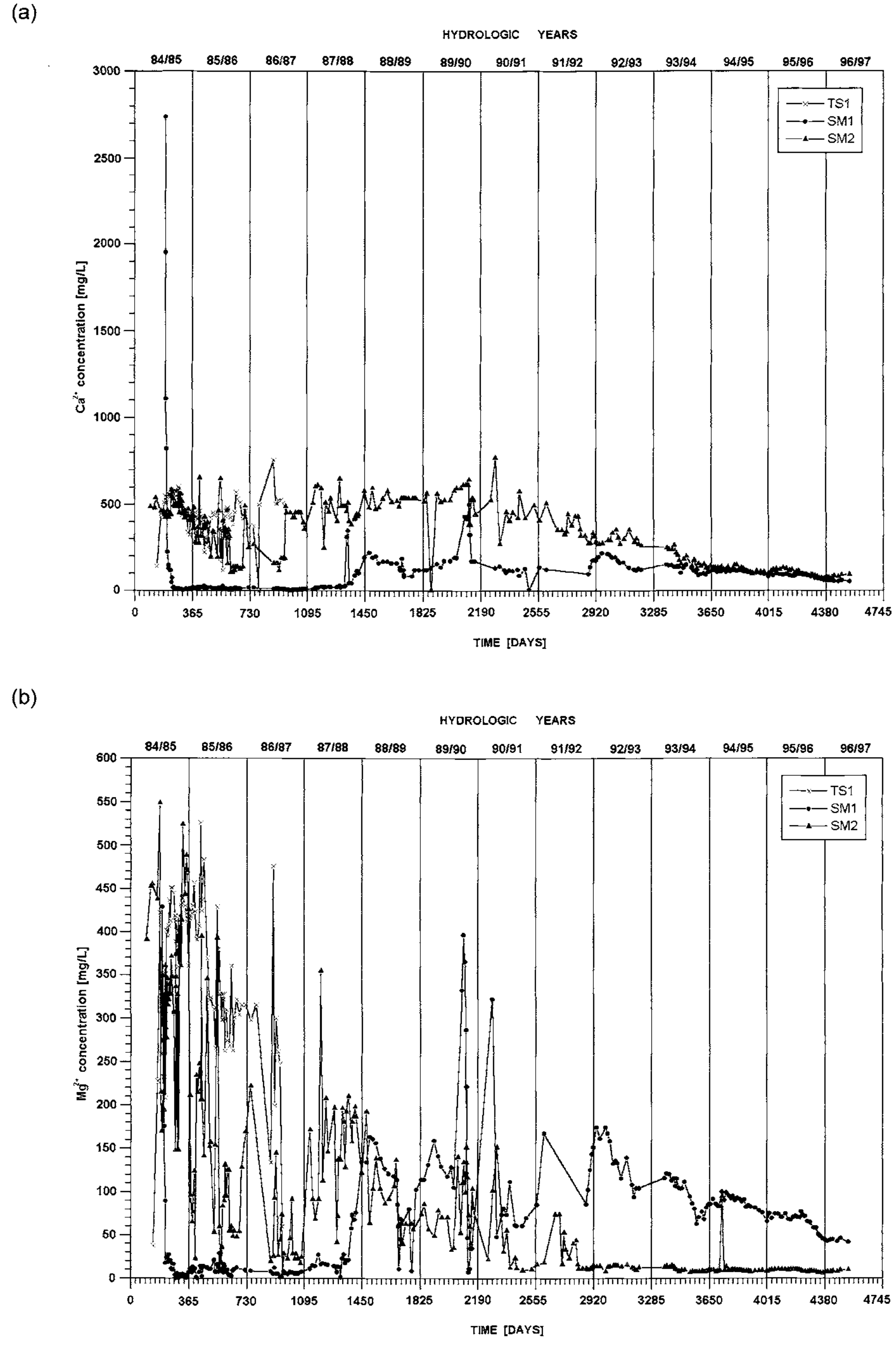


Figure III.6.18. (a) Calcium and (b) magnesium leaching from the surface coal mining waste layer 1.5 m thick of different buffering capacity. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1984–1996).

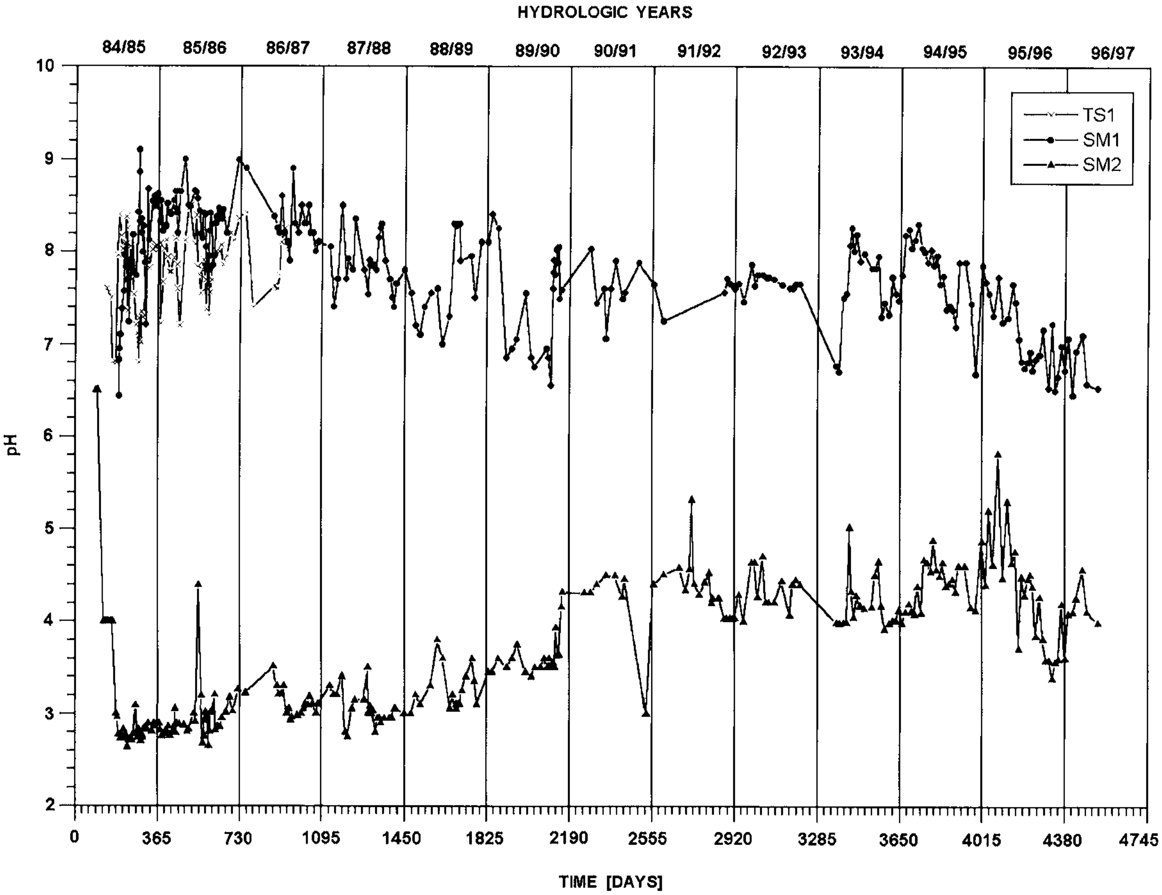


Figure III.6.19. pH values in the leachate from the surface layer of coal mining waste 1.5 m thick of different buffering capacity. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1984–1996).

and calcic (potassic, sodium) feldspar. Hydrogen ions displace Al^{3+} ions from their position in the lattice of clay minerals, dissolve kaolinite and react with feldspars, forming alumino-rich clay minerals, while Ca^{2+} is released into solution according to the reactions (Palmer, 1978; Lapakko, 1987):

$$(Al{\cdot}6H_2O)^{3+} + H_2O \rightarrow (AlOH{\cdot}5H_2O)^{2+} + H_3O \quad \text{(III.6.7)}$$

$$Al_2Si_2O_5(OH)_4 + 6H^+ \rightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O \quad \text{(III.6.8)}$$

$$CaAl_2Si_2O_8 + 2H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} \quad \text{(III.6.9)}$$

These reactions seem to be major acid consuming ones at the stage of deep acidification of the material SM2. Temporary growth of chloride and sodium concentrations proves the decapsulating effect of preceding physical decomposition of particle size.

In addition in the younger non-acidified material (SM1), weathering decomposition of rock grains rendered available new loads of dolomite formerly encapsulated in rock particles that somewhat extended the decreasing buffering capacity of the material, which was reported by other authors also (Toran, 1987).

Both sulfate concentrations and chemical composition of leachate from the 7 year old material TS1 from the top youngest Westphalian C series buffered by Ca^{2+} and Mg^{2+} carbonate minerals (mainly dolomite), which are uniformly disseminated in the rock matrix, displayed a considerable stability at the level controlled by the carbonate and gypsum equilibria in the system Ca–Mg–C–O–H–S (Garrels and Christ, 1965; Brookins, 1988).

III.6.4.2.2.3. Trace elements leaching

The water balance that has been presented and the mechanisms of acid generation are common for most mining wastes. Since pH and Eh are critical factors controlling the release and leaching of trace elements, the acidification of pore solution in oxic conditions in the anthropogenic vadose zone of mining waste dumps should cause mobilization of heavy metals. Particularly susceptible to release are trace elements occurring directly in the centers of acidification, i.e. those being the major or accessory components of sulfides. Of different mining rejects, coal mining waste is the most abundant, but the least hazardous material also in terms of trace element concentrations, which do not exceed the range of average values for soil (Table III.6.4). In buffered material, as well as in low-buffered mine wastes in the phase I, and in the initial stage of the phase II, when buffering capacity is above the critical level and acidification has not yet developed, no release of trace elements in elevated concentrations is observed.

Acidification of the low-buffered material and simultaneously about a twofold increase of Eh results in a release into leachate of almost all analyzed elements, of which SiO_2, Zn and Mn are in amounts more than an order of magnitude higher than from the same material in the buffered phase. Metals appeared in the acidic leachate from 10–22 years old waste in a descending concentration order: $(Fe^{2+}) > Zn > Al > Mn > Sr > Li > Ni > B > Co > (Fe^{3+}) > Cu > Cd$ (Fig. III.6.20). Iron plays a different role in the various stages of leaching under acidic conditions. In the initial stage of a deep acidification when pH drops below 3 and Eh $\approx$ 0.3, iron can appear in pore solution in

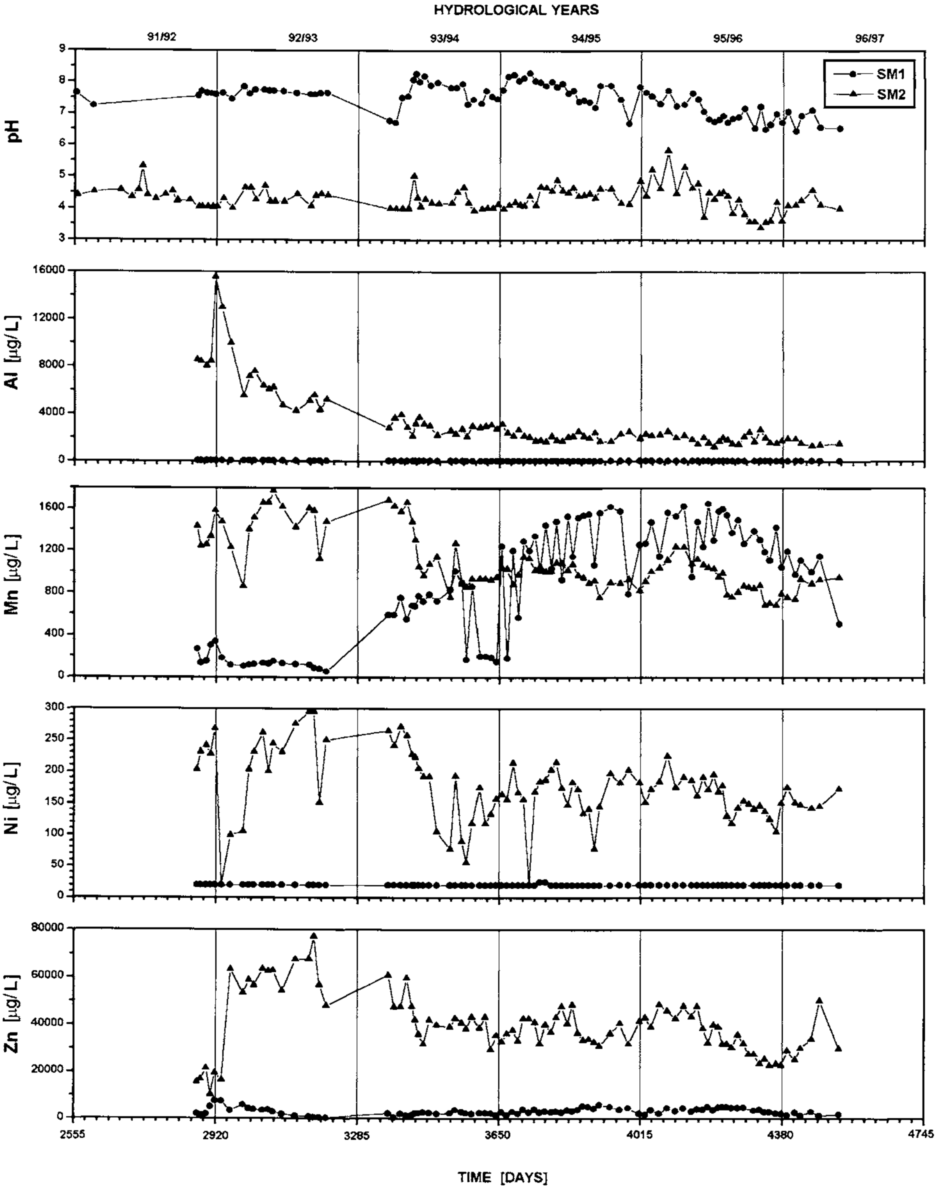


Figure III.6.20. Aluminum, manganese, nickel and zinc leaching from the surface layer of coal mining waste 1.5 m thick of different buffering capacity exemplified in the results of the hydrologic years 1992–1996. Long-term lysimetric studies in the 12 years' natural hydrologic cycle (1984–1996).

fairly high concentrations, from several to >100 mg Fe dm^{-3} (waste 10–12 years old), mainly as Fe^{2+} and $FeSO_{4aq}$ species. Along with gradually increasing pH to ≈ 4 at Eh ≈ 0.45, iron readily precipitates forming goethite and crystals of secondary sulfate minerals (melanterite, copiapite, halotrichite), abundant as coatings in disposed rock material 18–22 years old. Concentrations of such elements as Zn, Al, Mn, Cd, Ni exceed more than tenfold the MCL for drinking water, according to SDWA, WHO and Polish national standards. Geochemical speciation with the use of computer programs WATEQ4F, Visual MINTEQ v. 2.01 and PHREEQC 2.7 shows that trace metals are present in leachate most frequently as Me^+ and $MeSO_{4aq}$ species.

Taking into consideration the volume of acidic leachate and its long-term impact, heavy metals released from mining dumps, also from coal mining waste, may pose a serious risk to the aquatic environment, while the most problematic metal contaminants are dependent on the mined mineral (Table III.6.6).

III.6.4.3. ***Formation of pore solutions along the profile of a waste dump***

Presented examples of long-term lysimetric studies show that even a layer of coal mining waste 1.5 m thick can be a serious source for vadose zone and groundwater contamination lasting for decades, while maximum contaminant release may have non-linear, time-delayed character. Chemical composition of pore solutions along the profile of coal mining waste dump that may be some scores of meters thick is controlled by the same factors as a surface layer i.e. by acid generation potential/buffering capacity and water exchange rate in the waste layers downward in the profile. Formation of pore solutions in a waste dump has been exemplified in the hydrogeochemical profiles of the anthropogenic vadose/saturated zone of the coal mine dumps about 11 m thick, constructed of the material analyzed above. This is shown for the Smolnica dump (SM) in Figure III.6.21 and for the Siersza-Misiury dump (TS) in Figure III.6.22.

In the hydrogeochemical profile of the Smolnica dump constructed of low-buffered material disposed in two layers, 3.5 and 7.5 m thick, which are 15 and 10 years old, respectively, both acidification and distinct differentiation of chemical composition of pore solutions have been observed (Fig. III.6.21). Concentrations of the major species in the pore solution in the waste layer show a typical vertical redistribution pattern, specific for the vadose zone in the conditions of the lack of equilibria constraints, and reflect decreasing water exchange rate in the subsequent waste layers downward the profile. Pore solution is the sulfate type, SO_4–Mg–Fe in the top layer 0–1.5 m and SO_4–Na–Mg in deeper layers of the profile. Low chloride concentrations (mean from 100 to 500 mg Cl/l) prove high water exchange rate (leachate from the fresh wrought waste contains several thousands mg Cl/l). Along the whole profile of the vadose zone, advanced oxidation of all textural forms of sulfides and precipitation of gypsum was observed. The chemical composition of the pore solution showed acidification up to pH 4.0 and extensive sulfate release (Table III.6.6). Sulfate mineralization in the pore solution along the whole profile of the vadose zone many times exceeded the MCL for drinking water according to Polish regulations (Directive of the Minister of Health, 2000), i.e. TDS up to 30 times and SO_4 up to 82 times, and according to WHO guidelines, up to 66 times (Galal-Gorchev, 1993); concentrations of SO_4 in pore solutions and leachate were also up to 10–16 times higher than MCL for liquid waste discharged to waters or soil (Directive of the Minister of Environment, 2002a). The chemical composition of water in the saturated toe layer is a resultant of mixing leachate from the overlaying vadose zone with groundwater of the saturated zone. Despite significant dilution, the concentrations of both TDS and SO_4 still

Table III.6.6. Examples of drainage, pore solution and leachate quality at several mining waste disposal sites.

Parameter, constituent (mg/l)	Coal mining waste, USCB, Poland						Ore mining waste, Canada^a and N. Guinea^b			
	Leachate from waste layer 1.5 m thick (lysimeters)		Pore solution along the dump profile				Tailing pond in uranium mine^a-seepage	Silver mine waste dump^a seepage	Under-ground copper mine^a water	Copper mines waste dumps-leachate^b
	SM1^1 1.5 m	SM2^1 1.5 m	SM^1 0–10 m	TS^2 0–10 m	PS^3 0–3 m	P^4 0–10 m				
Waste age (years)	9–10	19–20	10–15	7	6–8	5–13	Abandoned	Active	Active	Active
pH (–)	6.70–8.24	3.92–4.64	4.0–5.2	5.8–8.5	4.04–7.62	3.39–7.35	2.0	2.8	3.5	4.0–9.2
Na	7.58–84.22	9.12–88.50			2,044–12,492	638.6–3,236.4				20–38
TDS	900.2–1,966.3	653.2–1,826.6	4,162–24,287	4,030–5,234	4,071–32,541	3,004–14,603				
Cl	4.28–335.2	20.21–198.3	84.8–1,276.2	123.4–493.6	50.0–12,131	52.9–3,164.6				
SO_4	384.6–997.6	377.4–1,188.8	2,829–16,511	2,541–3,711	1,521–5,010	1,762–8,187	7,440	7,650	1,500	
Al	<0.06–0.06	2.11–15.54			<0.06–0.166	<0.06–11.63	588.0	359		2–25
As						<0.05– < 0.05	0.74	25.0	0.05	
Cd	<0.005–0.005	<0.005–0.035			<0.005	0.005–0.173				<0.001–0.028
Cu	<0.01–0.02	0.018–0.100			0.047–1.936	0.098–0.970	3.6	89.8	16.5	0.001–235
Fe	<0.01–0.03	<0.01–0.07			0.31–14.28	<0.01–90.78	3,200	1,190	10.6	0.13–0.2
Mn	0.057–1.246	0.76–1.77			0.229–4.785	0.070–2.508	5.6	78.3	6.4	12–32
Ni	<0.02– < 0.02	0.077–0.295			<0.02–0.411	<0.025–0.501	3.5	8.0	0.06	
Pb	<0.05– < 0.05	<0.05–0.05			<0.05– < 0.05	<0.050–0.428				<0.001–0.003
Zn	0.383–7.402	10.05–77.25			0.458–4.698	0.149–320.52				0.001–3.0

Coal mining waste dumps in Poland (own data): [1]SM–Smolnica waste dump, low-buffered waste; [2]TS–Siersza waste dump, buffered waste; [3]PS–Piast waste dump; [4]Przezchlebie waste dump.

[a]After Hutchinson and Ellison (1992) (Reference: Paine, 1987).

[b]After Jeffery et al. (1988).

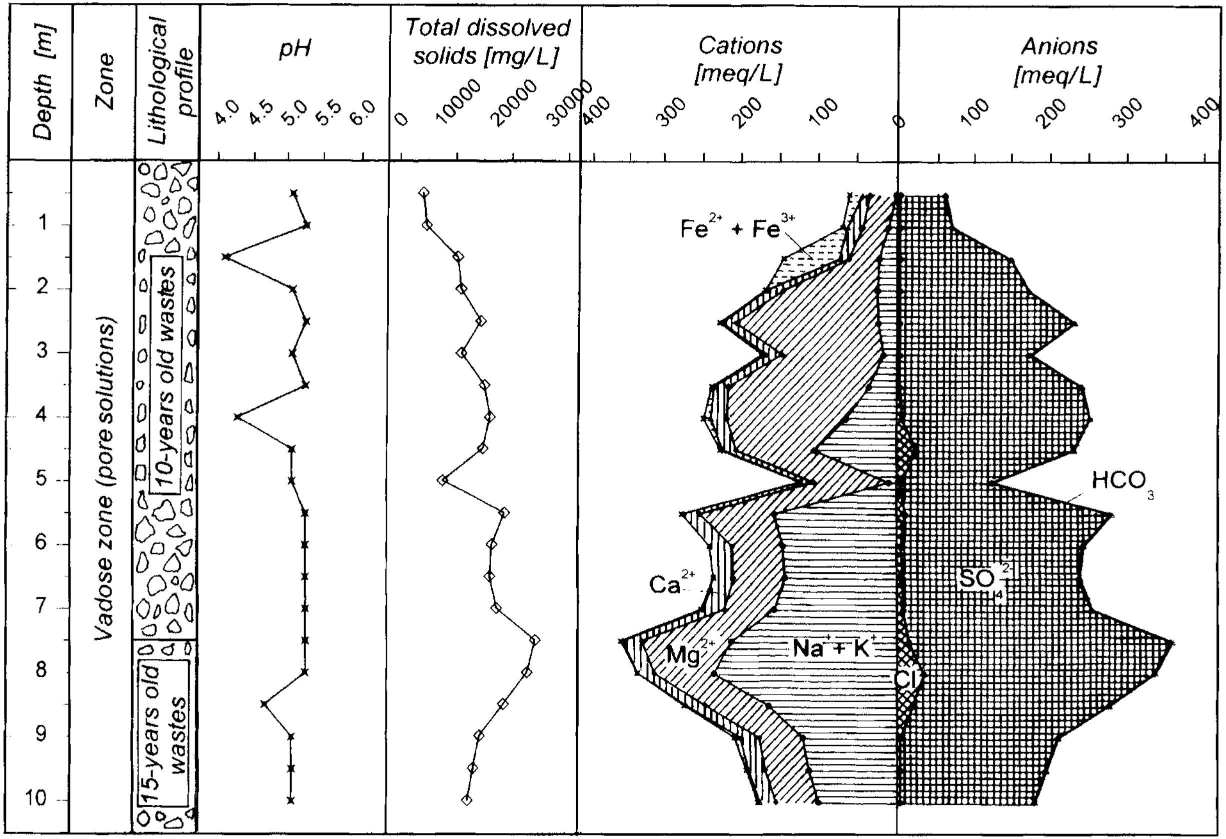


Figure III.6.21. Hydrogeochemical profile of pore solution within the low-buffered, acid generating waste SM (Smolnica dump).

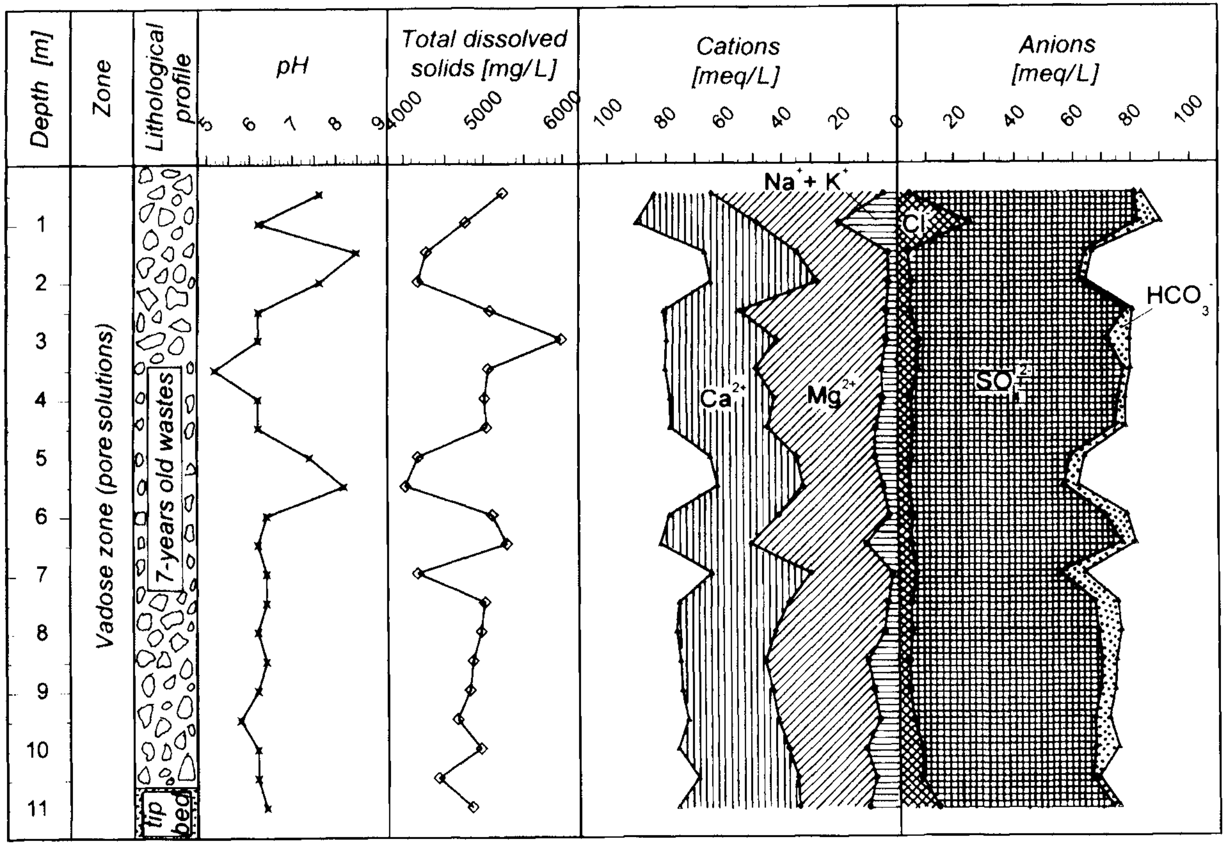


Figure III.6.22. Hydrogeochemical profile of pore solution within the buffered, non-acid generating waste TS (Siersza dump).

exceeded MCL by about an order of magnitude, causing serious deterioration of the groundwater quality.

In the profile of low chloride, buffered waste 7 years old (TS), the chemical composition along the profile is controlled by the equilibrium with gypsum and carbonate, and differs substantially from the pattern in the non-buffered material. Due to equilibria limitations, the concentrations of constituents along the whole profile are practically uniform (Fig. III.6.22). Pore solutions are of SO_4–Mg–Ca type, Mg:Ca ratio (in equivalent units) is close to 1, pH close to neutral, and gypsum precipitation is abundant along the whole dump profile. Due to the equilibrium constrains, the concentrations of both TDS and SO_4 are determined by the gypsum solubility (Table III.6.6). They are therefore significantly lower than the unconstrained concentrations in non-buffered wastes, though still 10–20 times higher than MCL for SO_4 in drinking water (Galal-Gorchev, 1993; Directive of the Minister of Health, 2000) and also several times exceeds MCL in liquid wastes discharged to water and soil (Directive of the Minister of Environment, 2002b).

The chemical composition of pore solution along the profile of another coal mining waste dump of the USCB, which consists of 3 layers of 1–13 years old material, also illustrates the time course of long-term environmental transformations of waste properties, from the buffered stage in the uppermost and youngest layer, through the acid generating stage in the middle layer and severe acidification of waste to pH 3.4 in the oldest layer. Elevated SiO_2 concentrations originate from the dissolution of kaolinite. High trace element release follows the sequence: $Zn \gg B > Fe > Ba > Sr > Al > P \approx Ni > Mn > Cu > Se \approx Mo \approx Cd$. The pollution potential of the oldest material appears to be the highest one (Fig. III.6.23, Table III.6.6).

This example also shows non-linear increase of the pollution potential of coal mining waste, resulting from the time-delayed depletion of the buffering capacity and acidification of the material. The data on leachate from acid coal mining and metal ore mining waste (Table III.6.6) prove the necessity of a careful evaluation and prediction of mining waste susceptibility to acidification and to adjust adequately the groundwater protection measures to the long-term leaching behavior of waste and to site-specific hydrogeological conditions.

III.6.4.4. Impact of mining waste dumps on the groundwater quality

Approximately 40–50% of dumping sites of high-volume waste all over the world, including mining waste, have been located in areas of unprotected aquifers used as a source of drinking water. The range and extent of the environmental impact of a mining waste dump, besides its short- and long-term pollution potential, largely depends on the hydrogeological conditions of the site, i.e. hydraulic conductivity and buffering properties of the bedrock and the dilution capacity of groundwater stream. The construction of a dump usually lasts for years; therefore, different layers and spatial parts of the dump display different pore solution exchange rate and its related chemical composition is dependent on the duration and mode of exposure to the atmospheric conditions. Hydrogeochemical profiles of the dumps illustrate this diversity (Figs. III.6.21–III.6.23). The construction period of the dump and its pattern, along with the heterogeneity of the disposed material,

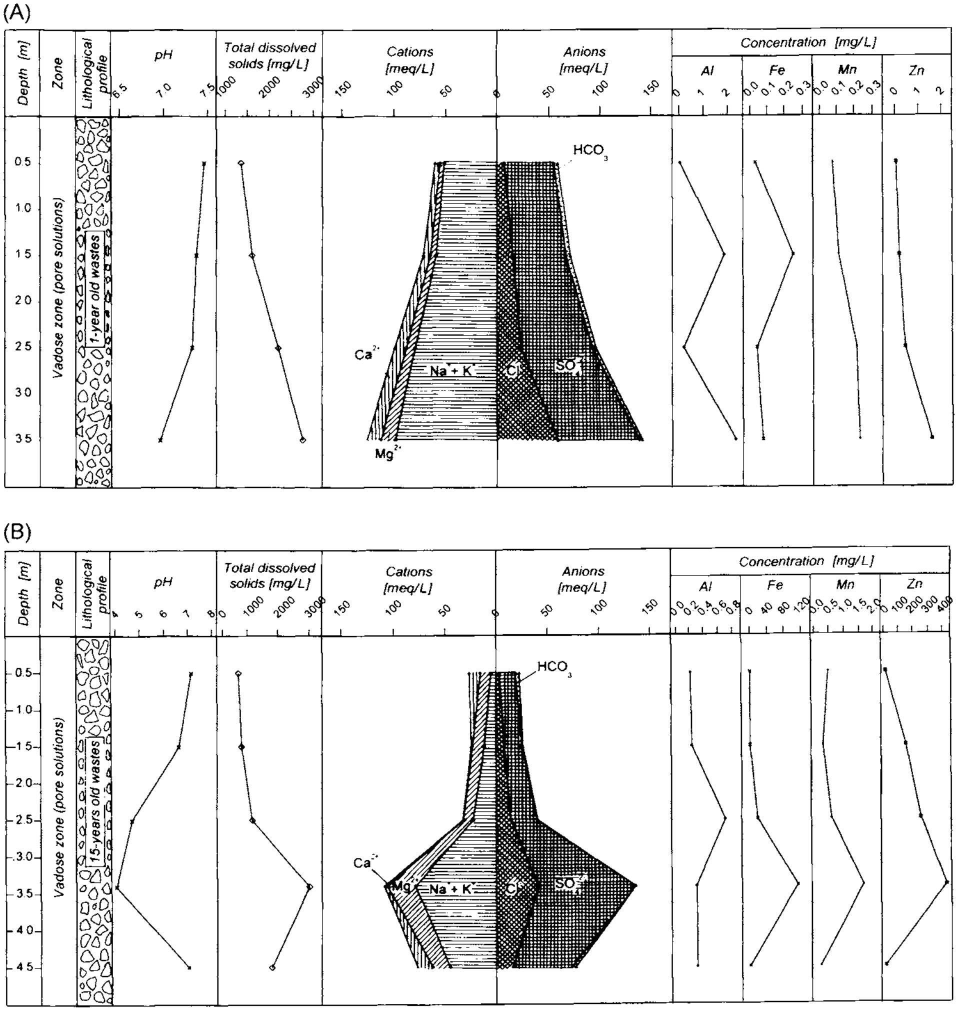


Figure III.6.23. Transformations of pore solution along the vertical profile of the Przezchlebie dump. Low-buffered waste undergoing changes in time from non-acidic (A – 1 year old waste) to acidic stage (B – waste layers 15 years old).

considerably affect the transformation of pore solution and leachate, and a resultant impact on the aquatic environment. Spatial and time-dependent variability of groundwater quality in the vicinity of a coal mining waste dump on the background of waste management and hydrogeological conditions will be exemplified here in the case study on the Smolnica coal-mining dump. The characteristics of material disposed, its leaching behavior and the pollution potential have been presented above, including results of long-term lysimetric studies on water balance (lysimeters SM1, SM2) and transformations of pore solution along the dump profile (SM).

III.6.4.4.1. Site characteristics

III.6.4.4.1.1. Waste characteristics and management

The Smolnica coal mining waste dump having total area $F_t = 130$ ha, thickness $H_t = 23$ m and volume $V_t = 13,845,000\ \mathrm{m}^3$ is located along the Bierawka river (USCB, Poland) (Fig. III.6.24). At the dump, weakly buffered granular coal mining waste of moderate to elevated chloride (0.050–0.245% Cl) and mean sulfide sulfur contents ($S_s < 1\%$) has been disposed in three layers since 1965, in the general direction N–S and E–W. Sulfide reactivity expressed as a sulfide half-life $t_{1/2}$ ranges from 1037 to 1440 days. Rock material heavily compacted by vibratory rollers remains permeable to air and water and due to rather high sulfide reactivity and low buffering capacity ($\xi = C_{\mathrm{buf}}/C_{\mathrm{ac}} \leq 0.70$) is susceptible to acidification in time (Twardowska et al., 1988, 1990). The older N part of the dump, constructed in 1965–1980 ($F = 34$ ha, $V = 7500 \times 10^3 \mathrm{m}^3$), from 1988 to 1997 was subject to residual coal recovery in the general direction W–E. After coal extraction by physical methods, waste has been re-disposed again. Technological processes caused disturbance of the primary constructed layers and increased exposure of waste to water and air during grinding, washing and sieving. Part E is the oldest part of the dump.

III.6.4.4.1.2. Hydrogeological conditions

The non-insulated quaternary aquifer in sandy gravel formations is underlined by impermeable tertiary muds. The free water table occurs 0.8–4.6 m below the ground surface. Groundwater in the dumping site area flows undisturbed in the general direction NE–SW to the riverbed (Fig. III.6.24).

III.6.4.4.1.3. Groundwater quality monitoring network

A local groundwater quality monitoring network (GWQM) consists of 28 wells (piezometers) installed in 1994 to yield groundwater samples from the uppermost quaternary aquifer up-gradient and down-gradient the waste management area. Water in the wells has been sampled 2–4 times a year. Isocontour maps (isopleths) of the hydrodynamic field and major water quality parameters were constructed by linear kriging using the SURFER computer program, Version 7 (Golden Software, Inc., 1999).

III.6.4.4.2. Groundwater quality transformations

Results of 9 years' (1994–2002) monitoring (Table III.6.7, Fig. III.6.25a–d) demonstrated generally stable good quality and lack of a strong anthropogenic impact on natural waters of the quaternary aquifer up-gradient of the waste dump. The leachate from the coal mining waste dump caused significant alteration of their chemical composition. It resulted in high (up to 80 times) increase of TDS and transformation of hydrogeochemical type of waters from SO_4–Ca into Cl–SO_4–Na, SO_4–Cl–Na–Ca–Mg or SO_4–Na–Ca down-gradient of the dump (Table III.6.7). Distinct trends in dynamics and directions of these transformations (Fig. III.6.25a–d) and analysis of cause–result nexus proved the controlling effect of such factors as waste age and management, as well as meteorological and hydrogeological conditions. In particular, the following general regularities were observed: (i) stable high sulfate concentrations,

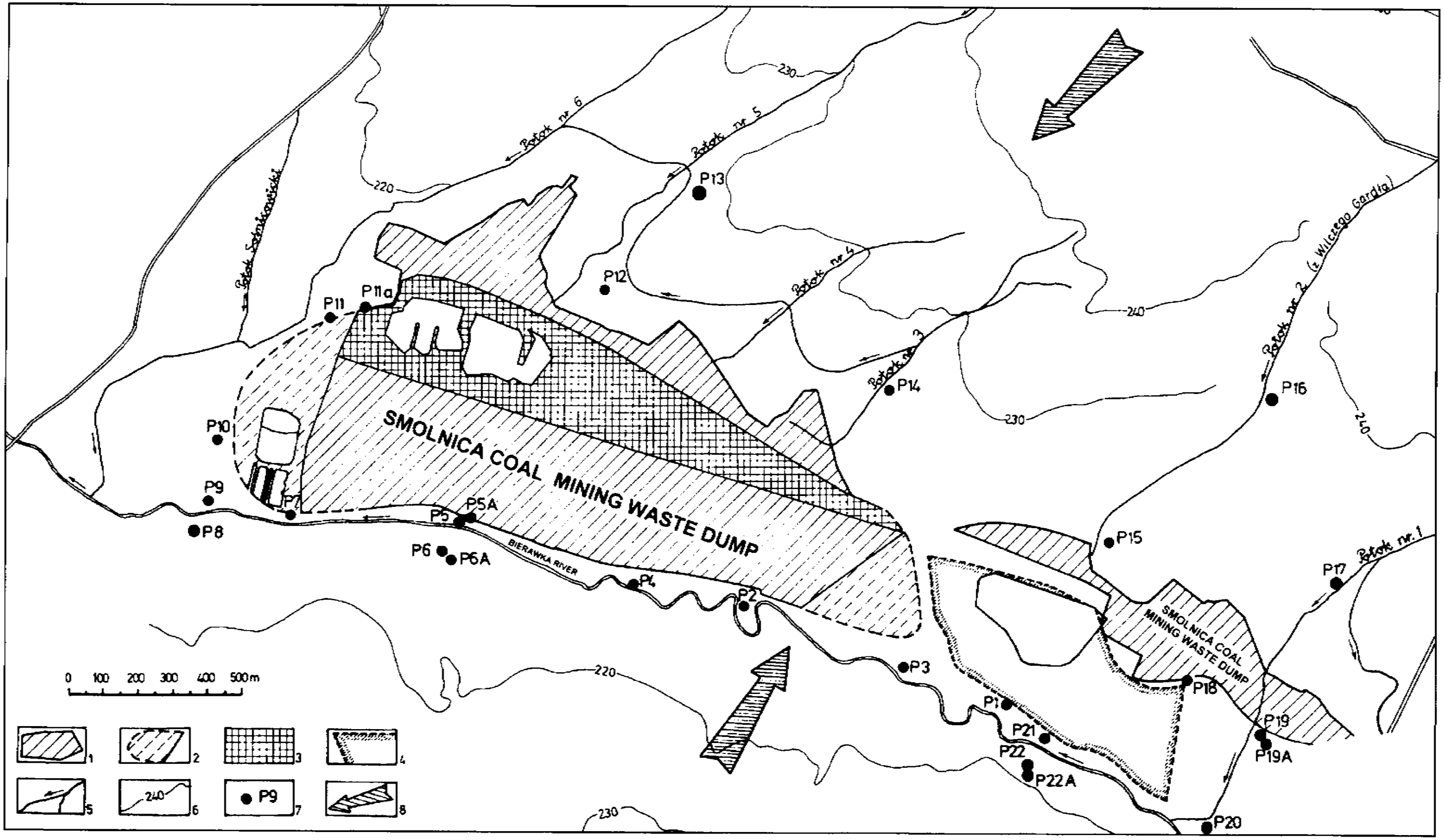


Figure III.6.24. Smolnica coal mining waste dump. Local ground-water quality monitoring network (LGWM). State in 12/1994. 1, Existing Smolnica coal mining waste dump; 2, planned final dump contour; 3, operational area of coal extraction plant; 4, planned municipal landfill; 5, water courses and rivers; 6, isopleths of ground level (m asl); 7, groundwater monitoring wells (LGWM network); 8, ground-water flow directions.

Table III.6.7. Transformations of groundwater quality in the Smolnica coal mining waste disposal site (USCB, Poland, monitoring data 1994–2002).

Parameter	Unit	Groundwater up-gradient of the dump	Groundwater down-gradient of the dump[a]			MCL for drinking water (Class A1 of surface water quality) – Polish standards[b]
			Part E: waste 20–38 years old	Central part: waste 15–30 years old + fresh rock	Part W: waste 10–20 years old	
pH, field		**5.35**–7.01	**2.51–6.41**	**5.73**–7.18	**6.13**–7.30	6.5–9.5 (6.5–8.5)
Conduct., field	μS/cm	214–466	1,855–**6,190**	**3,240–18,500**	1,212–**8,100**	2,500 (1,000)
Eh, field	mV	+146– + 344	−96.0– + 542	−78– + 144	−63– + 350	
Hardness, $CaCO_3$	mg/l	64.6–188.6	**742.6–2,363.3**	**1,067.9–4,071.9**	**543.8–2,456.4**	60–500
Ca^{2+}	mg/l	20.71–47.53	241.01–690.74	254.67–721.34	104.80–581.53	
Mg^{2+}	mg/l	3.12–16.98	34.20–**155.10**	**104.95–551.70**	**68.55–244.00**	50
Na^{2+}	mg/l	4.05–10.80	**263.73–1,174.85**	**587.55–3,403.45**	27.94–**1,368.5**	200.0
K^+	mg/l	0.91–2.41	8.33–20.47	19.06–90.63	12.07–87.64	
NH_4-N	mg/l	0.00–**4.96**	**1.184–10.08**	**1.00–8.68**	0.218–**6.720**	0.5 (0.5)
NO_2-N	mg/l	<0.001–0.019	<0.001	<0.001–0.004	<0.001–0.007	0.1
NO_3-N	mg/l	0.207–7.60	0.018–2.040	0.032–2.315	0.006–3.807	50.0 (50.0)
HCO_3^-	mg/l	5.49–24.12	0.00–122.03	9.15–705.97	18.31–360.0	
Cl^-	mg/l	8.16–29.58	257–**1,127**	204–**3,498**	22.22–**1,096.5**	250.0 (250.0)
SO_4^{2-}	mg/l	47.72–130.7	**1,013.3–2,846.9**	**1,958.3–7,362.4**	**495.33–3,595.6**	250.0 (250.0)
PO_4^{3-}	mg/l	0.009–0.087	0.002–0.094	0.006–0.098	0.001–0.050	5.0 (0.4)
SiO_2	mg/l	2–22	10–20	4–20	1–12	
TDS	mg/l	192–420	2,426–5,344	4,020–15,220	1,240–7,312	
COD	mg/l	7.41–54	15.20–**207.4**	24.48–**610**	9.76–**149.2**	(25.0)
C org.	mg/l	4.24–16.23	5.31–13.54	6.61–40.6	6.31–16.49	
Al	mg/l	<0.06	<0.06–**1.905**	<0.06–**0.614**	<0.06–**1.33**	0.2
B	mg/l	<0.10–0.10	<0.10–0.1	<0.1–0.6	<0.1–0.125	1.0 (1.0)
Ba	mg/l	0.059–**0.105**	0.025–0.095	0.022–0.026	0.037–0.065	0.7 (0.1)
Cd	mg/l	<0.003	<0.001–**0.070**	<0.001–**0.020**	<0.001–**0.011**	0.003 (0.005)

(continued)

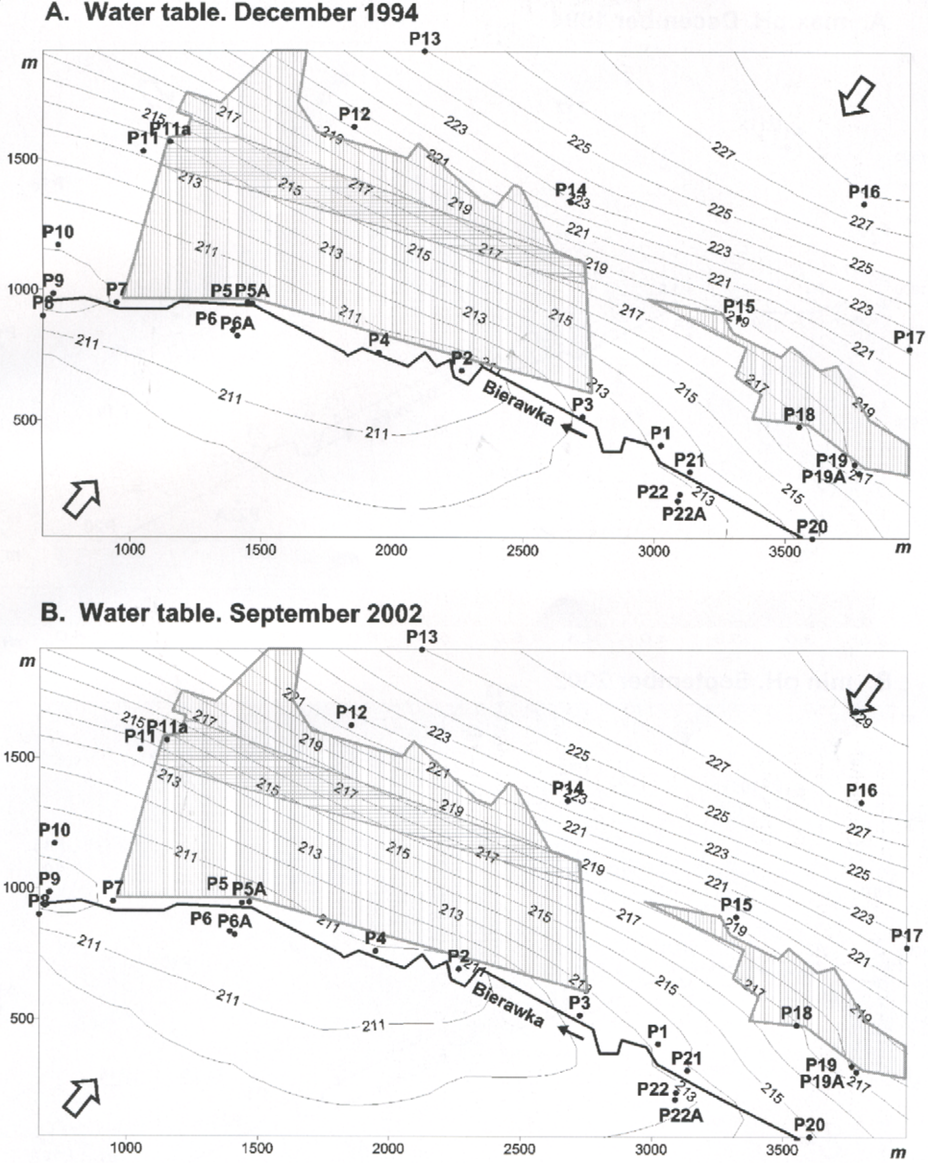
Table III.6.7. (Continued)

Parameter	Unit	Groundwater up-gradient of the dump	Groundwater down-gradient of the dump[a]			MCL for drinking water (Class A1 of surface water quality) – Polish standards[b]
			Part E: waste 20–38 years old	Central part: waste 15–30 years old + fresh rock	Part W: waste 10–20 years old	
Co	mg/l	<0.005–0.04	0.001–0.09	0.05–0.15	<0.001–0.09	
Cr_t	mg/l	<0.001–0.004	<0.001–**0.275**	0.010–**0.1784**	<0.001–**0.14**	0.05 (0.05)
Cu	mg/l	0.001–0.01	<0.001–**0.075**	0.010–0.033	<0.001–0.024	1.0 (0.05)
Fe	mg/l	<0.001–**8.57**	**28.43–297.3**	**20.68–158.4**	0.02–**92.09**	0.2 (0.3)
Mn	mg/l	<0.001–**1.45**	**4.18–14.09**	**5.253–15.897**	0.03–**12.53**	0.05 (0.05)
Ni	mg/l	<0.001–**0.04**	0.017–**0.107**	0.016–**0.570**	<0.001–**0.124**	0.02 (0.05)
Pb	mg/l	<0.005–**0.015**	<0.001–**0.120**	<0.001–**0.14**	<0.001–**0.08**	0.01 (0.05)
Zn	mg/l	<0.001–0.27	<0.001–**11.93**	<0.001–0.478	<0.001–0.62	3.0 (3.0)

[a] Values exceeding MCL are in bold.

[b] Directive of the Minister of Health (2000); Directive of the Minister of Environment (2002a).

(a)



A. Water table. December 1994

B. Water table. September 2002

Figure III.6.25. Hydrodynamic field and distribution of contaminants in groundwater of Smolnica dump site (m asl). A, State on 08/12/1994 (sampling series I, LGWM network); B, state on 05/09/2002 (sampling series XV, LGWM network). Kriging estimates, linear model, anisotropy: ratio 2.5, angle 15 (SURFER computer program, Version 7, Golden Software, Inc., 1999). (a) Map of hydrodynamic field; (b) distribution of pH values; (c) distribution of SO_4^{2-} concentrations; (d) distribution of Cl^- concentrations.

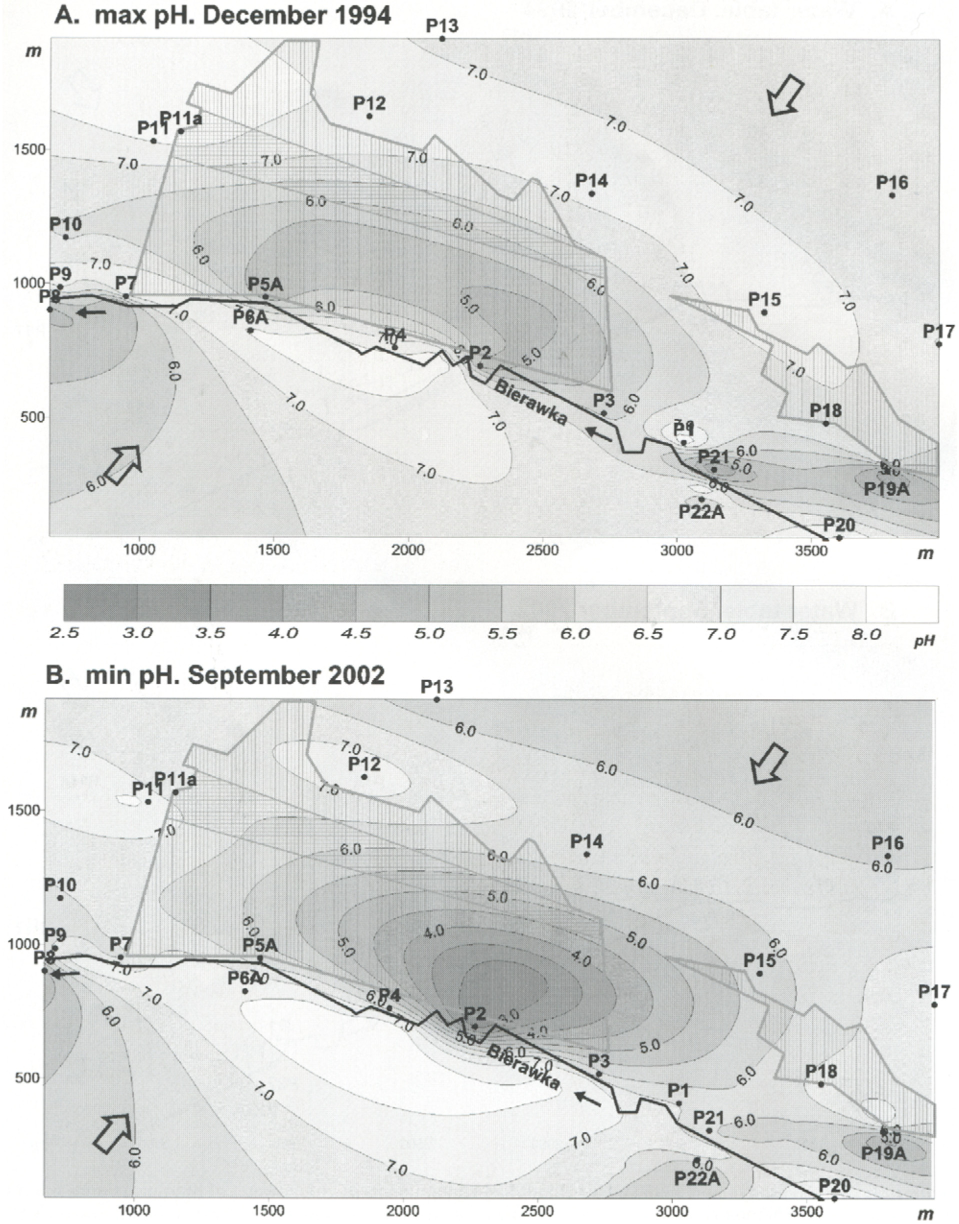


Figure III.6.25 (continued)

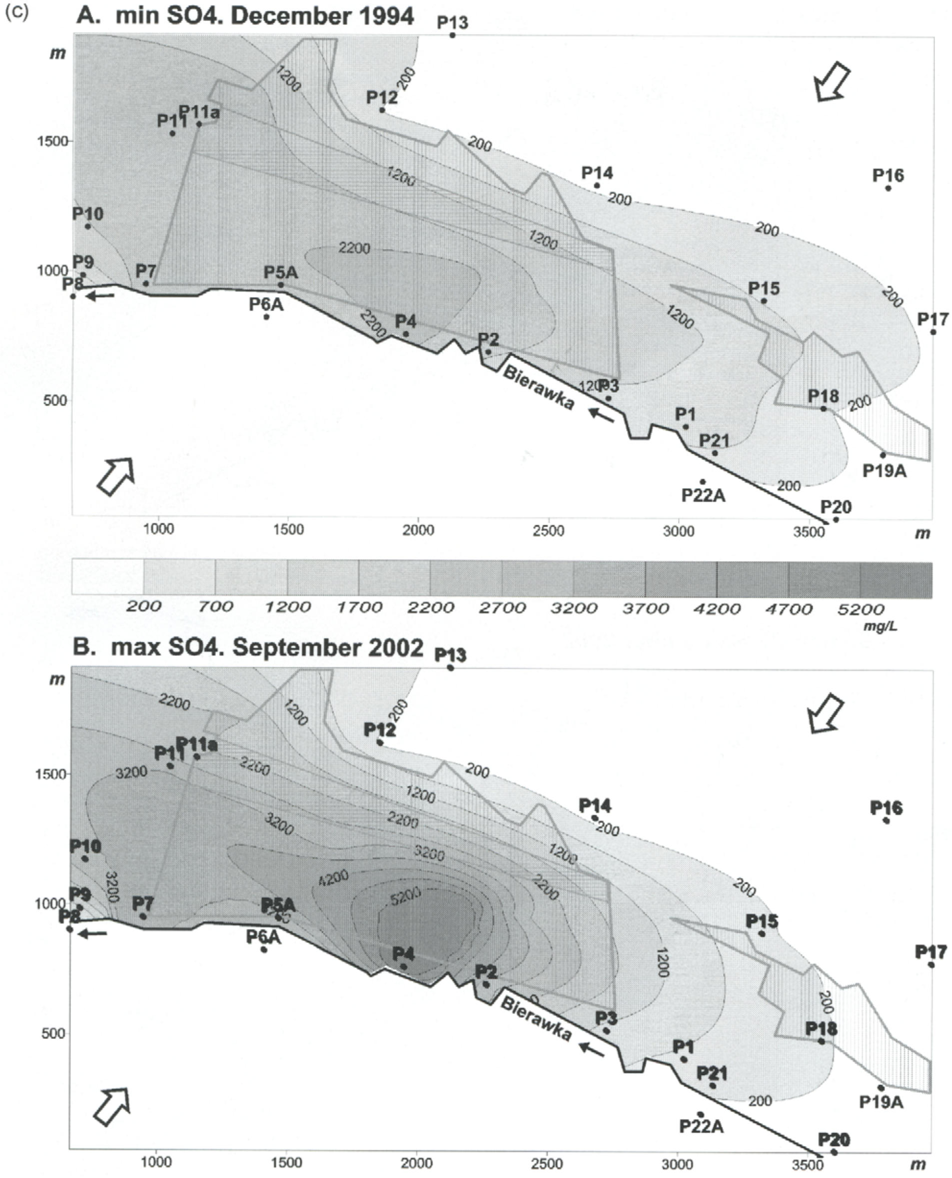
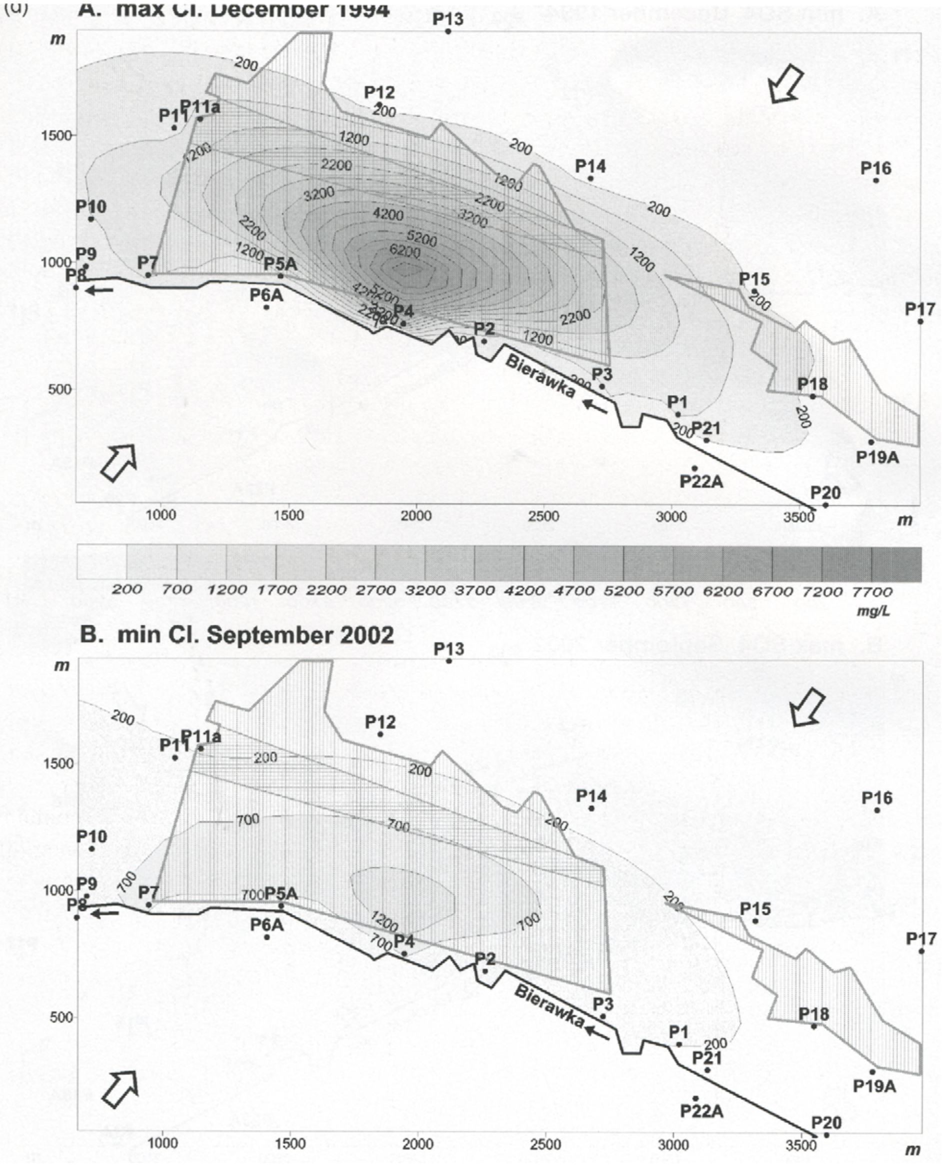


Figure III.6.25 (continued)

acidification up to pH 2.5; moderate or relatively low, gradually decreasing chloride salinity of groundwater affected by leachate from the oldest (20–38 years old) undisturbed E part of the dump; (ii) wide range of pH (mostly moderately acidic), high chloride and sulfate salinity of groundwaters receiving leachate from the central part of the waste dump, predominantly 15–30 years old, which was the most affected



(a) A. max Cl. December 1994

B. min Cl. September 2002

Figure III.6.25 (continued)

anthropogenically by joint impact of old waste deposits and current management operations; in these waters, the highest concentrations of chloride (decreasing trend) and sulfate (increasing trend) at weakly acidic pH were observed; (iii) pH values predominantly ≥6.5, decreasing chloride salinity and increasing sulfate concentrations in groundwaters receiving leachate from the W part of the dump (10–20 years old) and influenced also with coal recovery activity in the NW section. High chloride salinity was caused by the disposal of freshly mined rock at the top of the dump, while the increase of sulfate concentrations distinctly correlated with the direction of waste extraction/disposal for coal recovery. The concentrations of constituents in groundwater down-gradient of the waste dump appeared to be influenced also by meteorological conditions: intensive precipitation after dry periods resulted in higher concentrations of sulfate being a resultant of generation/release processes. Groundwaters affected by leachate from the dump also showed high contents of Fe and Mn (1–2 orders of magnitude with respect to MCL and background concentrations) and elevated maximum concentrations of Al, Cd, Ni, Pb and Zn, particularly in waters receiving leachate from the oldest E part of the dump. The adverse alteration of groundwater quality down-gradient of the coal mining waste dump has made the impacted aquifer unfit for any use.

The natural barrier against the expansion of contaminants from the dump in the SW direction is the Bierawka river, which drains the quaternary aquifer. Therefore, in the presented case study, a strong deterioration effect of the coal mining waste dump is spatially limited. The dilution/adsorption effect of bedrock in the vadose zone causes considerable reduction of trace metal concentrations (Zn, Ni), while iron in oxic conditions tends to precipitate in the form of hydroxides, abundant in the drainage ditches of the dump.

In other sites of the USCB, though, where the dumps are sited up-gradient of the settlements, thorough degradation of the usable quaternary aquifer has occurred as a result of macro-components leaching (sulfates, chlorides, TDS) despite the well-buffered mining waste disposed and qualification of the material as non-acid generating waste. This caused a necessity of using remote sources of tap water supply for a number of settlements.

Other numerous case studies on ARD or acid mine drainage (AMD) show similar environmental behavior of mining wastes with respect to potential for acidity generation and major ion composition; the acidic leachate from metalliferous waste contains considerably higher concentrations of mobilized heavy metals due to their high content in a waste rock (Table III.6.6) (Cnoquette et al., 1995; De Vos et al., 1997; Herring et al., 1998; Munroe and McLemore, 1999). As ARD generation creates a serious environmental problem both in active and old mining waste disposal sites, the European Union with its almost 2000 mining sites, of which almost 1000 is abandoned, should pay close attention to the environmental behavior of these sites.

Waste rock geochemistry and the long-term weathering characteristics of mining waste appear to be a key issue for predicting the potential of active or abandoned mine waste disposal sites for ARD, its detrimental or toxic effect and for undertaking preventive attenuation measures (Yeates, 1993; Price and Kwong, 1997; Zahner et al., 1997; Smith, 2001).

III.6.5. Conclusions

1. Bulk non-hazardous mining waste, either disposed at dumping sites or used in civil engineering as common fill, may cause long-term deterioration of groundwater quality.
2. The most important intrinsic factors controlling the contamination potential and its spatial and time-dependent transformations are the hydraulic conductivity,

permeability to air, soluble compound contents in the freshly mined waste rock and occurrence of geochemically unstable minerals (e.g. sulfides), which cause long-term generation and release of new loads of primary (e.g. acidity, sulfates) and secondary contaminants (e.g. trace metals). The external factors comprise meteorological, hydrogeologic, hydrogeochemical and hydrological conditions and the anthropogenic impact of waste management at the disposal site.

3. Sulfidic mining wastes, among them coal mining waste exposed to atmospheric conditions, should be considered as a long-term source of groundwater contamination, lasting for decades. The specificity of this material is an occurrence of short- and long-term pollution potentials. While the short-term pollution potential originating from the initial load of soluble macro-components (TDS: chlorides, sulfates) contained in fresh wrought material is well recognized, the long-term leaching behavior induced by sulfide oxidation is often neglected due to its non-linear, time-delayed character and failure in its evaluation by a singular regulatory leach test. This leads to wrong qualitative and quantitative assessment of the environmental risk of high-volume mining waste other than hazardous, e.g. coal mining waste.
4. The contaminant release and transport within sulfidic mining waste, e.g. in coal mining waste dumps and civil engineering constructions (river and lagoons embankments, ground leveling), occurs predominantly in the vadose zone conditions of water infiltration. Water balance of a surface layer of mining waste rock about 1.5 m thick is unstable, while the infiltration water flow within the dump is, in general, constant.
5. The majority of non-compacted and compacted granular mining wastes, among them coal mining waste, are permeable to vertical water infiltration and air penetration.
6. The chemical composition of pore solution within the dump profile is determined by the vertical redistribution of contaminant loads unrestricted by equilibria constraints (chlorides and sulfates balanced by alkali and hydrogen ions), acid generation potential (sulfide oxidation), buffering capacity at pH $\approx$ 7.0 (occurrence and forms of Ca–Mg carbonates: calcite, dolomite) and solid/liquid phase equilibria (equilibrium with carbonates and gypsum, pH–Eh).
7. The highest short-term contamination potential is from waste rock having relatively high chloride salinity; the highest long-term contamination potential is due to low-buffered acid generating waste of high metal content (e.g. from metal ore mining). High acidification and long-term macro- and trace component release generally occur in weathered mining waste several years old.
8. Sulfide minerals' reactivity varies in a wide range determined by their textural form and shows certain regularity depending upon their position in the stratigraphic profile of the carboniferous sequence. The kinetics of sulfide decomposition, which can be described by a first-order reaction, generally display high stability for the particular rock material and do not show acceleration in time that would have suggested considerable changes in prevailing oxidation mechanism.
9. Just part of the total sulfide load is available for the oxidation and acid-sulfate release process. The oxidizable sulfides in the material become gradually accessible in subsequent portions; the accessibility increases in older waste material in the uppermost layer of waste about 1.0–1.5 m thick due to the weathering degradation of the rock grains, which reduces their size.

10. Buffering of generated acid loads by carbonate minerals in waste rock is based mainly on their equilibrium-constrained dissolution in microenvironments of the heterogeneous porous matrix. There is a different availability of buffer load depending on the carbonate dispersion and specific surface. This causes a tendency to acidification of a buffered material in long dry periods. Hence, to neutralize ARD permanently, buffering capacity of the material should be much in excess with respect to its acid generation potential.
11. The extent of an adverse effect and required protective measures in the dumping area are site-specific and depend also on the buffering capacity of the vadose zone bedrock and ability of receiving ground and surface waters to dilute life cycle contaminant loads released from the dump. General evidence shows deep deteriorating impact of both active and old closed mining waste disposal sites on groundwater quality.

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Further reading

Web sites for further information

http://minerals.usgs.gov/minerals/pubs/country/

http://www.enviromine.com/ard/Eduardpage/ARD.HTM

http://www.state.sd.us/denr/DES/mining/adti.htm.http://www.enviromine.com/ard/Acid-Base%20Accounting/Quality.htm

http://www.enviromine.com/ard/Microorganisms/roleof.htm

http://www.enviromine.com/ard/Mineralogy/Petrology%20ard%20Mineralogy.htm

http://www.epa.gov/epahome/index/sources.htm