Solid Waste: Assessment, Monitoring and Remediation
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III.7
Coal combustion waste

Irena Twardowska and Jadwiga Szczepańska

III.7.1. Introduction

III.7.1.1. Coal combustion as a source of energy

The large-area contamination problems caused by coal-based electric utilities in the second half of the 20th century directed efforts to the reduction of particulate and gaseous emissions from coal-fired power plants to the atmosphere. The problem of fly ash (FA) emission has been solved successfully, immediately creating another problem of environmentally safe coal combustion waste (CCW) disposal and use. In turn, reduction of gaseous emission affects the structure and properties of CCW.

Coal combustion residues are one of the most abundant high-volume waste materials. Their proportion in the total waste stream highly depends upon the role of coal in power production, and is as a rule the highest in coal producing countries (Twardowska, 2003a). Despite stepping up development of alternative sources (oil, gas, nuclear, hydro and other renewables), the position of coal in power production is still strong and is also expected to be significant in the future (see Chapter III.6).

In 2000, coal provided over 23% of global primary energy needs and generated about 39% of the world's electricity (WCI, 2002e, after IEA, 2002a). At the beginning of 21st century, coal remains to be the major fuel used for generating energy worldwide. Countries heavily dependent on coal for electricity include the ones with the highest population that are also major producers of hard coal (China, USA and India, which supply 66.6% of global hard coal production), and a number of other countries, which comprise both suppliers and importers of coal.

In China, the greatest world coal producer, in 2000 electricity generation based on coal accounted for 78–84% (IEA, 2002a; WCI, 2002e). In the USA, the second biggest coal producer after China, electric utilities burn over 90% of the total coal output (Collins, 1992) to supply 52% of the nation's electricity according to 2001 data (WCI, 2002e). The third place as a coal producer holds India (8.5% of the total global hard coal production), where unlikely other stagnating coal markets, accelerated growth of output occurs to fulfill the increasing demands in power generation. Currently, Indian coal fired power plants comprise 77% of electricity output (2000 data, WCI, 2002e). National sources for all India estimate an increase of coal consumption to 725 Mt in 2011–2012 (Prasad et al., 2000); 500 Mt (72%) of coal is slated to go in 2009/2010 for power generation (Gale, 1999). This means an extremely challenging 2.3-fold growth in the next decade compared to the current hard coal production in the country (312.5 Mt in 2001). The ABARE report (2002) assesses the prospects for thermal coal consumption for electricity generation in India by 2010 with an average annual growth rate of about 3%, which is at much lower realistic level (WCI, 2002a, after ABARE, 2002).

A number of countries use coal as an important component in a balanced energy mix. According to the World Coal Institute (WCI, 2002e), major steam coal importers in 2001 were Japan, Republic of Korea and Chinese Taipei (Taiwan), which imported 2.1, 1.2 and 1.1% of the global output, respectively, while 15 Member States of the European Union (EU15) imported in total 145.4 Mt (3.8% of the global output). All these countries showed significant increase of steam coal import in 3 years since 1998. In the EU15 thermal coal import increased in this short period for 34% (WCI, 1999, 2002b), despite permanent general decrease of hard coal consumption in last two decades (1981–2001) and further projected declining trend by 2010 with an annual rate of −0.8% (WCI, 2002a, after ABARE, 2002).

The overall prognoses on global energy production based on coal compared to 1999 through to the year 2010 forecast an average annual growth of 1.9%. The majority of this increase is expected for electricity production in developing Asian economies, in particular in the ASEAN countries, India and China, with average annual growth rate of about 9.5, 3 and over 2.5%, respectively. Japan, Korea and Chinese Taipei (Taiwan) are projected to remain the largest importers of thermal coal (WCI, 2002a, after ABARE, 2002). In Japan, from 1975 to 1998, the total power production grew 2.3 times, while coal-based power generation increased 7.5-fold. The market share of coal-based power production in Japan increased 3.5-fold, from slightly more than 4.5% in 1975 to 15% in 1998. The Federation of Electric Power Companies in Japan estimates that coal will maintain its market share in the future composition of the Japanese power sector at the level of 20–21%, while further increase of electricity generation by 2008 up to 24% compared to 1998 is anticipated (WCI, 2000). This will assure a balanced energy portfolio for Japan and a safe broad diversity of fuels.

The growth of cost-effective coal-fired generation of electricity in some developed economies, such as the USA and Australia (1.5–2% per annum by 2010) is also expected (WCI, 2002a).

The emerging markets for coal-based electricity generation include selected developing countries, where electrification rates vary significantly (Fig. III.7.1). China in 2000 already reached the rate of electrification over 98% that was close to OECD average (99.2%); 78% (WCI, 2002e) to 84% (IEA, 2002a) of electricity in China was coal-fired. Philippines and Thailand experience dynamic growth of electrification that substantially exceeds world average (72.8%) and will shortly reach OECD level. Sub-Saharan Africa is suffering from acute energy shortage with an average of only 23%, while a number of these countries is placed much below this low level (e.g. Mozambique, Ethiopia, Uganda). South Africa greatly differs from the rest of Sub-Saharan countries: it has raised its electrification rate to 66.1% (88% of power generated is based on coal) and shows further rapid development. Similar fast growth of electrification occurs in Indonesia that is currently close to the developing countries with an average (64.2%). In India and Nigeria the electrification rate is still below 50% and requires a significant increase in power generating capacity (WCI, 2002c,d). These data illustrate both worldwide dispersion of coal use for electricity

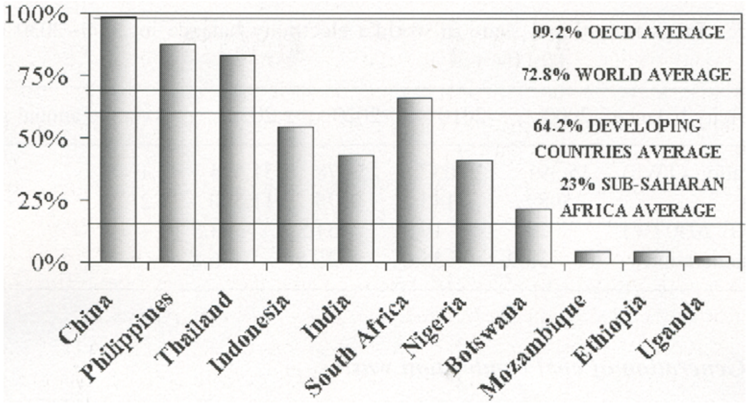

Figure III.7.1. Electrification rates for selected developing countries in 2001 (after IEA, 2002a,b).

production, and uneven present and future distribution of coal-fired power generation. African and Asian development in the area of energy to the great extent is going to be based on coal.

At present, in Asia Pacific coal has become the major source of energy generation, supplying in 2001 over 40% of primary energy in the region (WCI, 2002b). Besides China and India where coal-based electricity generation accounted 78 and 77%, respectively (2000 data), also in Australia 77% of power production is dependent on coal (WCI, 2002e).

The biggest European coal producer (2.7% of the global output in 2001) is Poland. Its electricity generation is almost entirely based on coal (96%). Besides Poland, other countries in Europe heavily dependent on coal as the source of electric power include Czech Republic (72%), and among the EU15 Member states Greece (67%), Germany (52.5%), Denmark (47%) and The Netherlands (28%). In the EU15 coal was used in 2001 for 27% of electricity generation (WCI, 2002e). In order to achieve a decrease in greenhouse gas (GHG) emissions under the Kyoto Protocol, EU15 plans to decrease solid fuel consumption, i.e. hard coal, lignite and peat that results in the negative growth rate projected by 2010.

The long-term World Energy Outlook (WEO) released in 2002 by the International Energy Agency (IEA) forecasts a 1.7% annual increase in energy demand and twofold increase in world electricity demand in the next three decades 2000–2030 (Table III.7.1). According to this prognosis, global primary coal consumption will rise at an average annual rate of 1.4% up to 2030. In all regions, coal use will become increasingly concentrated in power generation, which will account for almost 90% of the increase in demand between 2000 and 2030. In developing countries coal-based electricity is set to more than triple by 2030. Most of the increase is projected to be in India and China where large, low-cost reserves will keep coal as the dominant fuel (WCI, 2002e, after IEA, 2002b). Therefore, coal will remain the largest source of electricity generation for the first three decades of a new Millennium.

Table III.7.1. Prognosis of coal share in world's electricity balance in 2000–2030 (after IEA, 2002a,b).

World electricity balance	2000	2010	2020	2030	Average annual growth (%)
Gross generation (TWh)	15,391	20,037	25,578	31,524	2.4
Coal (TWh)	5989	7143	9075	11,590	2.2
Growth 2000–2030 (%)	0	19.3	51.5	93.5	
% of gross generation	38.9	35.6	35.5	36.8	

III.7.1.2. Generation of coal combustion waste

Coal-based power production results in generating a huge amount of CCW worldwide. Coal statistics reflect on the one hand, the range of CCW in the total waste stream, and on the other hand, non-uniformity of distribution of this waste in particular countries, producers and users of coal. Despite of the omnipresence of CCW, the statistical data concerning its generation and managing in the different countries of the world are fragmentary.

The OECD last available data for 19 member countries (without the USA, Canada, Spain and eight other OECD members) concerning waste from power generation in the 1990s gives the total as 166.66 Mt, which comprise besides CCW also other waste, e.g. from fuel oil (OECD, 1999). The largest contributions to this total were from Japan, Germany, Poland, UK, Australia and Turkey (57.3, 19.6, 18.0, 13.0, 11.0 and 8.7 Mt, respectively). In 2001, Poland produced 15.8 Mt CCW from electricity, and 3.0 Mt CCW from thermal energy generation, total 18.8 Mt (Central Statistical Office, 2002). Of these countries, which are coal producers, the exceptionally high position of Japan as a fuel importer is probably due to the high development of power-consuming industries. Earlier sources (Shao Yi, 1992) report that only 4.0 Mt of CCW was generated in this country in 1989. According to incomplete data, EC15 (without Spain, Austria, France and Luxembourg), produced a total of 49.93 Mt of waste from all the sources of power generation, and of this the contributions of Germany (39%) and the UK (26%) amounted to 65% of the total (OECD, 1999). Annual waste generation from these sources reported by EUROSTAT (2001) for 10 of 15 EC Member States for the years 1993–1999 accounted for 54.14 Mt; 71% of this amount was share of Germany (47%), and of the UK (24%). Of 29 European countries that comprise EC15, 3 associated and 11 candidate countries, data on annual waste generation from electricity and thermal energy production in this period were available only for 15 countries that produced in total 96.43 Mt of power plant waste. Germany, Poland and the UK generated 57% of this amount.

Divergence and incompleteness of both sources of the statistical data is a serious obstacle in the accurate assessment of the amount of CCW generated by OECD member states and European countries. For a number of other countries, no reliable statistics on CCW generation is available.

In the USA, in 1998 over 100 Mt of CCW were produced (Butalia and Wolfe, 1999; Chugh and Sengupta, 1999). According to American Coal Ash Association (ACAA) in 1992, 74.4 Mt of CCW was generated (Tyson, 1994). ACAA survey data for 1996 evaluate CCW amount for 92.45 Mt (Stewart, 1997, 1999). It consists predominantly of FA (58.3%), bottom ash (15.8%), boiler slag (2.5%) and FGD solids (23.4%) (Stewart, 1999).

In India, the coal consumption for power production in 1996–1997 was 196 Mt, and around 75 Mt of CCW was generated annually. This huge amount of CCW, which consists of about 80% of FA and 20% of bottom ash (BA), is due to use of high ash (30–50%) low-grade coal; thereby coal ash has been generated at an average rate of 5 t/MW/day (TIFAC, 1990). A further growth of CCW to 120 Mt at the beginning of the new Millennium (2000–2001) and up to 290 Mt in 2011–2012 has been anticipated at coal consumption for power generation of 299 and 725 Mt, respectively (Prasad et al., 2000).

III.7.1.3. Coal combustion waste disposal

The beneficial properties of CCW make it suitable for a wide array of commercially and technically proven applications. The traditional leading markets for CCW use are cement and concrete production, structural fills, road base and sub-base, as well as blasting grit/roofing granule. Other markets and reuse options for CCW as an engineering material are advancing (Collins, 1992; Cabrera and Woolley, 1994; Tyson, 1994; Butalia and Wolfe, 1999; Chugh and Sengupta, 1999; Stewart, 1999; Twardowska, 2003a,b; see also Chapter VI.8), with a goal of full use of these materials in a technically sound, commercially effective and environmentally safe way. Nevertheless, the utilization of CCW is still far from achieving this target for various reasons of a different character. Limiting factors which are of particular importance include: inadequate legislation, discrepancy between the CCW generation rates and demand for the end product, availability of competing materials for lower costs, experience of professionals involved in the production and marketing as well as the prejudice of potential end users and regulators. As a result, a large portion of the total CCW stream is still being disposed of in surface ponds or landfills. The rate of CCW disposal in a local or regional scale is a resultant of the joint effect of these factors, hence the differences between the countries with respect of CCW utilization (Twardowska, 2003a).

In 1992, CCW disposal in the USA accounted for 55.9 Mt (75.2% of the annual production) (Tyson, 1994). Also the most recent data refer to 25% of CCW utilization in the USA (Butalia and Wolfe, 1999; Chugh and Sengupta, 1999; Stewart, 1999). ACAA survey results for 1996 evaluated total CCW disposed for 69.6 Mt (75.3%), and utilized for 22.8 Mt (24.7%). Boiler slag, BA and FA are the primary CCW utilized at a rate 93.3, 30.3 and 24.7% of the amount generated, respectively (Stewart, 1999). Flue gas desulfurization (FGD) scrubber sludge and fluidized-bed combustion (FBC) products are the least utilized CCW in the USA (6.9% in 1996). Hence, about 75% of CCW are currently disposed of annually.

The data for China are limited and for 1989 (Shao Yi, 1992) CCW production was 62 Mt. Of this 22 Mt (33%) is reported to be utilized, while 67% (about 40 Mt per annum) is being disposed of.

In India, almost all CCW generated are disposed of. The data concerning the rate of utilization reported is from hardly 2–5% (Kumar et al., 1996) to 2–3% of the total amount generated (Prasad et al., 1999, 2000). CCW in India is usually disposed of hydraulically as a slurry containing 20–25% of a mixture of FA and BA in unlined surface ponds with an open circuit. Taking into consideration the amounts of CCW already produced (75 Mt) and a forecast for 2011–2012 of 290 Mt/a, the situation with CCW management in this country is going to be critical.

In Poland, of 18.8 Mt of CCW from electricity and thermal power generation in 2001, 13.8 Mt (73.1%) was utilized, while permanent disposal of and temporary storage accounted for 4.3 and 0.71 Mt (23.0 and 3.8% of the annual production), respectively. The total amount of CCW stored in the disposal sites was evaluated by the end of 2000 as being 312.3 Mt (Central Statistical Office, 2002). Huge amounts of CCW are stored in disposal sites worldwide, and the amount of CCW at these sites is growing continuously with the intensity depending upon its utilization rate.

These data show that despite all the efforts of reuse proponents to change the way CCW are classified in the legislative arena and to consider ash, slag and flue gas desulfurization solids (FGDS) from power production entirely as beneficial raw materials (Collins, 1992; Mishra and Seth, 1999), disposed CCW must be regarded as waste.

III.7.1.4. ***Regulatory framework***

CCW falls within the European definition of waste expressed in Council Directive 75/442/EEC on waste as last amended by Commission Decision 96/350/EC. An additional condition that the substance or object should be listed in the 16 categories of waste presented in Annex I (*vide* Chapter I, Annex A) is also fulfilled with respect to CCW, which belong to the category Q9 (residues from pollution abatement processes). The CCW are also included in the European list of wastes (Commission Decision 2000/532/EC as amended by Commission Decision, 2001/118/EC), where waste is categorized principally on the basis of origin or composition of the material. CCW are coded under category 10 (wastes from thermal processes), subcategory 10 01 (wastes from power stations and other combustion plants (except 19), codes 10 01 01, 10 01 02, 10 01 05 and 10 01 07, which comprise slag, BA and FA from hard coal and lignite, as well as FGDS. CCW are not considered hazardous wastes (Council Directive 91/689/EEC, 1991), though in view of Council Directive 75/442/EEC on waste, the disposal of CCW, as any waste, at any stage must not cause harmful effects to the environment.

In Poland, CCW disposal is regulated by the Waste Act of 27 April 2001, and the Directive of the Cabinet of 18 March, 2003. According to this Directive, disposal of FA and other CCW from coal combustion (10 01 01 and 10 01 02) is currently charged for the disposal ~US $4 per ton. Dry FGDS and slag from lime desulfurization process are charged for the disposal ~US $2 per ton.

In the USA, the basis for stepping up the reuse options is an exclusion of CCW, i.e. FA, BA waste, slag waste and flue-gas emission-control waste from fossil-fuel combustion from RCRA (1984) requirements. This exclusion is listed in 40 CFR 261.4. in the category of solid wastes that are not hazardous wastes. Despite this amendment enacted since 1980, some state regulations have set particularly stringent requirements for siting, constructing and managing CCW disposal facilities and reuse projects. Cost of CCW landfilling ranges from US $7 to $30 per ton depending upon the specific conditions (Chugh and Sengupta, 1999).

In India, no environmental regulations concerning CCW disposal and post-closure reclamation exist up to now. There are also no requirements concerning soil conservation or reclamation (CMPDIL, 1986; MOEF, 1992).

III.7.1.5. Environmental issues

The resentful approach of a certain part of decision-makers and of public opinion to CCW in the USA is based on its properties, which indicate that this material may pose an environmental risk while exposed to atmospheric conditions due to high concentration of trace metals, leachability of soluble constituents and its airborne character. The environmental compatibility of the products made with use of CCW should also be proven. The development of "clean energy" technologies and desulfurization of flue gases result in changes of the amount and properties of an end product depending upon the applied FGD process. This, in turn, influences its environmental behavior during disposal and utilization.

The structure of disposed CCW usually somewhat differs from that of CCW produced due to different proportions of kinds utilized. Because of predominance of FA, which accounts for $>70\%$ of the CCW generated in power plant (excluding FGD solids), and its lower utilization rate compared to BA and boiler slag, the proportion of FA in the total CCW disposed of increases up to $\geq 80\%$.

Traditional ways of CCW disposal are surface ponds (lagoons) or landfills. FA is transported hydraulically to surface ponds or lagoons and disposed of in a form of FA:water pulp, conventionally at slurry concentrations $\geq 20\%$ wt, or as dense slurry assuring transportability to the disposal site, approximately 50% wt (1:1). The lagoons are generally waterlogged and hence form an anthropogenic saturated zone that may easily contact with the natural vadose and saturated zones of unprotected aquifers.

In dry compacted landfills, CCW are disposed pneumatically. Landfills need about 25% of the space required by ponds of the same volume, liquid:solid (L:S) ratio is much lower than that in surface ponds. The water flow is adequate to handle the infiltration rate of atmospheric precipitation and a surface run-off in the vadose zone. Both in dry and wet disposal facilities, leaching of contaminants from FA by water will occur, though the mechanism and dynamics of the process are different due to the different water flow conditions in the saturated and vadose zones. FGDS either form an integral part of the disposed FA, or are generated and disposed separately, depending upon the applied FGD process. The disposal options for FGD solids also include ponding and landfilling of natural- or forced-oxidation dewatered sludge (Collins, 1992).

For both disposal systems, i.e. ponding and landfilling, a long-term environmental evaluation of disposed FA in relation to the actual field conditions is necessary, as it has direct environmental and economic consequences. "Pure" FA is predominant in the world's generation of CCW, in particular in the electric utilities, which either do not use the desulfurization of flue gases or use a wet or semi-dry desulfurization process with low content of FA in the end product. Hence, an evaluation of long-term environmental behavior of this kind of material is of a particular interest for the constructors and managers of dumping sites, as well as for potential end users of FA as high-volume material for structural fill.

This chapter is focused on FA characterization with respect to the long-term environmental implications of its disposal. The possibilities of CCW use for control of other sources of contamination from high-volume waste were also considered. Environmental impact of FA was exemplified in two case studies of the environmental behavior and time-delayed transformations of pore solutions in FA surface pond. The studies are presented on the background of the characteristics of FA composition and properties related to pollution potential to the environment. The impact on the groundwater quality is exemplified in the ash pond site of MSEB in Maharashtra, India. Post-closure changes of power plant waste pollution potential with respect to macro-compounds and trace metals are illustrated by the screening survey in the Przezchlebie disposal site (Upper Silesia Coal Basin USCB, Poland).

III.7.2. Properties of hard coal combustion waste related to pollution potential to the environment

III.7.2.1. Characteristics of freshly generated "pure" FA

III.7.2.1.1. Particle size distribution

Electric utilities usually burn coal supplied from several mining areas. In the USCB area, coal from different coal seams is supplied to power plants from many coal mines located within a radius of 50 km. Nevertheless, petrographical and phase composition and physicochemical characteristics of "pure" CCW from pulverized hard coal burning in conventional boilers display certain similarity and stability between years. Particle size distribution in FA is log-normal, the fraction <0.06 μm comprises over 50% wt, and ranges generally from 55 to 80% wt, while grains bigger than 260–320 μm do not occur (Fig. III.7.2). BA is a coarser and less uniform material. The fraction >1 mm may reach up to 30% wt, while the fraction <250 μm comprises about 50% wt.

III.7.2.1.2. Petrographical and phase composition

In this waste, which originates from high-temperature transformations of carboniferous rocks, amorphous components dominate over crystalline phases and range from 77 to $>80\%$. They include a glass phase and amorphous relics of clay minerals. In petrographical composition two types of particles are predominant: irregular or oval aggregates surficially sintered or glazed, and round grains (Table III.7.2). Round grains glazed thoroughly or partially are more frequent in finer fractions. The grains partially glazed are filled with very fine dehydrated amorphous relics of clay substances. Amorphous aluminum oxide (Al_2O_3) is partially soluble in acids and alkali, though insoluble forms like corundum α-Al_2O_3 or γ-Al_2O_3 are more abundant.

Crystalline phases are minor components of FA. Among them, secondary ones are definitely dominant. Primary phases are represented entirely by quartz and potassium feldspar. Among crystalline phases, there is a considerable proportion of mullite $3Al_2O_3{\cdot}SiO_2$ ($\sim$ 15–20%), which prevails over phases containing iron (hematite/maghemite Fe_2O_3 and spinels: magnetite ($FeO{\cdot}Fe_2O_3$), hercynite ($FeO{\cdot}Al_2O_3$), magnesium

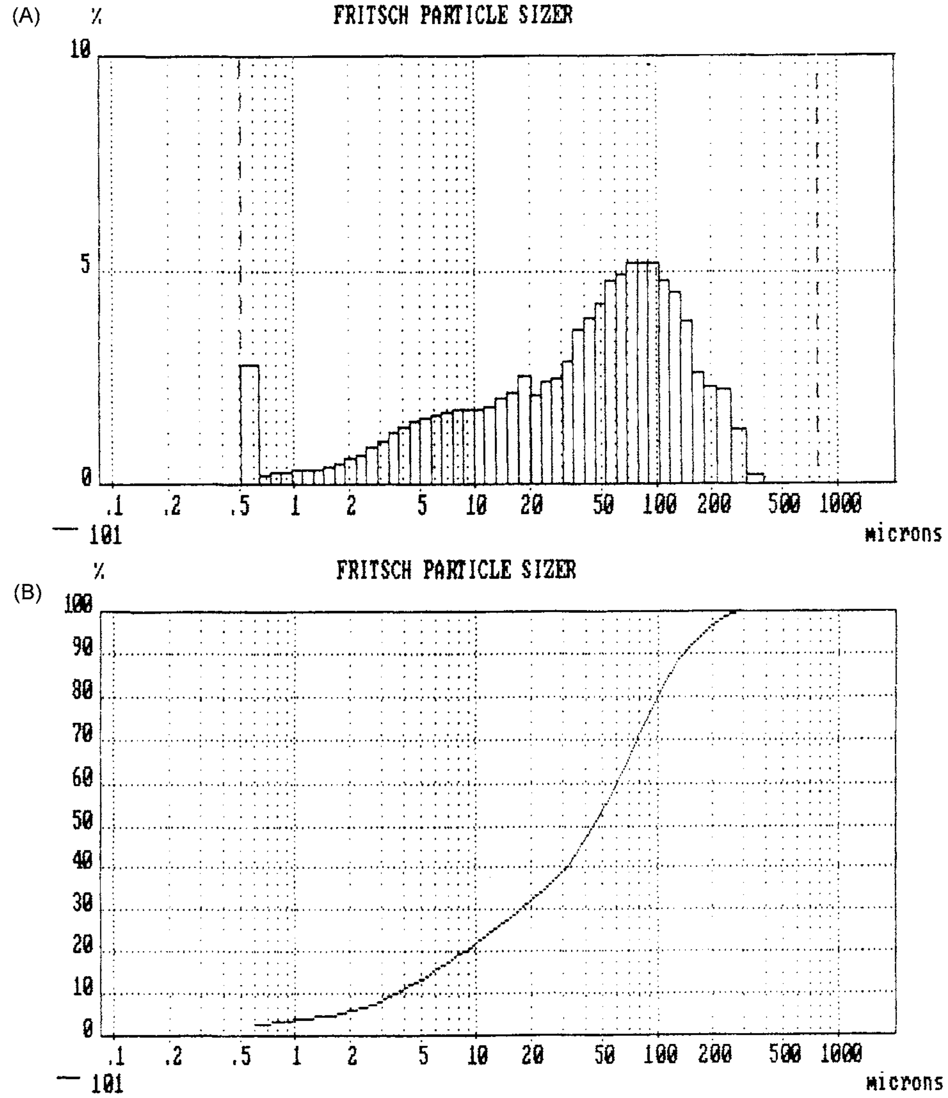

Figure III.7.2. Example particle size distribution in "pure" power plant FA. (A) Particle size frequency distribution. (B) Cumulative particle size frequency distribution.

ferrite ($MgO{\cdot}Fe_2O_3$) or mixed crystals between hercynite and magnetite). Trace or accessory amounts of sulfates occur predominantly in the form of anhydrite $CaSO_4$. Calcium oxides are present in mixed structures of C_4AF or C_2F phases. Also some amount of $Ca(OH)_2$ and phase C_4AH_{12} (hydrated calcium aluminate of $4CaO{\cdot}Al_2O_3{\cdot}12H_2O$ type) has been identified. Magnesium is present in small amounts as magnesium ferrite. FA contains also a small admixture (~3–4%) of unburnt coal (quick coke), which occurs in the form of porous particles of a skeleton structure.

Table III.7.2. Petrographical composition of FA from hard coal combustion, "pure" (FA) and containing FGD solids from dry (FA + D-FGD) and semi-dry process (FA + SD-FGD, in % v/v (after Ratajczak et al., 1999).

Components	Origin and kind of FA					
	"Pure" FA		FA + D-FGDS			FA + SD-FGDS
	R-1	L-1	R-2	R-3	O-1	L-2
Mullite aggregates[a]	57.5	47.6	22.5	35.6	10.0	34.3
Glaze spheres[b]	23.7	35.8	42.6	17.0	34.7	35.0
Unburnt coal matter	8.8	11.1	7.0	7.8	6.7	12.9
Quartz grains	2.7	2.3	1.0	1.3	1.0	3.6
Non-transparent spheres magnetically receptive	4.9	2.9	5.0	5.6	7.7	2.6
Primary and secondary carbonate aggregates[c]	–	–	21.9	32.7	39.9	11.6
Other	2.4[G]	0.3	–	–	–	–
Total	100.0	100.0	100.0	100.0	100.0	100.0

R – FA from the Rybnik power plant; L – FA from the Laziska power plant; O – FA from the Opole power plant (Poland); G – gypsum.

[a,b] In aggregates and spheres occurs an admixture of other components of FA.

[c] Primary carbonate minerals are represented by calcite, secondary minerals comprise calcium oxide, portlandite and anhydrite.

In general, the phase composition of FA from Polish power plants (Ratajczak et al., 1999) (Table III.7.3) is similar to that from other European (Garavaglia and Caramuscio, 1994) and US power plants (Mattigod et al., 1990, 1999).

III.7.2.1.3. Chemical composition

"Pure" FA from power plants of the USCB belongs to alkaline aluminum silicate material (van der Sloot et al., 1984). The ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) = 1.3-3.9$ is close to the available data for FA from European power plants fired by hard coal, where it ranges from 1.5 to 3.6 (this value reflects alkalinity of FA expressed as the ratio of buffering and acidifying agents: the sources of acidity are sulfide oxidation and aluminum hydrolysis). For FA considered typical for Indian power plants (Mishra and Seth, 1999; Singh, 1999) this ratio ranges widely from 0.64 to 4.25 with a domination of low-buffered material with low CaO content. For eight power plants of National Thermal Power Corporation Ltd. (NTPC), the average ratio is 1.30, for National Aluminum Co. Ltd. (NALCO) power plant it is 2.35. Combustion processes result in concentration of most macro-elements (except S and C) and trace elements (except Hg, I and F) by about an order of magnitude compared to the content in the coal that is burned (Table III.7.4). In "pure" FA the prevailing form of sulfur is sulfate sulfur, which accounts for about 74% of S_t, and organic sulfur (23% S_t). Concentrations of trace metals in "pure" FA (in mg/kg) show declining order (Table III.7.3) [10^3 mg/kg] (Ba $>$ Sr $>$ Mn $>$ V) $\gg$ [$\geq 10^2$ mg/kg] (Rb, Cr, Zr, Ce, Zn, Ni, Cu) $>$ [$>$10 mg/kg] (Co, Pb, La,Y, Nd, Sc, Th, Cs, As) $>$ [$\cong$ 10 mg/kg] (Sm, Be, U, Mo, Br, Sb) $>$ [$<$10 mg/kg] (Yb, Hf, Bi, W, Se) $>$ [10^{-1} mg/kg] (Eu, Ta, Tb, Lu, Hg, Cd, Ag) $\gg$ [10^{-2} mg/kg] (Au, Ir). Fluoride occurs in amount of 90–120 mg/kg. Comparison of the elemental composition of FA from Polish (Ratajczak et al., 1999; Twardowska, 1999a; Twardowska and Szczepańska, 2001, 2002, 2003) and other European coal-fired power plants (Garavaglia and Caramuscio, 1994; Meij and Schaftenaar, 1994) that partly use coal imported from Poland (Mukherjee and Kikuchi, 1999), as well as from Indian (Khandekar et al., 1999; Mishra and Seth, 1999; Pradhan et al., 1999; Das, 2000) and the US power plants (Mattigod et al., 1999) shows high similarity (Twardowska, 1999a; Twardowska and Szczepańska, 2002, 2003). This is due to properties of hard coal that despite of variability in different seams and regions exhibits also definite common features that also result from elements behavior during combustion and gasification (Mukherjee and Kikuchi, 1999). Only minor changes in the ranking of elements by concentration are observed. Therefore, the observations derived from environmental behavior of FA from hard coal combustion in power plants of the USCB (Poland) can be generalized to a considerable extent.

Concentrations of 16 PAHs in the "pure" FA matrix (Table III.7.5) have been found to be low ($<$300 μg/kg), of this naphthalene was predominant ($\sim$80% of the total). Phenanthrene and acenapthalene were present in lower amounts, while PAHs proven to be carcinogens, including the five recommended for monitoring by WHO, seven displaying the lowest risk-based concentrations (RBC) after US EPA (Smith, 1994) and two representing priority group 1 in the list of 100 hazardous substances under CERCLA (1980) prepared by US EPA and ATSDR (1988), did not occur in detectable concentrations (analytical method: HPLC/fluorescence detection).

Table III.7.3. Phase composition of FA from hard coal combustion, "pure" (FA) and containing FGD solids from dry (FA + D-FGD) and semi-dry (FA + SD-FGD) process, qualitative identification (after Ratajczak et al., 1999).

CCW kind and origin	Mineral phase												
	CaO	Po	Mu	An	Q	C	Sk	Pl	He	Ma	Gr	Gy	Amorphous
"Pure" FA													
R-1	−	−	++	−	++	−	−	−	−	+	−	−	+++
L-1	−	−	++	+?	++	−	−	+?	−	+?	−	+?	+++
FA + D-FGDS													
R-2	++	−	++	++	+	+	−	−	−	+?	−	−	++
R-3	++	−	++	++	+	+	−	−	−	+?	−	−	++
O-1	+	−	+	+	+	++	−	−	−	−	−	+?	++
FA + SD-FGDS													
L-2	−	+	+	+?	+	+?	−	−	−	+?	−	−	++

R – FA from the Rybnik power plant; L – FA from the Laziska power plant; O – FA from the Opole power plant (Poland).

Mineral symbols: An – anhydrite; C – calcite; Gr – granite; Gy – gypsum; He – hematite; Ma – magnetite; Mu – mullite; Pl – plagioclase; Po – portlandite; Q – quartz; Sk – potassic feldspar.

Occurrence of the identified phase: +++, abundant; ++, mean; +, low; +?, trace, close to the detection limit, or a presence that cannot be excluded due to coincidence of diffraction peaks; −, lack or below the X-ray detection limit.

Table III.7.4. Elemental composition of pure FA from different coal-fired power plants compared to coal.

Constituents	The Netherlands[a]		Italy[b]	India			USA[c]	Poland[d,e]		
	Coal	FA	FA	Coal[f]	FA[g]	Coal ash[g]	FA	"Pure" FA[d]	Rybnik PP[e]	
									1973–1995	1997–mean
Major constituents (wt %)										
Al	1.65	15.0	14.0	0.85	14.94 (12.43–19.29)	12.76–13.90	8.88–15.13	12.77 (10.03–13.95)	12.81–14.66	13.95
C	73.2	4.3		78.11						
Ca	0.14	1.2	1.27	0.20	0.94 (0.07–3.43)	1.43–1.55	0.87–4.40	2.51 (0.61–4.63)	1.46–2.64	2.93
Cl	0.06	0.004								
Fe	0.51	4.7	5.03	0.75	3.42 (1.49–5.41)	2.79–2.80	8.27–19.93	5.48 (4.74–6.70)	4.69–9.90	5.67
K	0.17	1.5	2.26	0.074	0.52 (0.08–0.94)	0.81	1.55–2.38	1.32 (0.71–2.36)	1.76–3.76	0.71
Mg	0.08	0.7	0.71	0.038	0.43 (0.28–0.72)	0.84–3.06	0.32–0.46	1.36 (0.49–1.66)	1.03–1.52	1.61
N	1.6	0.3		1.56						
Na	0.04	0.4	0.3	0.051	0.19 (0.07–0.28)	0.36	0.01–0.84	1.38 (0.29–2.18)	0.38–0.91	2.18
P	0.01	0.10				0.24	0.25–0.44	0.26 (0.12–0.34)	0.065–0.34	0.21
S	0.7	0.1	0.39	1.89	0.14 (0.03–0.87)		0.50–0.87	0.33 (0.10–0.78)	0.18–0.58	
Si	2.82	25.7	23.3		29.01 (25.92–30.24)	26.51–27.22	19.97–24.47	26.75 (22.53–28.50)	21.37–24.64	23.15
Ti	0.08	0.8	0.9	0.045		0.72	0.54–0.86	0.58 (0.44–0.67)	0.16–1.10	0.60
Trace elements (mg/kg)										
Ag								0.84 (<0.4–1.7)		<0.4
As	3.7	34	40	3.72			10–149	37.3 (2–120)	15–48	17
B	43	163								
Ba	158	1438	1000	67.50	400	120–350	466–1702	1264.3 (927–1600)		1528
Be	3.3	29	16					11.2 (7–21)		8.0
Br	5.4	1.6						12.4 (7–21)		7.0
Cd	0.10	0.9	0.2	0.06				1.3 (0.5–2.7)		<0.5
Ce	17	151						124.8 (114–141)		48

(continued)

Table III.7.4. (Continued)

Constituents	The Netherlands[a]		Italy[b]	India			USA[c]	Poland[d,e]		
	Coal	FA	FA	Coal[f]	FA[g]	Coal ash[g]	FA	"Pure" FA[d]	Rybnik PP[e]	
									1973–1995	1997–mean
Co	5.8	52		2.29	14	5–25		44.6 (21–74)	12–122	36
Cr	14.4	131	133		145	40–100	179–319	154.7 (87–230)	20–253	170
Cs	1.0	9						20.5 (13–27.3)		22.6
Cu	16.6	151	130	6.28	72	20–60	66–165	123.4 (70–167)	30–199	104
Eu	0.4	4						2.3 (2.0–2.7)		2.3
F	80	127							90–120	
Ga	2.0	18			50	15–25	24–52		85	
Hf	1.2	11						5.2 (4.5–6.0)		4.9
Hg	0.16	0.23						1 (<1)		<1
I	2.2	0.6								
La	7.6	69			108	15–20		62.2 (51.1–70)		65.2
Mn	46	415	431	12.40			117–380			
Mo	3.0	27					19–81	11.2 (<5–15)	10	7.0
Ni	11	98	105	6.10			112–155	138.8 (45–276)	32–151	93
Pb	8.5	77	68	3.67	95	10–30	24–69	195.2 (43–507)	47–223	69
Rb	9.2	84		5.05			103–188	145.8 (120–176)		176
Sb	0.8	7	5.0				<10–80	9.5 (4.2–4.14)	7.5	5.6

Sc	3.3	30						27.12 (18.3–31)		29.2
Se	2.2	13	13	1.29	10	1–8	9–13	9.7 (<3–43)	<1–1.02	<3
Sm	1.8	16						10.7 (9.1–12.1)		11.4
Sr	107	971	1000		164	40–350		704 (406–1214)		543
Th	2.9	26	26	1.342	112	39–85		23 (21–25.1)		25.1
Tl	1.0	9	2.0							
U	1.5	13	10	0.436	21	8–27	16–25	10.6 (7.6–13.7)		7.6
V	29	262	197		321	55–150	179–374	278 (129–459)	500–570	244
W	1.0	9						6.4 (<3–9)		<3
Y					47	20–50		60.2 (46–84)		50
Zn	24	218	65	11.89	295	180–460	135–390	199.2 (16–507)	70–389	135
Zr							156–244	170 (162–179)	70–80	162

[a] After Meij and Schaftenaar (1994).

[b] After Garavaglia and Caramuscio (1994).

[c] After Mattigod et al. (1999).

[d] After Ratajczak et al. (1999).

[e] Twardowska (2003a–c) and Twarowska and Szczepanska (2003).

[f] After Khandekar et al. (1999).

[g] After Khandehar et al. (1999), Mishra and Seth (1999), Pradhan et al. (1999) and Das (2000).

Table III.7.5. Concentrations of polynuclear aromatic hydrocarbons (16 PAH), and polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) in power plant FA, "pure" (FA) and containing FGD products from dry (FA + D-FGD) and semi-dry (FA + SD-FGD) process.

Kind and origin of CCW	PAH (μg/kg)				PCDD, PCDF (tetra- to octa-) (ng/kg)			
	16 PAH (EPA)	6 PAH[a] (WHO)	7 PAH[b] (EPA)	2 PAH[c] (EPA)	PCDD	PCDF	PCDD + PCDF	I-TEQ
"Pure" FA								
L-1	262.9	2.7	3.0	<0.06	12.51	5.46	17.98	0.69
FA + D-FGDS								
R-2	311.6	3.8	2.9	<0.06	40.15	1.31	41.46	0.05
O-1	182.0	2.8	3.0	<0.06	25.02	7.87	32.89	0.36
High-FA + SD-FGDS								
L-2/su	42.9	0.9	2.2	<0.06	70.81	6.49	77.29	0.72
L-2	40.8	1.9	2.3	<0.06	2.26	0.84	3.11	0.04
Low-FA + SD-FGDS								
DB	39.1	5.0	3.0	<0.06	5.56	3.95	9.50	0.31
Range of RBC (US EPA data, after Smith, 1994), μg/l, μg/kg								
Tap water	0.92–1500	0.92–1500	0.92–920	0.92	1.1[H]			
Residential soil	8800–3100 × 10^3	8800–3100 × 10^3	8800–8800 × 10^3	8800	10,000[H]			
Industrial soil	39,000–41,000 × 10^3	39,000–41,000 × 10^3	39,000–39,000 × 10^3	39,000	46,000[H]			

R – CCW from the Rybnik power plant; L – CCW from the Laziska power plant; O – CCW from the Opole power plant (Poland); DB – CCW from the DRAX "B" power plant (Denmark); su – start-up phase. H – sum of hexachlorodibenzo-*p*-dioxins only.

16 PAH by US EPA: Naphthalene, acenaphtylene, acenaphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene.

[a] 6 PAHs recommended for monitoring by WHO (Fluoranthene Flth, benzo[b]fluoranthene BbF, benzo[k]fluoranthene BkF, benzo[a]pyrene BaP, benzo[ghi]perylene BghiP, indeno[1,2,3-cd)pyrene INP.

[b] 7 PAHs proven carcinogens after US EPA: Benzo[a]pyrene BaP, dibenz[ah]anthracene DBahA, benzo[b]fluoranthene BbF, benz[a]anthracene BaA, indeno[1,2,3-cd]pyrene INP, benzo[k]fluoranthene BkF, chrysene CHR.

[c] 2 PAHs the strongest carcinogens after US EPA: Benzo[a]pyrene BaP, dibenz[ah]anthracene DBahA.

An earlier evidence of PCDDs and PCDFs identification in FA and flue gases from municipal waste incinerators, fossil-fuelled power plants, fireplaces, etc. (DCC, 1978; Rappe, 1980) suggested that these hazardous compounds could be formed in any combustion process. The analysis of FA for PCDD and PCDF confirmed their occurrence in this material, but in much lesser, ng/kg range (Table III.7.5), which is in conformity with the more recent data (Huang and Buekens, 1995). Opposite to the referred data (DCC, 1978; Rappe, 1980; Huang and Buekens, 1995), in analyzed material PCDDs were definitely major constituents. They comprised 70% of the total PCDD + PCDF yield in the "pure" FA.

III.7.2.1.4. Radioactivity

The process of coal combustion results also in the increase of radioisotope concentration in FA. For the 25 years' period 1977–2002, the increase of ^{226}Ra, ^{232}Th and ^{40}K content in FA compared to coal ranged from 2- to 4.5-times (Twardowska, 2003c). Radioisotope content in FA is in general considerably higher than mean concentrations in the lithosphere (Table III.7.6), but still more than an order of magnitude lower than the threshold level 10 kBq/kg of total Ra-isotopes, which qualifies waste as a radioactive material in compliance with Polish Standard PN-88/Z–70071. According to Polish Standards for stowing materials PN-93/G–11010, FA can be thus unrestrictedly used for hydraulic stowing of mine workings. All FA fulfill also the criterion $^{226}\text{Ra} < 350$ Bq/kg and $^{228}\text{Ra} < 230$ Bq/kg, which defines a permissible level for the disposal of and using a material for civil engineering works at the surface. The natural radioactivity level of FA in many cases, however, exceeds parameters $f_1 \leq 1$ and $f_2 \leq 185$ established by the National Polish Institute of Construction Techniques for assessing the applicability of material for production of construction materials. These parameters, which define the maximum acceptable level of γ- and α-radiation, respectively, are being evaluated as follows:

$$f_1 = 0.00027C_{\mathrm{K}} + 0.0027C_{\mathrm{Ra}} + C_{\mathrm{Th}} \leq 1, \qquad f_2 = C_{\mathrm{Ra}} \leq 185,$$

where C_{K}, C_{Ra} and C_{Th} are the concentrations of isotopes ^{40}K, ^{226}Ra and ^{228}Ra.

FA that does not fulfill these requirements cannot be used for production of construction materials. Variable f_1 and f_2 coefficients for Polish FA imply a requirement of analysis for radioactivity level of every portion of FA, which is considered to be used for this purpose. Scarce data for Indian FA showed increase of the radioactivity level for ^{226}Ra in the range from 6.2 to 4.2-fold compared to coal and from 5.0 to 2.6-fold compared to soil, and exceeded the average value for soil from >2 to >5 times. Concentrations of ^{228}Ra exceeded the corresponding concentrations in coal from 8.9 to 4.5 times and in soil from 7.5 to 2 times, and average value for soil from >2 to >3.5 times. Elevated concentrations of U and Th in FA from combustion of coal from the Talcher coalfields in India (Table III.7.4) also suggest the need of paying heed to this question, which up to now is beyond consideration in that country and has been commented as negligible on the basis of an unknown number of samples analyzed for ^{226}Ra and ^{228}Ra, which indeed displayed the concentrations within safety limits (Raghuveer, 1999).

Table III.7.6. Range and mean concentrations of radionuclides in coal combustion waste compared to coal and lithosphere (Poland and India).

Material	Concentration of radionuclides (Bq/kg)			Radiation coefficients[a]	
	^{40}K	^{226}Ra	^{228}Ra	f_1	f_2
Rybnik power plant, Silesia, Poland (1977–1997)[b]					
FA	917 (497–1106)	116 (< 18.5–197)	78 (43–122)	0.90 (0.47–1.26)	116 (< 18.5–197)
FA + D-FGDS[b]	746 (666–805)	103 (57–124)	88 (74–102)	0.86 (0.79–0.94)	103 (57–124)
Boiler slag	756 (336–908)	93 (28–153)	68 (30–103)	0.74 (0.35–0.98)	93 (28–153)
All Polish power plants					
(1980–1995)[c]					
FA	701 (33–1386)	124 (< 1–395)	89 (< 1–194)	0.91 (0.04–1.44)	124 (< 1–395)
Boiler slag	541 (1–1260)	95 (2–335)	70 (1–210)	0.70 (0.04–1.63)	95 (2–335)
(1996–2000)[d]					
FA	716 (20–1664)	114 (8–363)	90 (2–206)	0.89 (0.07–1.77)	114 (8–363)
Boiler slag	591 (20–1120)	99 (5–482)	77 (1–188)	0.75 (0.04–2.08)	99 (5–482)
2001[e]					
FA	680 (56–1062)	119 (11–268)	92 (2–141)	0.90 (0.04–1.36)	119 (11–268)
Boiler slag	590 (57–1047)	89 (9–198)	73 (5–130)	0.71 (0.16–1.19)	89 (9–198)
Coal (1977–1997)					
Coal	316 (115–438)	37 (21–81)	24 (14–34)	0.28 (0.16–0.39)	37 (21–81)
Lithosphere					
Soil and rock	380 (100–700)	25 (10–50)	25 (7–50)		
Indian power plants (after Raghuveer, 1999)					
Coal ash		55.5–133	55.5–82.5		55.5–133
Coal		9–31.5	6–21		9–31.5
Construction materials					
Concrete/cement		33–74	30–85		33–74
Brick		52–96	37–126		52–96
Lithosphere					
Soil		26 (11–52)	26 (7–48)		26 (11–52)
Rock, stone, sand		15–111	4–167		15–111

[a] Coefficients defining applicability of material for production of construction materials with respect to the natural γ- and α-radiation. Regulatory limits: $f_1 < 1$ (for γ-radiation); $f_2 < 185$ (for α-radiation) (ITB, 1995).

[b] Data on routine analysis of CCW from Rybnik power plant for radioactivity carried out by Laboratory of Radiometry, Central Mining Institute in 1977–1997; data for FA + D-FGDS are from 1990 to 1997.

[c] After Central Statistical Office, 1997 (data of the Central Laboratory of Radiological Protection).

[d] After Central Statistical Office, 2001 (data of the Central Laboratory of Radiological Protection).

[e] After Central Statistical Office, 2002 (data of the Central Laboratory of Radiological Protection).

III.7.2.2. Effect of FGD processes on FA composition

III.7.2.2.1. Process characterization

The FGD processes, which have been developed as a part of clean energy technologies, may exert a considerable effect on the properties of FA, depending upon the composition and proportion of FGDS and the FA in the end product (EP). In general, widely used technologies of FGD can be defined as dry, semi-dry, mixed and wet processes, which differ by the reagent used, method of the reagent injection and the kind of the reaction product (e.g. Collins, 1992; Anonymous, 1995a–c; Blaszczak and Buzek, 1998; Punshon et al., 1999). In the dry methods, the reagent is injected in the dry form, and the end product is also dry. In the semi-dry methods, the reagents are injected thoroughly or partially wet, while the end product is dry. In the wet methods, both the input reagent and the reaction product are wet. The majority of currently used methods are based on lime in the form of limestone, quicklime, slaked lime or dolomite lime as a reagent for binding SO_2. This results in calcium compounds enrichment in the end product, which is highly dependent upon the used desulfurization technology (Twardowska, 1999b).

In the dry method, limestone or pulverized limestone is injected into the boiler furnace, where the calcium carbonate decomposes thermally to form calcium oxide and carbon dioxide. A portion of SO_2 and all of the SO_3 reacts with CaO to form $CaSO_4$. The flue gas desulfurization solids in the dry process (D-FGDS) are the newly formed $CaSO_4$ and the unreacted excess of CaO. They are carried along with the coal FA out of the boiler, forming the end product (FA + D-FGDS), which is highly alkaline due to the excess of CaO with respect to the initial SO_2 (Ca:S = 2.5–3.1). Due to a low efficiency of desulfurization (20–40% for conventional pulverized coal fired boilers) and sorbent use (10–15%), the dry processes are being replaced by semi-dry or wet methods and generally treated as transitory ones. For fluidized-bed boilers (FBB), end product also consists of FA and spent limestone sorbent containing $CaSO_4$, unreacted CaO, MgO and inerts (Collins, 1992; Mukherjee and Kikuchi, 1999). The efficiency of this process ranges from 85 to 95% due to different operational parameters.

The semi-dry desulfurization process consists of injecting a pulverized suspension of slaked lime into the flue gas flowing through the reactor, where calcium hydroxide reacts with SO_2 in flue gas. The temperature of the process is 15–20°C higher than the dew-point of a Ca:S ratio of 1.2–1.8. The primary reaction component is $CaSO_3$, which further partially oxidizes into $CaSO_4$. The final end product is separated from the flue gas in the bag filters or electrostatic precipitators. The end product (FA + SD-FGDS) is a dry powder, which consists of FA and the reaction products of the injected slaked lime and the SO_2 in the flue gases containing $CaSO_3$, $CaSO_4$, $Ca(OH)_2$, $CaCO_3$ and moisture. The efficiency of the process is from 70 to 80% up to 90%. Efficiency of sorbent use is about 45%. These processes are offered by a dozen firms (e.g. ABB-NID one-stage process). Due to addition of FGDS, the amount of the end product, i.e. FA along with FGDS, increases by 20–30%.

Combined methods are coupling elements of the dry and semi-dry processes, i.e. pulverized limestone injection into the boiler with post-furnace humidification in an activation reactor, e.g. ER (Rybnik) or LIFAC process (Anonymous, 1995b,c). The first stage is a typical dry process. In the second, post-furnace stage of the combined process, the flue gas is moisturized by injecting water into a specially designed activation reactor, with, or without addition of slaked lime. Within this reactor, the unreacted CaO is converted into $Ca(OH)_2$, which readily reacts with SO_2. The efficiency of desulfurization is similar as in the semi-dry process, and reaches 80–90%. By closely controlling the parameters of the process, in particular the temperature in the reactor, the CaO conversion and SO_2 reduction can be maximized, up to >90%. Due to addition of FGDS, the amount of the end product, i.e. FA along with FGDS increases by 20–30%. The end product is similar as in the one-stage semi-dry process described above (FA + SD-FGDS). In some semi-dry processes, FA and the reaction product of desulfurization are collected separately. In this case, dry end products consist of "pure" FA and low-FA flue gas desulfurization solids (low-FA-FGDS). The compositions of end products from dry and semi-dry desulfurization process are presented in Table III.7.7.

Currently, the most worldwide spread desulfurization methods are wet processes, mainly based on the limestone as a sorbent of SO_2 (Punshon et al., 1999). In the USA, they account roughly for 80% and in Germany for 90% of all the applied desulfurization processes. The process consists in a sorption of SO_2 in a water suspension of ground limestone in scrubbers and adsorption columns. The end product is calcium sulfate and sulfite crystals in the form of water suspension separate from FA. The excess of Ca used in the process is low (Ca:S = 1.03–1.05) and the pH of the suspension is 5.5–6.0. The efficiency of the desulfurization process exceeds 90%. The wet FGD processes do not influence the properties of other CCW (FA, BA, slag), but cause formation of

Table III.7.7. Phase composition of end products from dry (FA + D-FGDS) and semi-dry FGD process (FA + SD-FGDS) with high- and low-FA content.

FGD process	FA + D-FGDS (Rybnik PP)	FA + SD-FGDS			
		High-FA[a]		Low-FA[b]	
		LIFAC	ABB-NID (Laziska PP)	RYBNIK (Rybnik PP)	FLÄKT (DRAX-B PP)
Phase composition (% wt)					
Fly ash	85	50–70	>80	2–4	9–12
$CaSO_3$	0.011	10–15	5.55	31–42	40–50
$CaSO_4$	3.54	10–15	3.14	12–14	7–12
$CaCl_2$	1.00		ND	1–2	1–4
$CaCO_3$	1.53	5–15	7.55	9–10	2–4
$Ca(OH)_2$	Trace			29–36	8–15
CaO	10.0	Trace	Trace		Trace
Moisture	ND	2–5	2–5	2	1–3
Crystal water	ND				7–11
Neutral compounds	ND		ND		3–5

ND – not determined.

[a]LIFAC, ABB-NID – flue gas desulfurization process with high-FA content in the end product.

[b]RE-RYBNIK, FLÄKT – FGD process with low-FA content in the end product.

a considerable amount of FGD solids that create problems with their management. The proportion of FGD solids with respect to other CCW in the USA accounts for about 28% (Collins, 1992) to over 23% (Stewart, 1999). The environmental behavior of FA when the wet desulfurization of flue gases is used does not differ from that of the "pure" FA from the power plants not using FGD process. The FGD products in the form of suspension contain 5–15% of solids before dewatering and need further fixation for stabilization.

In 1990, the total utilization of FGDS in the USA as a percentage of production accounted for 1.1% (Collins, 1992), in 1992 it was reported to be 2% (Tyson, 1994), and in 1996–1997 it reached 6.9–7% (Butalia and Wolfe, 1999; Stewart, 1999), while the utilization of other CCW accounted in total for 24.8% of production in 1992 and remained at the same level in 1996–1997 (24.7%). In Germany, FGDS use, mainly in the wallboard industry, is considerably higher. Recent research and demonstration projects have indicated that dry and wet FGD materials can be safely and cost-effectively utilized also in highway construction, mine reclamation and agricultural applications (Butalia and Wolfe, 1999; Punshon et al., 1999).

III.7.2.2.2. Characteristics of FA properties resulting from FGDS admixture

The admixtures of FGDS significantly influence properties of end products, depending upon the applied technology of desulfurization (Twardowska, 1999b). The final end product of the dry desulfurization process (FA + D-FGDS) is FA (~70–80%) with the reaction products from the dry desulfurization process (D-FGDS). They consist of unreacted CaO and reaction products, mainly anhydrite $CaSO_4$, as well as minor amounts of $CaCO_3$ and $CaCl_2$ (Table III.7.7). The chemical composition of FA + D-FGDS showed significant increase of S_t, Ca and carbonates compared to the "pure" FA (Table III.7.8). Due to the presence of unreacted CaO, the end product is reactive and highly alkaline. The high proportion of FA (70–80%) moderates reactivity of the FGD reaction products.

The end product of the semi-dry process consists of dry FA and the reaction products of the injected limestone and SO_2 in the flue gases. The reaction products from FGD consist of calcium compounds: sulfite $CaSO_3$, sulfate $CaSO_4$, hydroxide $Ca(OH)_2$, carbonate $CaCO_3$ and accessory amount of chloride $CaCl_2$. The composition of the end product from the semi-dry desulfurization processes, in particular the proportion of calcium compounds, depends upon the proportion of FA, which differs significantly for different systems and varies from 2 to 75%. Accordingly, the end products can be thus either high- or low-FA material. The content of $CaSO_3$, which is a main component of the end product, generally ranges from 10 to 60%, $CaSO_4$ occurs in accessory amounts, and $Ca(OH)_2$ prevails over $CaCO_3$ (Table III.7.7).

The proportion of FA and FGD reaction products determines the chemical composition of the end product of a semi-dry process (FA + SD-FGDS) (Table III.7.8). The end product of semi-dry ABB-NID process implemented at the Laziska power plant (Poland) displayed several times higher sulfur and calcium contents compared to the pure FA from the same plant. The alkalinity of the end product expressed as the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3)$ (van der Sloot et al., 1984) was close to that of a pure FA. Because of the presence of chemically unstable sulfides, the end product showed thixotropic properties.

Table III.7.8. Elemental composition of FA containing FGD solids from dry (FA + D-FGDS) and high-FA semi-dry process (FA + SD-FGDS) compared to pure FA.

Element	Rybnik power plant		Opole power plant	Laziska power plant	
	FA (1973–1993)	FA + D-FGDS (1990–1995)	FA + D-FGDS (1993–1994)	FA (1994–1995)	FA + SD-FGDS (1995)
Macro-elements (% wt)					
Al	13.94 (12.82–14.60)	11.74 (9.96–13.26)	10.46 (8.93–11.84)	14.53 (14.49–14.58)	10.83
Ca	**2.12 (1.47–2.63)**	**8.62 (6.59–10.66)**	**13.63 (11.68–16.05)**	**2.84 (2.82–2.89)**	**8.12**
Cl	0.21	ND	ND	ND	ND
Fe	6.68 (4.69–9.91)	5.45 (4.27–6.73)	5.36 (5.05–5.52)	5.10 (4.86–5.13)	4.45
K	2.36 (1.76–2.76)	1.79 (1.59–2.08)	1.99 (1.72–2.32)	2.48 (2.39–2.58)	1.73
Mg	1.18 (1.03–1.52)	0.97 (0.88–1.03)	1.66 (1.39–1.84)	1.81 (1.58–1.87)	1.17
Na	0.58 (0.39–0.91)	0.53 (0.35–0.69)	0.67 (0.59–0.74)	0.46 (0.44–0.48)	0.53
P	0.18 (0.06–0.35)	0.31 (0.22–0.37)	0.16 (0.09–0.21)	0.28 (0.26–0.29)	0.30
S	**0.37 (0.18–0.78)**	**1.78 (1.16–1.97)**	**1.11 (0.77–1.72)**	**0.30 (0.28–0.32)**	**2.22**
Si	22.47 (21.52–24.82)	18.40 (15.69–20.57)	18.99 (17.38–20.81)	22.85 (22.82–22.88)	20.54
Ti	0.53 (016–1.10)	0.59 (0.13–1.16)	0.64 (0.57–0.67)	0.68 (0.61–0.75)	0.50
Trace elements (mg/kg)					
As	42 (33–48)	27 (12–39)	20 (15–22)	26–28	26
Ba	1528	879–1066	1230 (1047–1346)	1372 (1262–1385)	913–1052
Cd	2.7 (<0.5–5)	1.2–1.6	3.1 (1.2–5)	1.7 (0.5–2.5)	1.2
Co	61 (12–102)	59 (16–92)	41 (31–49)	40	18–30
Cr	166 (20–253)	156 (40–197)	130 (107–160)	143 (122–165)	56–136

Cu	120 (30–197)	121 (25–151)	147 (129–182)	134 (98–170)	31–88
F	105 (90–120)	105	ND	ND	ND
Ge	<5	<5	<3	<3	<3
Mn	580 (360–840)	590 (200–650)	590 (550–660)	720	ND
Mo	7–10	<5–7	<3–9	15	6
Ni	109 (32–151)	108 (35–132)	90 (78–105)	90	24–69
Pb	112 (21–223)	84 (45–174)	92 (67–108)	64 (50–90)	22–104
Sb	5.6	5.4–5.9	7.8	9.5–11.6	4–16
Sr	543	438–487	725 (568–948)	630	368–444
Tl	ND	1.76	1.7	2.7	0.65
V	244–500	183–220	270	251	178–185
Zn	218 (70–280)	193 (80–260)	175 (116–220)	193 (143–225)	36–190

Elements showing distinct increase in FA + FGD compared to pure FA are bold; ND – not determined.

Comparison of data leads to a general conclusion that despite many different and variable sources of coal supply to power plants (usually, to each power plant from several, up to 20, mines and coal seams of the USCB), the general pattern of trace element occurrence in FA matrix remained similar within the years studied. The occurrence of D-FGD products in FA generally resulted in a decrease of metal concentrations in FA + D-FGDS as an effect of addition of low-metal FGD solids, though no strong effect of reaction products from dry desulfurization (D-FGD products) on trace metal concentrations in FA + D-FGDS has been observed. The concentration range of each metal for representative samples FA + D-FGDS compared to "pure" FA was within the deviation caused by the heterogeneity of fuel in the different power plants and did not show regular trends due to the relatively low proportion of D-FGDS in the end product. Nevertheless, comparison of metal contents in FA(R) and FA + D-FGD(R) analyzed in parallel suggested the reducing effect of D-FGDS admixture on the end product (Tables III.7.8 and III.7.9).

On the other hand, up to 2–3-fold decrease of metal concentrations in high-FA end product containing SD-FGD products has been found. This can be explained by the "diluting" effect of trace metal-free reaction products (calcium sulfite, sulfate and carbonate compounds), comprising up to 60% of the high-FA + SD-FGD end product.

An extremely low trace metal content occur in the low-FA + SD-FGD solids. They appeared to be approximately 5–10 times lower than these in the high-FA + SD-FGD end products. This proves FA is the main source of trace metals in the end products from the FGD process.

Therefore, FGD solids from dry and semi-dry FGD processes may have a considerable effect on the end product properties and release of constituents from this material due to its influence on pH, contents and forms of sulfur and calcium compounds, as well as on concentrations of trace elements. With respect to trace element contents, FGD products caused a positive "diluting" effect on the FA (Tables III.7.8 and III.7.9).

Concentrations of the total 16 PAHs in the FA matrix containing D-FGD solids ranged from 182 to 312 μg/kg. They appeared to be close to those of "pure" FA, also with respect to quantitative composition and proportions of PAH compounds. While no distinct effect of dry FGD process on PAH occurrence was noticed, the semi-dry process results in reduction of 16 PAHs content both in high-FA + SD-FGDS and in low-FA + SD-FGDS close to an order of magnitude, mainly due to the decrease of naphthalene content, which was a dominant compound (Table III.7.5).

In FA with FGDS, concentrations of dioxins and dibenzofurans occur in the low, ng/kg, range. The low formation of these compounds in highly effective power plant boilers is mainly due to complete combustion resulting in non-soothing flames. The highest concentrations of PCDDs and PCDFs were found in the end product from dry desulfurization of flue gases (FA + D-FGDS), where also the highest PAHs content occurred. In the "pure" FA, PCDD + PCDF content was about half of that found in FA + D-FGDS, while PAHs were present within the same range. Both high-FA and low-FA semi-dry desulfurization processes cause about an order of magnitude reduction of these hazardous compounds in the end product. Also in this material, opposite to the referred data (DCC, 1978; Rappe, 1980; Huang and Buekens, 1995) PCDDs were definitely the major constituents. They comprised in the "pure" FA 70%, in FA + D-FGDS 76–97%, and in FA + SD + FGDS 58–72% of the total PCDD + PCDF yield.

Table III.7.9. Concentration of trace metals in parallel samples of power plant FA, pure and containing FGD solids from dry and semi-dry process with high- and low-FA content.

CCW	Concentration of trace metals (mg/kg)									
	As	Cd	Cr	Cu	Ni	Pb	Sb	Se	Tl	Zn
"Pure" FA										
R-1	41.0	<2	170	104	93	69	ND	<3	ND	135
L-1	28.0	1.56	46.8	62.7	58.0	80.9	11.60	<1.07	2.66	97.6
FA + D-FGDS										
R-2	17.0	1.32	40.8	45.9	44.1	51.7	7.45	<1.02	1.76	106
O-1	2.85	1.62	54.1	65.8	49.0	67.3	8.19	<0.99	1.70	154
High-FA + SD-FGDS										
L-2/su	16.0	1.10	38.7	41.7	39.9	45.1	8.00	<1.07	1.57	69.6
L-2	<1.02	1.22	23.1	31.1	24.4	21.6	4.06	<1.05	0.652	35.9
Low-FA + SD-FGDS										
DB	<1.05	<0.50	3.63	2.45	3.57	4.84	0.714	4.79	0.053	7.32
Range of RBC (US EPA data, after Smith, 1994), mg/l, mg/kg										
Tap water	0.011	0.018	0.180	1.40	0.73	3.7×10^{-6}	0.015	0.180	0.0029	11.0
Residential soil	23	39	390	2900	1600	0.0078	31	390	6.3	23,000
Industrial soil	310	510	5100	38,000	20,000	0.1	410	5100	82	310×10^3

FA – pure power plant fly ash; FA + D(FGD) – FA containing reaction products from dry FGD process; FA + SD(FGD) – FA containing reaction products from semi-dry flue gas desulfurization process; (R) – Rybnik power plant; (O) – Opole power plant; (L1) – Laziska power plant; (L2/su) – start-up stage of ABB-NID semi-dry desulfurization process, high-FA end product; (L2) – Laziska power plant, operational stage of ABB-NID semi-dry desulfurization process, high-FA end product; (DB) – DRAX-B power plant, FLAKT semi-dry desulfurization process, low-FA end product.

The reduction of PCDD + PCDF content in end products from the SD-FGD process was mainly due to the dramatic decrease (>80%) of PCDD concentrations (Table III.7.5).

Blending FGD reaction products results also in the reduction of FA + FGDS radioactivity compared to the "pure" FA (Table III.7.6).

Therefore, FGDS from dry and semi-dry FGD process may have a considerable effect on the end product properties and release of constituents from this material due to influence on pH, content and forms of sulfur and calcium compounds and concentrations of trace metals. With respect to trace metals content, FGD products exert positive "blending" effect on the FA. The semi-dry desulfurization process causes considerable reduction of organic compounds of a proven carcinogenicity, though their occurrence is generally low and non-problematic. The phase and chemical composition of FGDS in dry ($CaSO_4$, residual CaO) and semi-dry process ($CaSO_3$, $CaSO_4$, $Ca(OH)_2$, $CaCO_3$) will affect also the environmental behavior of the disposed or utilized end product.

III.7.2.3. Hydrogeological parameters of FA

Both from the environmental and technological aspects, hydrogeological parameters of FA:water mixtures are of a special importance, in particular hydraulic conductivity k (m/s), the time of solidification t_s (days) and penetration resistance R (kPa). These parameters define circulating conditions of pore solution in the material and permeability to air, which determine the extent of contaminant migration and sealing properties of FA:water mixture.

III.7.2.3.1. Hydraulic conductivity

The presented data show that CCW contain high concentrations of mainly inorganic contaminants, of which trace metals are of a special concern due to high mobility and proven toxic effect of many of them (some metals are also proven carcinogens). This material disposed of in surface impoundments or exposed to the atmospheric conditions when used as a structural fill, may be a source of a serious contamination of groundwater resources, provided the toxic compounds can be mobilized from the matrix and migrate to the aquatic environment. From this standpoint, the hydrogeological parameters defining the ability of solutions to penetrate through the waste layer are crucial for evaluating pollution potential of the waste, besides the concentration of contaminants in the material and their susceptibility to mobilization. The major parameters, which define filtration properties of material, are effective porosity n_e responsible for transport of solutions and hydraulic conductivity k. In turn, total porosity, pore structure and the specific surface of the material play an important role in release and migration of contaminants. The typical pore structure and hydraulic properties of FA, "pure" and containing reaction products from the dry desulfurization process (FA + D-FGDS) in the form of solidified mixture 1:1 (wt) with distilled water, is presented in Table III.7.10 and in Figures III.7.3–III.7.5. The effective porosity n_e of these wastes ranged from 16.9 to 26.4%, which is characteristic of materials of high and very high porosity (Pazdro and Kozerski, 1990). The FA + D-FGDS has much lower porosity due to the cementitious effect of calcium carbonate and sulfate, though still considerably higher than natural clays. The values of hydraulic conductivity for "pure" FA at the level of $k \geq 10^{-8}$ m/s do not fulfill the criteria of impermeability both

Table III.7.10. Hydraulic conductivity parameters of CCW compared to natural soils.

Material		Density (g/cm^3)		Porosity (%)		Pore specific surface (m^2/g)		Mean pore diameter (μm)	
No.	Kind, symbol[a]	Bulk, ρ_d	Specific, ρ_s	Total, n_t	Effective, n_e	Total, S_t	Capillary voids, S_e	Total, d_t	Capillary voids, d_e
"Pure" FA									
1	R-1	1.1773	1.6037	26.58	26.40	0.461	0.250	1.9599	3.5816
2	L-1	1.0479	1.3658	23.24	21.13	4.913	0.402	0.1806	2.0068
FA + D-FGDS									
3	R-2	1.0620	1.2830	17.23	16.03	1.231	0.231	0.5271	2.7581
4	O-1	1.0306	1.3329	22.68	22.25	1.463	0.316	0.6018	2.7369
Natural soils									
5	Clay	2.1441	2.7048	20.73	11.23	7.583	0.236	0.0510	0.8883
6	Loam	1.9401	2.4427	20.25	2.25	22.514	0.019	0.0188	2.3949

R – FA from Rybnik power plant; L – FA from Laziska power plant; O – FA from Opole power plant (Poland).

[a] "Pure" FA – power plant FA without desulfurization products; FA + D-FGDS – FA containing reaction products from dry FGD process.

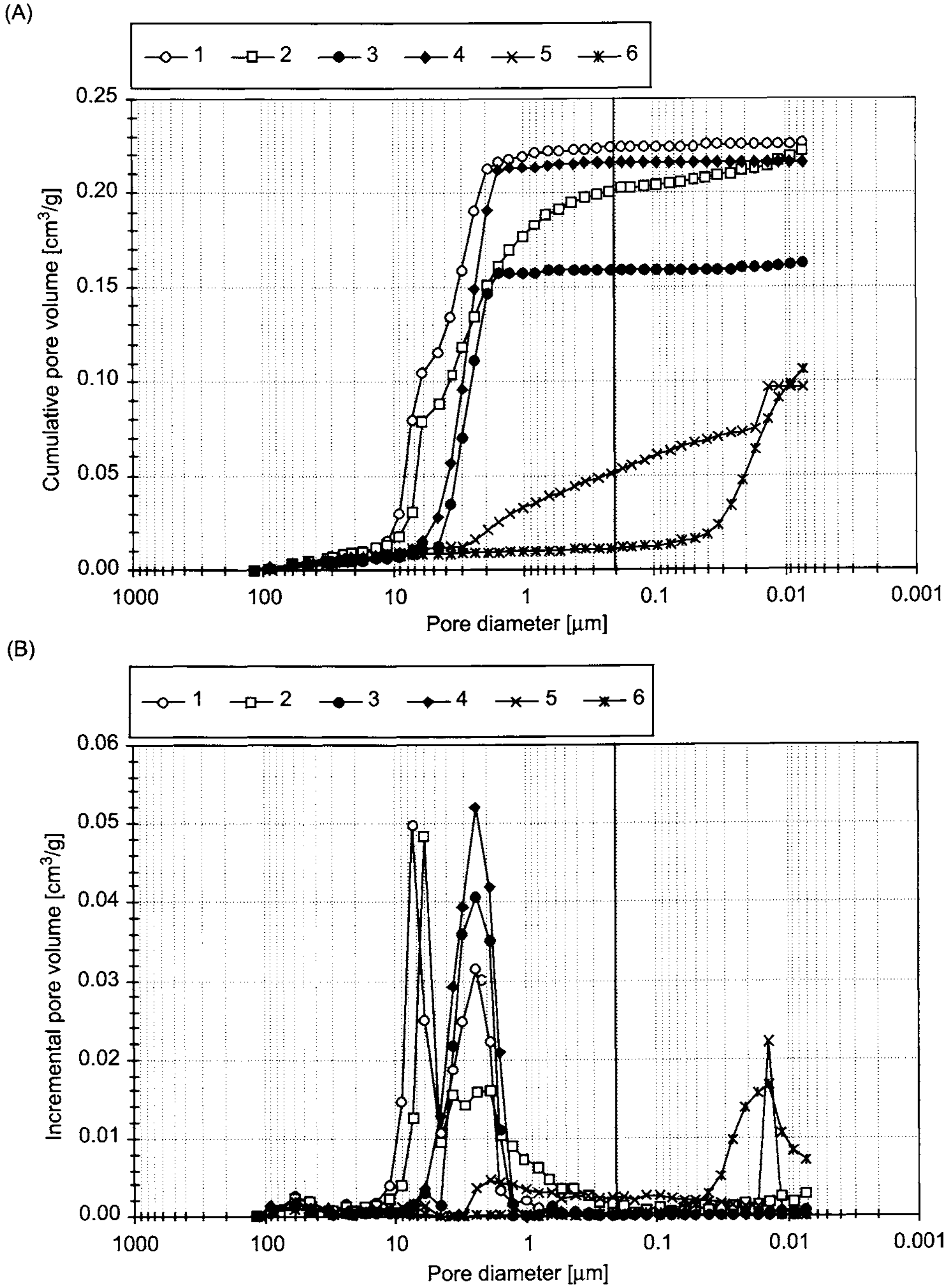

Figure III.7.3. Pore structure of solidified CCW: water mixtures (1:1 wt) compared to natural soils. (A) Cumulative and (B) incremental pore volume (cm^3/g) vs. pore diameter (μm). 1 – "pure" FA from the Rybnik power plant; 2 – "pure" FA from the Laziska power plant; 3 – FA + D-FGDS from the Rybnik power plant; 4 – FA + FGDS from the Opole power plant; 5 – clay; 6 – loam.

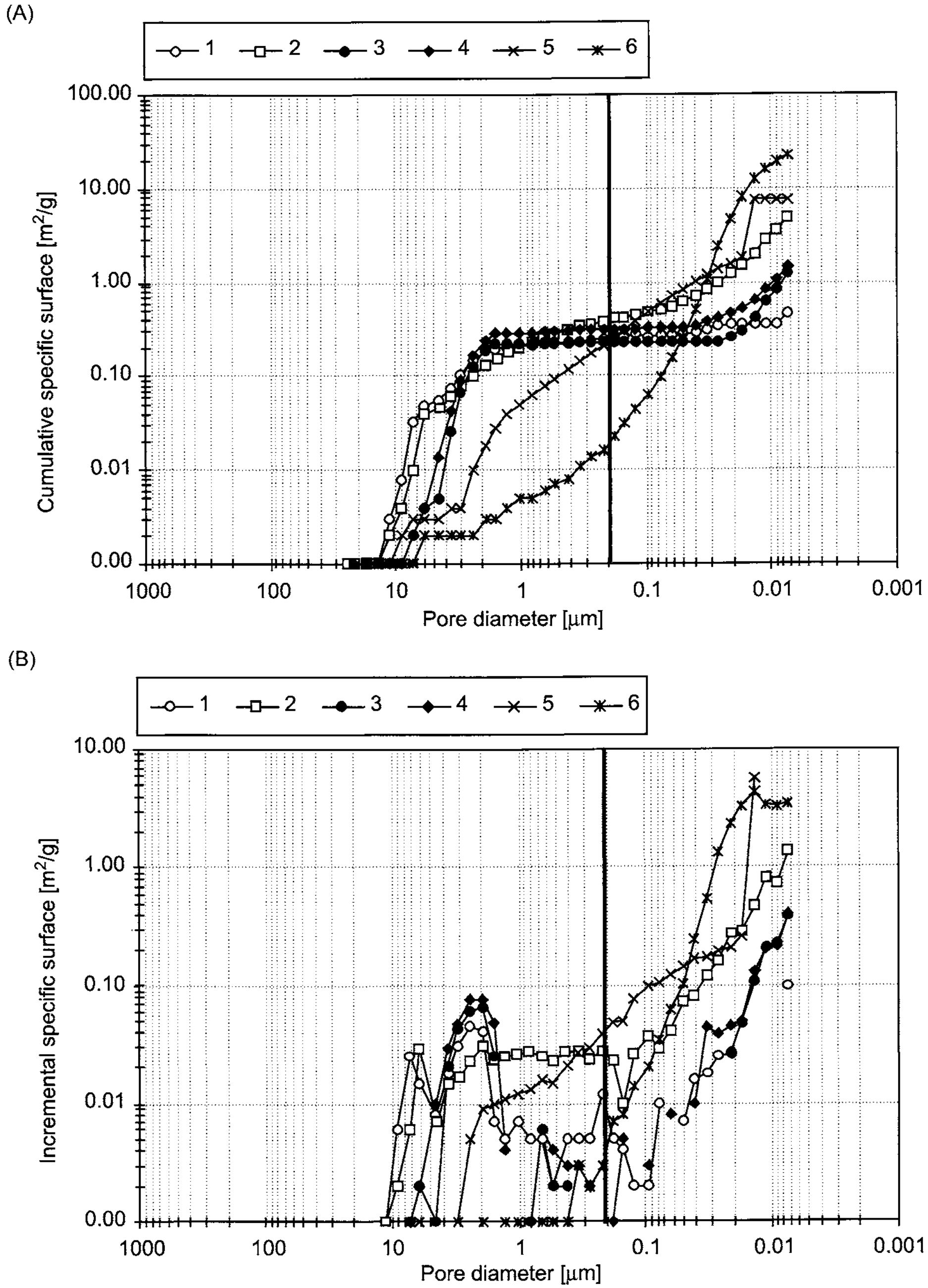

Figure III.7.4. Pore structure of solidified CCW: water mixtures 1:1 (wt) compared to natural soils. (A) Cumulative and (B) incremental specific surface (m^2/g) vs. pore diameter (μm). 1 – "pure" FA from the Rybnik power plant; 2 – "pure" FA from the Laziska power plant; 3 – FA + D-FGDS from the Rybnik power plant; 4 – FA + FGDS from the Opole power plant; 5 – clay; 6 – loam.

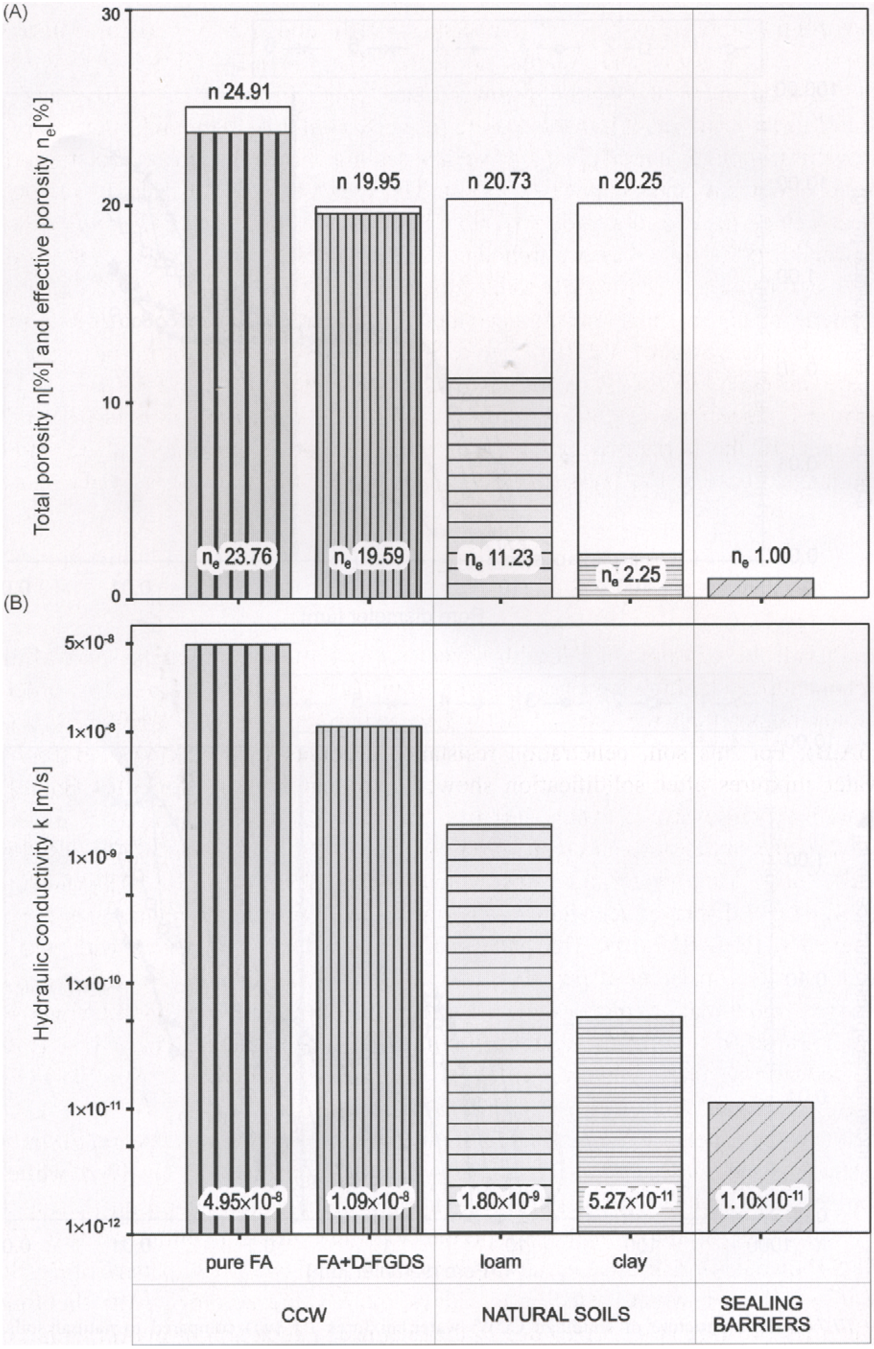

Figure III.7.5. Hydraulic properties of solidified CCW: water mixtures 1:1 (wt) compared to natural soils and sealing materials. (A) Total porosity *n* (%) and effective porosity n_e (%); (B) Hydraulic conductivity *k* (m/s). 1 – "pure" FA from the Rybnik power plant; 2 – "pure" FA from the Laziska power plant; 3 – FA + D-FGDS from Rybnik power plant; 4 – FA + FGDS from Opole power plant; 5 – clay; 6 – loam.

for horizontal flow (Pazdro and Kozerski, 1990) and for a vertical infiltration (Table III.7.11, Witczak and Adamczyk, 1994). The FA + D-FGDS has a hydraulic conductivity an order of magnitude lower than "pure" FA ($k = 10^{-9}$–10^{-8} m/s) and hence fulfills the criterion of impermeability for horizontal flow in groundwater reservoirs. These values, though, classify it as a weakly sealing material with respect to vertical infiltration (Witczak and Adamczyk, 1994). The rocks considered in hydrogeology as practically impermeable to a horizontal flow in an aquifer ($k = 1.0 \times 10^{-8}$ m/s) (Pazdro and Kozerski, 1990) do not assure sufficient barrier properties with respect to the vertical infiltration of water from the surface to the groundwater layer. The mean infiltration rate of atmospheric precipitation in Poland accounts for 100 mm/yr, which is adequate to the vertical infiltration rate of 3.2×10^{-9} m/s. This means that the infiltration water may percolate through the rocks of the hydraulic conductivity $k = 3.2 \times 10^{-9}$ m/s at a gradient = 1. Therefore, FA mostly does not fulfill the criteria of impermeability both with respect to the horizontal and vertical water flow. The leaching and transport of contaminants from the FA layer to the groundwater by the percolating water can thus occur.

III.7.2.3.2. Penetration resistance

Generally, all the mixtures of FA with water (1:1 wt) after solidification (16–24 days) were characterized by high R-values, ranging from 1000 to 19,000 kPa, i.e. 1–2 orders of magnitude higher than the ones of natural cohesive soils such as boulder clay (Fig. III.7.6A,B). For this soil, penetration resistance accounts for 190 kPa. Therefore, the FA:water mixtures after solidification showed excellent sealing properties against air penetration (Twardowska, 1999a,b, 2003b).

The R-values of mixtures based on pure FA appeared to be the lowest (1100–1200 kPa) (Fig. III.7.6A). Mine water mixtures which were 1:1 wt with FA + D-FGDS and FA + SD-FGDS displayed R-values roughly an order of magnitude higher than the ones with pure FA (Fig. III.7.6B). The pattern of $R = f(t)$ for 1:1 mixtures with water of different salinity consisting of pure FA, FA + D-FGDS and FA + SD-FGDS suggested that in the solidification process of these end products different mechanisms were involved: Phase 0 – instant chemical binding (FA + SD-FGDS); Phase I – gravitational dewatering and evaporation losses (FA, FA + D-FGDS, FA + SD-FGDS); Phase II – chemical binding (FA + D-FGDS).

The changes of penetration resistance of pure FA:water mixtures appeared to be very slow. It was a one-phase process, where almost entirely phase I was involved, while the role of phases 0 and II were negligible. The process of solidification and changes of R-value of water mixtures with end products of dry desulfurization process FA + D-FGDS showed different, specific for this kind of material two-phase pattern of R-values. In the initial phase I, which lasted up to 5 days, the R-value was low. After this time, a sharp increase of R-value occurred due to the chemical interaction of matrix with a pore solution (phase II). The chemical process of solidification was similar to the hydration and cementation of a lime mortar. Mixtures consisting of FA + D-FGDS showed the shortest solidification time (15–20 days) and the highest R-values (13,000–19,000 kPa). Use of high-salinity water for mixture preparation resulted in an increase of R-value of

Table III.7.11. Classification of rocks as protective barriers insulating groundwaters against vertical infiltration (after Witczak and Adamczyk, 1994).

Proposed class name (after Witczak and Adamczyk, 1994)	Vertical hydraulic conductivity k, m/d (m/s)	Examples of rock	Class name
Practically non-insulating	1×10^{-1} ($>1.1 \times 10^{-6}$)	Loamy sand, sandy loam, loam/low-fissure rocks	Very highly permeable
Very weakly insulating	From 1×10^{-1} to 1×10^{-3} (from 1.1×10^{-6} to 1.1×10^{-8})	Silt loam, sandy clay loam, low-fissure rocks	Highly permeable
Weakly insulating	From 1×10^{-3} to 1×10^{-5} (from 1.1×10^{-8} to 1.1×10^{-10})	Clay loam, silty clay loam	Medium permeable
Medium insulating	From 1×10^{-5} to 1×10^{-6} (from 1.1×10^{-10} to 1.1×10^{-11})	Sandy clay	Low permeable
Well insulating	From 1×10^{-6} to 1×10^{-7} (from 1.1×10^{-11} to 1.1×10^{-12})	Lean clay	Very low permeable
Very well insulating	$<1 \times 10^{-7}$ ($<1.1 \times 10^{-12}$)	Boulder clay	Practically impermeable

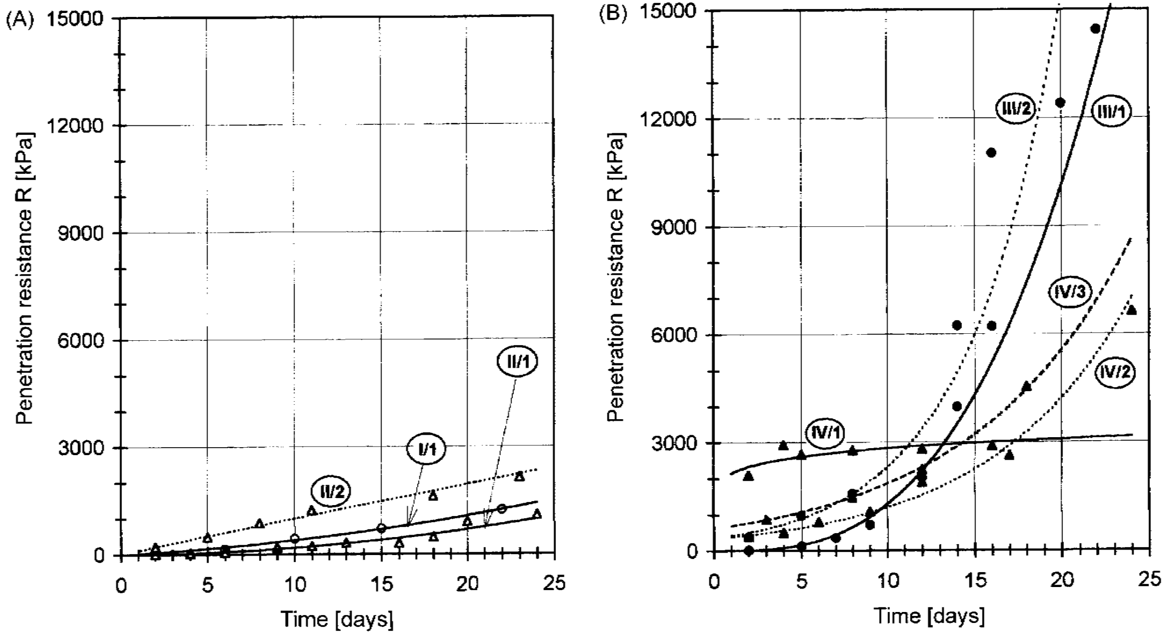

Figure III.7.6. Kinetics of solidification and increase of sealing properties of FA: water mixture (1:1, wt) against air penetration. A – "pure"FA; I/1 – low-alkaline "pure" FA from the Rybnik power plant (LA-FA). Mine water of Cl–SO_4–Na type, TDS 3.9 g/l, pH 8.15; II/1 – high alkaline "pure" FA from the Laziska power plant (HA-FA). Mine water of Cl–SO_4–Na type, TDS 3.9 g/l, pH 8.15; II/2 – high-alkaline "pure" FA from the Laziska power plant (HA-FA). Synthetic saline water of Cl–Na type, TDS 50.0 g/l, pH 7.2; B – FA + FGDS; III/1 – FA + D-FGDS, Rybnik power plant. Mine water of SO_4–(Cl)–Na–Ca type, TDS 2.9 g/dm^3, pH 8.06; III/2 – FA + D-FGDS, Rybnik power plant. Synthetic saline water of Cl–Na type, TDS 50.0 g/l, pH 7.2; IV/1 – FA + SD-FGDS from ABB-NID process, Laziska power plant. Mine water of SO_4–(Cl)–Na–Ca type, TDS 2.9 g/l, pH 8.06; IV/2 – FA + SD-FGDS from ABB-NID process, Laziska power plant. Synthetic saline water of Cl–Na type, TDS 50.0 g/l, pH 7.2; IV/3 – FA + SD-FGDS from ABB-NID process, Laziska power plant. Saline mine water of Cl–Na type, TDS 59.2 g/l, pH 7.23.

FA + D-FGDS mixtures. The effect of saline water was similar to that observed for mixtures with pure FA.

During the solidification of water mixtures with end products of the ABB-NID semi-dry desulfurization process (high-FA + SD-FGDS), the major role in the changes of *R*-value occurred for phases 0 and I. In the short-term phase 0, which lasted up to 2 days, the *R*-values depended both on chemical composition of water and characteristics of the matrix. The changes of *R*-value in this phase appeared to be specific for high-FA + SD-FGDS mixtures and were attributed to the fast chemical reactions, mainly of chemical water binding in matrix (Fig. III.7.5B). After phase 0, these mixtures showed considerable *R*-values (from 300 to 2100 kPa), from 1 up to >2 orders of magnitude higher than the respective *R*-values for mixtures with pure FA and also with FA + D-FGDS. In the next phase I, the characteristics of a matrix seemed to be the most important. In a long period up to 25 days the slow gradual, almost linear increase of *R* up to >7000 kPa occurred. In the phase 0, the highest *R*-values were displayed for the mixture of high-FA + SD-FGDS with a moderately mineralized water. In the phase I, use of highly saline mine water did not cause increase of *R*-value of these mixtures compared to low or moderately mineralized water. The long period of solidification and certain thixotropic properties of FA + SD-FGDS mixtures with water reduce the reuse potential of this end product as a sealing material against air penetration, particularly in a wet climate.

III.7.3. Pollution potential from FA

III.7.3.1. Weathering transformations of "pure" FA

The chemical composition of FA shows that this material is highly enriched in major and trace elements compared to the parent rock of its origin. Reliable assessment of the potential environmental impact of FA stored in the disposal sites or used for the production of construction materials that will be exposed to the atmospheric conditions during their life cycle, or application as soil amendment, which becomes increasingly popular in some countries, in particular in India, requires a knowledge of the qualitative and quantitative weathering transformations of FA in time under the actual field conditions. These transformations, which resulted from contact of FA with water, exert a determining influence on the leaching behavior of macro- and trace elements. Here, the transformation of pollution potential of "pure" FA from hard coal combustion has been discussed as a most abundant kind of CCW disposed and stored in FA ponds worldwide.

In general, in the FA weathering model, four major phases have been distinguished (Janssen-Jurkovičová et al., 1994). In the *phase 1*, intensive dissolution of highly soluble salts and oxides, along with ion exchange occurs between the liquid and solid phase at the surface of FA particles. The most characteristic aspect for this phase is an exothermic process of CaO hydration accompanied by a strong rise of pH values above 11–12. The major processes in *phase 2* consist of the devitrification of the amorphous glass phase at high pH, exposure of the amorphous relics of clay minerals filling FA particles, release of amphoteric constituents and formation of secondary phases at gradually decreasing pH values. In the *phase 3*, diffusion processes are considered to be predominant, and a slower continuation of the development of the secondary amorphous Mg–Al–Si phases exposure at the interface with the glass matrix occurs. The further aging processes in the *phase 4*, are considered to result in formation of clay minerals (kaolinite, smectite) at lower $pH < 9-10$ at the interface between solution and amorphous phase (or zeolites at $pH > 9-10$).

Janssen-Jurkovičová et al. (1994) attribute the decrease of pH to the dissolution and screening by precipitates of a more reactive exterior glass phase and exposure to leaching of a less reactive interior one. It seems, though, that this process should be explained rather by the proven exposure of interior amorphous relics of clay minerals due to the devitrification of a glassy superficial phase. This results in the development of the aluminum hydrolysis reactions. Different sources refer to equilibrium with gibbsite $Al(OH)_3$ or aluminum hydrolysis as solubility controlling factors for Al (Schofield and Taylor, 1954; Hem, 1968; Brookins, 1987; Hutchinson and Ellison, 1992; Garavaglia and Caramuscio, 1994; Blaszczak and Buzek, 1998). In the FA, amorphous aluminum hydroxides along with silica are the prevailing phases. The pH of a solution determined by the hydrolysis reaction of aluminum ions is close to pH 5.0. The pattern of pH formation at the wash-out (I) and dissolution (II) stages observed in the simulated leaching cycle (Twardowska and Szczepańska, 2002) and field studies presented below fits well with this scheme.

Our own observations of weathering transformations of "pure" FA from Polish power plants during long-term column leach experiments and field surveys showed massive macro-constituent release at highly alkaline pH 9.8–12 in *phase 1*, which occurred with subsequent decrease of pH. The dynamics of macro-constituents release were adequate to wash-out stage I of leaching presented in Chapter III.1, and the stabilization of leaching at a relatively low level at pH which had decreased to $<7-7.5$ in *phase II* (which is adequate to dissolution stage II). A number of secondary minerals were also formed in stage II. The extent of pH increase in *phase 1* and subsequent decrease in *phase 2* was found to be highly dependent upon the CaO content and the value of the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3)$. At the mean concentration in FA of $CaO \leq 3\%$ wt and the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) \leq 3.0$, the pH values in *phase 1* are less alkaline (pH 11–10) and the decrease of pH in *phase 2* is faster and deeper, up to $pH < 7-6$. This material was termed as low-alkaline (LA). At CaO at the level $\geq 4\%$ wt and the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) > 3$, the pH values in the *phase 1* are strongly alkaline (up to $pH \geq 12$) and their decrease in the *phase 2* is slower and stabilizes at the slightly alkaline level (up to pH 7.5). This material was consequently termed high-alkaline (HA).

The newly formed minerals observed in the different parts of weathered FA layer were portlandite $Ca(OH)_2$ and calcite $CaCO_3$ as products of CaO hydration and carbonation by atmospheric CO_2. The typical secondary mineral was ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, hydrated calcium aluminates of C_4AH_n type ($4CaO\cdot Al_2O_3\cdot 12H_2O$), and occasionally calcium sulfaluminates of $C_3A\cdot CaSO_4\cdot H_{12}$ type or in the form of mixed crystals with C_4AH_{12} phase. As a transitory mineral, gypsum $CaSO_4\cdot 2H_2O$ was also present, which showed gradual depletion in time. These minerals, along with amorphous phases, are in conformity with phases observed by de Groot et al. (1989) and Janssen-Jurkovičová et al. (1994) in weathered FA from Dutch power plants and seem thus to be typical for FA weathering transformations at the transitory *phase II* and stabilization *phase III*. These observations comprise, though, a relatively short period of time and do not supply a satisfactory knowledge on a life-cycle environmental behavior of FA in actual field conditions.

Though FA has become for years a focus of extensive studies in order to develop a reliable unified and systematic approach to evaluation of the leaching behavior of inorganic granular waste based on general geochemical principles (van der Sloot et al., 1984, 1991, 1993, 1994, 1996, 1997; van der Sloot, 1996; Tiruta-Barma, 2000; Twardowska and Szczepańska, 2001, 2002, 2003), there are still significant uncertainties in the long-term prognosis of environmental impact of this waste placed at disposal sites or used for large-area application (e.g. for soil amendment), in particular of impacts on groundwater and soil (Ghuman et al., 1999; Rowe et al., 2001; Twardowska et al., 2003; Wang et al., 2003; Ziemkiewicz, 2003a,b). Long-term environmental impact of FA ponds in different stages of weathering of waste material was exemplified in two case studies: (i) an operational ash pond sited in the Erai River basin (MSEB, Chandrapur, Maharashtra, India); (ii) a reclaimed FA pond in the dewatering stage of the post-closure period sited in a disused sand quarry (Silesia, USCB, Poland). Selection of these sites remote from each other was inspired by two premises. On one hand, it was intended to show the similarity of the leaching behavior of hard coal FA from different sources, on the background of the disposal/management approach. On the other hand, lack of FA ponds under operation in Silesia enabled parallel field leaching studies at the initial stages of leaching in the same area.

III.7.3.2. Leaching behavior of FA at the (I) wash-out and (II) dissolution stages (a case study: ash pond under operation, MSEB, Maharashtra, India)

III.7.3.2.1. Characteristics of a disposal site

The FA pond construction and management is typical for the current FA disposal practice in India based on the least cost. The major method of CCW utilization is wet disposal in the surface ponds sited in the areas of unprotected aquifers, with open water circuit and overflow discharge of surplus water to the nearest river. The slurry consists of a mixture of FA and BA in the general proportion 80/20, as it is generated in the power plant (Prasad et al., 1999). Controls over these sites have been given a low priority due to failure to recognize the adverse environmental impact of the disposed CCW. This waste is considered harmless, predominantly on the basis of short-term leaching tests simulating (II) dissolution stage at a lowest rate of release and applied to a freshly generated material (Singh and Gambhir, 1996; Singh, 1999) or monitoring of surplus overflow impact on the river water quality (Raghuveer, 1999).

A surface pond for disposal of coal ash slurry from the Maharashtra State Electricity Board (MSEB) at Chandrapur was sited in 1983–1984 in the Erai River basin, in the submerged depression with a total area of 27 km^2 in the valley of Kankaiya nallah (stream), a tributary of the Erai River (Fig. III.7.7). The stream water was impounded by constructing a masonry dam across the catchment near Chargaon village, thus giving rise to a large settling pond. No specific lining has been provided to insulate the pond from the aquifer. The pond filling is being performed by progressively extending the ash slurry pipeline and changing its alignment. Ash slurry is disposed at the rate of approximately 50,000 m^3/day and contains 20–23% v/v of ash. The ash pond has a storage capacity of approximately 116 million m^3 and is expected to fill in 30 years. The excess water as

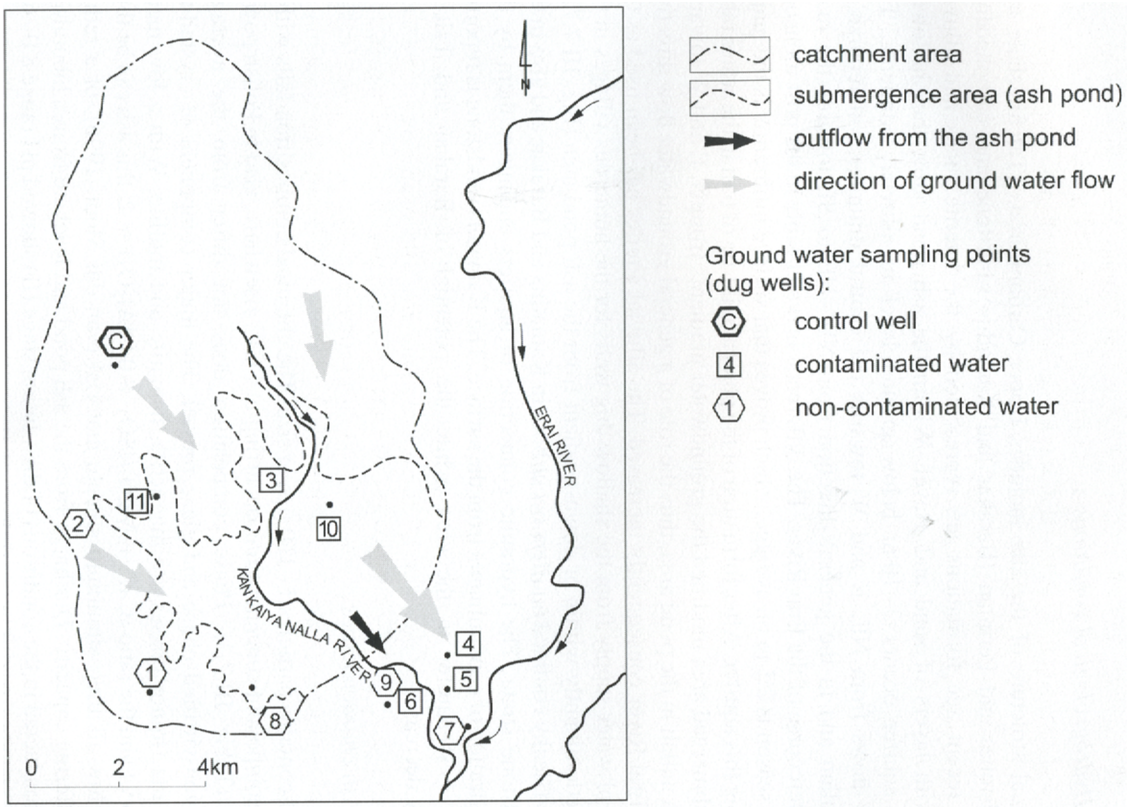

Figure III.7.7. General map of MSEB coal ash pond under operation (Maharashtra, India) and location of groundwater sampling points (wells). C – control well upgradient of the ash pond; 1–8, 10, 11 – dug wells; 9 – outflow of excess water from the ash pond; 11, 3, 10 – contaminated aquifer within the ash pond; 4, 5, 6 – contaminated aquifer down-gradient of the ash pond; 2, 1, 8, 7 – non-contaminated well water beyond the impact of the ash pond.

the overflow passes the weir in the spillway area is discharged directly into the Kankaiya nallah.

The average annual precipitation (1346 mm/a) is distributed within the year in a way typical for the region: heavy rains of a monsoon period are followed by 7 months of dry weather. Temperature ranges from 10 to 45°C.

III.7.3.2.2. Hydrogeological conditions

The geological structure of the site includes Upper Carboniferous (Talchir shale and pebbly sandstone) and Permian (Barakar and Kamathis sandstone and carbonaceous shale). The recent age formations are represented by the laterite rocks and alluvial sediments with layers of sand and gravel. Within the ash pond area, the shallowest unprotected aquifer occurs 3–10 m below ground level in alluvial sediments. The groundwater flows from NE, E and W towards the central drainage watercourse of Kankaiya nallah and in the general direction from NW–NE to SE towards the main drainage watercourse of the Erai River. The difference in water table in the post monsoon and summer season is 2.5 m on average, which proves that surface infiltration is the major source feeding this aquifer. After formation of the pond a build-up of 6 m in the water table below the submerged area modified the groundwater gradients from N, E and W towards the Kankaiya nallah in the pond area, thus the role of a general groundwater flow direction towards the Erai River consequently increased. The alluvial aquifer has been used as the main source of water supply from the shallow dug wells for the numerous villages in the area sited predominantly within or down-gradient from the ash pond area (Fig. III.7.7).

In this area, leaky confined aquifers occur both in Kamathis and Barakar and also in the Talchir sandstone strata. The hydraulic connection of aquifers endangers them by the potential infiltration of contaminants from the surface. The Kamathis sandstone is reported to form the best aquifer in the area, while the potential of Barakar and Talchir progressively decrease.

III.7.3.2.3. Ash characteristics

This material contains particles 1–150 μm in size. The chemical composition falls within the range of component concentrations occurring in CCW elsewhere, also in Polish power plant waste (Table III.7.3). Phase composition does not differ from the average. Amorphous non-vitrified phase and glaze prevail. The major component of crystalline phases is quartz; minor phases are magnetite, hematite and mullite. With a low mean CaO = 2.0% wt and the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) \approx 2$, this ash can be thus classified as low-alkaline aluminum silicate material (van der Sloot, 1996), of a rather moderate buffering capacity. Discharge from the ash pond and leachate from a laboratory column test conducted in the conditions of dissolution stage (II) showed pH range 8.0–6.0 (Singh and Gambhir, 1996; Singh, 1999), which indicates a potential for acidification.

III.7.3.2.4. Survey of groundwater quality in the vicinity of CCW disposal site

In the ash pond under operation, in conformity with the *phases 1, 2* and *3* of the FA weathering model (Janssen-Jurkovičová et al., 1994), two generic leach patterns of the disposed material are anticipated to occur (van der Sloot et al., 1993, see also Chapter III.1): wash-out stage (I), when the soluble compounds unrestricted by equilibria limitations are readily released from the freshly generated material after its disposal at the site, at high pH; dissolution stage (II) when the leached loads are controlled by solubility of constituents limited by equilibria constraints, at pH decreasing to the lower values close to neutral. The resultant concentration and pH values will depend upon the proportion of the CCW freshly disposed and already washed out, of the different pattern of compounds release, as well as on the dilution potential and water quality of the recipient groundwater stream. Hydrogeological/hydrological parameters of the pond are determined by the two major water streams under the saturated zone conditions: (1) outflow of the excess water from the pulp over the weircase discharged directly to the surface recipient (river) and (2) vertical infiltration of water through the CCW layer to the groundwater stream and horizontal flow of groundwater in the general direction towards the Erai River.

A survey conducted by AIC Watson Consultants Pvt. Ltd. (1996) to evaluate the impact of the ash pond on the usable groundwater resources in the area, in order to undertake adequate remedial measures, was commissioned by MSEB in response to the World Bank request. The problem of a possible deterioration of the groundwater quality by the seepage from ash pond was brought to the notice of the MSEB during the supervision of the power plant facilities in 1994. The quality of the groundwater within the ash pond and in its vicinity was assessed in 1996 on the basis of water sampling from 11 dug wells in the villages, as well as from the discharge of the overflow water from the ash pond (Fig. III.7.6). Water was sampled in triplicate with an interval of 2 weeks. As a control, the dug well in Chalbardi village up-gradient of the ash pond was selected as the one unaffected by the ash disposal.

The survey (Fig. III.7.7, Table III.7.12) showed significant adverse changes of water quality in the shallowest unprotected alluvial aquifer within and down-gradient of the pond, which was revealed mainly in the multiple increase of macro-constituent concentrations typical for the leachate from the power plant ash (TDS, chloride, sulfate hardness, Ca, Mg). Contents of trace elements (B, Cd, Cr(VI), Pb, Hg), fluoride and nitrate also distinctly increased compared to the background concentrations. Nevertheless, except Hg which showed permanent excess concentrations, trace metals only occasionally exceeded MCL (Cd, Pb) due to pH values (7.4–8.3) within the stability field for the majority of these elements (Garrels and Christ, 1965; Brookins, 1987; van der Sloot et al., 1994, 1996). The most dramatic changes, which disqualify this water, occurred within the ash pond (wells 11, 3 and 10). Down-gradient of the ash pond (wells 4, 6, 5) water quality, though improved due to dilution, was still not fit for use. There is groundwater deterioration due to the adverse impact of the ash pond on the macro-component concentrations. Low concentrations of contaminants, which are present in the excess water, are discharged as an overflow through the weir. These contaminants result from the high proportion of ash used in the slurry prepared with fresh water in an open circuit. There is a short contact time of the ash with the water in the slurry and in the surface layer of the ash pond. These data, along with the accelerated laboratory leach tests, which are inadequate relative to the actual field conditions, are often used as a proof of a lack of adverse impact of unlined ash ponds on groundwater resources (Singh and Gambhir, 1996; Singh, 1999). The release of macro-contaminants at a high rate during the vertical

Table III.7.12. Groundwater quality in sampling points located in the vicinity of coal ash pond site and direction of groundwater flow in wash-out I and dissolution II stages (MSEB Chandrapur, Maharashtra, India); concentrations in mg/l (mg/dm^3).

Parameter	Location of sampling points with respect to coal ash pond and the direction of groundwater flow												DWS[a] (MCL)	DL
Sampling points	Control well up-gradient	Wells up-gradient			Well shielded by riverbed	Discharge (overflow weir)	Wells within the ash pond			Wells down-gradient				
	C	2	1	8	7	9	11	3	10	4	5	6		
Color	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1	<0.5	<0.5	<0.5	<0.5	<0.5	5	0.5 Hazen
Odor	OL	OL	OL	OL	OL	SU	OL	OL	OL	OL	OL	OL		
Turbidity	0.19	0.66	0.18	<0.01	<0.01	7.2	<0.01	0.2	0.13	0.1	<0.01	0.16	5	0.01
pH	8.35	7.66	7.75	7.81	7.79	7.96	7.51	7.45	7.37	7.41	7.67	7.36	6.5–8.5	0.1
Alkalinity $CaCO_3$	**268.5**	**266.7**	**319.3**	**236**	194.7	82	**560**	**360**	**512**	**320.7**	**717.33**	**322**	200	–
Total dissolved solids (TDS)	330	438.7	810	394.7	359.3	290	**3513**	**2716**	**2122.7**	**1824.7**	**1332**	**1173**	500	–
Total hardness $CaCO_3$	194	286.7	**460**	264	216	168	**1172**	**1010**	**720.7**	**884**	147.33	**660**	300	–
Calcium Ca	48	78.13	**90.4**	72.3	69.9	57.6	**174.13**	**190.4**	**93.87**	**156.1**	24	**178.4**	75	–
Magnesium Mg	36	22.2	**56.9**	20.3	9.4	5.83	**179.65**	**129.8**	**118.1**	**109.8**	21.22	**52**	30	–
Chloride Cl	16.56	44.16	82.84	47.4	21.28	28.4	**817.4**	**733.4**	**377.4**	**384.3**	75.09	183.9	250	–
Sulphate SO_4	150	1	88.3	1.73	81.3	97.5	**658**	**376.7**	**435.8**	**210**	**317.5**	83	200	0.1
Fluoride F	**1.41**	0.94	0.66	0.5	0.041	**1.68**	**1.24**	0.428	**1.107**	0.78	**1.55**	0.263	1	0.018

Nitrate NO_3	0.24	0.52	2.47	0.69	0.21	0.109	*5.98*	*4.58*	*3.36*	*4.95*	0.3	3.62	45	0.01
Arsenic As	0.001	0.0065	0.011	0.016	0.0071	*0.037*	0.0072	0.011	0.03	0.011	0.006	0.0064	0.05	0.001
Boron B	0.07	0.097	0.126	0.054	0.054	*0.45*	*0.318*	*0.211*	*0.383*	*0.179*	*0.43*	*0.107*	1	0.01
Cadmium Cd	<0.001	0.0013	0.0027	0.003	0.005	0.001	*0.008*	*0.007*	**0.02**	*0.006*	*0.0057*	*0.0063*	0.01	0.001
Chromium Cr^{6+}	0.006	0.0063	0.0057	0.004	0.004	0.01	*0.008*	*0.012*	*0.008*	*0.008*	*0.0075*	0.0063	0.05	0.001
Copper Cu	0.011	0.0061	0.0073	0.004	0.005	0.003	0.016	0.013	0.009	0.011	0.0157	0.014	0.05	0.001
Iron Fe	**0.31**	**0.388**	**0.325**	0.247	0.173	0.55	0.213	**0.516**	0.152	0.205	0.2027	0.174	0.3	0.001
Mercury Hg	<0.001	**0.0025**	**0.0037**	**0.004**	**0.002**	**0.006**	**0.002**	**0.004**	**0.005**	**0.005**	**0.002**	0.001	0.001	0.001
Lead Pb	0.016	0.004	0.012	0.005	0.005	0.0007	**0.06**	**0.054**	*0.023*	0.051	0.0047	*0.031*	0.05	0.001
Selenium Se	0.004	0.008	0.013	0.005	0.006	0.0096	0.0058	0.007	0.006	0.008	0.005	0.004	0.01	0.001
Zinc Zn	0.037	0.107	0.068	0.035	0.052	0.012	0.0073	0.053	0.061	0.096	0.067	0.086	5	0.001
Phenols	0.001	**0.015**	**0.022**	**0.022**	**0.025**	**0.028**	**0.28**	**0.04**	**0.037**	**0.039**	**0.026**	**0.083**	0.001	0.001
α radiation Bq/l	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	Absent	0.04
β radiation Bq/l	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	Absent	0.08

C – Control groundwater from Chalbardi village, DL – detection limit.

Value – exceeds MCL; *Value* – exceeds the background level.

Sampling points (Fig. III.7.6): 1 – Tadoli village, 2 – Ghodpeth village, 3 – Kachrala village, 4 – Tirwanja village, 5 – Kawathi village, 6 – Chhota Nagpur village, 7 – Wichota village, 8 – Chargaon village, 9 – discharge from FA pond, 10 – Awanda village, 11 – Gunjala village.

[a]DWS – Drinking water standard established by Bureau of Indian Standards according to IS 10500, 1991 = SDWA/EPA.

percolation through both the freshly generated and previously disposed ash layers has a significantly longer contact time which is generally neglected.

Adequately carried out and interpreted standard leach tests would have ensured reliable short-term risk assessment from any granular material including CCW at the wash-out (I) and dissolution (II) stages (Twardowska and Szczepańska, 2002). Archival data (Zawisza et al., 1990, 1993) on pre- and instant post-closure monitoring of the drainage, leachate and circulation water from the closed circuit and of the groundwater quality at the predominating dissolution stage II of constituent release from the disposed low-alkaline FA at the Przezchlebie fly ash pond (USCB, Poland) confirm the discussed pattern of leaching behavior of FA at this stage (Table III.7.13).

In the presented case of coal ash disposal pond of MSEB (Maharashtra, India), a further extension of groundwater deterioration in space and time is anticipated during the planned 30 years long disposal of power plant ash in a huge area. In the presented survey, contamination of the deeper aquifer has not yet been observed. However, in the long run, the hydraulic connection of aquifers poses a serious threat due to downward development of contamination (Twardowska et al., 1999, 2003).

III.7.3.3. Leaching behavior of FA at the delayed release (III) stage (a case study: fly ash pond of Rybnik power plant in the post-closure period, USCB, Silesia, Poland)

The above study exemplifying the pollution potential of a power plant ash pond in the operational period, which lasts usually for several years and reflects wash-out (I) and dissolution (II) stages, was discussed for the case study of ash pond in Maharashtra, India. While the short-term risk assessment to the environment from CCW is easy to define, the long-term prediction is much more difficult due to the complicated nature of kinetically determined long-range transformation processes, which might be easily overlooked. The leaching behavior of FA in the surface pond in the post-closure period at the delayed release (III) stage (van der Sloot et al., 1993, see Chapter III.1) is exemplified here in the case study on the Przezchlebie fly ash surface pond of Rybnik power plant (USCB, Silesia, Poland).

III.7.3.3.1. Location and characteristics

The fly-ash pond for disposal of Rybnik power plant wastes was sited in an unused 20 ha sand quarry having a maximum depth of 20 m (Fig. III.7.8). The hydraulic disposal of FA to the pond in a closed circuit started in 1979 and lasted for 12 years. In 1982–1983 due to construction of embankments of coal mining wastes, the FA disposal in the pond was continued above the surface level. The location of pulp outlet was changed several times.

The total area of FA disposal increased to 53 ha and its volume reached 23 million m^3. In the following years, the construction of the pond was further developed through increasing the height of embankments and construction of new sections. The anthropogenic FA layer 25–30 m thick replaced finally the extracted primary sand layer.

Since 1984, the amount of FA disposal decreased, up to the site closure in 1991. In the post-closure period, due to gradual dewatering of the pond, hydrogeological conditions within the FA layer changed from saturated to vadose zone conditions. In order to control

Table III.7.13. Monitoring of groundwater quality in the area adjacent to the Przezchlebie fly ash pond of the Rybnik power plant (USCB, Poland) prior to and after the site closure (after Zawisza et al., 1993).

Parameter	Monitoring wells (Quaternary aquifer)			Drainage outlet	Effluent below the front dam	Collecting reservoir in water circuit	Effluent below the railway	MCL for drinking water[a]
	P1b	P1a	P10					
Quality parameters prior the site closure (1989–1991)								
pH	8.3–6.5	6.6–6.4	8.3–7.9	8.0–9.1	7.3	7.8–8.4	7.8	6.5–9.5
Cl	19.6–13.5	29.4–31.2	23.4–25.0	**888–685**	**734**	**700–684**	**940**	250
SO_4	247–204	**276**–190	10.7–9.1	**1829–1215**	**1648**	**1263–1214**	**2351**	250
TDS	13,848–9220	2118–908	351–62	4366–2972	3467	3143–2913	5896	
Quality parameters after the site closure (1992–1993)								
pH	6.6–8.1	6.9–8.3	7.5	8.7	8.0–7.5	8.5–7.4	8.0–7.5	6.5–9.5
Cl	17–20	32–10	20	**665**	**277**–192	**600–713**	**1107–975**	250
SO_4	222–207	248–209	7.0	**1370**	**1609–605**	**1360–1254**	**2795–1885**	250
TDS	3158–2111	621–550	117	3680	3541–1575	3481–3650	6852–7222	

Values exceeding MCL are bold.

[a] Polish regulations: Directive of the Minister of Health (2000).

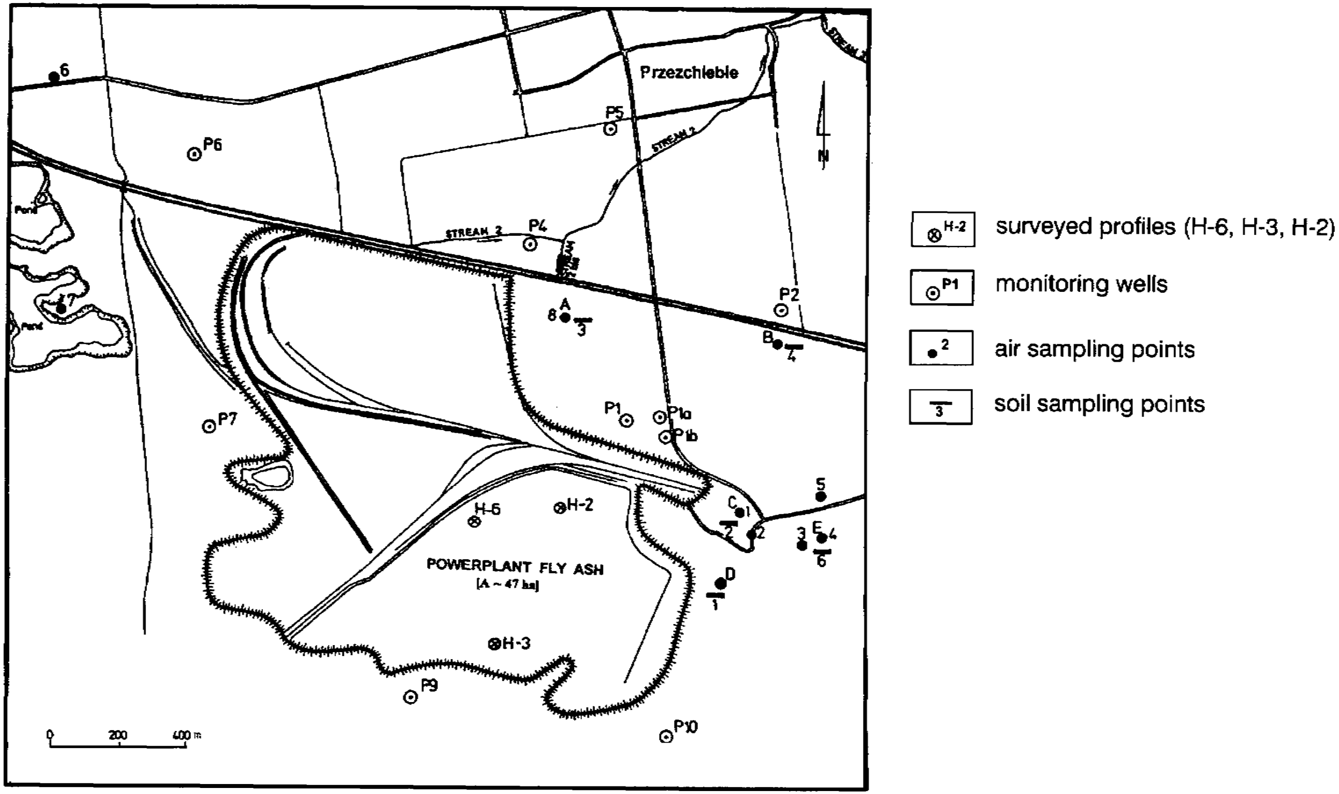

Figure III.7.8. General map of the Przezchlebie fly ash pond of the Rybnik power plant (Silesia, Poland) in the post-closure period. Location of monitoring wells (P1–P10) and screening boreholes (H-2, H-3, H-6).

dusting, the dump surface was stabilized by carbamide resins spread from a helicopter and in the following years it was reclaimed by grass cover. Due to full reuse of FA in Silesia, no new surface ponds have been constructed since then.

III.7.3.3.2. Meteorological and hydrogeological conditions

Annual precipitation in the area ranges from 559 to 866 mm; pH of the precipitation in the area adjacent to the pond in the W–E direction of dominating winds ranged in 1989–1993 from acidic to close to neutral (pH 3.5–7.4, mean 5.6).

The geological structure of the site is represented by Quaternary, Tertiary and Triassic sediments. The Quaternary formations in the site area are about 20 m thick in the W and about 50 m thick in the E directions. They comprise both permeable (sand and sand gravel) and low permeable sediments (clays and silts). The upper Quaternary aquifer in sandy sediments is of discontinuous character. The water table, at a depth 0.3–4.7 m under the ground surface, is free and only locally it is tense.

The Quaternary groundwater monitoring network includes 10 wells, drainage, leachate and reservoir of circulating water, where only basic parameters (pH, TDS, Cl, SO_4, Fe and Mn) were measured (Fig. III.7.8, Table III.7.13). After site closing, the monitoring of groundwater terminated.

III.7.3.3.3. Fly ash characteristics

FA from the Rybnik power plant has been characterized in detail in the previous subchapters, in Tables III.7.2–III.7.10, and in Figures III.7.2–III.7.6 as a representative material of typical composition and properties. FA from the Rybnik power plant can be classified as LA aluminum silicate material with CaO ranging from 2.07 to 3.70% wt, mean 2.98% wt and the ratio $(CaO + MgO)/(SO_3 + 0.04Al_2O_3) = 1.7–3.6$, mean 2.6. In this respect, this range is typical for "pure" FA from European power plants fired by hard coal.

III.7.3.3.4. Methods of field survey

The applied procedure of evaluating long-term leaching behavior of "pure" FA at the disposal site should have been both reliable and fast, which could be assured by direct measurements. The field survey conducted in 1993 was based on the assessment of qualitative and quantitative transformations of pore solution in FA layer at the Przezchlebie pond in the post-closure period. The pond after dewatering was already converted into an anthropogenic vadose zone. This newly formed zone was sampled along the vertical profile in the three drilled boreholes up to 11 m deep (H-2, H-3, H-6) (Fig. III.7.9). FA core samples of a natural moisture content were transported in air-tight plastic bags to the laboratory, where pore solution was extracted by the pressure method under nitrogen and analyzed for the metal content by standard methods using ICP-OES technique (ICP Perkin Elmer Plasma 40). For anionic compounds, a High Throughput Capillary Electrophoresis System Model 270A-HT Perkin Elmer was applied. The elemental speciation in pore solution and QA/QC testing was performed with use of a geochemical computer programs WATEQ 4F and Visual MINTEQ ver. 2.01.

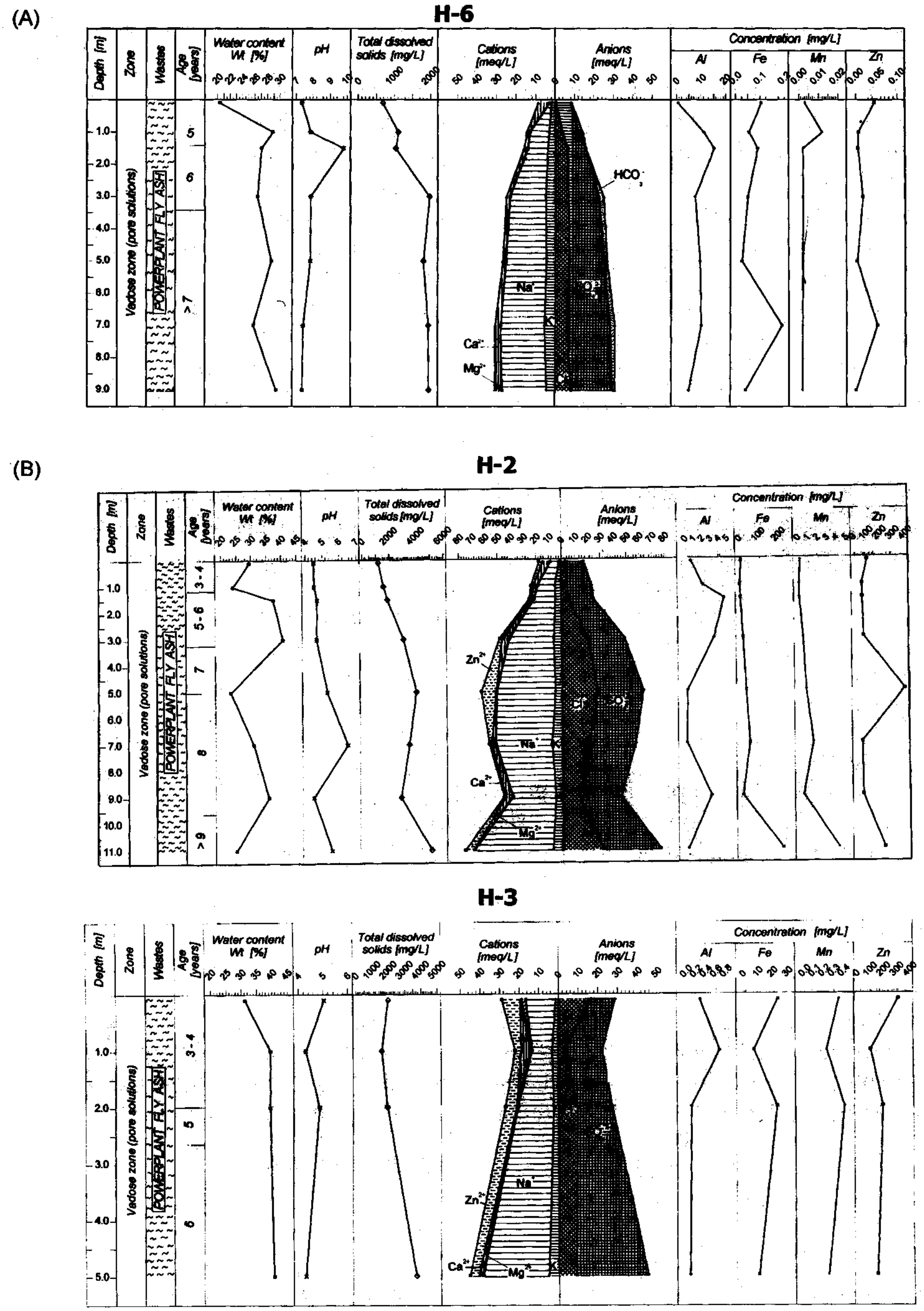

Figure III.7.9. Hydrogeochemical profiles of macro-components in pore solutions in the layer of alkaline FA from the Przezchlebie fly ash pond of the Rybnik power plant in the post-closure period. (A) Dissolution (II) phase (profile H-6); (B) Delayed release (III) phase (profiles H-2 and H-3).

III.7.3.3.5. Field screening studies

The results of analysis of pore solutions along the three vertical profiles of the FA disposal pond in the post-closure period after 12 years operation displayed the pattern of leaching behavior at the delayed release (III) stage that has not been considered or reported before with respect to FA. The material disposed in the pond is of a different hydraulic conductivity, from high in the non-compacted to moderate in compacted state ($k = 10^{-3}$–10^{-4} cm/s) typical for fine and mean sands, and has a high porosity ($n = 0.58 - 0.50$). After closure, the water flow pattern changed during the dewatering of the FA layer from saturated zone conditions typical for the operating stage into vadose zone conditions, when vertical percolation of atmospheric precipitation had started. Chemical composition of pore solutions along the FA dump profiles displayed significant transformations, which reflected both the altered water flow (vertical downward redistribution of ions) and the equilibria conditions. The comparison of the pore solution characteristics along the H-6, H-2 and H-3 profiles reflected the character of these changes (Table III.7.14, Figs. III.7.9, III.7.10a–e). While the pore solution in FA in H-6 profile, which showed lower specific density, hydraulic conductivity and moisture content still reflected the dissolution stage II under operating conditions (pH 7–10), the composition of pore solution in the looser FA profiles H-2 and H-3 indicated alteration of buffering properties of the system that could be defined as delayed release III stage. It resulted in the decrease of pH from alkaline values to acidic ones, ranging from 4.3 to 6.5, and release of trace metals in accordance with the changed stability conditions. The composition of pore solutions along the profiles H-2 and H-3 compared to H-6 suggested that the major buffering mechanisms controlling pH after depletion of carbonates comprised reactions involving hydrolysis of aluminum ions from amorphous phases exposed to the direct contact with percolating water due to the devitrification of glaze. The first stage hydrolysis reaction:

$$(\mathrm{Al{\cdot}6H_2O})^{3+} + \mathrm{H_2O} = (\mathrm{AlOH{\cdot}5H_2O})^{2+} + \mathrm{H_3O^+} \qquad \log K \approx 5 \tag{III.7.1}$$

Further weathering transformations of the solid phase were directed to formation of the secondary minerals within the amorphous phase, which was reported also by Janssen-Jurkovičová et al. (1994). Composition of pore solutions and phase analysis of material indicated that these processes in simplified form can be described as equilibrium–non-equilibrium reactions between kaolinite and gibbsite at the stage of their formation, and dissolved silica and water, discussed by Garrels and Christ (1965). In particular, the following reactions that involve amorphous phase might be considered as major ones controlling pH and ionic composition of pore solutions at this stage:

- Second stage of aluminum hydrolysis and gibbsite formation:

$$\begin{gathered} 2\mathrm{Al^{3+}} + 6\mathrm{H_2O} = \mathrm{Al_2O_3{\cdot}H_2O(c)} + 6\mathrm{H^+} \\ \log K = 5.7 = \log[\mathrm{Al^{3+}}] + 3\mathrm{pH} \end{gathered} \tag{III.7.2}$$

- Dissolution of silica and kaolinite formation that may congruently limit the activity of dissolved aluminum:

$$\begin{gathered} 2\mathrm{Al^{3+}} + 2\mathrm{H_4SiO_{4(aq)}} + \mathrm{H_2O} = \mathrm{H_4Al_2Si_2O_9(c)} + 6\mathrm{H^+} \\ \log K = 1.0 = \log[\mathrm{Al^{3+}}] + \log[\mathrm{H_4SiO_4}] + 3\mathrm{pH} \end{gathered} \tag{III.7.3}$$

Table III.7.14. Concentration range of constituents in pore solutions along the vertical profiles of the Przezchlebie fly ash pond of the Rybnik power plant (USCB, Poland) in the post-closure period: Dissolution II (profile H6) and delayed release III stages (profiles H2 and H3).

Parameter constituent	Concentration in pore solution (mg/L, mg/dm^3)							
	Profile H-6 (0.1–9.0 m)		Profile H-2 (0.1–11.0 m		Profile H-3 (0.1–5.0 m)		MCL[a] (Polish)	RBC[b] US EPA
	Min	Max	Min	Max	Min	Max		
pH	7.50	*9.80*	*4.46*	*6.50*	*4.29*	*5.04*	6.5–9.5	
μS cm^{-1}	961	2150	1194	1913	1119	1756	2500	
Macro-constituents								
TDS	681	1976	1198	5079	1564	3712		
Ca	31.98	112.62	2.95	110.73	5.95	98.60		
Mg	0.269	3.250	2.17	7.17	4.18	26.26		
Na	26.10	*516.90*	150.25	*1393.53*	*231.28*	*765.64*	200	
K	66.60	216.87	72.10	320.00	55.64	202.44		
NH_4-N	< 0.05	*1.67*	0.32	*1.26*	< 0.05	*1.22*	0.5	3.70
NO_3-N	6.41	15.03	6.55	18.40	10.85	37.40	50.0	58.0
Cl	19.24	*294.60*	108.15	*1116.06*	108.60	*589.62*	250	
SO_4	*362.69*	*1054.26*	*687.31*	*2134.09*	*581.64*	*1742.05*	250	
HCO_3	38.44	147.05	< 0.50	4.27	< 0.50	< 0.50		
SiO_2	4.83	17.26	65.46	281.18	135.19	313.66		
PO_4	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	0.2	
Trace elements								
Ag	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	0.01	0.18
Al	*0.744*	*15.260*	< 0.060	*4.662*	< 0.060	*0.663*	0.2	110
B	< 0.01	*3.064*	*2.869*	**7.987**	**3.343**	**10.460**	1.0	3.30
Ba	0.069	0.204	0.096	0.341	< 0.002	0.488	0.7	2.60
Be	< 0.002	< 0.002	< 0.002	**0.012**	**0.002**	**0.007**		0.0016
Cd	< 0.003	< 0.003	*0.013*	**0.175**	**0.045**	**0.167**	0.003	0.018

Cr	*0.059*	*0.170*	< 0.010	*0.97*	*0.121*	*0.310*	0.05/0.03	37/0.18
Cu	0.069	0.200	< 0.005	0.036	< 0.005	0.042	1.0	0.73
F	*1.62*	**7.85**	**8.03**	**33.76**	**12.98**	**30.17**	1.5	2.20
Fe	0.027	0.191	*3.891*	*209.30*	*7.222*	*23.59*	0.2	
Li	0.537	**3.512**	0.430	**4.000**	0.345	**2.548**		0.73
Mn	< 0.002	0.012	**0.081**	**4.061**	**0.222**	**0.399**	0.5	0.18
Mo	0.088	**1.480**	0.086	**1.412**	0.090	**0.361**		0.18
Ni	< 0.025	< 0.025	< 0.025	*0.062*	< 0.025	< 0.025	0.03	0.73
Sr	0.503	1.304	0.229	1.784	0.152	1.565		22.0
Ti	< 0.005	< 0.005	< 0.005	0.050	< 0.005	0.040		
V	0.076	**1.120**	< 0.010	**0.900**	0.020	0.115		0.26
W	< 0.010	0.400	1.044	7.800	1.910	7.700		
Zn	0.004	0.052	**57.33**	**382.31**	**102.80**	**308.86**	3.0	11.0

Values in *italic* exceed Polish MCLs for drinking water: Values in **bold** exceed RBC by US EPA.

[a] MCL for drinking water (Polish regulations: Directive of Minister of Health, 2000).

[b] RBC by US EPA, 1994 (Smith, 1994).

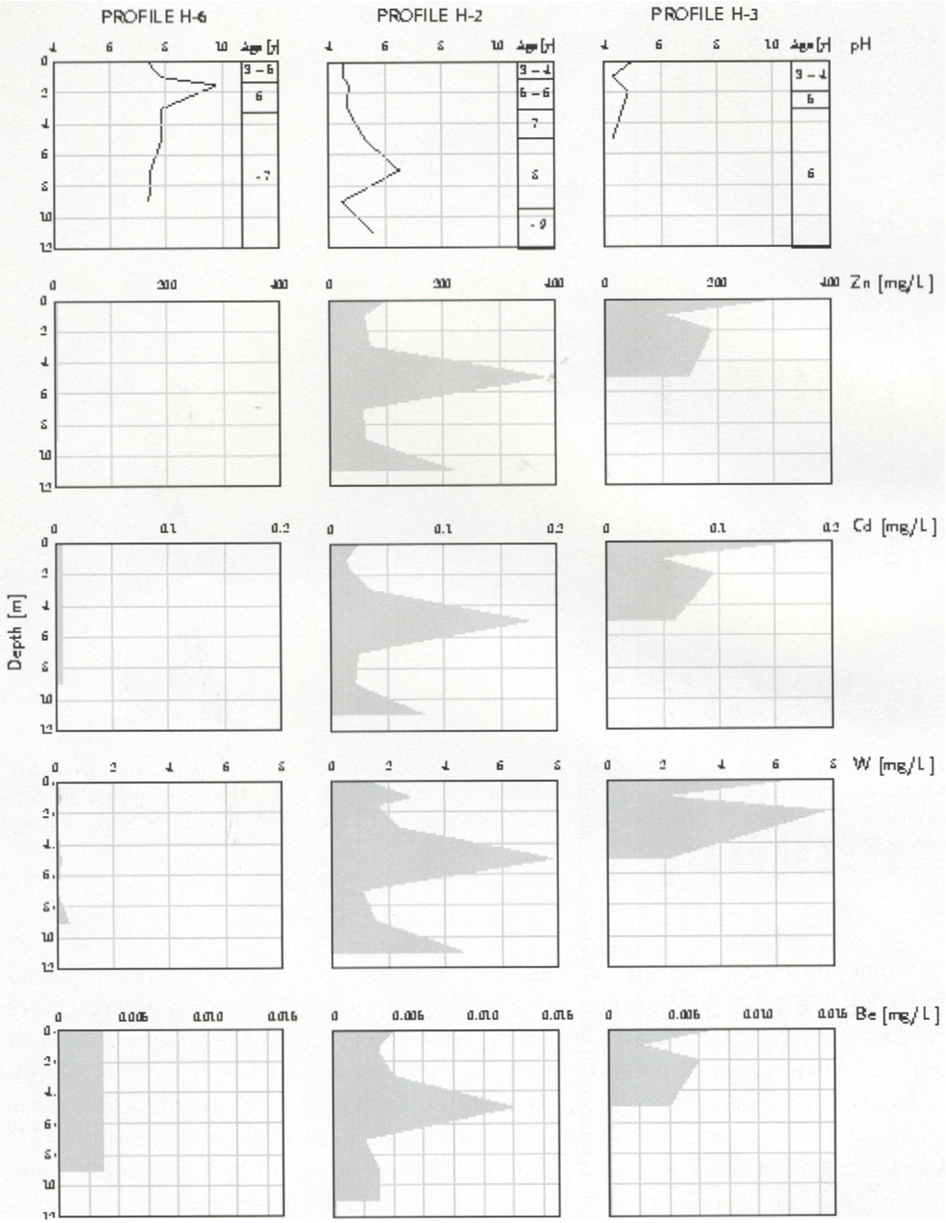

Figure III.7.10a. Chemical transformations of pore solutions along the vertical profiles of the Przezchlebie fly ash pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (a) pH-controlled high increase (Zn, Cd, W, Be).

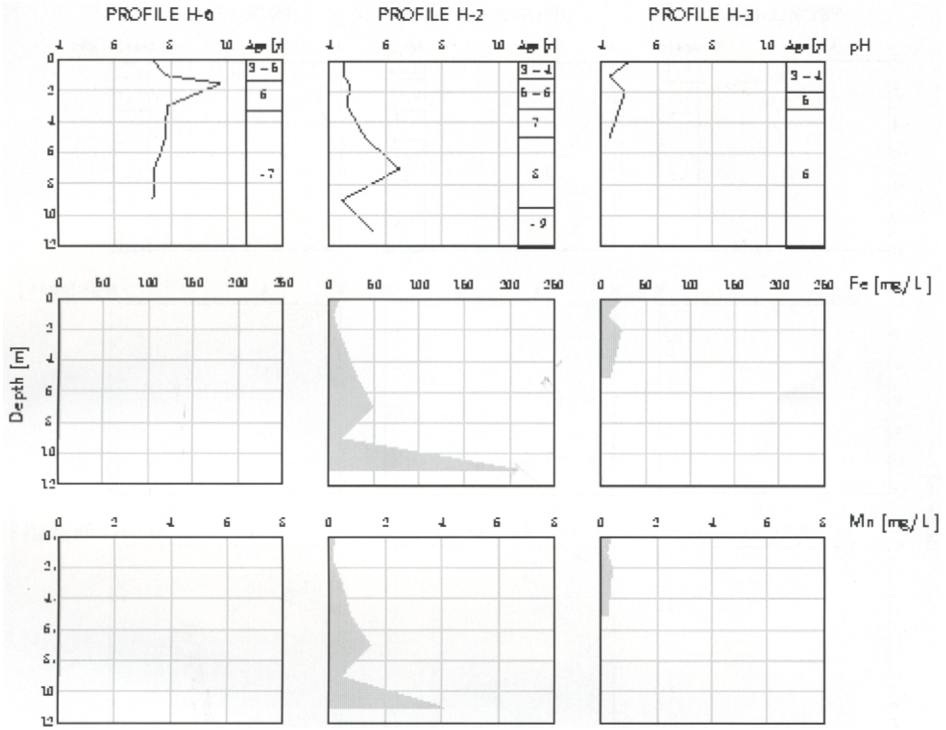

Figure III.7.10b. Chemical transformations of pore solutions along the vertical profiles of the FA pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (b) pH-dependent high increase (Fe, Mn).

The solubility product for the dissolution of solid amorphous silica to form dissolved silica is $10^{2.6}$. At this value the stability of kaolinite was found to be the greatest (Garrels and Christ, 1965). More complicated composition and nature of relations between the solid and liquid phase in the system FA – pore solution resulted in the formation of predominantly mixed crystal phases. Depletion of dissolved Al^{3+}, acidification of pore solution and simultaneous considerable increase of dissolved silica along the profiles H-2 and H-3, as well as formation of ettringite and other minerals of hydrated sulfaluminate type as secondary crystalline phases, confirmed this general scheme of reactions occurring in the delayed release III stage and explained the nature of acidification of pore solutions.

This dissolution resulted in a large non-linear release of heavy metals from the FA and a significant increase in contamination potential of the FA with respect mainly to the groundwater and eventually soils in adjacent area in case of uncontrolled dusting (decrease of pH in leachate to 4.3–4.5) and delayed extensive release of Zn, Mo, Mn, Li, F, Cd, Be, B in hazardous concentrations, and Fe, Cr, Al, SO_4, Cl, NO_3, NH_4, K, Na and TDS several times above their MCL values for drinking water. The chemical composition of pore solutions displays a pattern reflecting equilibria limitations for particular metals and their

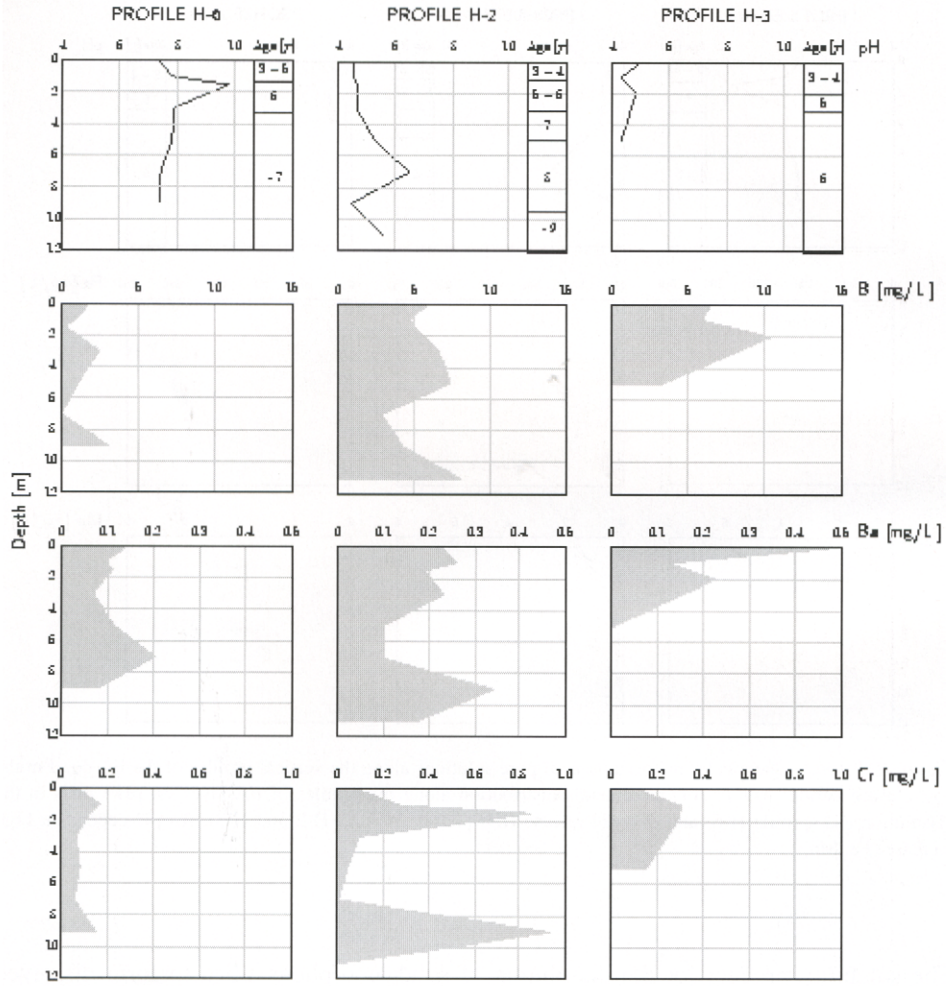

Figure III.7.10c. Chemical transformations of pore solutions along the vertical profiles of the FA pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (c) pH-controlled moderate increase (B, Ba, Cr).

stability fields under the different pH–Eh conditions along the vertical profiles of FA layer, including changes from oxic conditions in the surface layer to locally anoxic environment in the deeper layers. In general, in conformity with pH–Eh-stability fields (Garrels and Christ, 1965; Brookins, 1987), metals can be grouped in accordance to similar release-dissolution response to pH as the controlling parameter, e.g.: I: (Zn–Cd–W–Be) (Fig. III.7.9a); II: (Fe–Mn) (Fig. III.7.9b) (reverse pH-dependent increase). Several metals show weak (III: B, Ba, Cr) (Fig. III.7.9c) or no influence of pH (IV: Li, Mo, Sr) (Fig. III.7.9d), while Al, Cu and V (Fig. III.7.9e) display opposite behavior

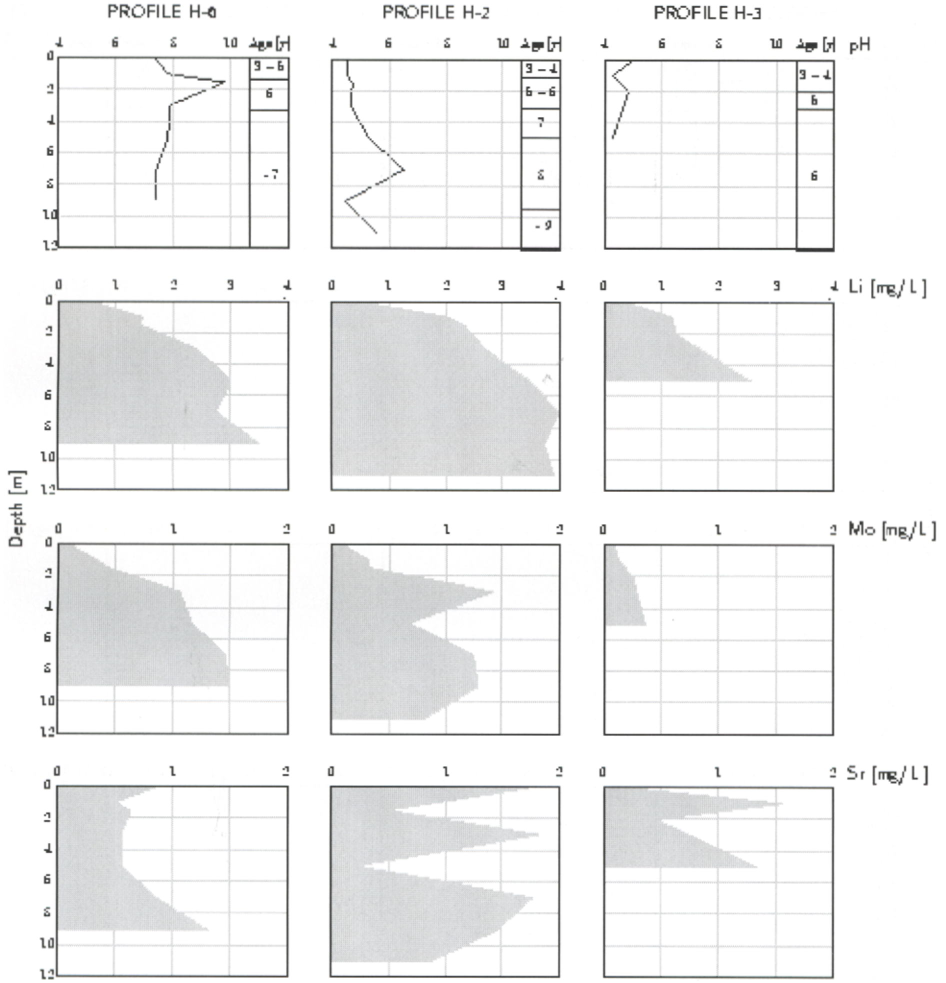

Figure III.7.10d. Chemical transformations of pore solutions along the vertical profiles of the FA pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (d) Weak influence of pH (Li, Mo, Sr).

(immobilization at pH 4.3–5.0), in case of Al well explained by formation of clay minerals and other aluminates. Leaching behavior of oxyanions appeared to be less pH-controlled and showed either high susceptibility to release in a wide range of pH in compliance with wide stability field (Mo), or lower dissolution rate at low pH (V). Molybdenum is a known toxin highly enriched in FA, therefore its unrestricted mobility is to be considered at every case of FA disposal or bulk use in the conditions of extensive environmental exposure. Other oxyanions of high toxicity such as As and Se, also considerably enriched in FA, were not analyzed in this survey. Other sources (Mattigod et al., 1990, 1999) report high

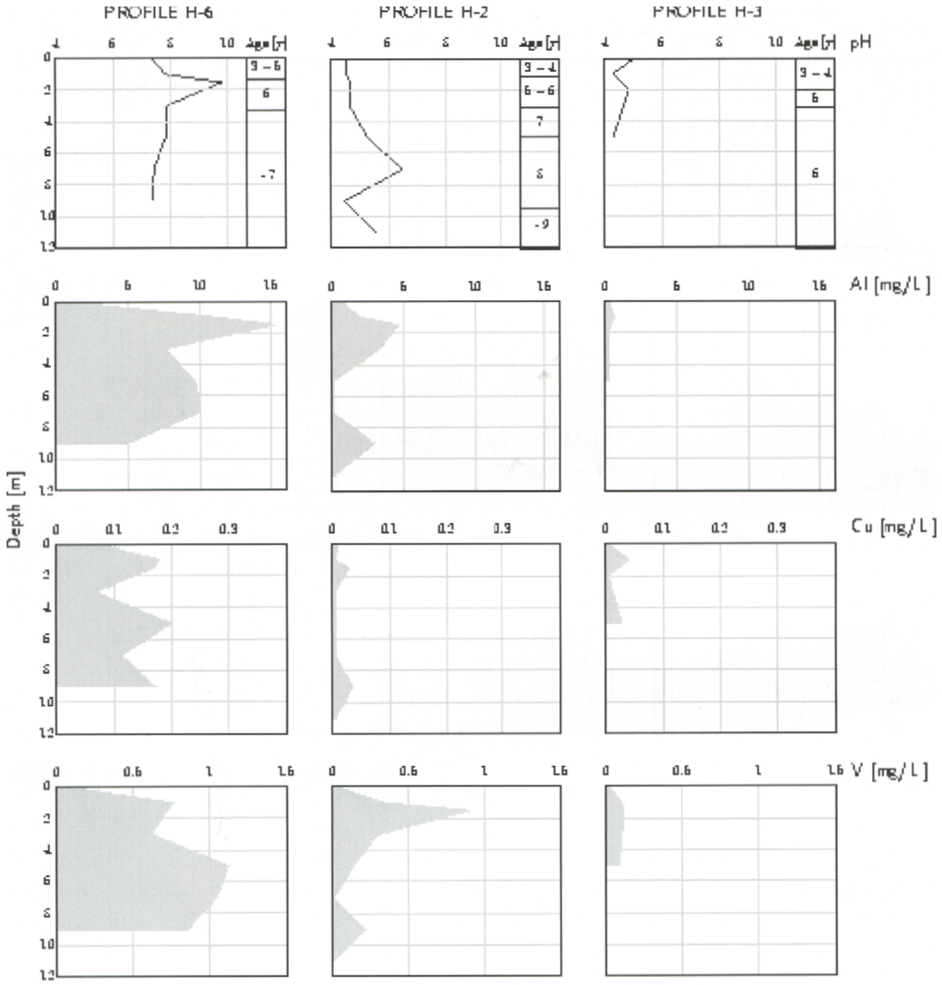

Figure III.7.10e. Chemical transformations of pore solutions along the vertical profiles of the FA pond in the post-closure period: patterns of trace metals distribution along the profiles of FA layer vs. pH values in the dissolution (II) (profile H-6) and delayed release (III) phases (profiles H-2 and H-3). (e) Immobilization at low pH (Al, Cu, V).

leachability of these elements from fossil-fuel combustion residues. Studies on speciation of As and Se during FA leaching (Eline et al., 1994) suggested sorption-controlled leaching process, while pH was to be a parameter controlling the kind of sorption phase and binding strength with respect to arsenate and selenite. At alkaline pH, Ca-minerals (portlandite or ettringite) and at acidic pH, amorphous iron oxides were considered as sorption phases, this last process to be modeled using a simplified sorption complexation model.

The speciation of pore solutions with the use of WATEQ 4F geochemical assessment computer program, showed occurrence of trace metals released to solution in the delayed release (III) stage predominantly as free ions or associated with sulfur as $MeSO_{4(aq)}$. Dissolved silica was specified as $H_4SiO_{4(aq)}$, which is in conformity with the mechanism of transformations and chemical composition of pore solution in the delayed release III stage.

Leaching characteristics of coal combustion FA deposits in the natural conditions, although similar to that reported by other investigators (de Groot et al., 1989; van der Sloot et al., 1991, 1996; Ghuman et al., 1999; Danker et al., 2001) shows significant differences in comparison with the data obtained in laboratory leaching tests. These differences are also emphasized by other authors (Fällman and Hartlén, 1994; Janssen-Jurkovičová et al., 1994; Meij and Schaftenaar, 1994; Twardowska and Szczepańska, 2002). Due to the much more complicated nature of the environmental interactions, the distortion of the time scale may cause serious qualitative and quantitative errors in prediction of the leaching behavior of the material. In particular, kinetically determined processes and reactions such as weathering, dissolution of amorphous phases and formation of secondary minerals, as well as effect of flow conditions upon the actual composition and ionic strength of pore solutions, is not adequately considered in these tests. Correct prediction of the leaching behavior of trace elements from the material requires the precise modeling of processes occurring within the macro-components of a material under the exposure conditions, which influence the factors controlling trace metal release (pH, Eh, specific surface and pore structure, organic matter, complexing agents) (van der Sloot, 1996; van der Sloot et al., 1997; Tiruta-Barma et al., 2000; Twardowska and Szczepańska, 2002).

In general, the study proved (i) possibility of discontinuous non-linear time delayed increase of pollution potential of disused non-hazardous large-volume waste in the dumping sites to the hazardous level due to externally or intrinsically induced transformations of the environmental exposure and alteration of controlling factor values; (ii) inconsistency of the laboratory leaching tests and the actual leaching behavior of trace metals, particularly at the conditions when composition changes are dictated by kinetically determined reactions. The tests reflected entirely wash-out (I) and dissolution (II) stages but not the delayed release (III) stage; (iii) and demonstrated the necessity of life-cycle screening/monitoring of CCW dumping sites for contaminant release as a function of the primary factors (pH–Eh, ionic strength, ionic composition of solute) and secondary controlling factors (L/S–liquid to solid ratio, water flow conditions) along the vertical profile of an anthropogenic or natural vadose zone. These data are to be utilized in the development of the long-term predictive hydrogeochemical models and their field validation, and for providing an early warning and remedial actions with respect to the particular site. The development of a reliable model requires parallel observations of hydrogeological conditions as well as of transformations occurring in the solid phase over time as a function of the exposure conditions.

The formation of pH (and Eh) as a function of time-dependent (kinetically defined) processes appeared to be a key issue for a correct prediction of the leaching behavior of waste with respect to inorganic trace elements controlled by the precipitation/dissolution reactions. With respect to As and Se (as arsenate and selenite), which were found to be the most important redox species in FA, the sorption-controlled leaching model with pH as a parameter defining the sorption phase and the reversibility of the process was suggested (Eline et al., 1994).

It should be added that so-called "low emission" from the FA pond (wet and dry deposition of FA particulates from the dump surface in the direction of dominating winds) can also adversely influence soils in the areas adjacent to the site: soil acidification in sampling point 1 to pH 4.2–4.9 compared to the background pH 5.4–7.7 in the area closest to the Przezchlebie fly ash pond (USCB, Silesia, Poland) (Fig. III.7.7) in the direction of dominant winds was already reported (Zawisza et al., 1993). In view of growing popularity in developing countries of concept of CCW (FA or coal ash) bulk use as a soil amendment, the processes not only within anthropogenic vadose zone layer, but also waste–soil interaction in the natural unsaturated zone should be the objective for long-term prediction. The studies carried out so far (Hockley et al., 1992; Sajwan et al., 1999) do not give yet strong basis for long-term prediction of these interactions for different systems.

III.7.4. Conclusions

Coal combustion, which currently generates about 39% of the world's electricity, will continue to be a major source of world power well into third Millennium. With 67% of world's coal output currently devolved to China, the USA and India, and heavy dependence of these countries on coal for power generation, a low rate of CCW use (33% (e), 25 and 2–5%, respectively) reflects the scale of FA disposal. Only few countries – small CCW generators – utilize it to the extent of 90–100%. Anticipating the highest world's energy growth based on coal in Asia in the first decades of the Millennium indicates that this is the most critical area with respect to CCW management in the near future.

About 10-fold higher concentration of trace elements compared to coal/lithosphere, the occurrence of highly leachable macro-components, high hydraulic conductivity and observed acidification of the most abundant low-alkaline FA in a long-range time due to devitrification of glass phase, generation of secondary minerals and regeneration of primary minerals from their amorphous relics are the major factors that lead to the conclusion that the potential risk to the environment from FA should be evaluated as high. The nature and extent of the risk varies at the different stages of weathering. The beneficial property of FA is its high penetration resistance, 1–2 orders of magnitude exceeding that of natural cohesive soils. It can thus be eventually used as a sealing material against air penetration.

Occurrence of xenobiotics (PAHs, PCDD, PCDF) in FA was found to be low. The radioactivity level of FA has been found to pose no risk to the environment and health provided it is not used for the production of construction materials. For this purpose, FA material cannot be used unrestrictedly and should be tested for the level of α- and γ-radiation before use.

Dry and semi-dry desulfurization processes generally caused the addition of calcium- and sulfur-containing compounds to FA reaction products from FGD process. Their proportion and kind in the end product depends on the applied process. Generally, an admixture of FGD solids results in a significant increase of leachable sulfate compounds, but also in much higher buffering capacity and lower concentrations of xenobiotics and trace metals in this product due to the "diluting" effect of FGDS, as well as generally low susceptibility to release due to permanent moderately alkaline to neutral pH values.

The leaching behavior of "pure" FA disposed in ash ponds appears to display all three basic stages of leaching, i.e. wash-out (I), dissolution (II) and delayed release (III) stages. In the first two stages, the contamination potential of FA is governed predominantly by the release of macro-components at pH values ranging from alkaline to close to neutral, hence the leaching of the majority trace elements is low, except of oxyanions of a wide stability field in solution (Mo, As, Cr(VI)). The deterioration of groundwater quality by high concentrations of leachable macro-components (TDS, chloride, sulfate, Ca, Mg) and also Mo, As and Cr(VI) may already render the shallow unprotected aquifer unusable at these stages, as was demonstrated in the case study on the MSEB ash pond in Maharashtra, India. In the dissolution stage (II) of the lowest dynamics of component leaching controlled by the equilibrium with gypsum, the sulfate content in leachate is high enough to render the groundwater non-potable. Equilibrium concentrations of macro-constituents in both stages are developed in a water stream due to a vertical redistribution of constituent load in the vadose zone or during down-gradient flow of water through the ash layer in the saturated zone of an ash pond.

The highest pollution potential to unprotected aquifers from the FA disposal was found to occur in the post-closure period in the delayed release (III) stage where the massive release of trace elements (Zn, Mo, Mn, Li, F, Cd, Be, B) occurred in hazardous concentrations, and Fe, Cr, Al, SO_4, Cl, NO_3, NH_4, K, Na and TDS were several times above MCL for drinking water. Despite years of extensive studies on FA focused on developing a reliable evaluation of the leaching behavior of granular waste, the information on the full three-stage cycle of FA leaching is still unsatisfactory. While a systematic approach to release of trace metals and also other inorganic components of waste as a function of controlling factors such as L:S (liquid to solid ratio) and pH is well advanced, a weak side of a long-term prognosis is a lack of the reliable long-term prediction model for controlling factors, in particular for pH changes due to proton release ion based on the one hand on the general geochemical principles, and on the other hand on the specificity of a material and a site. This has been the main reason for a failure in recognition of a long-range time-delayed possibility of FA acidification and hence of a massive release of trace metals in hazardous concentrations. The change of pH (and Eh) as a function of time-dependent (kinetically defined) processes appeared to be a key issue for a correct prediction of the leaching behavior of waste with respect to inorganic trace elements.

There is also evidence that easily detectable, obvious and visible adverse impact of ash disposal ponds on unprotected aquifers in their vicinity quite frequently remains neglected induced changes of controlling parameters. A field validation by means of a life-cycle monitoring/screening of waste disposal site is the most reliable instrument for the evaluation of the actual situation and the verification of predictive models, which eliminate a chance of the wrong decision. For these purposes, monitoring of the anthropogenic and natural vadose zone in the disposal site is the best source of early-warning information. Considering the high costs of the equipment and its maintenance for the stationary vadose zone monitoring, the concept of mobile installations for a periodical survey of factors controlling release of contaminants (e.g. pH, Eh and conductivity) along the vadose zone profile of CCW and a detailed survey of controlled contaminants (concentrations of constituents in pore solutions, in particular of trace elements) in the case of detected systematic changes should provide the required information on the behavior of a material and particular contaminants in a waste in the most cost-effective way. Therefore, we consider monitoring is required to provide an early warning and to permit effective remedial actions.

Direct analysis of pore solutions gives the most reliable results and can be based either on temporary drillings, or on stationary sets of porewater samplers. The first option seems to be the most convenient and cost effective, in particular in the developing countries with the limited availability of a trained staff and difficulties in maintaining the permanent monitoring network.

The presented case studies confirm that CCW from coal combustion, though considered non-hazardous and fit for use in a multitude of commercially proven applications, should not be treated the same way as a natural raw material despite of a strong pressure of proponents of this approach, among them of the ACAA (Stewart, 1999). Uncontrollably disposed, this waste may pose a high short-term risk to shallow unprotected aquifers and soil, and its further non-linear time-delayed increase, which would render an area environmentally problematic. Another conclusion that should be derived, is a need of a careful long-term environmental evaluation of a bulk use of FA under the conditions of the vast environmental exposure of the unprocessed material, e.g. as soil amendments. It should take into consideration the possibility of soil contamination with trace elements in all stages of geochemical transformations.

To facilitate CCW disposal and utilization in an environmentally safe way and to prioritize its use, besides reliable environmental risk assessment prediction models, testing procedures, and life-cycle monitoring, countries that are high CCW generators need national strategies of power plant waste control, treatment and disposal methods within a general waste management strategy. These strategies should provide a legislative and regulatory framework within which adequate enforcement procedures can be implemented that would make uncontrollable FA disposal highly unprofitable. The enforcement procedures should comprise a well-balanced system of precepts, prohibitions and charges for disposal (fees, penalties) that would encourage power plants as waste generators to support financially the environmentally safe utilization of CCW by the waste reuse industry on a cost-benefit basis, in order to reduce charges for the disposal and to assure competitiveness of these products in the market. The current practice in India shows that under the conditions of the lack of the Resource Conservation Act and of financial incentives for CCW end users from waste generators, their products cannot compete financially with natural raw materials, and a fast growth of FA market remains a wishful thinking. The lack of properly working system of finance transfer from waste generators to utilization industries seems to be a serious obstacle for growing of CCW market also in the USA, despite of an adequate and properly implemented regulatory framework.

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