Solid Waste: Assessment, Monitoring and Remediation
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VI.8

Bulk use of power plant fly ash in deep mines and at the surface for contaminant and fire control

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VI.8.1. Introduction

Despite a number of beneficial properties and stepped up use in a wide array of field-proven applications, coal combustion waste (CCW) cannot be just renamed a raw material to solve the environmental problems posed by its generation and disposal. CCW is considered a waste as soon as it enters the waste stream and is disposed of or temporarily stored and not utilized in an environmentally safe way. As has been shown in Chapter III.7, CCW is not an inert material and may create a serious threat to the environment, in particular to ground water resources, up to a hazardous level in a long-range period. Therefore, CCW management must fulfill the criteria of environmental safety. Having in mind its diverse characteristics, both positive and negative, sound management of CCW should go beyond safe storage and disposal and take into account the possibility of reducing its volume through bulk use. The current practices show that this goal is not easy to achieve in the countries that are large CCW generators (Table VI.8.1). Up to now, the optimistic examples of thorough utilization used to back up the idea of CCW being renamed a by-product are relevant solely for the smallest CCW generators (e.g. the Netherlands or Denmark), where a very limited CCW production (≤1 Mt) does not exceed the market demand. In the USA, which holds the second position after China in coal production and coal-based power generation in the world, CCW generation was estimated to increase from about 80 Mt in 1990 to over 100 Mt in 1999 (Butalia and Wolfe, 1999; Adriano and Weber, 2001). In 1992, 74.4 Mt of CCW was reported by American Coal Ash Association (ACAA, after Tyson, 1994) to be generated in the form of coal ash, i.e. fly ash (FA) (59.6% wt.) and bottom ash (BA) (17.1%), boiler slag (5.0%), and FGD solids (18.3%). ACAA survey data for 1996 showed increase of CCW generation to 92.5 Mt, i.e. for almost 20% (Stewart, 1999). The rate of its utilization, though, has not changed much, and during this decade accounted roughly for 25% of the amount produced. The traditional markets comprise predominantly cement/concrete and in lesser amounts production of other construction materials (e.g. blocks, bricks, tiles, lightweight aggregates), structural fill, road base and sub-base, blasting grit and roofing granules, as well as miscellaneous minor applications such as filler in asphalt, anti-skid material, grouting, toxic waste stabilization and solidification, fillers in plastics and paints, wallboard manufacture, zeolite production, etc. These markets, though, cannot assure

Table VI.8.1. Examples of annual coal combustion waste generation and use in selected countries – large FA generators, Mt (%).

CCW management	USA							India	Poland	UK	Japan
	1990[a]	1992[b]	1996[c]					1998[d]	1998[e]	1989–1998[f]	1989[g]
Products, markets	Total	Total	FA	BA	BS	FGDS	Total	Total	Total	Total	Total
Generation, Mt (% of total)	78.75	74.4	53.88 (58.3)	14.58 (15.8)	2.33 (2.5)	21.65 (23.4)	92.45 (100)	75.0	17.76	12.54–13.00	3.925
Utilization, Mt (% of generation)	19.28 (24.5)	18.4 (24.8)	14.74 (27.3)	4.42 (30.3)	2.18 (93.3)	1.50 (6.9)	22.84 (24.7)	1.5–4 (2–5)[c]	11.39 (64.1)	6.12 (48.8)	1.920 (49.0)
Cement/concrete	7.25 (9.2)	7.2 (9.7)	7.28[h] (13.5)	0.69[h] (4.73)	0.00[h] (0.00)	0.06[h] (0.28)	8.04[h] (8.70)	x	–	0.73 (5.8)	1.421 (36.2)
Building materials, blocks	–	–	–	–	–	–	–	xx	–	3.92 (31.3)	0.173 (4.4)
Flowable fill/ structural fill	3.78 (4.8)	2.4 (3.2)	2.25 (4.17)	0.65 (4.46)	0.04 (1.72)	0.06 (0.28)	3.00 (3.24)	–	7.29 (41.0)	1.10 (8.8)	–
Road base/ sub-base	1.84 (2.4)	2.2 (3.00)	0.68 (1.26)	0.66 (4.53)	0.00 (0.00)	0.11 (0.51)	1.44 (1.56)	–	–	–	0.134[i] (3.4)
Blasting grit/ roofing granule	1.67 (2.1)	1.9 (2.6)	0.00 (0.00)	0.15 (1.03)	1.97 (84.6)	0.00 (0.00)	2.13 (2.30)	–	–	–	0.058 (1.5)
Other markets listed below:	4.74 (6.0)	4.7 (6.3)	4.52 (8.39)	2.28 (15.6)	0.16 (6.87)	1.27 (5.87)	8.23 (8.91)	–	4.10 (23.1)	0.37 (3.0)	0.077 (2.0)
Asphalt filler	0.131 (0.17)	–	0.15 (0.27)	0.03 (0.20)	0.05 (2.14)	0.00 (0.00)	0.22 (0.24)	–	–	–	[i]
Snow, ice control	1.56 (1.98)	–	0.00 (0.00)	0.61 (4.18)	0.10 (4.29)	0.00 (0.00)	0.71 (0.77)	–	–	–	–
Grouting	0.31 (0.39)	–	[h]	[h]	[h]	[h]	[h]	–	–	0.25 (2.0)	–

Mining application	0.054	–	0.69	0.06	0.00	0.03	0.77	x	4.10	–	–
	(0.07)		(1.28)	(0.41)	(0.00)	(0.14)	(0.83)		(23.1)		
Wallboard	0.036	–	0.01	0.00	0.00	0.79	0.81	–	–	–	–
	(0.05)		(0.02)	(0.00)	(0.00)	(3.65)	(0.88)				
Waste stabilization solidification	–	–	1.75	0.23	0.00	0.05	2.04	–	–	–	–
			(3.25)	(1.58)	(0.00)	(0.23)	(2.21)				
Miscellaneous[j]	2.647	–	1.91	1.34	0.01	0.40	3.66	–	–	0.12	0.077
	(3.36)		(3.54)	(9.19)	(0.43)	(1.85)	(3.96)			(1.0)	(2.0)
Agriculture and fisheries	–	–	0.01	0.01	0.00	0.00	0.02	xx	0.00	0.00	0.058
			(0.02)	(0.07)	(0.00)	(0.00)	(0.02)		(0.0)	(0.0)	(1.5)

FA = Fly ash; BA = Bottom ash; S = Boiler slag; FGDS = Flue gas desulfurization solids; xx – major amount; x – minor amount.

[a] ACAA data 1990, after Collins, 1992.

[b] ACAA data 1992, after Tyson, 1994; CCW use: FA 27%, BA 28%, S 75%, FGDS 2%.

[c] ACAA data 1996, after Stewart, 1999.

[d] Estimate, after Prasad et al., 2000 and Ray, 2000.

[e] Electricity and thermal energy generation: After Central Statistical Office, 1999 and State Environmental Protection Inspectorate, 1997; For full data on power generation in 1985–2001 see Table VI.8.2.

[f] National Power/Power Generation data 1989, after Clarke, 1994 and OECD Environmental Data, 1999.

[g] Japan Coal Ash Assn., 1989, after Clarke, 1994.

[h] Data for grouting are given together with cement/concrete.

[i] Data for road base and asphalt filler together.

[j] Miscellaneous = waste stabilization and solidification (if not given separately) and other low-volume applications such as fillers in plastics and paints, zeolite production, etc.

absorption of all, or at least of a more substantial proportion of the CCW generated (Collins, 1992; Clarke, 1994; Tyson, 1994; Butalia and Wolfe, 1999; Chugh and Sengupta, 1999; Stewart, 1999).

In India, at present coal and power production, around 75 Mt of CCW as coal ash is generated annually, and a further growth to 290 Mt by 2011–2012 is anticipated. The current coal ash utilization level is negligible and according to a rough estimation ranges between 2 and 3% (Prasad et al., 1999, 2000), and 6% (Ray, 2000). The major areas of bulk application are production of building materials (bricks, cement, tiles) and in agriculture as soil amendment and fertilizer. This last area seems to be particularly attractive to India as high-volume low-technology application, and potential sink for almost unlimited amounts of CCW, in particular when a visible growth of crop after application up to 600 t/ha was observed (Tripathi et al., 1997; Singh and Tripathi, 2000). In view of the mostly low lime content in Indian CCW (1–3% CaO) typical also for the majority of this waste in other countries, which displays low neutralizing capacity, along with 10-fold enrichment with heavy metals compared to burned coal, including mobile oxyanions of proven toxicity, and adverse weathering transformations of its properties due to devitrification (Twardowska and Szczepanska, 2002), large-area uncontrolled agricultural use may lead to irreversible soil contamination in the long-range period (Twardowska et al., 2003). These premises resulted in a ban on CCW use in agriculture in many countries, e.g. in the EU Member States, and also in Poland and limited use in other countries (e.g. in Japan) as environmentally problematic application. The safe utilization of CCW in agriculture, particularly for industrial dumping sites reclamation with use of technical species (Sloan and Cawton, 2001), e.g. aromatic plants growth (Kanungo, 2000) though seems sound and prospective, does not solve the problem of bulk utilization of FA.

These examples show that FA utilization is still far from being satisfactory in the developed countries, and almost none in the developing ones that use coal for power generation. The major limiting factors for higher extent of CCW utilization are saturation of traditional markets and availability of competing materials at lower processing, transportation and handling costs, apart from other reasons, such as possible prejudice of end users and regulators, as well as insufficient experience of professionals dealing with processing, distribution, advertising, contraction, regulations, etc.

The ways of improving the situation with CCW utilization that should bring about substantial progress include:

- A carefully elaborated legislative and regulatory mechanism based on the adequate system of charges, fees and penalties for CCW disposal and requirements with respect to the site construction that would induce the generators to seek the possibilities of CCW utilization in the environmentally safe way on the cost-benefit basis, through the supporting financially the CCW utilizing industries to assure their competitiveness in the traditional and new markets.
- Harmonization of CCW handling techniques with further use.
- Development of new potential markets for high-volume CCW use, which are at least equally technically sound, commercially proven and environmentally safe as traditional materials. An attractive field of high-volume CCW application is its use for specific purposes in deep coal mines or at the surface.

- Promotion and advertising actions, and demonstration projects supported also by governmental agencies showing particular beneficial qualities and advantages of different CCW applications.

In Poland, a remarkable growth of CCW use occurred, from 32.1% in 1985 to 73.4% in 2001, when 18.8 Mt of power plant wastes were generated, out of which 13.8 Mt of the annual production was utilized (Table VI.8.2) (Central Statistical Office 1994, 1997, 1999, 2001, 2002). This places Poland at the top of the countries that produce comparably high amounts of CCW with respect to the percentage of its use. This success should be owed mainly to the proper use of legislative and financial instruments. To a considerable extent, this high position of Poland in CCW utilization is also due to the extensive application of FA in deep mine workings. Since the second half of the 1980s, FA utilization underground has become increasingly popular in Poland. In the 1990s, the amount of FA utilized this way was growing particularly fast. In the area of the Upper Silesia Coal Basin (USCB), where 4.8 Mt of CCW (29.6% of the total) were generated in 1996, 4.5 Mt, i.e. 93.7% of this waste was utilized (State Environmental Protection Inspectorate, 1997). The rate of CCW use in the USCB comprised 48.2% of the total quantity utilized in Poland in 1996. According to the data of 1994 concerning the structure of CCW utilization in the region, 85.0% of the total amount generated was used underground. The rest was utilized for conventional applications, mainly for production of cement and building materials (11.7%), and the remainder in road construction and as structural fills (State Environmental Protection Inspectorate, 1995). New administrative division of the country in 1999 and formation of Silesia land in new borders that comprise the USCB, but also new areas, makes comparison with the latest data somewhat complicated. In 2001, electricity and thermal energy production in Silesia land resulted in generation of 5.6 Mt of CCW, of that 4.8 Mt, i.e. 84.4% was used (State Environmental Protection Inspectorate, 2002). Up to the end of 1994, 65 coal mines of the USCB utilized at least 17.4 Mt of CCW. By the end of 1996, this amount increased to 24.2 Mt; by the end of 1999, it accounted for about 34 Mt and continues to grow in time with the same intensity limited by the availability of CCW. Up to now, no other country can boast of comparable achievements in this field including the USA where for mining reclamation a negligible amount of 0.06 Mt in 1990 was reported to be used (Collins, 1992). In 1996, over 10 times more, i.e. 0.77 Mt (0.83% of total) was applied in the mining in the USA that is still a very low amount (Stewart, 1999).

Technically and technologically, power plant FA use underground has become a routine process in Poland during the last decade and it does not create problems. This field of application has been proven to be technically sound and commercially effective. The prerequisite of CCW use as a beneficial by-product, besides technical and commercial efficiency, is environmental safety. Considering the predominance of FA in CCW (from 72 to >80% of total CCW excluding FGD solids), and its lower utilization rate compared to BA and boiler slag, this chapter is focused on the environmental aspects of FA use in deep mine workings and on the surface. According to Polish statistics, FA handling techniques have a profound influence on its utilization. The lowest utilization rate shows coal ash transported hydraulically (slightly over 53%) which is due to its form and weight that makes it extremely inconvenient for further use, while dry FA is utilized almost thoroughly (92–93% in 1998–2001) (Table VI.8.2). "Pure" FA is the most abundant

Table VI.8.2. Generation and use of coal combustion waste (CCW) in Poland, 1985–2001 (after Central Statistical Office, 1994, 1997, 1999, 2001, 2002).

Year	Generated					Used						Stored				
	Mt					Mt	% of generated					Mt				
	CAM	FA	S	FGD-S	∑CCW	∑CCW	CAM	FA	S	FGD-S	∑CCW	CAM	FA	S	FGD-S	∑CCW
1985	–	–	–	–	27.3	8.8	–	–	–	–	32.1	–	–	–	–	168.1
1990	–	–	–	–	26.6	11.3	–	–	–	–	42.5	–	–	–	–	260.9
1992	–	–	–	–	21.7	10.0	–	–	–	–	46.3	–	–	–	–	267.4
1993	–	–	–	–	21.5	10.3	–	–	–	–	48.0	–	–	–	–	275.8
1995	–	–	–	–	20.1	12.5	–	–	–	–	62.2	–	–	–	–	318.5
1996	–	–	–	–	20.6	13.2	–	–	–	–	64.3	–	–	–	–	325.3
1998	9.0	4.1	2.8	2.6	18.5	12.5	53.6	91.9	86.3	57.4	67.5	239.1	27.6	20.6	4.1	291.4
2000	9.1	4.6	2.5	3.1	19.3	14.3	53.2	93.3	86.0	97.7	73.9	244.3	46.4	18.3	2.1	311.1
2001	8.6	5.2	2.3	2.4	18.5	13.2	46.5	93.2	88.3	96.7	71.3	246.6	45.3	18.1	0.9	310.9
1998	Electricity and thermal energy production				17.8	11.4	–	–	–	–	64.1	–	–	–	–	248.9
2000					18.1	13.7	–	–	–	–	75.7	–	–	–	–	251.7
2001					18.8	13.8	–	–	–	–	73.4	–	–	–	–	312.3

CAM – coal ash (FA/S mixtures transported hydraulically); FA – fly ash (dry); S – slag; FGD-S – flue-gas desulfurization solids (lime methods); ∑CCW – total coal combustion waste.

waste in electric utilities, which do not use desulfurization of flue gases, and in the ones using wet desulfurization process that is predominant in the USA, Germany and in most of the other countries using desulfurization of flue gases. Typically it accounts for 70–80% of the ash generated by conventional coal-fired power plants. Considering the widespread application of wet desulfurization of flue gases in power plants, the environmental evaluation of this kind of reused material is of particular interest for the potential end-user.

Environmental aspects of FA utilization underground were evaluated here on the basis of a study carried out in 24 deep coal mines of the USCB in Poland, which used FA routinely in the last decade. Pure FA originated from two power plants (Rybnik and Laziska, which produce 1600 and 1520 MW, respectively). FA with products of dry FGD process (FA + D-FGDS) originated from the Rybnik and Opole power plants, and FA containing products of ABB-NID semi-dry desulfurization process (FA + SD-FGDS) came from the Laziska power plant. Various options of bulk FA utilization at the surface were also analysed.

The major purposes of FA use discussed here are based on the specific hydrogeological and hydrogeochemical properties of this material, both adverse and positive, presented in detail in Chapter III.7. The basic premises of these applications and their limitations can be summarized as follows:

- All the low-ratio water mixtures of FA after solidification show excellent sealing properties against air penetration. Their penetration resistance ($R = 1000–19,000$ kPa) is 1–2 orders of magnitude higher than that of natural cohesive soils such as boulder clay ($R = 190$ kPa).
- FA has a high water retention capacity exceeding 50% wt.
- Hydraulic conductivity of pure FA at the level of $k \geq 10^{-8}$ m/s does not fulfill the criteria of impermeability both for horizontal water flow and for a vertical infiltration. This material can be classified as a very weakly insulating one similar to silt loam or sandy clay loam and cannot be used as a sole protective barrier against water infiltration.
- Due to high leachability and the concentration of macro-components and trace elements being an order of magnitude higher than in natural soils, among them toxic oxyanions as As, Mo, Se, Cr^{6+} and insufficient buffering capacity of low-alkaline FA, this material can be a source of long-term aquatic and terrestrial environment contamination at all three stages of leaching, i.e. wash-out (I), dissolution (II) and delayed release (III) stages.
- The best hydrogeological and hydrogeochemical parameters are displayed by high-alkaline FA, in particular FA + D-FGDS containing products of dry flue gas desulfurization lime process. These show the lowest hydraulic conductivity, up to impermeability to horizontal flow ($k = 10^{-8}–10^{-9}$ m/s), lack of tendency to acidification and hence of the massive trace elements release in the delayed release (III) stage, the shortest solidification time, the best sealing properties against air penetration and the highest water retention capacity.
- Low-water mixtures with FA containing products of semi-dry desulfurization process (FA + SD-FGDS) besides being improved in basic properties compared to pure FA such as air penetration resistance or lack of the tendency to acidification and hence of the delayed release (III) stage, display adverse features caused by the presence of

chemically instable sulfites, in particular a long period for solidification and certain thixotropic properties, which reduce reuse of this material at the surface in a wet climate or underground in wet workings.

The bulk use of FA underground and at the surface is thus focused on the utilization of its properties as an excellent sealing material against air penetration that has no competitor in this respect among the natural alternative materials, and its high water retention capacity. This way, FA utilization for these purposes would not just reduce the amount of disposed CCW waste, but would improve environmental quality and safety in the areas of CCW utilization. At the same time, environmental requirements dictate the need of taking into consideration and suppression of the adverse parameters of FA, such as low barrier properties with respect to water infiltration and high leachability of macro-components and problematic trace elements.

VI.8.2. Fly ash application underground

VI.8.2.1. Purposes of FA application

The main direct purposes of FA application in deep coal mines are liquidation of useless drifts, peat shafts and sealing of mined out and abandoned workings, backfilling (stowing) of mine workings and stopping construction for fire prevention and control, methane control and reduction of greenhouse effects caused by methane release to the atmosphere, simplification of a ventilation system, and reduction of surface deformations due to subsidence, as well as a component of binding material. Sealing properties of FA against air penetration create wide demand for CCW in deep mines as irreplaceable and infallible raw material, easily available and manageable. In mine workings CCW, predominantly FA, and in lesser amounts (up to 10%) also BA, are being used in the form of a dense mixture with mine water, or less frequently with flotation slurry from coal preparation process. The worst quality highly saline or/and of elevated radioactivity mine waters are used for mine water:FA mixtures are prepared for two reasons:

- To use the high water retention and binding capacity of FA for adequate reduction of contaminant loads discharged with mine waters to the surface receiving waters;
- To protect high quality ground water resources.

In addition to the major purposes, utilization of FA underground eliminates to a great extent a burden caused by a surface disposal of this airborne and highly leachable waste. While generated quantities of FA increase, the availability of appropriate disposal areas decreases and the costs of new disposal areas rise significantly. Nowadays, requirements for siting and managing disposal sites have become very stringent. No less important is eliminating the threat of the so-called secondary "low emission" of dust from the pond surface, as well as of an impact on the ground and surface waters in the vicinity of the disposal site.

Besides benefits, this material used underground may also cause adverse side effects, resulting from high leachability of constituents from its matrix. The extent of these side effects largely depends upon geological, hydrogeological, and hydrological conditions in the site of FA use, as well as upon the material properties.

VI.8.2.2. Methods of FA utilization underground

In Polish practice, FA is loaded in a dry state directly from electrostatic precipitators into railway or road tankers through a hermetic connection, and transported to the unloading station at a mine. Again, through the hermetic connection, with use of compressed air, it passes to a feeder, where it is mixed with mine water in the required proportion and pumped to a retention tank. From the tank, the dense (low-water) FA mixture is transported underground gravitationally by pipelines to an outlet, behind the barrier (stopper) in the backfilled working (Fig. VI.8.1). The mine water:FA ratio is determined by the transportability of the mixture, the distance of the outlet from the retention tank at the surface, and the time of the mixture solidifying. The most frequent mine water:FA ratio is 1:1, up to 0.8:1 by weight. The deposited mixture undergoes gradual dewatering. An excess of water joins the mine drainage system and is pumped to the surface. Partially or thoroughly, the residual water is directed back to the circuit of mine water. The excess water from FA mixture is discharged to the surface recipients (rivers) either directly, or through the mine water-collecting pipeline. The amount of water and discharged loads of contaminants prescribed by the permit depend on the mine water and dissolved constituent load balance and the dilution capacity of the recipient. Besides compulsory environmental impact assessment (EIA) to be submitted by the FA utilizing company to the Environmental Protection Department to obtain a permit for its utilization underground for each mine, mine workings and kind of FA, an extensive study on the environmental evaluation of FA use in deep mines in different hydrogeological conditions was conducted in 1993–1996. As was already mentioned above, the assessment comprised FA originating from the three power plants (Rybnik, Laziska and Opole), being used in 24 coal mines of the USCB.

VI.8.3. Environmental evaluation of fly ash use in deep mine workings

VI.8.3.1. Criteria of the environmental impact assessment

Utilization of the large quantities of CCW in the underground mine workings in the form of dense FA:mine water (or FA:slurry) mixture creates entirely an new environmental issue. For its evaluation, adequate criteria should be applied, regarding the general regulations, acts and methods of EIA, as well as FA properties and its environmental behavior in the new array of applications under specific conditions. Transformation in time, mechanism and dynamics of release, and immobilization of contaminants from FA mixtures and their migration (depending upon the interaction with the disposal environment) are factors to be considered. In brief, the criteria of the EIA of FA may be formulated as following:

- The basic parameters for evaluation of the environmental effect of power plant waste deposition underground should be the load of contaminants in mine water used for the mixture preparation and the mobilizable contaminant load in FA per mass unit.

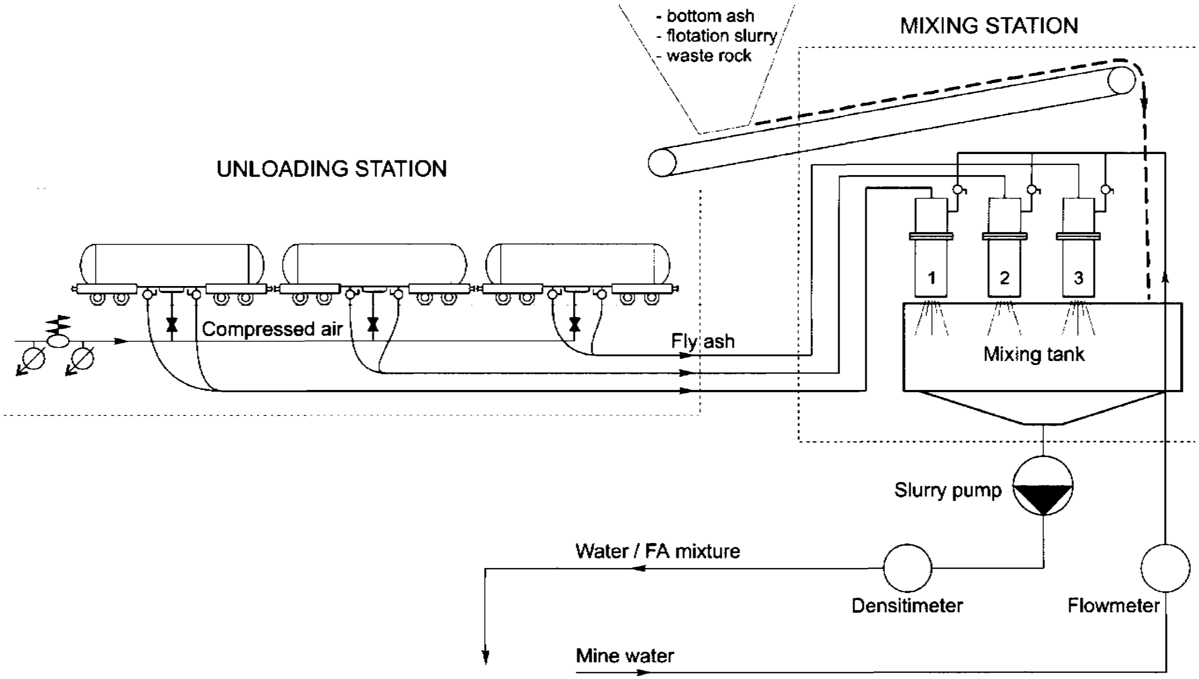

Figure VI.8.1. Scheme of installation for dense water:FA mixtures preparation and use in deep mine workings (after UTEX Ltd, Poland).

- The basic criterion should be the balance of actual input and output pollutant loads in the dense FA:mine water (slurry) mixture, with regard to the quality requirements of the recipient.

A concentration-based approach does not display clearly either the amount of contaminant released, or retained in the fly-ash matrix. The load-based criteria assure obtaining objective data on either adverse or beneficial environmental effects of CCW used in mine workings in the form of dense FA:mine water mixture. These criteria permit separate evaluation of the amount of pollutants introduced to the system by mine water and released or retained by FA. The positive or adverse environmental impact is thus evaluated as negative or positive load balance in outflow from the mixture compared to the load introduced to the mixture with mine water.

Environmental evaluation of FA use underground should also comprise: (i) assessing pollution potential of FA vs. transformations of waste properties with time; (ii) long-term prognosis of contaminant loads release/retention balance from mine water:FA mixture, in compliance with its disposal environment; (iii) characterization of hydrogeological and hydrogeochemical conditions in working or abandoned mines with regard to protection requirements of major groundwater basins (MGWBs); (iv) radioactivity level in mine workings resulting from utilization of CCW; (v) prognosis of post-closure hydrogeological and hydrogeochemical conditions in the mine where FA was used. An integral part of the EIA of FA utilization in deep mines should be environmental monitoring within the eventual impact radius.

On the grounds of the above criteria and procedure, extensive testing and research to characterize CCW for developing the guidelines of its environmentally safe use underground, for each particular case of application in the form of a dense mixture with mine water (or slurry), have been carried out. The environmental evaluation was a basis for obtaining a permit for FA utilization in each seam of each particular mine and revealed a variety of different issues in seemingly similar cases.

Characteristics of FA properties, elemental composition and leaching behavior, as well as hydrogeological characteristics of FA:mine water mixtures have been discussed in Chapter III.7.

VI.8.3.2. Ground water protection requirements

In the area of FA utilization underground, the critical protection areas (CPAs) of the MGBW should be considered and protected against contamination from this source. FA utilization at any rate may not pose a threat to the usable ground water resources. Kleczkowski (1990) defined usable ground water horizons (UGWH) and MGWB on the basis of the qualitative and quantitative criteria. Groundwater basins defined as MGWB are the fragments of UGWH of better hydrogeological conditions. With respect to qualitative criteria, two basic classes of water have been distinguished: (I) to be used for drinking water supply; (II) not considered to be used for drinking water supply. Waters belonging to Class I comprises four sub-classes (a, b, c, d) depending upon the need for water preparation: Ia – very good, no need for preparation; Ib – good, no need for preparation; Ic – concentrations of pollutant(s) slightly above the maximum permissible level MCL, easy to treat; Id – MCL considerably exceeded, preparation required.

The following criteria have been used for defining MGWBs in the Carboniferous strata: (i) potential capacity of water intake $>70\ m^3/h$; (ii) potential capacity of group water intakes $>10{,}000\ m^3/h$; (iii) water quality fulfills I class criteria. With respect to the Carboniferous MGBW, these criteria are applied both to well and mine water intakes. Carboniferous MGWBs are used mainly as mine intakes, to lesser extent as wells. In the areas of water shortage, for selection of Quaternary MGWB and UGWHs, individual quantitative criteria, which are lower than the basic ones, are being used. With respect to MGWB, the potential capacity of a well should be $>40\ m^3/h$, and a group intake should be above 2000 m^3/d. The potential capacity of a single well for UGWH should be no less than 5 m^3/h. The quality of water should fulfill the criteria of classes Ia–d.

That either UGWHs or MGWBs are not jeopardized by FA utilization is to be confirmed by the EIA.

VI.8.3.3. Characteristics of mine waters

Mine waters are a component of a dense FA:water mixture and therefore exert a considerable effect on its properties, environmental behavior and pollution potential. Optimization of the environmental effect of FA use underground requires thus adequate mine water management.

Waters occurring in the Carboniferous strata in the USCB represent different chemical composition and total dissolved solids (TDSs) ranging over wide limits from 0.1 to 230 g/l. It reflects hydrogeological zonality in the stratigraphic column typical for sedimentation basins, which is characterized by the general trend of downward increase of mineralization independent from the age of the stratigraphic column (Różkowski and Przewlocki, 1987; Różkowski, 1995). In the profile of the Upper Carboniferous in the USCB, explored by mine workings up to a depth of about 1200 m, three vertical hydrochemical zones can be distinguished: (I) infiltration, (II) mixed and (III) connate waters. In the upper zone of the active water exchange, young infiltration waters of a low salinity occur. The middle zone is of a transitional character and contains mixed infiltration and connate waters of a slow recharge rate and TDS from several to <30 g/l. The lower zone contains stagnating connate brines of TDS up to 370 g/l. The hydrogeochemical anomalies, which result from geological and anthropogenic factors, disturb this general regularity. Of the geological factors, the major ones are an occurrence of a sealing horizon formed of Tertiary clay sediments insulating the Carboniferous strata from the percolation of the atmospheric precipitation, observed decreasing permeability of Carboniferous sandstone with the depth and an occurrence of halite deposits in the Tertiary sediments. Another major group of factors modifying chemical composition and mineralization of mine waters is mining activity, which evokes mainly mixing waters from different zones due to long-term drainage, infiltration of contaminated waters from the surface as well as sulfide oxidation in the Carboniferous rocks. Waters of the upper zone in the depth range 1–500 m are of HCO_3–SO_4–Ca–Mg or SO_4–Cl–Ca–Mg type, TDS ranging from <1 to about 25 g/l. Mixed waters represent generally SO_4–Cl–Na type. The roof of the lowest zone of connate waters, which is represented by brines of Cl–Na or Cl–Na–Ca type, generally occurs at a depth of 400–500 m. Mine water is generally slightly alkaline ($pH \leq 7.8$), more rarely slightly acidic ($pH \geq 6.4$) or acidic ($pH < 4$). Examples of elemental composition and load balance of typical saline mine waters of the USCB are presented in Tables VI.8.3 and VI.8.4 as input. Water inflow to mines of the USCB ranges from 0.5 to 7.4 m^3/min. The mines were classified by Wilk (1965) as the ones of high (>5 m^3/min), moderate (from >2 to ≤5 m^3/min) and low water inflow (≤2.0 m^3/min).

Of the trace elements, mine waters frequently contain high concentrations of Ba (up to 100 mg/l). Other elements occur in concentrations below 1 mg/l, in the range from 0.1 to 0.001 mg/l or in concentrations below the detectable level (e.g. Mo, V). The concentrations of trace elements in mine waters are governed by stability constraints and at the actual pH range are generally low. Nevertheless, the concentrations of metals in saline mine waters often exceed MCL for drinking water (in particular Mn, Pb, Ni, Cd) and in general are elevated compared to low-TDS Quaternary ground waters (Tables VI.8.3 and VI.8.4). In some seams saline mine waters display elevated or high natural radioactivity levels, up to 390 kBq/m^3 (Lebecka and Tomza, 1989).

Discharge of saline mine waters to the low-flow surface receiving waters in the USCB area results in the off-class deterioration of their quality and therefore the reduction of discharged contaminant loads becomes critical for the mine economy.

VI.8.4. Environmental effects of dense mine water:FA mixture use in dry mine workings

VI.8.4.1. General trends

Utilization of FA in mine workings in the form of dense mine water:FA mixtures, besides other effects beneficial for the environment, i.e. reduction of surface deformation (subsidence), fire prevention and methane control, simplification of a ventilation system and liquidation of old mine workings (goafs), results in a significant reduction of mine water discharge to the surface receiving waters and of loads of the majority of contaminants contained in the saline mine waters used for the preparation of pure FA: mine water mixtures.

Environmental evaluation of FA containing desulfurization products from dry and semi-dry process based on the load balance of contaminants retained in mine water: FA + FGDS mixture and released in the outflow of the excess water showed, similarly to pure FA, a generally positive effect of utilizing this material in deep mines in the form of a mixture with mine waters (Twardowska, 1999b).

The output concentrations of the majority of contaminants are higher in leachate than in the input mine water as a result of the release from pure FA or FA + FGDS. The output loads of these contaminants in leachate (Cl, Na, TDS, trace metals) are though considerably lower than the respective input loads in mine water used for preparation of mixtures with FA, mainly due to the permanent binding of water in the solidifying mixture that accounts from 50% up to 65% wt. related to the FA mass, along with a respective load of dissolved constituents. In some cases, also reduction of concentrations of some constituents in the excess outflow occurs, due to precipitation or sorption. This way utilization of CCW underground has a positive effect on the water quality of surface receiving waters. The leachate composition and the contaminant balance (reduced and released loads) for pure FA and FA + FGDS deposition underground may vary considerably depending upon

Table VI.8.3. Concentrations and load balance of dissolved constituents in the input mine water and output leachate from mine water:low alkaline FA mixture 0.8:1 wt., and contents of leachable constituents in solidified material. Pure low alkaline fly ash (LA-FA) from the Rybnik power plant.

Parameters, constituents	Mine water – Borynia mine		Leachate from water – fly ash mixture 1:1		Leached (+) or bound (−) loads	Solidified mixture – leachable load
	Input 0.8 m^3/t		Output 0.458 m^3/t (46%)			
Parameters	C_{in}, mg/l	L_{in}, g/t	C_{out}, mg/l	L_{out}, g/t	$\Delta L = L_{in} - L_{out}$, g/t	$\sum L_{1-3}$, g/t
μS/cm	36,000	–	30,000	–	–	–
pH	7.45	–	7.43	–	–	10.96–9.04
Alkalinity, meq/L	**2.60**	**2.08**	**0.6**	**0.22**	**− 1.86**	25.0
Hardness, meq/L	115.20	92.16	129.06	47.32	**− 44.84**	73.15
Hardness $CaCO_3$	5765	4612	6459	2368	**− 2244**	3661
Hardness Ca	69.97	55.97	128.34	47.06	**− 8.92**	72.78
Hardness Mg	**45.23**	**36.19**	**0.72**	**0.26**	**− 35.92**	0.37
Macro-constituents						
Ca	1402.28	1121.83	2572.00	943.07	**− 178.76**	1458.4
Mg	**550.0**	**440.0**	**8.70**	**3.19**	**− 436.81**	4.55
Na	**9285.2**	**7428.2**	**6292.9**	**2307.1**	**− 5122.56**	3664.4
K	165.92	132.73	213.4	78.25	**− 54.49**	585.8
NH_4^+ - N	0.19	0.152	1.4	0.513	0.36	4.85
NO_3^- - N	0.713	0.567	1.406	0.515	**− 0.055**	0.09
Cl^-	**18,656**	**14,295**	**14,100**	**5170**	**− 9754.8**	7843.2
SO_4^{2-}	8.64	6.91	1441.96	528.72	521.81	639.7
HCO_3^-	**158.6**	**126.91**	**36.61**	**13.42**	**− 113.49**	366.10
CO_3^{2-}	0.0	0.0	0.0	0.0	0.0	390.06
OH^-	0.0	0.0	0.0	0.0	0.0	102.05
PO_4^{3-}	**0.064**	**0.051**	**0.035**	**0.013**	**− 0.038**	0.51
TDS	**30,220**	**24,176**	**24,682**	**9050**	**− 15,126**	15,390
COD	1008.8	807.1	1132.8	415.4	−391.7	1711.5

Trace elements						
Al	<0.060	<0.048	<0.060	<0.022	ND	ND
Ba	**92.23**	**73.79**	**0.396**	**0.145**	**−73.64**	ND
Cd	**0.11**	**0.088**	**0.06**	**0.022**	**− 0.066**	<0.075
Co	**0.14**	**0.112**	**0.11**	**0.040**	**− 0.072**	0.05
$\mathrm{Cr_t}$	0.02	0.016	0.25	0.092	0.076	0.65
Cr(VI)	0.004	0.003	0.01	0.0033	0.0003	0.33
Cu	**0.19**	**0.152**	**0.07**	**0.026**	**− 0.126**	0.10
Fe	**0.23**	**0.184**	**0.10**	**0.034**	**− 0.15**	<0.075
Mn	**0.63**	**0.504**	**0.05**	**0.018**	**− 0.486**	<0.075
Mo	<0.025	<0.020	0.523	0.239	0.239	ND
Ni	0.09	0.072	0.13	0.048	**−0.024**	0.19
Pb	0.17	0.136	0.18	0.066	**− 0.070**	<0.075
V	<0.01	<0.008	<0.01	<0.004	ND	ND
Zn	**0.11**	**0.088**	**0.09**	**0.033**	**−0.055**	<0.075

ND – not determined; Constituents showing the reduction of concentrations and/or loads in leachate compared to the input mine water are bold.

Table VI.8.4. Concentrations and load balance of dissolved constituents in the input mine water and output leachate from mine water:high alkaline mixture 1:1 wt., and contents of leachable constituents in the solidified material. Pure high alkaline fly ash (HA-FA) from the Laziska power plant.

Parameters, constituents	Mine water – Moszczenica mine		Leachate from water – fly ash mixture 1:1		Leached (+) or bound (−) loads	Solidified mixture – leachable load
	Input, 1.0 m^3/t		Output, 0.42 m^3/t (42%)			
Parameters	C_{in}, mg/l	L_{in}, g/t	C_{out}, mg/l	L_{out}, g/t	$\Delta L = L_{in} - L_{out}$, g/t	$\sum L_{1-3}$, g/t
µS/cm^{-1}	46,300	–	49,200	–	–	–
pH	7.60	–	12.27	–	–	7.71–7.67
Alkalinity, meq/l	1.55	1.55	11.00	4.62	3.07	10.25
Hardness, meq/l	127.90	127.90	192.12	80.69	**− 47.21**	116.06
Hardness $CaCO_3$	6401	6401	9614	4038	**− 2363**	5809
Hardness Ca	84.50	84.50	191.70	80.51	**− 3.99**	94.60
Hardness Mg	**43.40**	**43.40**	**0.42**	**0.18**	**− 43.22**	21.46
Macro-constituents						
Ca	1694.2	1694.2	3841.5	1613.43	**− 80.77**	1896.2
Mg	**528**	**528**	**5.12**	**2.15**	**− 525.85**	260.95
Na	9950.4	9950.4	10,339.8	4342.72	**− 5607.68**	6614
K	216.4	216.4	501.2	210.50	**− 5.90**	662.45
NH_4^+- N	**10.08**	**10.08**	**7.00**	**2.94**	**− 7.14**	9.97
NO_3^-- N	**0.218**	**0.218**	**0.062**	**0.026**	**− 0.192**	0.33
Cl	20,380	20,380	23,620	9920.4	**− 10,459.6**	15,300
SO_4^{2-}	**7.82**	**7.82**	**7.41**	**3.11**	**− 4.71**	1040.93
HCO_3^-	94.58	94.58	0.00	0.00	**− 94.58**	625.42
CO_3^{2-}	0.00	0.00	30.01	12.60	12.60	0.00
OH^-	0.00	0.00	170.01	71.82	71.82	0.00
PO_4^{3-}	**0.342**	**0.342**	**0.036**	**0.015**	**− 0.327**	0.32
TDS	37,445	37,445	39,556	16,613.5	**− 20,831.5**	27,500
COD	889.2	889.2	925.6	388.75	**− 500.45**	3267

Trace elements						
Al	0.243	0.243	ND	ND	ND	ND
Ba	125.2	125.2	ND	ND	ND	ND
Cd	0.05	0.05	0.06	0.025	− **0.025**	1.10
Co	0.21	0.21	0.32	0.134	− **0.076**	0.15
Cr	0.03	0.03	0.29	0.122	0.092	1.00
Cr(VI)	0.001	0.001	0.173	0.073	0.072	1.00
Cu	0.06	0.06	0.08	0.034	− **0.026**	0.50
Fe	0.19	0.19	0.39	0.16	− **0.03**	1.40
Mn	0.11	0.11	0.13	0.055	− **0.055**	0.15
Mo	<0.025	<0.025	0.207	0.087	0.087	ND
Ni	**0.33**	**0.33**	**0.23**	**0.097**	− **0.233**	0.30
Pb	**0.35**	**0.35**	**0.33**	**0.14**	− **0.21**	0.50
V	<0.01	<0.01	ND	ND	ND	ND
Zn	0.03	0.03	0.16	0.067	0.037	0.40

ND – not determined; Constituents showing the reduction of concentrations and/or loads in leachate compared to the input mine water are bold.

the resultant effect of the interaction of two components – mine water and FA of different chemical composition (also upon the content and composition of FGDS). Concentrations of macro constituents and trace metals in the output solutions (leachate) compared to input (mine water) showed significant changes resulted both from the release of soluble constituents of FA and from the binding of dissolved constituents in mine water (Twardowska, 1999a,b). Examining leachate from the different low- and high-alkaline systems in deep mines and at the surface and the computer simulation of pore solution speciation with use of a geochemical computer models WATEQ4F (Ball and Nordstrom, 1991, 1994), MINTEQA2 (Allison et al., 1991) and PHREEQC (Parkhurst, 1995; Parkhurst and Appelo, 1999) proved that pH along with equilibrium constraints were the major factors controlling leachability of macro-constituents and trace elements.

VI.8.4.2. Effects of mine water:pure FA mixture utilization underground on contaminant loads discharged from mines

VI.8.4.2.1. Chemical composition of leachate from dense mine water:pure FA mixtures

The effect of FA characteristics, in particular of its alkalinity, on the leachate composition is exemplified in Tables VI.8.3 and VI.8.4. The typical changes compared to the input mine water common for both low- and high-alkaline FA:mine water systems consist of: (i) transformation of Ca–Mg hardness in the input mine water into almost entirely Ca hardness in leachate, while Mg appears to be thoroughly suppressed with Ca equilibria constraints; (ii) increase of K, which is a minor component of both input mine water and leachate; (iii) considerable increase of output COD for low-saline input water, and slight increase of COD at high COD and salinity of input mine water. Amphoteric trace elements and oxyanions distinctly increase in the leachate especially chromium, present mainly in a hexavalent form Cr(VI), and molybdenum. Pb displays considerable stability, while V appears to be resistant to mobilization. High enrichment of fluoride in the outflow was also observed.

In general, trace element concentrations in leachate follow leaching patterns caused by solubility/stability criteria, pH being the main controlling factor (Brookins, 1987; de Groot et al., 1989; van der Sloot et al., 1991, 1996, 1997). The ionic strength and chemical composition of the solution resulting from the interaction of mine water with FA exerts considerable effect on trace element release or binding and results in substantial diversity in leaching behavior of FA.

The differences in alteration of mine water chemical composition, which result from the contact with FA in low-alkaline and high-alkaline systems were found to be specific for these systems.

In low-alkalinity saline mine water systems (Table VI.8.3), the chemical composition of leachate is dictated by equilibrium with gypsum. The typical transformations of the output leachate from the mixture compared to the input mine water can be summarized as follows: (i) frequent pH stabilization at the moderate alkalinity level; (ii) decrease of carbonate contents in parallel with increase and stabilization of sulfate at the concentration dictated by the equilibrium with gypsum; (iii) frequent decrease of chloride and sodium concentrations due to complexation at Cl–Na type of input waters, which results in the adequate reduction of TDS; (iv) increase of nitrogen (N) compounds. Due to pH range within the stability field of the majority of trace metals, weak metal release or reduction of Ba (due to precipitation of $BaSO_4$), Cd, Co, Cu, Fe, Mn and Zn occurs in the output leachate. Ni displays an increasing trend due the vast stability field in solution in a broad pH range and high content in FA.

In high-alkalinity FA:mine water systems (Table VI.8.4), chemical composition of leachate is governed by carbonate equilibria, which determine a pattern of the qualitative transformations of the input mine water. In general, the most characteristic trends in these systems are as follows: (i) increase of pH value, up to pH $>$ 12; (ii) strong increase of alkalinity in parallel with carbonate hardness and decrease of sulfate hardness (iii) increase of chloride and Na concentrations due to release from FA matrix; the intensity of release is higher if Cl–Na salinity of the input mine water is low; (iv) increase of TDS as a result of increase of chlorides balanced by alkali ions and of carbonate hardness; (v) decrease of sulfate concentrations that adversely depends upon the SO_4 content in the input mine water and is deeper if the SO_4 concentrations in the input mine water are high; (vi) frequent distinct decrease of nitrogen compounds (ammonia and nitrate). Concentrations of trace metals in leachate strongly depend upon their stability field at elevated pH. Most of the metals in such systems with pure high alkaline FA show a general moderate increase. Trace metal concentrations in the leachate usually somewhat exceed the maximum permissible concentration level for drinking water (MCL).

The decrease of N compounds and sulfate contents in leachate from high alkaline FA:mine water mixtures or the reduction of Cl, Na and TDS in leachate from low alkaline FA:mine water mixtures is not an explicit rule and in some systems does not occur, which is due to the variety of chemical composition and physiochemical parameters of both FA and mine waters used for mixture preparation.

VI.8.4.2.2. Load balance

Generally, the leachate quality is worse than that of the input mine water. Nevertheless, the permanent binding of input water in high-TDS mine water:FA mixture up to 65% wt. results in a considerable reduction of the discharged loads of contaminants compared to those in the input mine water, including almost all trace metals (except Cr_t Cr(VI) and Mo), N compounds, major parameters and macro components like chloride, hardness, Na, K, TDS and COD, and in high alkaline systems or at high sulfate input water also sulfate (Tables VI.8.3 and VI.8.4, Fig. VI.8.2a,b). The most environmentally beneficial effect is the high reduction of discharged contaminant loads resulting from the preparation of FA mixtures of highly saline, acidic, high trace metal mine waters from the deep seams at the ratio assuring transportability at the minimum leachate, usually 1:1 or less. The adverse effect of pure FA use underground is an increase of pH value in excess outflow up to strongly alkaline pH $\geq$ 12 in the highly alkaline systems and mobilization of amphoteric metals like Cr and Ni. Oxyanions such as Mo show high mobility in a wide range of pH, both in neutral and alkaline systems. The released excessive loads, though, can be effectively minimized by the optimization of the mine water:FA ratio.

The application of a better quality, low-TDS mine water fit for any other purpose for preparation of dense mine water:FA mixtures should be avoided in order to protect usable ground-water resources and because of a strongly reduced or even completely lacking environmentally beneficial effect of contaminant binding. A comparison of the load

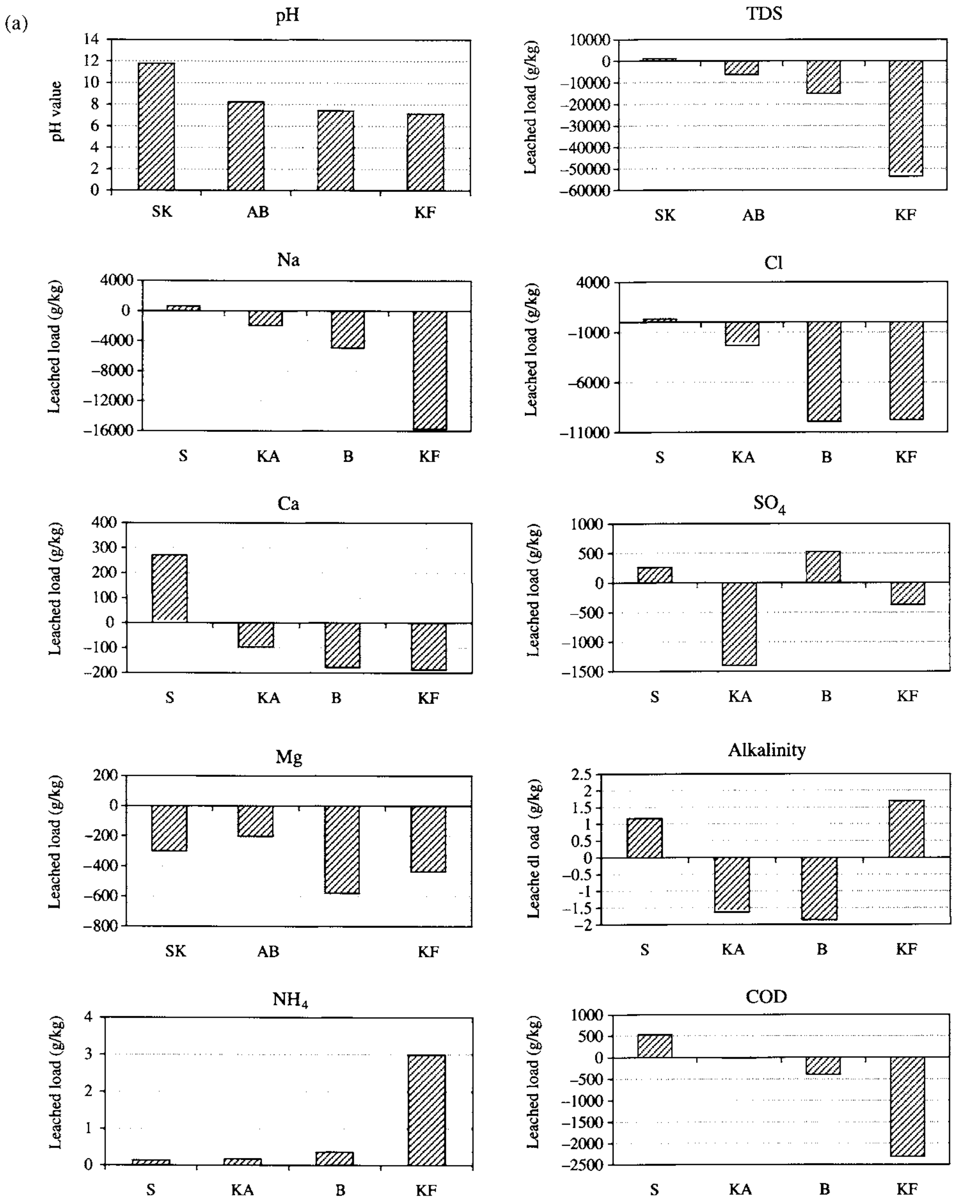

Figure VI.8.2. (a) Effect of mine water salinity in mixture with pure FA (1:1, wt.) on binding (−) or release (+) of macro-constituent loads. Material: Low alkaline FA from the Rybnik power plant. Mine water of increasing Cl–Na salinity in the TDS range from 2 to 100 g/l from different coal mines (USCB, Poland): Sosnica (S), Knurow-Aniolki (KA), Borynia (B) and Knurow-Foch (KF). TDS values: 2.7 g/l (S); 8.3 g/l (KA); 30.2 g/l (B); 93.7 g/l (KF). (b) Effect of mine water salinity in mixture with pure FA (1:1, wt.) on binding (−) or release (+) of trace element loads. Material: Low alkaline FA from the Rybnik power plant. Mine water of increasing Cl–Na salinity in the TDS range from 2 to 100 g/l from different coal mines (USCB, Poland): Sosnica (S), Knurow-Aniolki (KA), Borynia (B) and Knurow-Foch (KF). TDS values: 2.7 g/l (S); 8.3 g/l (KA); 30.2 g/l (B); 93.7 g/l (KF).

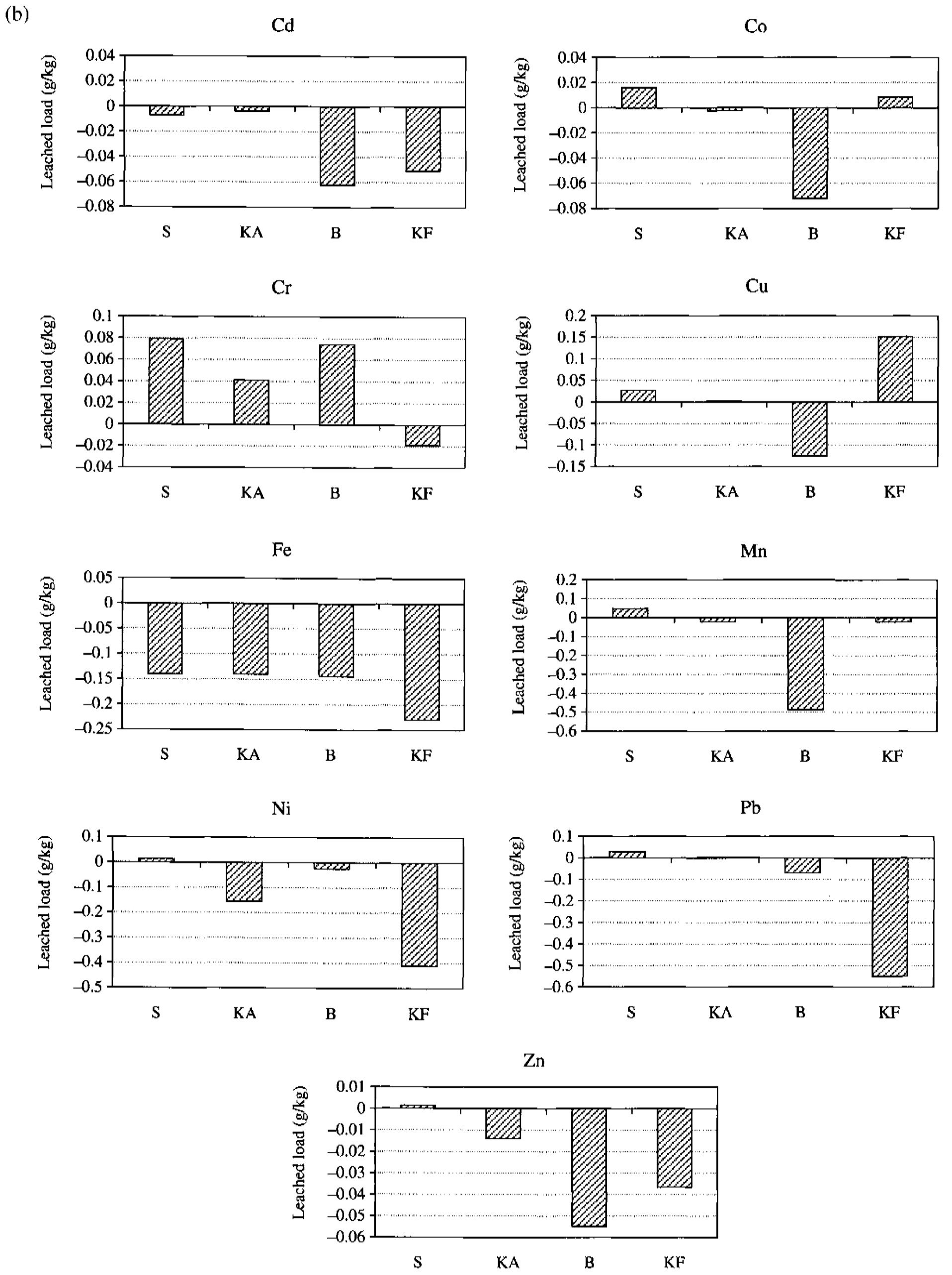

Figure VI.8.2. (Continued).

balance for a mixture of low- to high-TDS mine water (Fig. VI.8.2a,b) clearly shows the domination of release over binding of almost all measured macro-constituents and trace elements if low-TDS mine water (S in Figure VI.8.2a,b) is being used for a mixture preparation. If moderate to high-TDS saline mine water is used, the binding effect prevails with respect to the both macro- and trace constituents (KA, B, KF in Figure VI.8.2a,b). If no other water is available, the maximum technologically possible reduction of mine water:FA ratio would allow achieving a substantial decrease of the leachate volume. This also decreases the excessive loads of contaminants in leachate that are to be discharged to the water:FA mixture preparation circuit that can be separated from a general mine dewatering system if the released loads reduce the discharged water quality.

VI.8.4.2.3. Leachability of constituents from the solidified mixture

After binding of added mine water in a process of formation of calcium silicates and aluminosilicates, sulfate hydration and crystallization, loss of excess water, and solidification of mine water:FA mixture placed in dry mine workings, leachate terminates. The solidification of pure FA mixtures lasts 23–24 days. The further leaching of soluble constituents from FA mixture may occur either in wet mine workings or after flooding the mine in a post-closure period. In such conditions, the release of constituents will follow the leaching behavior pattern for monolith material, and will show low dynamics that is not addressed here.

To evaluate total load of the potentially leachable constituents in solidified dense FA mixtures, a standard leaching test of crushed material at liquid to solid ratio $L:S = 2$ according to EN 12457–1 (2002) in triplicate sequence was used. It displayed somewhat different leachability for low- and high-alkaline systems (Tables VI.8.3 and VI.8.4, Fig. VI.8.3a,b).

Low-alkaline solidified mixtures showed similar pH range as the outflow, but in some cases also increase of pH range of eluates up to values $11 < pH < 9$ (Table VI.8.3, Fig. VI.8.3a,b), while the pH range of eluates from the solidified high-alkaline mixture, opposite to the low-alkaline one, was definitely lower than that in dewatering stage, within slightly alkaline values (Table VI.8.4). The total leachable loads of TDS, Cl, Na and Ca-hardness in both systems were close to that retained in the material from mine water. High COD and high NH_4-N leachable loads originated from FA. The leachable load of sulfates in the low alkaline system was comparable to that released in the dewatering stage, while in the high alkaline system it was up to over three orders of magnitude higher than in the outflow. Most of the trace elements appeared to be stable in a solid phase at the actual pH range and unsusceptible to mobilization, similar to those in leachate at the dewatering stage of a mixture. The dynamics of constituent leaching from the monolithic solidified material will be naturally much lower.

The decreasing trend of pH values in both systems during sequential leaching signals the possibility of acidification of the material in course of a longer time if constant vertical infiltration through the FA mixture placed in mine workings occurs under the vadose zone conditions. Shifting from the highly alkaline to acidic pH values of pore solution in FA surface pond in the post-closure period with all the consequences of massive heavy metal mobilization have been already observed (Twardowska and Szczepanska, 2002) (see also Chapter III.7). The similar non-linear time-delayed trace

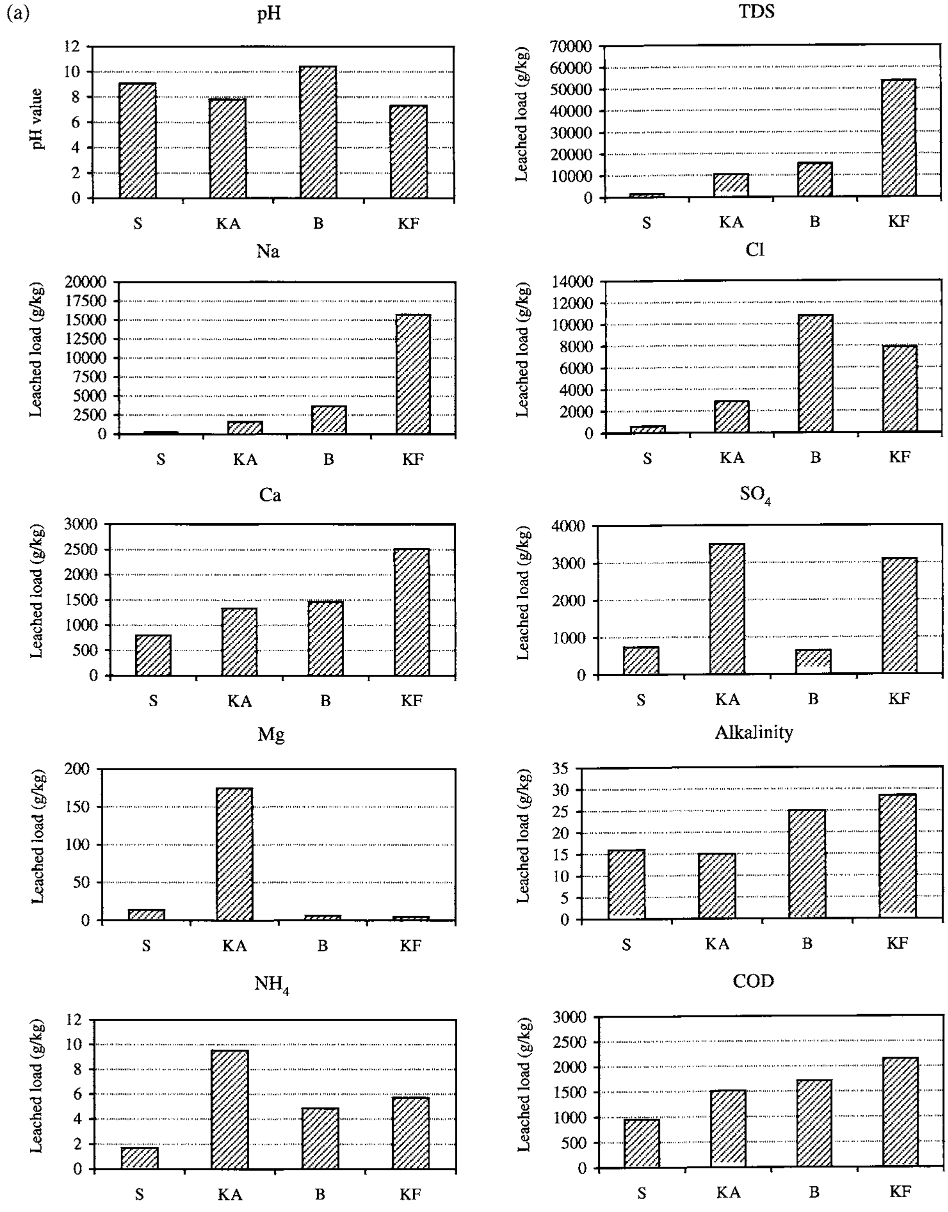

Figure VI.8.3. (a) Contents of leachable macro-constituents in solidified mixtures of pure low alkaline FA with mine water of increasing salinity of Cl–Na type (1:1, wt.). Material: Low alkaline FA from the Rybnik power plant. Mine water of Cl–Na salinity in the TDS range from 2 to 100 g/l from different coal mines (USCB, Poland): Sosnica (S), Knurow-Aniolki (KA), Borynia (B) and Knurow-Foch (KF). TDS values: 2.7 g/l (S); 8.3 g/l (KA); 30.2 g/l (B); 93.7 g/l (KF); (b) Contents of leachable trace elements in solidified mixtures of pure low alkaline FA with mine water of increasing salinity of Cl–Na type (1:1, wt.). Material: Low alkaline FA from the Rybnik power plant. Mine water of Cl–Na salinity in the TDS range from 2 to 100 g/l from different coal mines (USCB, Poland): Sosnica (S), Knurow-Aniolki (KA), Borynia (B) and Knurow-Foch (KF). TDS values: 2.7 g/l (S); 8.3 g/l (KA); 30.2 g/l (B); 93.7 g/l (KF).

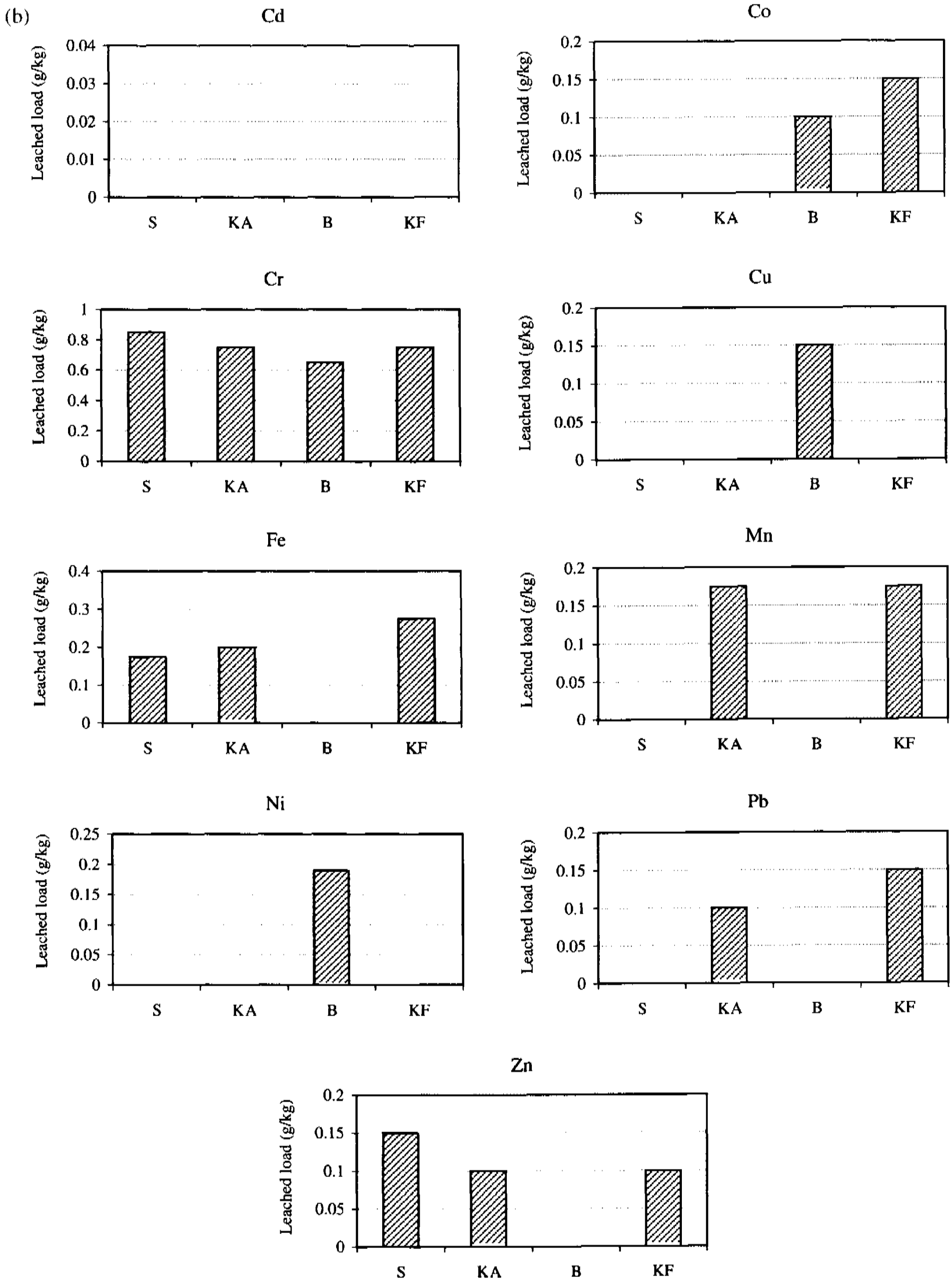

Figure VI.8.3. (Continued).

metal release might occur also in the FA layers underground provided that they are exposed to the vertical percolating of infiltration water directly from the surface or from the recoverable ground water resources. This suggests caution in placing FA mixtures in such infiltration zones if the reliable long-term predictive modeling of pH changes does not exclude the possibility of acidification.

VI.8.4.3. Effects of slurry:pure FA mixture utilization underground on contaminant loads discharged from mines

Instead of mine water for preparation of a transportable FA mixture, non-dewatered slurry from the flotation process in coal preparation plants can be used. The amount of slurry required for assuring the gravitational transportability of mixture is higher than for mine water, i.e. a ratio of slurry:FA of 2:1 by weight. This way of FA mixture preparation gives an opportunity of utilizing slurry underground and substantially reduces costs by resignation from filter press dewatering of slurry and its disposal at the dumping sites.

This method of preparing transportable FA mixtures is less popular than using mine water as it is more problematic and expensive. It needs a more precise electronically operated process of mixture preparation to keep exact parameters (density, flow rate) of mixture and slurry pumps must be used for slurry transport to the installation (Fig. VI.8.4).

The balance of contaminant retention and release using slurry for preparation of FA mixtures, similar to use of mine water, depends on the properties of FA and the liquid phase in the slurry. The leachate quality and load balance for such mixture with use of moderately alkaline and saline slurry and low alkaline FA from the Rybnik power plant were found to improve substantially compared to these in the input slurry due to the reduction of Cl and Na concentrations, TDS and Mg hardness, and low concentrations of trace metals (<MCL) resulting from the slightly or moderately alkaline pH values within their stability field in the solid phase (Twardowska, 1999a). In general, leachate quality from these mixtures was similar to those from adequate systems with mine water. Significant reduction of COD and a high increase of nitrogen compounds, mainly ammonia in leachate was specific for these systems, and usually did not occur in output from mine water:FA mixtures. Because of high input water retention in the mixture (from 57 to >70%), almost all the released loads of macro-constituent and trace metal loads in leachate were substantially lower than those in the input solution. Nevertheless, due to a moderate salinity of slurry water, the total load balance of contaminants was less favorable than for mixtures with brine mine water, as the highest load reduction occurred when waters of high salinity at low mine water:FA ratio were used.

Here, another system of acidic slurry (pH 3.78) from the Jastrzebie mine in a mixture at a ratio 0.7:0.3 with low-alkalinity FA has been analyzed with regard to environmental impact (Table VI.8.5). In this system, FA showed very good buffering properties, transforming pH of an output leachate into slightly alkaline one that remained as such after sequential extraction in triplicate of the solidified mixture. Similar to the alkaline system, reduction of Cl, Na, K and TDS concentrations in leachate compared to the input solution occurred. The differences in alteration of leachate characteristics compared to the alkaline slurry consisted in an increase of Mg-hardness and alkalinity, at practically stable SO_4 content in output. The adverse alteration comprises almost 10-fold increase of COD.

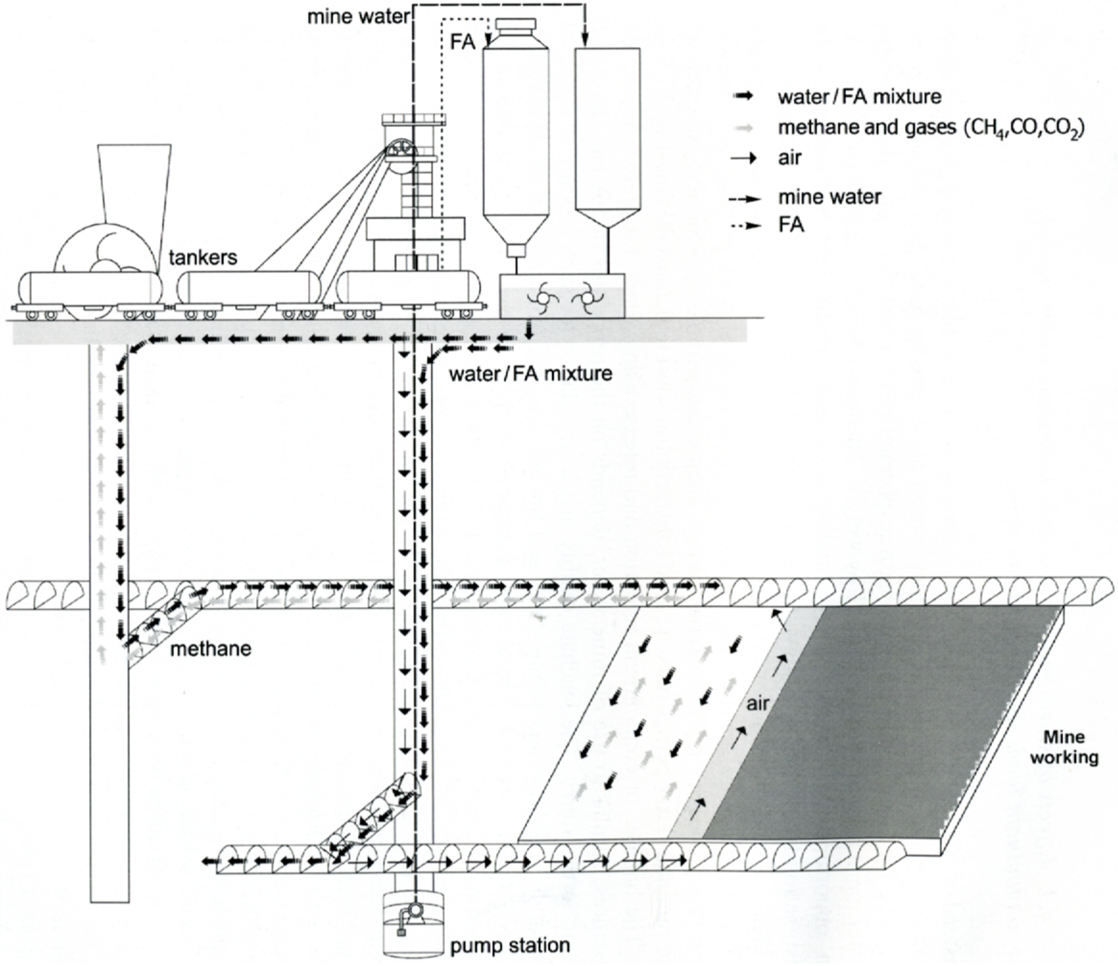

Figure VI.8.4. Scheme of installation for flotation slurry:FA mixture preparation to be utilized in deep mines (after UTEX Ltd., Poland).

Table VI.8.5. Concentrations and load balance of dissolved constituents in the input slurry water and output leachate from acidic flotation slurry:low alkaline FA mixture 2:1 wt., and contents of leachable constituents in solidified material. Pure low-alkaline FA from the Rybnik power plant.

Parameters, constituents	Slurry water – Jastrzebie mine		Leachate from slurry – fly ash mixture 2:1		Leached (+) or bound (−) loads	Solidified mixture – leachable load
	Input, 0.756 m^3/t		Output, 0.211 m^3/t (28%)			
	C_{in}, mg/l	L_{in}, g/t	C_{out}, mg/l	L_{out}, g/t	$\Delta L = L_{in} - L_{out}$, g/t	$\sum L_{1-3}$, g/t
µS/cm	10,500	–	10,000	–	–	–
pH	**3.78**	–	**7.84**	–	–	7.92–8.20
Alkalinity, meq/l	0.00	0.00	2.80	0.472	0.472	17.0
Acidity, meq/l	**7.70**	**6.05**	**0.00**	**0.00**	**− 6.05**	0.00
Hardness, meq/l	43.05	33.90	60.49	10.20	**− 23.702**	134.31
Hardness $CaCO_3$	2154	1696	3027	510	**− 1186**	6722
Hardness Ca	42.15	33.19	48.77	8.22	**− 24.97**	125.35
Hardness Mg	0.90	0.71	11.72	1.976	1.268	8.96
Macro-constituents						
Ca	844.88	665.36	977.54	164.8	−500.51	2512.2
Mg	11.0	8.663	142.5	**24.03**	15.367	109.0
Na	**1955.4**	**1539.9**	**1509.9**	**254.6**	**− 1285.2**	862.6
K	**82.96**	**65.33**	**39.87**	**6.386**	**− 58.608**	132.5
NH_4^+-N	10.32	8.127	14.65	2.47	**− 5.656**	8.57
NO_3^--N	**0.685**	**0.539**	**0.125**	**0.021**	**− 0.518**	0.105
Cl^-	**3922**	**3088.6**	**3498**	**589.88**	**− 2498.8**	2821.0
SO_4^{2-}	**1888.7**	**1487.4**	**1877.6**	**316.6**	**− 1170.76**	4360.8
HCO_3^-	–	–	170.85	28.80	28.81	1037.3
CO_3^{2-}	–	–	0.0	0.0	0.0	0.0
OH^-	–	–	0.0	0.0	0.0	0.0
PO_4^{3-}	0.026	0.0048	0.029	0.0049	−0.0155	0.76

(continued)

Table VI.8.5. (Continued)

Parameters, constituents	Slurry water – Jastrzebie mine		Leachate from slurry – fly ash mixture 2:1		Leached (+) or bound (−) loads	Solidified mixture – leachable load
	Input, 0.756 m^3/t		Output, 0.211 m^3/t (28%)			
	C_{in}, mg/l	L_{in}, g/t	C_{out}, mg/l	L_{out}, g/t	$\Delta L = L_{in} - L_{out}$, g/t	$\sum L_{1-3}$, g/t
TDS	**9242**	**7278.3**	**8354**	**1408.8**	**− 5869.53**	12,005
COD	166.4	130.96	1203.6	1373.2	71.92	11,718
Trace elements						
Al.	<0.060	0.047	0.643	0.108	0.0612	ND
Ba	0.238	0.187	0.312	0.053	**−0.135**	ND
Cd	**0.14**	**0.109**	**0.01**	**0.002**	**− 0.109**	0.10
Co	**0.16**	**0.125**	**0.06**	**0.010**	**− 0.1158**	0.175
Cr_t	0.02	0.015	0.04	0.007	**− 0.0089**	0.35
Cr(VI)	0.008	0.006	0.013	0.002	**− 0.0041**	0.145
Cu	**1.22**	**0.960**	**0.37**	**0.062**	**− 0.898**	0.10
Fe	**70.1**	**55.17**	**0.03**	**0.005**	**− 55.20**	0.01
Mn	**11.45**	**9.01**	**2.86**	**0.482**	**− 8.535**	<0.075
Ni	**0.29**	**0.227**	**0.12**	**0.020**	**−0.208**	0.30
Pb	**0.09**	**0.071**	**0.04**	**0.007**	**− 0.0641**	<0.075
V	<0.01	0.008	0.016	0.003	−0.0052	ND
Zn	**1.80**	**1.417**	**0.49**	**0.08**	**− 1.335**	0.125

ND – not determined; Constituents showing the reduction of concentrations and/or loads in leachate compared to the input slurry water are bold.

The favorable effect on leachate compared to the input solution was a dramatic reduction of high metal concentrations due to shifting pH values into their stability field, in particular Fe, Mn, Zn, Cu, Cd, Ni, Pb, and Co. Slight increase of amphoteric and oxyanionic metal concentrations, like Al, Cr, Cr(VI), Mo, V, all within MCL for drinking water, does not create any problems, as the output loads of these metals showed significant reduction. This example shows a particular beneficial effect of FA application in mines having problems with high-metal acidic waters, which is equally frequent in coalfields and metal ore mines in the world (e.g. in the USA, the UK, Australia, South Africa). In this most prospective field of FA application, the neutralizing and metal-reducing effect is due to the direct neutralization, but the most long-term effect consists in prevention and termination of acidity generation from the sulfite oxidation resulting from perfect sealing of a mined out or abandoned workings against air penetration.

VI.8.5. Environmental effects of mine water:fly ash mixture use in wet mine workings

In the case of application FA in the form of dense low-ratio mine water:FA mixture in dry mine workings insulated either from the infiltration zone of the recoverable ground water resources or from the inflow of saline waters from the upper seams, the leachate is limited entirely to the outflow of the excess water from the deposited mixture. Under the complicated hydrogeological conditions of mines, further leaching of FA mixtures by infiltration water either from the surface or from the upper seams may occur in wet seams and in the post-closure period due to water logging of dry seams.

The simulation of leaching behavior of high-alkaline FA:mine water mixture comprised the actual and potential cases of mine operating: (A) low-TDS mine water:FA mixture deposited in the infiltration area of recoverable ground water resources; (B) saline mine water:FA mixture deposited in the infiltration area of recoverable ground water resources; (C) saline mine water:FA mixture deposited in the area of roof inflow from static resources of saline mine water (Twardowska, 1999a). Flow-through leaching cycle comprised two phases (0 – dewatering and 1 – vertical in filtration under the vadose zone conditions, up to 2.5-fold cumulative pore water exchange rate). The phase I covered wash-out (I) and dissolution (II) stages. Both the results of simulation (Table VI.8.6) and the long-term practice of FA utilization in deep mines shows, that the most environmentally beneficial and safe option is utilization of FA mixtures with saline mine water in dry mine workings insulated from the recoverable ground water resources. Use of saline waters intensifies and accelerates solidification of FA layer, which is an additional advantage. Vertical infiltration of water through freshly deposited high-alkaline FA appeared to strongly enhance contaminant loads release from the mixture, roughly at an order of magnitude compared to the dewatering phase (0) and in concentrations exceeding MCL either in the both stages (e.g. for the case (A): pH, K, NH_4-N, COD, Cr(VI) and Mo) or in the wash-out (I) stage (for the case (A): Na, NO_2-N, SO_4, Cr_t). In the case (A) the released load origins from the FA matrix.

Utilization of FA mixtures with saline mine water in the feeding zone of recoverable ground water resources (case B) caused release in the infiltration phase of almost the total load of soluble constituents introduced into the mixture with saline water (Cl and Na),

Table VI.8.6. Concentration range of selected constituents in leachate and loads leached from the 2 m thick layers of water:FA mixture 1:2 wt. in simulated conditions of a vertical rain- or mine water infiltration in wet mine workings.

Parameters, constituents	(A)		(B)		(C)		MCL[a], mg/l	(A)		(B)		(C)	
	Concentrations							Loads					
Parameters	0	I	0	I	0	I[b]		0	I	0	1	0	I[b]
Water exchange rate	0.189	2.516	0.170	2.324	0.152	0.524		0.189	2.516	0.170	2.324	0.152	0.524
pH	7.62	8.25–**11.46**	**10.78**	**7.86–11.16**	7.66	7.90–8.16	6.5–8.5						
Alkalinity, meq/l	1.0	0.45–6.30	2.20	1.8–4.65	1.5	1.8–3.05		79.55	3608	160.00	2973	98.86	463,864
Hardness, meq/l	2.21	0.31–2.55	79.11	1.4–15.32	97.9	14.12–23.58		175.80	843.26	5753.4	11,169	6452	9336
Hardness $CaCO_3$	110.59	15.51–127.61	3959	70.06–766.68	4899	706.6–1180							
Macro-constituents, mg/l													
Na	362.35	313.8–15.3	**33,031**	**16,701–3615.4**	**32,021**	**29,403–33,177**	800	28,823	183,547	2,402,254	11,528,140	2,110,476	7,028,259
K	**167.65**	**199.2**–20.6	**542.03**	**653.8–104.5**	**532.59**	**403.6–456.4**	80	13,336	126,691	39,420	317,699	35,103	101,429
NH_4^+-N	**12.09**	**20.16**–1.01	**15.82**	**18.2**–1.08	**38.22**	**12.6–41.75**	10	961.71	6986	1150	5318	2519	ND
Cl^-	127.2	254.4–31.8	**35,340**	33,880–5745	**53,480**	**50,200–53,600**	1000	10,118	129,393	2,570,182	19,018,125	3,524,818	11,730,545
SO_4^{2-}	**864.5**	384.2–9.61	**864.54**	144.09–47.11	**1022**	**911.8**–125.11	500	68,767	220,096	62,876	145,962	67,345	174,268
TDS	1761	1508–288	90,133	52,756–9640	89,628	80,523–87,760		140,080	919,917	6,555,127	33,226,782	5,907,300	19,341,570
COD	128.2	**141.02**–76.92	**13,230**	**4615–1128**	**10,049**	**10,801–13,524**	125	10,198	138,409	962,199	3,672,283	662,349	2,524,420
Trace elements, mg/l													
Al	0.519	1.287–0.82	<0.06	0.204–1.073	<0.06	1.528–0.528	3	41.28	ND	<4.36	ND	<3.95	ND
Cd	<0.001	0.1–0.3	**0.45**	0.12–0.01	**0.44**	0.14–0.13	0.4	<0.08	4.19	6.54	52.23	10.54	33.02
CrVI	**0.436**	**0.492–0.15**	**0.401**	**0.283–0.149**	**0.194**	**0.193–0.309**	0.1	34.68	279.08	29.16	216.55	12.79	48.98
Cu	0.05	0.02–<0.001	0.11	0.08–0.01	0.11	0.14–0.10	0.5	3.98	9.75	8.00	42.25	7.25	25.93
Mo	**2.699**	**2.985–2.334**	**2.37**	**3.509–2.307**	**2.488**	**1.312**–0.122	1	214.69	ND	172.36	ND	163.98	ND
Ni	0.03	<0.001–0.01	**0.93**	**0.63**–0.04	**0.82**	**0.77–0.68**	0.5	2.39	4.71	67.64	263.73	54.05	172.27
Pb	0.04	0.23–<0.001	0.28	0.42–0.05	0.47	**0.66–0.60**	0.5	<0.79	38.83	20.36	174.93	30.98	122.11
Zn	<0.001	0.21–<0.001	<0.001	0.37–<0.001	<0.001	0.64–0.12		<0.08	47.46	<0.073	75.02	<0.066	52.68

FA – high alkaline FA from Laziska power plant. (A) Low TDS water:FA mixture, simulated rain water infiltration, flow rate 4.74 mm/d; (B) 50 g Cl/L-Na brine:FA mixture, simulated rain water infiltration, flow rate 4.74 mm/d; (C) 50 g Cl/L-Na brine:FA mixture, simulated brine roof inflow, flow rate 20 mm/d. Phase 0 – dewatering; Phase I – vertical infiltration under the vadose zone conditions; ND – not determined.

[a] Polish regulations for liquid waste discharged to waters and soils (Directive of the Minister of Environment, 2002).

[b] Solidification.

along with the loads of the macro-constituents and trace elements leached from the FA matrix in several times higher concentrations and amounts than in the case (A): Ca-hardness, COD, K, trace metals: Ni, Pb, Zn, Cd, Co, Cu, Mo, Mn, Fe. Despite a gradual release of these loads, the leachate displayed long-term deterioration. The positive effect of contaminant retention in the dewatering phase in both cases (A and B) was thus strongly reduced or annihilated in the infiltration phase. Therefore, due to adverse impact of soluble constituents release from the FA matrix on the infiltration water quality, any direct contact of FA mixtures with the feeding zone of recoverable ground water resources should be avoided. In particular, application there of FA mixtures prepared with use of saline mine water should be considered intolerable.

Utilization of FA mixtures in the zone of infiltration of saline waters from the static resources causes temporary increase of leached loads of contaminants prior to the cementation of the FA layer. If the released loads play a negligible role in the total soluble constituents' balance discharged to the receiving waters with the mine drainage, this temporary situation may be accepted as a low-impact one.

The presented results show a general adverse effect of mine water:FA exposure to vertical infiltration of water due to the contact with the recoverable ground water resources or with their feeding zone. Our long-term practice of FA utilization in underground mine workings shows that the most environmentally beneficial and safe option is utilization of FA mixtures with saline mine water in dry mine workings insulated from the recoverable ground water resources. In the light of our vast experience, the reports on the beneficial effect of FA on the ground water under the conditions of a permanent direct contact (Paul and Singh, 1995) should be treated as a particular case and cannot be generalized. Also other authors, in view of evidence of exhaustion of FA/coal ash alkalinity over extended time periods, point out the need of predicting the overall leaching behavior of CCW, in particular placed in environments where acid mine waters occur. For this purpose, the mine water leaching procedure (MWLP) was developed to sequentially leach particular CCW with the target mine's groundwater to evaluate leaching behavior of trace elements as alkalinity is exhausted (Ziemkiewicz et al., 2003a,b). Thus, in every case of the planned use of FA in mine workings, the long-term prognosis of the environmental effect of FA utilization in the actual hydrogeological conditions should be carried out to avoid unnecessary risk.

VI.8.6. Effect of FGD solids on the environmental behavior of dense mine water:FA + DGDS mixtures utilized underground

VI.8.6.1. General trends

The trends reflecting the environmental behavior of FA mixtures containing FGD solids from dry and semi-dry processes are similar to those for pure FA and displayed a generally positive environmental effect, predominantly due to retention of water in the mixture, and partly due to equilibria limitations, which cause permanent binding of a substantial part of the contaminant loads in the mixture. The resultant effect can be summarized as follows: the output concentrations of the majority of contaminants are higher in leachate than in the input mine water as a result of the release from FA + FGDS, while the output loads are considerably lower due to high retention capacity of the material. The leachate composition and the contaminant balance for FA + FGDS deposition underground may vary considerably according to mine water and FA composition, to the great extent determined by the composition and content of FGDS. The characteristics of FGDS and FA + FGDS mixtures from dry and semi-dry processes are presented in Chapter III.7, while the effect on the aquatic environment of the use of FA containing FGD solids has been discussed in detail elsewhere (Twardowska, 1999b). Here, it will be summarized in brief.

VI.8.6.2. Effect of using FA + D-FGDS mixtures with mine water on the contaminant balance

The environmental behavior of low-ratio mine water mixtures with FA containing products of the dry desulfurization process (FA + D-FGDS) is highly determined by the content of unreacted CaO in these products, which assures the best hydrogeological and hydrogeochemical parameters: the lowest hydraulic conductivity, up to impermeability to the horizontal flow ($k = 10^{-8}-10^{-9}$ m/s), the best sealing properties against air penetration (penetration resistance $R = 13,000-19,000$ kPa, which is an order of magnitude higher than that of pure FA mixtures and 2 orders of magnitude higher than that of natural cohesive soils such as boulder clay $R = 190$ kPa), the shortest solidification time (mean 17 days), the highest water retention capacity (60–75%), lack of tendency to acidification and hence of the massive trace elements release in the delayed release (III) stage. The excess of CaO results in high pH and alkalinity of the leachate and thus is similar to the leachate composition and the load balance for the pure high-alkaline pH, in particular in the mixture-dewatering phase 0. Similar systematic behavior of high-alkaline material from the different power plants and processes dictated by pH values is illustrated in Figure VI.8.5 a,b.

The release of macro-constituents for this system is determined by carbonate equilibrium constraints. The general pattern of contaminant release displays low leachability of sulfates from FA and high Ca-carbonate hardness of leachate, lack of chloride complexation and frequent decrease of N compounds. The highest leachability of trace elements show Cr_t, mainly in the Cr(VI) form, and Mo. Most of the other trace elements occur in the leachate in elevated concentrations compared to the input mine water, though the load balance for both macro- and trace constituents shows high retention capacity of the mixture with high TDS water in the dewatering phase 0 (Figures VI.8.5 a,b, and V.8.6a,b – case B). The load balance of low-TDS water for almost all leached constituents including trace elements exhibits predominance of release over binding in the dewatering phase (Twardowska, 1999b). Leachability of macro-constituents and trace elements from ground solidified mixtures of FA + D-FGDS was found to be generally lower than that of pure high-alkaline FA (Fig. VI.8.5 a,b) and higher than from pure low-alkaline FA mixtures with mine water of moderate and high TDS. The binding of macro- and trace constituents in FA + D-FGDS mixtures with high-TDS mine waters in solidified mixture (1) appeared to be considerably higher than in the adequate mixture with low-alkaline pure FA (Fig. VI.8.6a,b – cases A and B). In actual conditions, due to significantly lower hydraulic conductivity and high cementation properties, much lower dynamics of constituents leaching from the solidified mixture is anticipated.

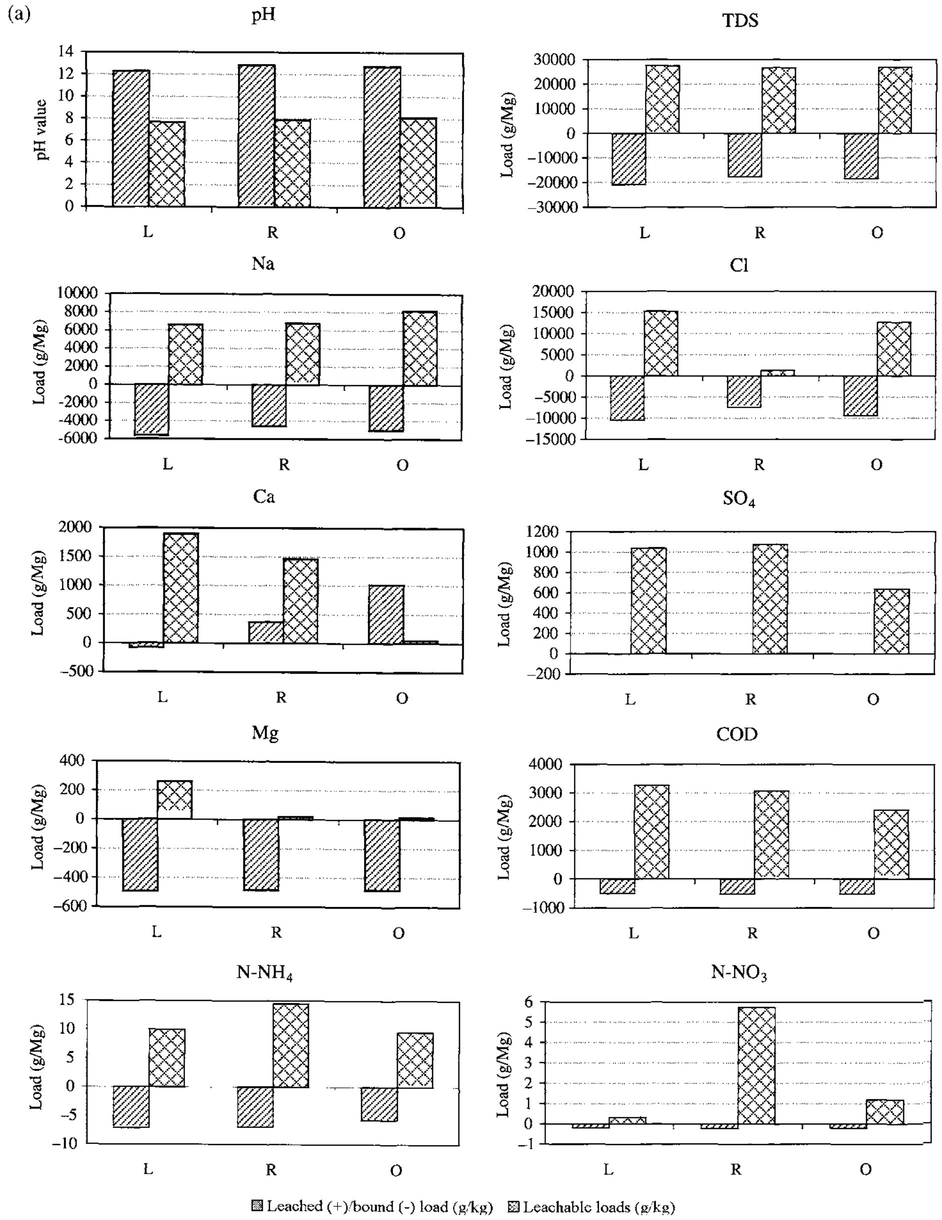

Figure VI.8.5. (a) Binding (−) and release (+) of macro-constituents from mine water mixtures with high alkaline pure FA or FA + D-FGDS (1:1 wt.) in the dewatering stage, and contents of leachable constituents in the solidified mixtures. Dense mixture components: Mine water from the Moszczenica mine of Cl–Na type, TDS 37.5 g/l; L – pure high alkaline FA from the Laziska power plant; R – FA + D-FGDS from the Rybnik power plant; O – FA + D-FGDS from the Opole power plant. (b) Binding (−) and release (+) of trace elements from mine water mixtures with high alkaline pure FA or FA + D-FGDS (1:1 wt.) in the dewatering stage, and contents of leachable trace elements in the solidified mixture. Dense mixture components: Mine water from the Moszczenica mine of Cl–Na type, TDS 37.5 g/l; L – pure HA-FA from the Laziska power plant; R – FA + D-FGDS from the Rybnik power plant; O – FA + D-FGDS from the Opole power plant.

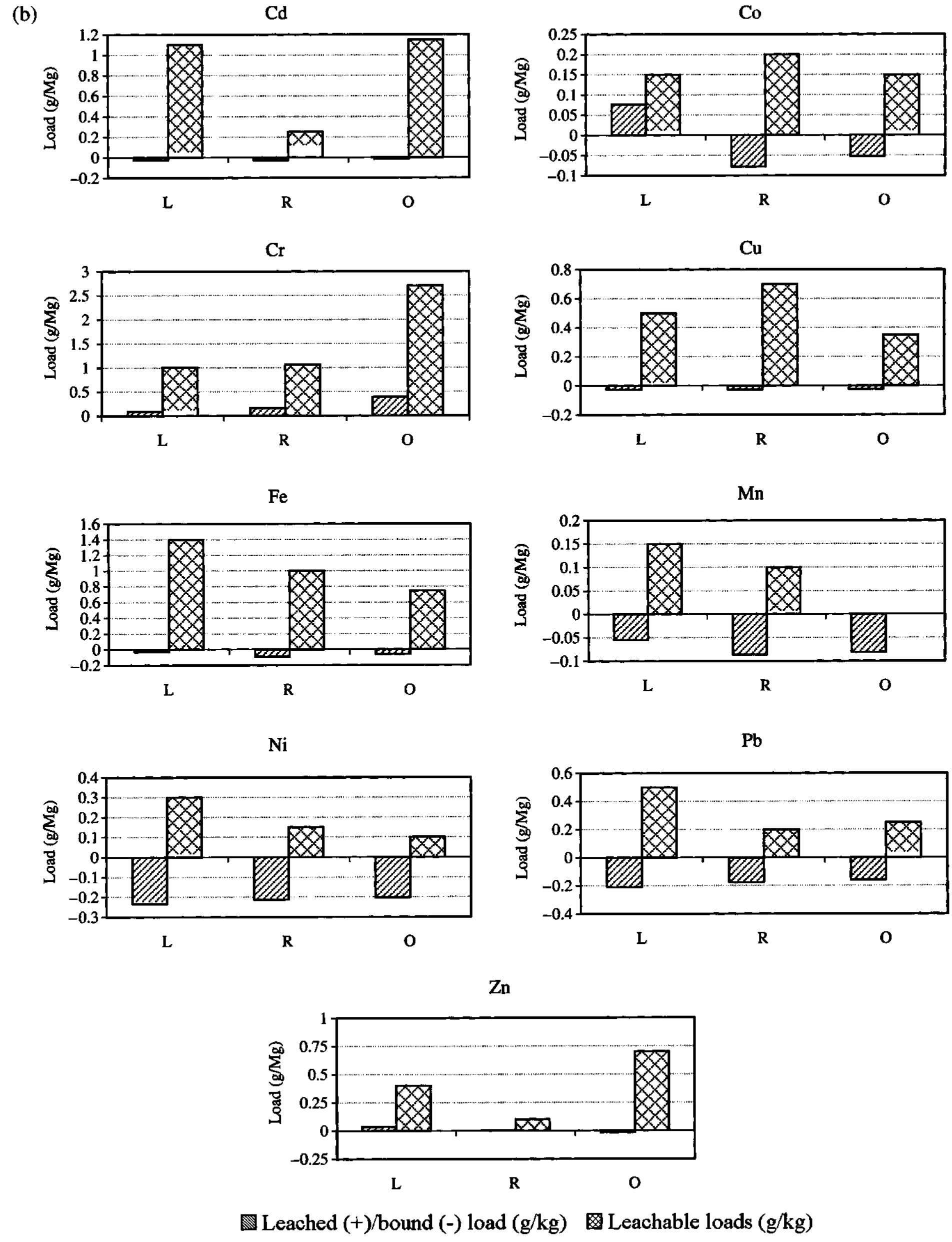

Figure VI.8.5. (Continued).

From the general pattern of constituent binding and release can be concluded that the most favorable load balance are mixtures of FA + D-FGDS with high-TDS mine water. Hence, to utilize thoroughly the binding capacity of FA + D-FGDS for reduction of contaminant loads discharged from mine drainage, mine waters of a high sulfate or

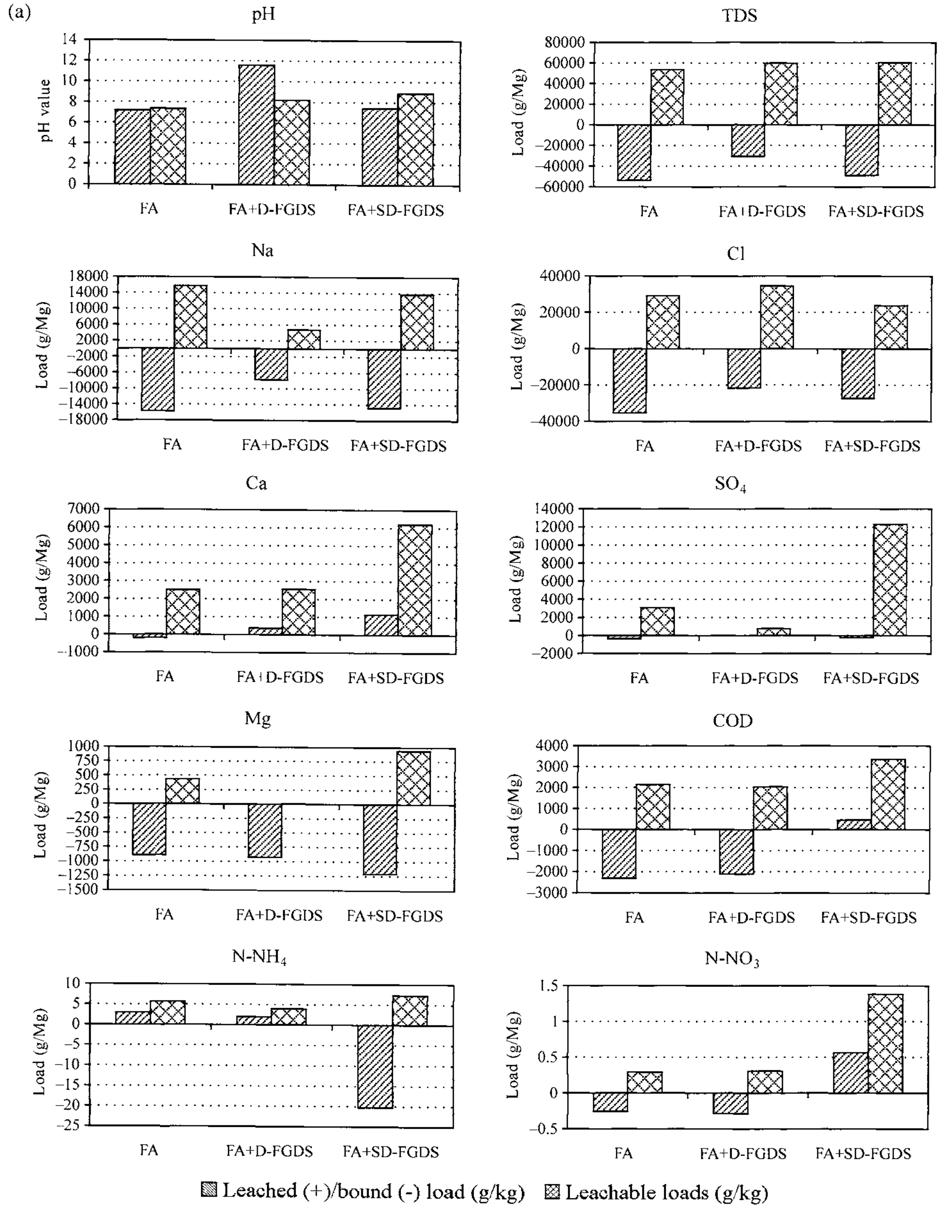

Figure VI.8.6. (a) Effect of content and kind of FGD solids from dry (D) and semi-dry (SD) process on binding (−) and release (+) of macro-constituents in the dewatering stage and contents of leachable constituents in solidified mixtures of FA + FGDS with mine water (1:1 wt.) utilized underground. Dense mixture 1:1 wt. components: Mine water from the Knurow mine of Cl–Na type, TDS ~ 100 g/l (94–96 g/l), pH 7.89–7.33; A – pure low alkaline FA from the Rybnik power plant; B – FA + D-FGDS from the Rybnik power plant; C – FA + SD-FGDS from the Laziska power plant, ABB-NID process. (b) Effect of content and kind of FGD solids from dry (D) and semi-dry (SD) process on binding (−) and release (+) of trace elements in the dewatering stage and contents of leachable trace elements in solidified mixtures of FA + FGDS with mine water (1:1 wt.) utilized underground. Dense mixture 1:1 wt. components: Mine water from the Knurow mine of Cl–Na type, TDS ~ 100 g/l (94–96 g/l), pH 7.89–7.33; A – pure low alkaline FA from the Rybnik power plant; B – FA + D-FGDS from the Rybnik power plant; C – FA + SD-FGDS from the Laziska power plant, ABB-NID process.

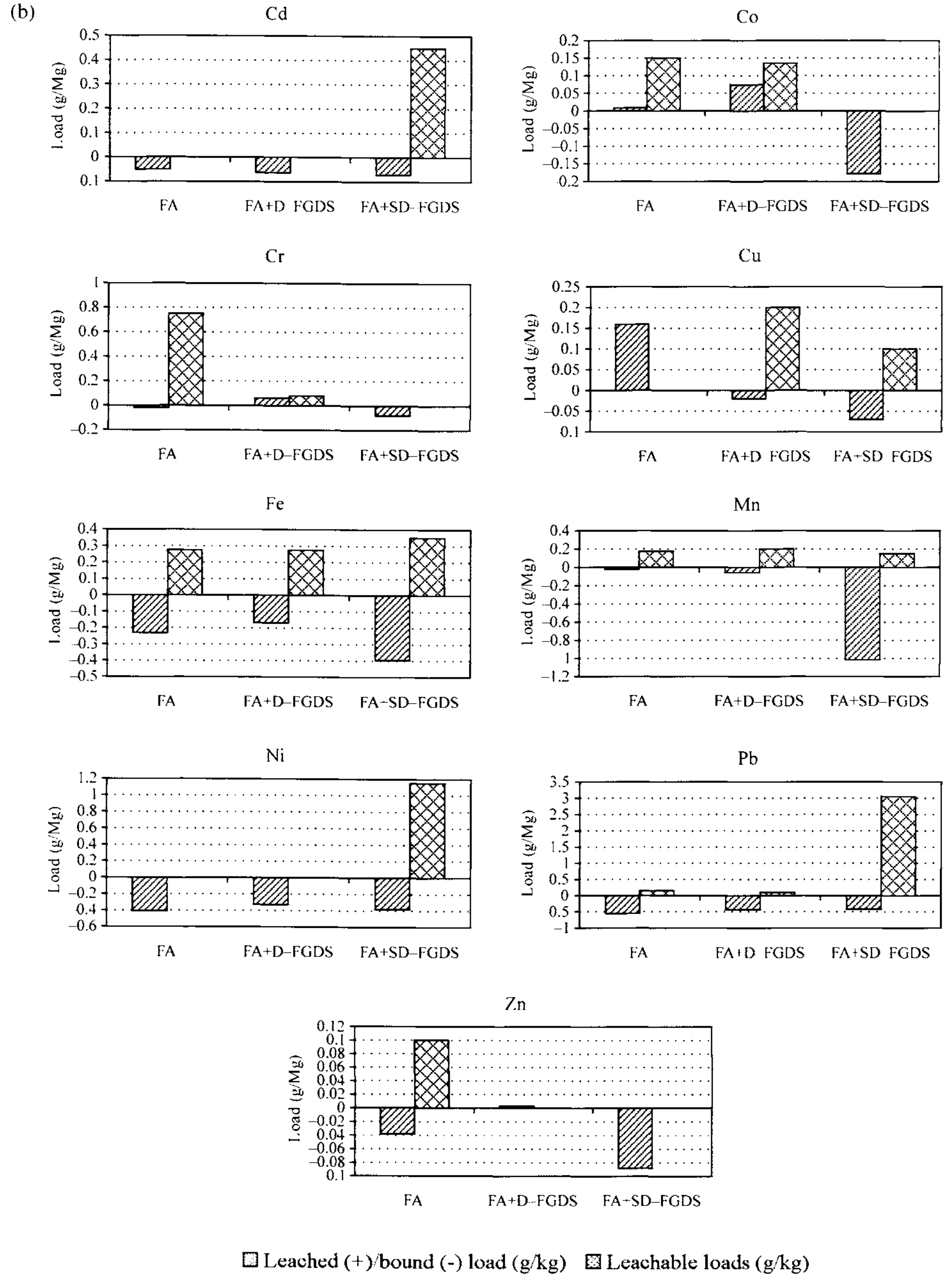

Figure VI.8.6. (Continued).

chloride salinity (TDS) should be used. In case of the deficiency of high-TDS waters, a closed circuit of mine water would be an optimum solution, provided it is technically sound and cost-effective. The leachability of dissolved solids, in particular sulfates, from the dewatered and solidified mixture despite the higher content in the matrix was similar to or lower than leachability from the high-alkalinity pure FA. In the potential conditions of post-closure flooding the mine, the constituent release is anticipated to be low due to the cementation and lower hydraulic conductivity of the solidified mixture. In general, due to the leaching behavior and cementitious properties, the mine-water–FA + D-FGDS mixtures appear to be the most advantageous CCW product with respect to the long-term effect on the aquatic environment.

Because of the low-efficiency of the D-FGD processes, its use is limited to the treatment of low-sulfur flue gas emission or to the first stage of SO_2 reduction and it is being gradually replaced by less cost-effective and simple, but more efficient semi-dry and/or wet processes. Nevertheless, this method will be probably still applied in many countries as a transitional process that gives an opportunity of utilize excellent properties of FA with the products of dry FGD process as a sealing material in the most environmentally beneficial way.

VI.8.6.3. Effect on the contaminant balance of using FA + SD-FGDS mixtures with mine water

Lower retention capacity and high leachability of sulfates, formed by the oxidation of sulfides, resulted in a lower efficiency of the permanent binding of soluble constituents in the mixture of high FA + SD-FGDS solids compared to pure high alkaline FA, while the binding capacity of this material generally appeared to be similar to that of low alkaline pure FA (Fig. VI.8.6 – A, C). The semi-dry desulfurization process results in the neutralization of the end product, hence the pH value of the outflow from the FA + SD-FGDS mixture remains close to neutral in all phases of leaching. The systematic leaching behavior of this material is similar to that of low-alkalinity pure FA and is controlled by equilibrium with gypsum following the typical major transformations of the input water, i.e. decrease of alkalinity in parallel with increase of sulfate and hardness, which is transformed from the Ca–Mg-type into the Ca-type. The major specific property of this system was invariably low alkalinity, either in the stage of the dewatering, or after solidifying. The adverse transformations specific for this material containing unstable sulfides as FGD reaction products, is high leachability of sulfates and Ca from the solidified phase, along with a high COD due to sulfide oxidation. Nitrogen compounds do not show systematic behavior, with a generally prevailing trend to reduction in the output. Permanently neutral pH values lead to a stability in the matrix of the majority of trace elements, among them amphoteric metals like Cr. Increase in the output showed oxyanions Mo and V in conformity with the general pattern of leaching behavior, with maximum in pH range close to neutral (Figure VI.8.6a,b – case C) (Brookins, 1987; de Groot et al., 1989).

The general trend of transformation of chemical composition of mine water used for mixture preparation with FA + SD-FGDS consisted in increasing concentrations of all the macro constituents except Mg and carbonates. These constituents comprised both major (Cl, SO_4, Na, Ca) and minor ones (K). Nevertheless, the load balance displayed the reduction of loads of practically all macro- and trace constituents in outflow compared to the input mine water except Ca, COD and Mo. The long time of solidifying and the highest potential leachability of sulfates compared to all analyzed mixtures with FA, both pure and with end products from dry FGD process, is the disadvantage of this material. The leachability of trace metals from the solidified mixtures of FA + SD-FGDS with low- and high-TDS mine water appeared to be similar, and for most of them within the range observed for other mine-water:FA systems. In comparison with these systems, Mo, Ni and generally low mobile Pb showed higher susceptibility to release, while Cr was distinctly less leachable.

In general, this material is applicable for use in dry mine workings. Occurrence of instable sulfides in the FA with a high SD-FGDS content results in the mentioned longer time of solidification and susceptibility to plastifying of solidified material in contact with water. Hence, this material should not be used in the wet mine workings.

VI.8.7. Dense mine water:FA mixtures as a sink of radioactivity in mine waters

As was shown in Chapter III.7, concentrations of radionuclides in CCW are distinctly elevated compared to the lithosphere and coal, from several times (^{40}K, ^{228}Ra), up to an order of magnitude (^{226}Ra). Nevertheless, this waste fulfills the criteria of unrestricted permit for their use in mine workings (total concentration of radionuclides < 10 kBq/kg) (PN-93/G-11010) as well as for the disposal at the surface and use for civil engineering works (^{226}Ra < 350 Bq/kg, and ^{228}Ra < 230 Bq/kg) (GIG, 1994) and is not classified as a radioactive waste. At the same time, some saline waters occurring in different Carboniferous seams of the USCB display high level of radioactivity, up to 390 kBq/m^3. The annual radium load discharged with mine waters to the surface recipients is estimated to be about 150 GBq (Lebecka and Tomza, 1989).

According to the Polish Standards PN-88/Z-70071 (1988), waters with Ra concentrations over 0.7 kBq/m^3 are considered liquid radioactive waste. Mine water is considered radioactive if the Ra concentration exceeds 1 kBq/m^3. According to the Directive No 23/70 of the Government Attorney regarding Use of Nuclear Energy (1970), the discharge of radioactive waters to the open surface reservoirs is permitted provided that Ra concentration does not exceed 1.1 kBq/m^3, i.e. 10-fold MCL for drinking water, which accounts for ^{226}Ra $= 0.11$ kBq/m^3. Such waters can be discharged to closed collecting sewers if the Ra concentration does not exceed MCL for drinking water by more than 100-fold, i.e. 11.1 kBq/m^3.

A considerable part of radioactive mine waters in the area of a positive radio-hydrogeological anomaly belongs to the Ra–Ba, low-sulfate type A. The rationale of the concept of using FA as a sink of radioactivity loads from high radioactive mine waters has been based on two major assumptions:

- FA, in particular with FGD solids, contain high concentrations of sulfate, hence have potentially high binding capacity for radium through co-precipitation with $BaSO_4$.
- FA has high water retention capacity (50–70%), hence may bind physically adequate radium loads along with high-radioactive waters also of a B type (low Ba, high-sulfate).

Practically, the radioactivity loads can be adequately reduced by use of high-radioactive waters for preparation of dense mine water:FA mixtures to be used routinely in mine workings for different purposes. From Ra–Ba waters radioactivity can be removed in parallel, both by chemical and physical binding. For Ra removal from Ra-waters of B type only physical binding can be applied.

The efficiency of Ra removal from mine water originating from three coal mines of the USCB, Poland, of radioactivity range $^{226}Ra = 2.171-103.208\ kBq/m^3$ and $^{228}Ra = 1.48-67.76\ kBq/m^3$ is exemplified in Table VI.8.7. For mine water:FA mixture preparation, pure FA from the Laziska power plant, and FA + D-FGDS from the Rybnik and Opole power plants were used, with sulfate content 0.74, 2.65 and 2.78% SO_4 wt., respectively. The results confirm excellent binding properties of FA for radionuclides, removed both chemically (co-precipitation with $BaSO_4$) and physically (water retention at the level from 60.0 to 85.75% wt. for water:FA ratio 1:1). In general, radioisotope residuum in outflow was similar, and independent from the input concentration. For FA + D-FGDS it was below MCL = $0.11\ kBq/m^3$ for drinking water, while in outflow from pure FA mixture the residual radioisotope concentration was somewhat higher, up to 2.5-fold MCL for ^{226}Ra. This reflects a little lower, but still very high binding capacity of pure FA for radioisotopes in high radioactive mine waters.

VI.8.8. Use of FA at the surface as a sealing agent

VI.8.8.1. Use of FA for preventive sealing of mining waste dumps

Besides an unquestionable environmentally beneficial use of FA underground, though not without certain limitations dictated by the hydrogeological conditions, there are other prospective fields of application of this material at the surface, aimed to use its sealing properties against air penetration, which are from 1 to 2 orders of magnitude higher than in natural cohesive soils. In this respect, FA has no competitors and thus should be strongly considered for the control of oxidation in the reactive material in order either to prevent, or to remediate the generation of pollutants or combustion processes. This area of application, though, creates serious side problems that result from the environmentally adverse properties of FA, in particular its fairly high permeability to vertical infiltration, high concentrations and leachability of contaminants, and possibility of their delayed release due to long-term transformations (see Chapter III.7). This sets the complicated task of optimization of FA use in a way that would permit to utilize in full its sealing properties and attenuate adverse impact, to achieve the most positive resultant effect.

One of these areas is use of FA for sealing mining waste dumps, e.g. coal mining waste that is the biggest amount of waste in Poland and creates environmental problems in coalfields worldwide due to susceptibility to self-ignition and long-term adverse environmental impact caused by sulfide oxidation and acidification of low-buffered waste with subsequent release of trace constituents from the material and the bedrock of the vadose zone lasting for decades. Due to the low consolidation properties of the considerable amount of Carboniferous rocks, self-ignition prevention requires application of expensive heavy compaction by vibratory rollers in thin layers. There is always a possible formation of local self-ignition centers at compaction failure or in older less heavily compacted dumps (see Chapter III.7). This has directed attention to seeking additional effective sealing means, of which FA was found the most promising. The development of methods of FA use as a sealing material was induced by a lack of self-ignition cases at the Przezchlebie coal mining waste dump where since 1969 coal mining waste from three coal mines with a minor amount of waste from six other mines together

Table VI.8.7. Reduction of the natural radioactivity of type A in mine waters with use of pure FA from the Laziska power plant and FA + D-FGDS (FA with products of desulfurization by dry method) from the Rybnik and Opole power plants.

Sample, treatment	Sampling date	Concentrations (kBq/m^3)		Reduction (%)	
		^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Mine water from the Chwalowice mine cross-cut I E, levels 390 and 550 m	09.1994	103.208 ± 8.26	67.76 ± 13.57		
Mine water as above + pure FA from the Laziska power plant (1:1 wt.)		0.234 ± 0.024	0.23 ± 0.08	99.77	99.66
Mine water as above + FA + D-FGDS from the Rybnik power plant (1:1 wt.)		0.058 ± 0.012	<0.05	99.94	100
Mine water as above + FA + D-FGDS from the Opole power plant (1:1 wt.)		0.087 ± 0.013	0.17 ± 0.07	99.92	99.75
Mine water as above + FA + D-FGDS from the Rybnik power plant (1:1.9 wt.)		0.075 ± 0.013	<0.05	99.93	100
Mine water from the Jankowice mine – shaft VIII, level 565 m	09.1994	80.986 ± 6.48	23.10 ± 4.65		
Mine water as above + pure FA from the Laziska power plant (1:1 wt.)		0.0279 ± 0.027	0.09 ± 0.06	99.65	99.61
Mine water as above + FA + D-FGDS from the Rybnik power plant (1:1 wt.)		0.095 ± 0.014	<0.06	99.88	100
Mine water as above + FA + D-FGDS from the Opole power plant (1:1 wt.)		0.050 ± 0.011	<0.05	99.94	100
Mine water from the Moszczenica mine-cross – cut W, level 406 m	09.1994	2.171 ± 0.175	1.48 ± 0.30		
Mine water as above + pure FA from the Laziska power plant (1:1 wt.)		0.111 ± 0.015	<0.06	94.89	100
Mine water as above + FA + D-FGDS from the Rybnik power plant (1:1 wt.)		0.051 ± 0.011	<0.06	97.65	100
Mine water as above + FA + D-FGDS from the Opole power plant (1:1 wt.)		0.123 ± 0.016	0.17 ± 0.07	94.33	88.51
Mine water as above + FA + D-FGDS from the Opole power plant (1:1.1 wt.)		0.040 ± 0.006	<0.03	98.16	100

with dry FA were disposed. Since 1973, the FA from the Rybnik power plant was disposed at this dump in the increasing amounts, up to its domination with respect to coal mining waste in 1979, when its location at the dump terminated and the separate hydraulic disposal to the FA pond began. During the separate disposal, acidification of coal mining waste started to develop. Due to predominant disposal of coarse run-of-mine waste (70%) and rock properties, coal mining waste material can be classified as practically non-insulating ($k > 1 \times 10^{-1}$ m/d), partially very weakly insulating against vertical infiltration ($k = 1 \times 10^{-1} - 1 \times 10^{-3}$ m/d) and having low barrier properties against air penetration that has caused pyrite oxidation practically throughout the dump volume. Such parameters are typical for a majority of coal mining dumps of the region. The first developed and patented methods consist in the alternate placing of horizontal layers either of the dry FA (slightly wetted to prevent dusting) or dense water:FA mixture with coal mining waste during the dump construction. The FA layer thickness is dependent on the material available, but is generally considerably thinner than coal mining waste for fast solidification (up to 0.5 m), while water:FA ratio should assure the highest density technically possible to achieve at mixture preparation and spreading at the dump at the spot (Fig. VI.8.7) (Twardowska, 1988, 1990). The major idea was to use the buffering capacity of both materials, in particular of FA at the initial stage, and its sealing properties against air penetration in the long-term period to neutralize generated acid loads during the construction of the upper coal mining waste layer and thus to temporarily enhance buffering capacity of the freshly disposed coal mining waste, but primarily to intercept further acid loads generation in the coal mining waste layer underneath. In parallel, the sealing effect of FA cover is used for prevention of self-ignition. The maximum reduction of water used for FA placing was aimed to save the high water retention capacity of FA for eventual retardation of leachate and dissolved contaminants percolation during the construction of the dump section, until the final top of the dump with a sub-surface drainage system on the layer of a well hydraulically insulating material is constructed to attenuate further water infiltration through the dump. This condition is difficult to realize and thus the amount of water used should assure convenient uniform spreading of the FA cover on the top and its fast solidification with the minimum of an outflow, considering its adverse properties and possibility of further contaminant leaching from the lower coal mining waste layer. This method of "blanket"-like horizontal placing of FA mixture assures adequate continuous insulation of sulfide-bearing wastes from air penetration at low costs, and due to separation from insulated wastes, enables future use of insulated waste without unwanted admixture of FA for various applications, e.g. for engineering constructions or residual coal extraction.

Another method (Fig. VI.8.8) (GIG, 1994) consists of placing coal mining waste in layers 3.6–3.7 m thick on the dump slope with a plough dumping conveyor alternately with the dense FA:water mixture delivered by pipe to the slope, to sink in the coal mining waste and to form a cover layer 0.25–0.4 m thick in the half-height of the slope. Along the toe of the dump a bank ~ 1 m high is to be formed to fill the space between the dump toe and the bank with a FA:water mixture to get the FA layer 0.5 m thick, where coal mining waste is to be disposed to allow the FA to thoroughly mix with coal mining waste. After completion of this layer, a new bank is to be constructed and the procedure repeated. The leachate is to be collected for reuse in the circuit for FA mixture preparation. The major aim of the method is protection of the waste dump against self-ignition.

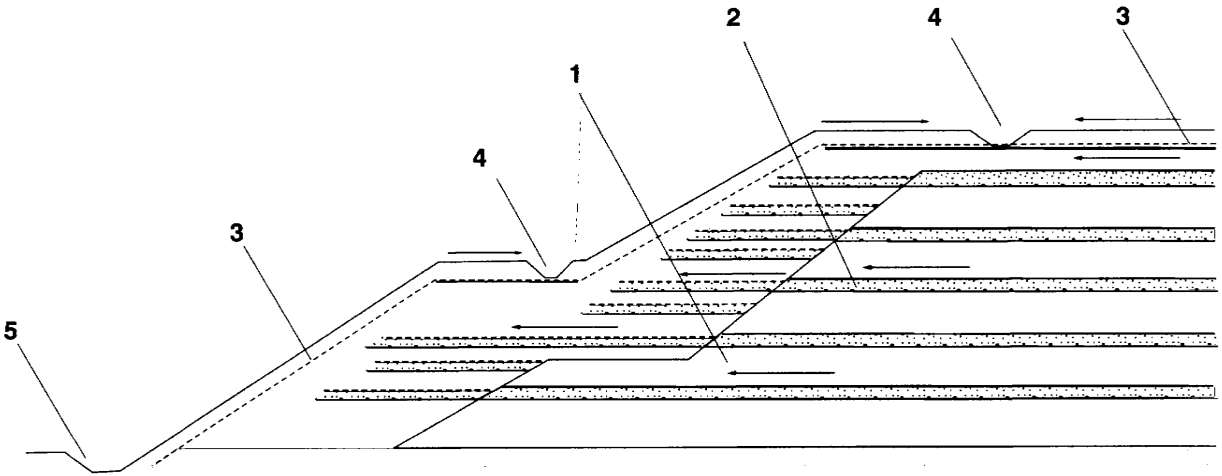

Figure VI.8.7. Construction of a coal mine waste dump with protective barriers in the form of blanket layers of dense water:FA mixtures.1 – coal mining waste; 2 – blanket layers of dense FA:water mixtures (≤0.5 m); 3 – subsurface drainage system; 4 – collecting drainage ditches on the top and terraces; 5 – toe drainage ditch.

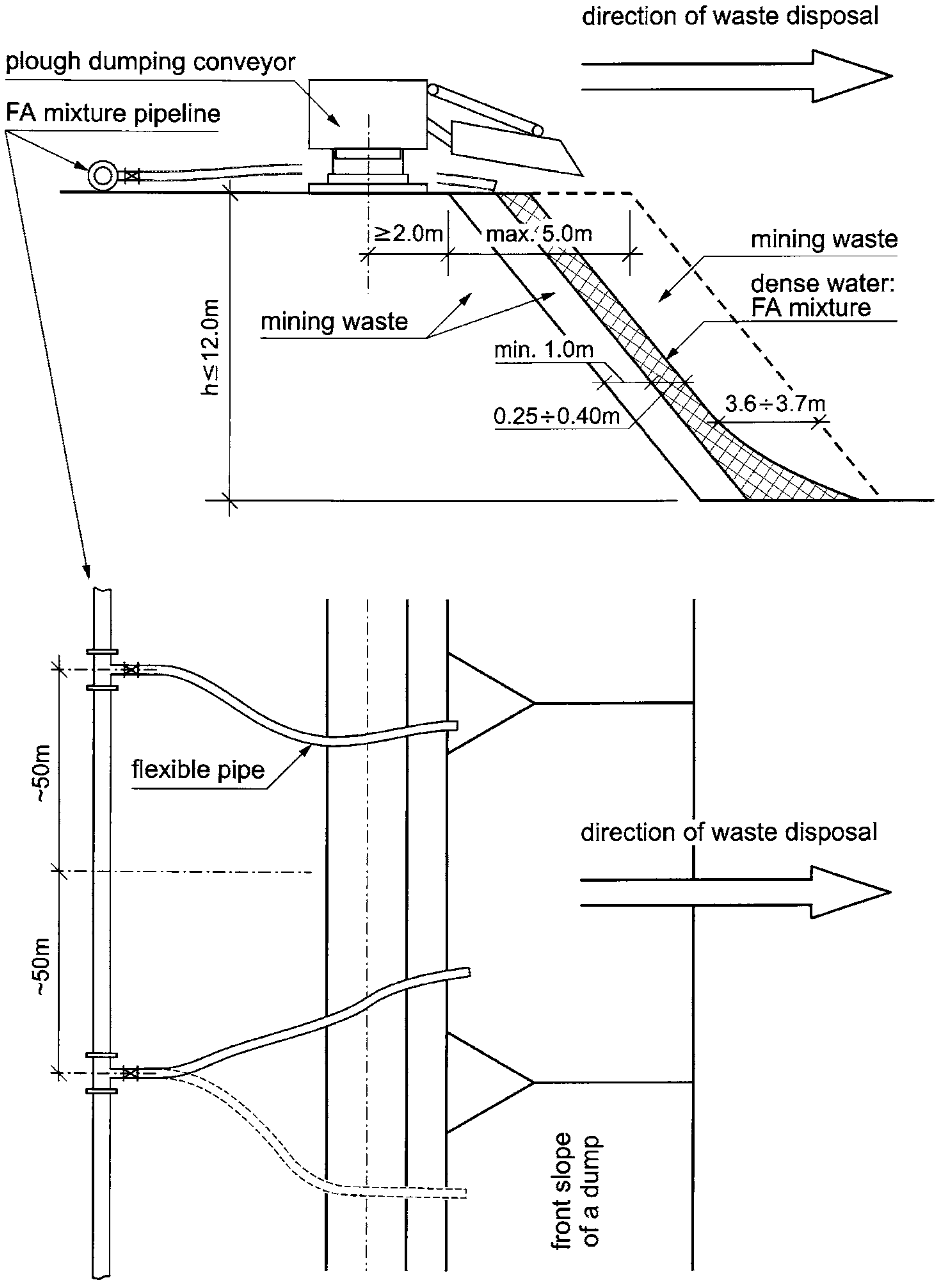

Figure VI.8.8. Construction of a coal mine waste dump sealed by dense water:FA mixtures placed at the front slope of a coal mining waste dump (after GIG, 1994).

This method was planned to be used at the Przezchlebie waste dump (INTECHKOP, 1994) to utilize the seasonal excess of FA generated in the Rybnik power plant. The project was not completed due to the lack of required amount of FA.

The modification of this method (Drąg, 1993) also considers thorough filling of the coal mining waste dump with the dense water:FA mixture delivered in two stages subsequently as water:FA mixtures of different density, 0.6:1 and 0.4:1 wt. at the top of the dump section separated with the banks to enable sinking the mixture into the lower coal mining waste layer and flowing down the working front slope of the dump. Besides self-ignition control, the method was claimed to prevent against the vertical infiltration and leaching of dissolved constituents from the dump.

This modification, which used partially FA + D-FGD from the Opole power plant in the limited scale in 5 ha of the total 180 ha was applied at the Maczki Bor central coal mining waste dump (USCB, Poland) where waste from several coal mines of the area has been disposed of. The dump has been sited in the mined out part of a sand quarry 10–30 m deep at the area of unprotected Quaternary aquifer of the usable groundwater horizon (UGWH) hydraulically connected with the Carboniferous aquifer. Despite an optimistic prognosis, a screening of the basic parameters in the swamp at the dump toe, as well as in the Quaternary and Carboniferous waters down-gradient of the dump sector sealed with dense water:FA mixture showed distinct adverse impact of the outflow and leachate from this sector, in particular alkalization of waters, enrichment of TDS, SO_4, Na, Cr, Zn, COD and transformation of water type into HCO_3–SO_4–Ca or HCO_3–SO_4–Na. This confirms high leachability and permeability of mixtures, and lack of barrier properties with respect to the vertical infiltration that should be strongly taken into account in case of using FA as a sealing agent for preventive purposes. In general, this method appeared to be unsuccessful and environmentally unfriendly. This case can be a good illustration of the importance of adequate technical solution to utilize beneficial and suppress adverse properties of dense FA mixtures used as insulating agent.

The simulation of contaminant leaching during 1.5-year exposure to the atmospheric conditions of 2 m layer of fresh-wrought coal mining waste sealed with a cover layer of pure low alkaline FA or FA + D-FGDS in the amount 10% wt. with respect to coal mining waste, in the form of dense water:FA mixture 0.6:1 illustrates the environmental behavior and interaction of these two kinds of wastes in the dump constructed according to the first of the presented methods (Twardowska, 1988) compared to the non-sealed (0) waste. This period of exposure comprised wash-out (I) and the transition the diffusion (II) stages (Fig. VI.8.9, Table VI.8.8). In the non-sealed layer, the leachate originated entirely from the precipitation. In the sealed layer, infiltration comprised also either the outflow of surplus water from the FA mixture, or the spare retention capacity, if added water is below the total retention capacity of FA. In the presented case, the sealing layer reduced the total amount of leachate from 19% (pure FA) to 27% (FA + D-FGDS). The major load of contaminants leached from the sealed layers came from the outflow, and was particularly high for the pure FA system that resulted in the unfavorable total load balance compared to unsealed layer for TDS, SO_4, Mg, COD, Cd, Cr, Mn, Ni, and Zn. For FA + D-FGDS system, where binding prevailed over release, the load balance was considerably lower for almost all leached constituents. The adverse property of both sealed systems was high release of Fl (in amounts from 1.7 g/t for pure FA to 8.74 g/t for

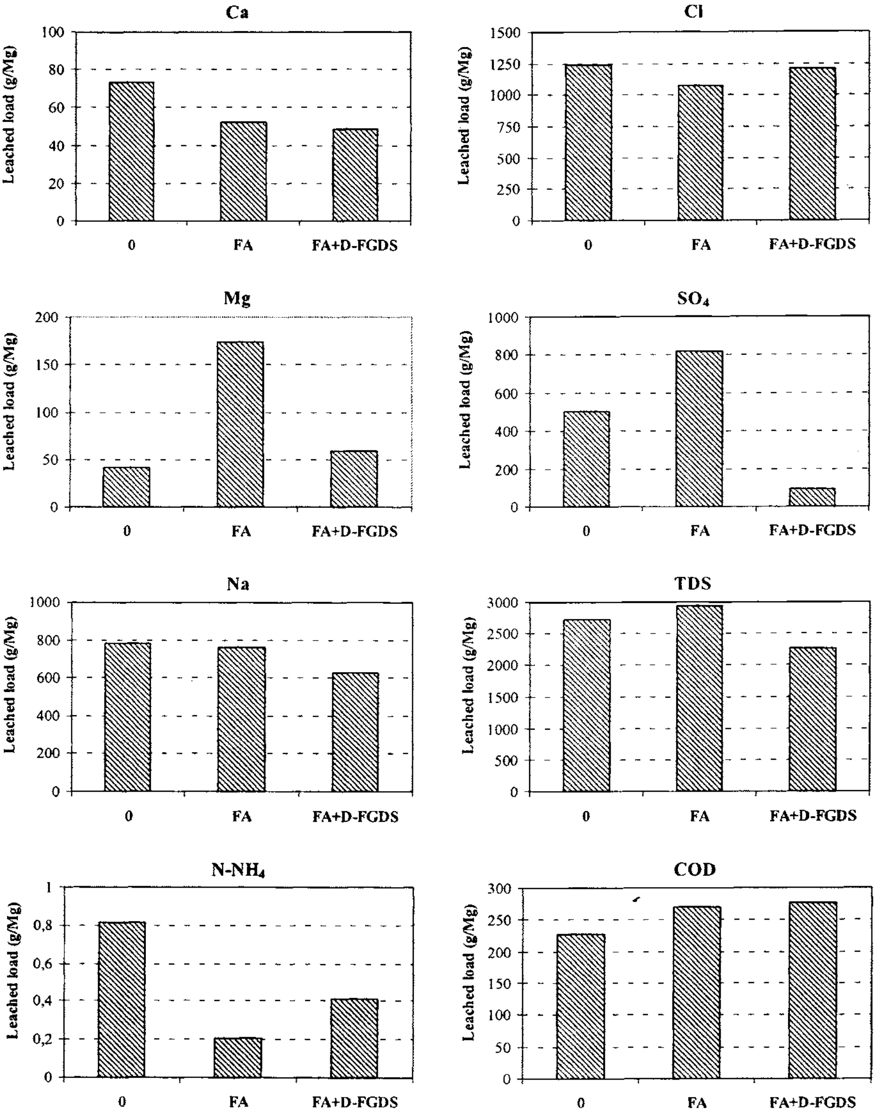

Figure VI.8.9. Environmental effect of contaminant release in the wash-out (I) stage from coal mining waste 2 m thick sealed surficially with the layer of dense water:FA and FA + D-FGDS mixtures 0.6:1 wt., compared to the unsealed coal mining waste dump; amount of FA = 10% wt. of coal mining waste. 0 – unsealed coal mining waste layer; FA – sealing layer of dense recirculation water:pure FA mixture; FA + D-FGDS – sealing layer of dense recirculation water:FA + D-FGDS mixture.

FA + D-FGDS compared to 0.37 g/t for unsealed waste) and Mo, and high COD that is typical for CCW. The further pattern of contaminant release, in particular in the Diffusion (II) stage shows high efficiency of the FA sealing cover in intercepting oxidation processes and pH correction, which is reflected in the several times lower,

Table VI.8.8. Concentration range of constituents in leachate from the 2 m thick layers of freshly disposed coal mining waste, surficially sealed with a layer of dense water:pure FA or FA + D-FGDS mixture 0.6:1 wt. compared to unsealed freshly disposed (and weathered) material in simulated conditions of 1 year's vertical rainwater infiltration (wash-out I and transition to diffusion II stages). *Sealing water:FA mixture*: FA: Low alkaline FA from the Rybnik power plant, 10% wt. of coal mining waste; Water: from closed circuit, TDS 3789 mg/l, Cl 1390 mg/l, SO_4 1039 mg/l; Mean daily precipitation 4.74 mm.

Parameters, constituents	Unsealed fresh/ (weathered) waste		Sealed with water: Pure FA: mixture		Sealed with water: FA + D-FGDS mixture[a]		MCL[b] mg/l
Parameters	I	I–II	I	I–II	I	I–II	
Water exchange rate, *R*	2.252	4.371–12.583	0.658	1.36–2.67	0.099	0.270–1.90	
Total leachate, *L/t*	56.67	110.00–316.67	68.18	140.91–456.82	6.684	18.182–127.807	
Conductivity, μS/cm	39,200	10,950–1220	38,200	8870–1201	62,500	58,400–8740	
pH	3.22	7.65–8.54 (7.96–8.0)[c]	6.94	8.35–8.38	7.48	7.46–8.09	6.5–8.5
Alkalinity, meq/l	0.00	2.1–5.5	0.40	6.0–5.95	0.85	0.8–2.35	
Hardness, meg/l	73.1	36.8–0.43	197.4	47.52–0.41	109.07	156.82–6.30	
Hardness Ca, meq/l	46.3	9.3–0.13	30.5	3.6–0.41	68.2	61.1–3.3	
Hardness Mg, meq/l	26.8	27.5–0.30	166.9	43.92–0.0	40.87	95.72–3.0	
Hardness $CaCO_3$, mg/l	3658	1842–21.52	9879	2378–20.52	5458	7848–315.3	
Macro-constituents, mg/l							
Ca	928.1	223.6–2.60	611.9	144.8–1.3	1367.8	1284.1–66.5	
Mg	326	334–3.69	2030	490–4.22	497	1164–36.4	
Na	**9321.2**	**2609–316.9**	**8778.8**	**2237.2–263.8**	**14,800**	**13,701–1502.9**	800
K	382.5	143.1–44.3	202.9	57.2–56.9	568.6	414.1–77.77	
NH_4^+-N	10.25	2.56–1.90	1.62	1.29–0.06	10.69	8.23–1.19	10
NO_3^--N	12.28	12.02–0.88	9.83	6.49–3.64	0.242	2.147–6.022	30
Cl^-	**16,320**	**3162**–65.28	**14,280**	**1428**–102	**29,316**	**27,348–2650**	1000
SO_4^{2-}	**4225.9**	**2881.8**–336.2 **(3280–1960)**[c]	**7396**	**4303.1**–299.2	**2085.2**	**1200.75**–86.45	500
HCO_3^-	0	128.14–311.19	24.40	358.8–356.9	51.86	48.81–143.39	
CO_3^{2-}	0	0–12	0	6–3	0	0	
PO_4^{3-}	0.038	0.052–0.05	0.22	0.198–0.092	0.024	0.020–0.016	3 (as P)
TDS	31,852	9360–1005	33,712	8876–984	55,076	49,368–4814	
COD	**3004.4**	**592.3**–25.7	**3519.4**	**412.0**–51.5	**10,922**	**6155.24–490.57**	125

Trace elements, mg/l							
Cd	0.1	0.06–0.1	0.21	0.17–0.1	0.15	0.14–0.03	0.4
Co	0.28	0.06–0.02	0.36	0.09–0.06	0.39	0.39–0.03	1
Cr$_t$	0.06	0.07–0.005	0.1	0.06–0.13	0.2	0.15–0.01	0.5
CrVI	0.006	0.008–0.003	0.006	0.003–0.011	0.04	0.034–0.004	0.1
Cu	0.08	0.07–0.01	0.12	0.25–0.04	0.12	0.03–0.01	0.5
Fe	0.22	0.09–3.57	0.22	0.13–40.2	0.25	0.39–0.05	10
Mn	0.78	0.03–0.11	2.2	0.35–0.19	0.36	0.21–0.15	
Ni	0.31	0.03–0.12	0.39	0.06–0.14	0.43	0.36–0.03	0.5
Pb	**1.89**	0.40–0.05	**1.32**	0.31–0.09	**0.98**	1.96–0.2	0.5
Zn	0.35	0.03–0.27	0.89	0.94–0.30	0.04	0.04–0.01	

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[a] Simulated leaching cycle 0.5 years.

[b] Polish regulations for liquid waste discharged to waters and soils (Directive of the Minister of Environment, 2002).

[c] Data for weathered ~ 1 years old material.

decreasing concentrations of SO_4 while in unsealed material the increasing sulfate generation due to pyrite oxidation is observed (Table VI.8.8).

Therefore, the reduction of outflow of surplus water from the sealing mixture is crucial for assuring positive environmental effect at all stages of FA application to reactive waste as a sealing agent. This supports the preference for using dense FA mixtures alternately as a uniform cover in a minor amount with respect to sealed material, and for minimization of water in the mixture to reduce the outflow. High content of free lime in the FA + D-FGDS enhances contaminant binding. Limited and continuously decreasing availability of this material due to shifting to the more efficient semi-dry and wet desulfurization methods is a definite obstacle to its wider use. One of the options is adding free lime to FA, in the best case as a waste product.

The use of FA as a sealing agent was exemplified here in application for coal mining waste, though it can be applied to any mining waste containing sulfide, among them to acidic metal ore mining waste of much higher pollution potential. This creates a wide area of a beneficial utilization of this waste.

In each case of selecting the optimum material and parameters, detailed testing of the material adequate to the area of application is required. For interpretation of experimental data, several simple computer programs are of use as supporting tools, e.g. geochemical programs MINTEQA2 (Allison et al., 1991), WATEQ 4F (Ball and Nordstrom, 1991, 1994) for chemical speciation and evaluation of saturation parameters, or the most developed and sophisticated geochemical computer program PHREEQC (Parkhurst and Appelo, 1999; Charlton and Parkhurst, 2002), in particular the newest version PHREEQC Interactive v. 2.8.0.0 (2003). Besides speciation, the program PHREEQC can be used for reaction-path, one-dimensional advective transport of contaminants and inverse geochemical calculations, including calculations of isotope equilibrium constants for implementations in geochemical models (Thorstenson and Parkhurst, 2002). Relatively simple programs POLLUTE (Rowe et al., 1994) or KYSPILL v.2 (Anonymous, 1997; Serrano, 1997) allow prognosis of contaminant migration from waste disposal sites to ground waters, though every program has definite simplifications and limitations and should not replace the testing procedure fit to the case.

VI.8.8.2. Use of FA for fire control in mining areas in emergency cases

VI.8.8.2.1. Use of FA mixtures for fire control and attenuation of environmental pollution caused by fire in mining areas

Another very promising and not yet fully utilized area of FA application is fire control in coal mining areas. The scale of this problem is different, from the local fires in coal mining waste sites to the vast areas of coalfields set on fire. An example of the last case and its environmental and economic consequences is Jharia Coalfields in Bihar, India, where of 258 km^2 operated by Bharat Coking Coal, 17.32 km^2 i.e. 6.7% of the total operated area was set on fire according to CMPDIL (1986), while the current situation appears to be even worse. In terms of the total devastation of the territory, which resulted in the evacuation of population, thorough destruction of the structures and vegetation, severe damage and development of high salinity of soils, surface and ground water resources, as well as air pollution (PAHs, CO, CO_2, SO_2, H_2S, NO_x) in the much bigger area and scale than that set on fire, this situation cannot be termed in other way than a disaster. The coking coal losses due to fires were estimated for 37 Mt, while total coal blocked by fires was evaluated at over 1.8 Bt (CMPDIL, 1988). The routine method of fire control is cutting off the sources of air. In the Jharia coalfield, five fires were reported to have been intercepted by placing three subsequent layers of seals (Malhotra, 2001). The primary seal consisted of placing a repeatedly compacted soil blanket in the fire area prepared by "fire digging" and vibrating to receive the seals with tyre-mounted equipment. The secondary seal comprised working out an overburden material and laying it in stages with repeated compaction, along with digging and compaction of developed cracks. The tertiary blanket was again formed of compacted soil.

The described procedure required moving and digging out enormous amounts of soil and overburden material of different, mostly fairly poor sealing properties, and repeated compaction of this material to enhance efficiency of sealing, all jobs in extremely difficult and dangerous conditions of active fire. Application of FA:water mixture as a sealing material of a proven, at least one order of magnitude higher penetration resistance than the natural cohesive soils, with no compaction required, would have achieved a better effect in fire control and attenuation of environmental damages caused by fire in a much simpler, safer, cost-effective and efficient way. FA is an abundant material in the area, thus its utilization as a best seal having no comparable alternatives is an inescapable conclusion and will allow use of a large amount of FA in the most beneficial way.

VI.8.8.2.2. Use of FA for endogenous fire control in coal mining waste dumps and interception of the environmental pollution caused by fire

Poor compaction properties of coal mining waste rock from the majority of Carboniferous seams of the USCB results in the elevated endogenous fire danger. It is particularly severe at the older high dumps constructed in thick (6–12 m) layers placed by a plough dumping conveyor and compacted at the top, while penetration of wind from a front side slope can easily occur. It results in sporadic, but extremely troublesome cases of self-ignition and environmental contamination of the same character as described above. The fire control at the closed sites or at the dumps under operation has been always a dangerous, time-consuming and expensive procedure that consisted of multiple re-compaction of an inflamed material in the fire centers, often under extreme emergency conditions.

Application of FA:water mixtures for fire interception at the Skalny coal mining waste dump in 1999 with use of combination of several simultaneously used technologies, which comprised absorption trenches, vertical hole injection, sealing inter-layers and spreading on the surface, along with partial sealing of slopes proved its high efficiency. It resulted in suppression of fire in 22 of 26 monitoring points registered as decrease of temperature and CO and other fire gases up to two orders of magnitude, which profoundly reduced air pollution within a large radius from the site (Golec and Mólka, 2000). Technological flowsheet of installation for fire control consisted of the stationary or mobile station for mixture preparation from dry FA being delivered in standard hermetic truck tankers and mine water in regulated optimum ratio. To enhance sealing properties, to the pure FA the waste lime may be added. From the mixing tank the ready mixture is pumped in steel pipes to the places of application. The general scheme of mixture preparation is similar to that used for any purpose, e.g. for utilization underground (Fig. VI.8.1), and can be applied also for fire control in coal seams in mining areas. This case study exemplifies high efficiency and prospects of FA use as sealing material for fire control in emergency cases, as well as for fire prevention, along with the parallel environmental protection effects.

VI.8.9. Conclusions

As practice shows, FA, both pure and containing flue gas desulfurization solids (FGDS from dry and semi-dry processes), can be widely and beneficially used underground and at the surface for a variety of applications where its sealing properties against air penetration, water retention and contaminant binding properties, which outclass the adequate properties of natural available materials, are the most crucial parameters.

Besides the main direct purposes of FA application (in the form of dense mixtures with mine water) in deep coal mines for sealing mined out and abandoned workings, backfilling of mine workings and stopping construction for fire prevention and control, methane control and reduction of a greenhouse effects caused by methane release to the atmosphere, simplification of a ventilation system, and reduction of surface deformations due to subsidence, high water retention and binding capacity of FA causes adequate reduction of contaminant loads discharged with mine waters to the surface recipients.

The most environmentally beneficial and safe way of utilizing FA, pure or containing dry or semi-dry desulfurization products (FA + D-FGDS or FA + SD-FGDS) underground as a sealing material is its use in the form of dense mixtures with saline or/and acidic low-quality mine waters or flotation slurry in the mine workings insulated from the recoverable usable ground water resources. Utilizing slurry underground reduces costs by resignation from filter press dewatering of slurry and its disposal.

Using FA or FA + FGDS in such workings, at an optimally high TDS/acidic mine water:FA ratio, which assures transportability of mixture to the place of deposition at minimum leachate will cause considerable reduction of aquatic environmental contamination in the period of mining and after mine closure. A particularly beneficial effect of FA application on the reduction of trace metal load was found in its application in mines having problems with high-metal acidic waters, which are equally frequent in coalfields and metal ore mines in the world. The use of good quality low TDS-mine waters for preparation of mine water:FA mixtures and utilization of FA in the feeding zones of recoverable ground water resources should be restricted. The mine water:FA ratio should be optimized for each system individually on the basis of the most effective contaminant load balance and the requirements of the transportability of the mixture to the place of deposition. For dry or moderately flooded mines, the optimum solution is to utilize all pumped mine water for FA mixture preparation in a closed circuit that would effectively and thoroughly eliminate discharge of pollutants to the surface receiving waters. As a rule, the mines in the USCB of low mine water inflow are working in such a no-discharge system.

Use of FA + SD-FGDS in dry mine workings appeared to be the most rational approach, taking into consideration long solidification time and certain thixotropic properties of this material.

Dense FA, and in particular FA + FGDS mixtures, used underground have appeared to be also an effective sink of high radioactivity loads from mine waters of the Ra–Ba type that shows reduction in outflow to a concentrations below MCL for drinking water.

Besides the environmentally beneficial use of FA underground, a prospective field of application of this material at the surface is its use for sealing coal mining waste dumps to prevent self-ignition and long-term adverse environmental impact caused by sulfide oxidation and acidification of low-buffered waste with subsequent release of trace constituents from the material and the bedrock of the vadose zone lasting for decades. In this respect, FA has no competitors and thus should be strongly considered for the control of oxidation in the reactive material in order either to prevent, or to remediate the generation of pollutants or combustion processes. This area of application sets the complicated task of optimization of FA use in a way that would utilize in full its sealing properties and attenuate adverse impact of massive release of contaminants from FA mixture in the wash-out (I) stage, to achieve the most positive resultant effect. The reduction of outflow of surplus water from the sealing mixture was found crucial for assuring positive environmental effect at all stages of FA application to reactive waste as a sealing agent. Of different types of CCW, FA + D-FGDS was found to be the most efficient in contaminant binding due to its high content of free lime. Limited and continuously decreasing availability of this material due to shifting to the more efficient semi-dry and wet desulfurization methods is a definite obstacle in its wider use. One of the options is adding of free lime to FA, in the best case as a waste product.

FA as a sealing agent can be applied to any mining waste containing sulfide, among them to metal ore mining waste of much higher pollution potential. This creates a wide area of a beneficial utilization of this waste.

Another very promising but not yet fully utilized area of using excellent sealing properties of FA is fire interception in the coal mining areas and dumping sites. Positive results of fire suppression at the coal mining waste dump in the USCB, Poland, suggest its wide application for fire control in coalfields and dumping sites.

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