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ON SOLIDIFICATION OF BY-PRODUCTS FROM DRY FLUE GAS DESULFURIZATION METHODS: WAWO AND FLUIDIZED BED COMBUSTION AS A WAY OF WASTE MANAGEMENT, UTILIZATION OR SAFE DISPOSAL

The alkalinity of FGD by-products is the main problem of their safe disposal. On the basis of preliminary experiments carried out at the Institute of Environmental Protection Engineering of the Wrocław University of Technology and literature data it can be reckoned that by-products obtained using FGD conditioning method (WAWO) and from fluidized bed boiler are characterized by binding properties. Such properties are due to pozzolanic reactions between ash compounds, unused sorbent (free CaO) and desulfurization by-products. Water extracts and filtrates from raw by-products and those after binding (due to reaction with water) were analyzed. Limiting standards of pH, chlorides, fluorides, sulfates (VI) and soluble substances were exceeded. Ash fixation by means of water significantly decreases the permeability of by-products and the concentration of washed out compounds. This property enables us to use the by-products from FGD plant (WAWO) for disposal sites' sealing.

1. INTRODUCTION

In Poland energy and fuel production achieves the first place not only due to SO₂ emission, but also because of the volume of waste which is annually disposed and generated. Immense volume of waste comes from flue gas desulfurization. Both utilization and safe disposal of wastes depend on the physical and chemical properties of the by-products and thus on the desulfurization method, conditions and ways of by-products generation, i.e. on the type of fuel, sorbent, process and by-product discharge. In West Europe the wet limestone method is commonly applied – dihydrate calcium sulfate (gypsum) as a waste product is generated, which after proper processing can be reused in cement industry, road building, agriculture [1]–[4]. In Poland there is not much demand for that sort of gypsum, and thus other FGD methods are needed. One of the FGD recommended method is the WAWO method.

WAWO is a two-phase process. In the first phase, a dry sorbent (limestone or dolomite) is injected into the combustion zone, where a temperature reaches 800–1000 °C. A residence time required is 1 second. The sorbent load varies with the

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sulfur content in the fuel. Due to processes occurring in this zone SO_2 is partially bound, and CaO and CaSO_4 are generated. The particles of the desulfurization products increase the particulate concentration in the flue gas stream. In the second phase, SO_2 is bound by alkaline liquid sorbent, i.e. by $\text{Ca}(\text{OH})_2$ suspension. The flue gases leaving the boiler pass through an air heater, where they are cooled down to the temperature of 130–200 °C and enter a reactor, in which the following processes take place:

- removal of about 30% of the dust particles carried in the flue gas stream,
- cooling down of the flue gas to the temperature of 90 or 110 °C according to the desired SO_2 removal efficiency,
- removal of SO_2 as the result of a liquid sorbent fixation.

The result of the process, that takes place in a reactor, is CaSO_3 in a dry form. Due to velocity variations in a reactor, coarse ash particles, which are generated during drying of particulate agglomerates formed in the reactor, precipitate. Final cleanup of gases from ash is carried out in electrostatic precipitator, where the flue gases are directed after leaving the reactor.

As a result of a preliminary study carried out at the Institute of Environmental Protection Engineering [5], [6] and the literature data [7], the following conclusions can be drawn. The wastes obtained using FGD conditioning method and from combustion in the fluidized-bed boilers are characterized by similar chemical composition and binding properties. Unlike synthetic gypsum generated by means of a wet method, the by-product formed in a semi-dry FGD process is regarded as a non-homogeneous, self-binding agent with pozzolanic properties [8].

The mixture of by-products and fly ash in a 1:1 proportion shows (after natural setting) a porosity similar to, and a permeability lower than, that of fly ash. This is due to the "pozzolana effect", i.e. the capability of fly ash to bind CaO along with generation of compounds with hydraulic properties in water environment. Desulfurization by-products affect the binding properties of the mixture. Such mixtures can be applied to ground leveling or land reclamation, and after activation with cement of appropriate quality – also to road building, mining or building materials production. However, the property that makes the mixture applicable to soil stabilization becomes a limiting factor in a safe disposal.

The construction of new disposal sites is a very costly investment. One of the main items in the budget are the capital investments necessary to seal the bottom and the embankments of the disposal site. Polyethylene, polypropylene or PVC foils, at least 1.5 mm thick, acidproof and oilproof are recommended for disposal site designing. The foils should be weatherproof, especially sunlight resistant. The imported high-quality polyethylene foil meets all these demands.

Ground sealing and enforcement with fly ash is a technique, which has been well-known and proven for many years in road construction, mainly to stabilize an earthen foundation. Soil surface is covered with a dense layer of a siliceous and fly ash composite.

The basic components of these composites are fly ashes from bituminous coal mixed in adequate proportions with an activator and liquid glass, whenever necessary.

In the presence of an activator, coagulation of liquid glass and soluble components of the activator is induced by the ions (mostly calcium ions) influencing the colloidal particles of the liquid glass.

Linings made from fly-ash composites can be laid on the disposal site bottom and embankments (with a maximum slope of 1:2.5). They are characterized by an appropriate elasticity, which does not change in time and remains stable after sowing with a variety of grass species. This natural protecting cover prevents excess drying and extends the duration of the chemical processes responsible for the endurance and tightness of the disposal sites. The lining sticks well to the background and to such bodies as concrete or steel, they are resistant to frost penetration and to activity of majority of chemical compounds disposed in various types of waste. The physico-chemical parameters of the lining depend on its composition and are characterized by the filtration coefficient, which should vary from 10^{-9} to 10^{-11} m/s.

The applicability of fly ash to the insulation of the disposal site bottom is assessed in terms of grain-size distribution, particularly the content of ash and clay fractions, which is mainly responsible for the filtering and sorbing properties of the fly ash.

Fly ash is the main component of the lining (90%). Thus, if the layer is to be at least 25 cm thick, it will be necessary to use approximately 300 kg of fly ash (approx. 3000 t/ha) to lay 1 m² of lining. In a fly ash/concrete layer, the resistance to water flow and leakage flow increase with time. A homogenized, packed fly ash/cement composite allows a more effective use of the disposal site capacity and reduces the space requirement for further development [11], [12].

The above-described advantages of the fly ash application to the construction of sealing layers at disposal sites allows us to recommend this economic utilization of ash-containing desulfurization by-products.

2. EXPERIMENTAL

In order to characterize an environmental impact due to particular wastes, it is necessary to determine:

- chemical composition and some physical properties of the waste,
- water solubility of the waste,
- physical and chemical parameters of the water extracts from the wastes (dynamic method) and filtrates (static method),
- content of heavy metals in wastes, water extracts and filtrates.

Seven samples of by-products were used for the tests. Sample No. 1 was taken from the particulate collection unit of the fluidized bed boiler in a power and heating plant in Lubań on March 10th, 1995. The other samples were taken in the power plant in Wrocław during the heating season of 1996/1997 from a hopper under the reactor (samples No. 1R, 2R, 3R) and from zone II of an electrostatic precipitator (samples No. 1EF, 2EF, 3EF). All samples were taken in the KW-3 boiler plant.

The analysis of the by-products consisted in determining their humidity, roasting losses, chemical composition, content of heavy metals and solubility. Humidity was deter-

mined by means of drying waste mass loss at the temperature of 373 K. Roasting losses were determined by means of roasting deposit mass loss at the temperature of 1273 K.

In order to carry out the chemical analysis, dried wastes were mineralized in the mixture of nitric and perchloric acids by means of microwave method. The metals were determined by flame photometry (Na, K, Ca) and atomic absorption spectrophotometry (heavy and transient metals). Free CaO was determined potentiometrically in glycol solution. Sulfur in the form of sulfates was determined by weight and expressed as SO_3 .

3. FILTRATION COEFFICIENT

Filtration coefficient (water permeability indicator) was examined by means of ZWK-2 apparatus at four hydraulic gradients (i) for each sample.

At the beginning the ring where sample is located was measured. Then the material examined was put to the ring and then to the apparatus. Next, distilled water was passed through the sample from the bottom to the top for at least 20 minutes. The aim of slow water flow is more exact air removing from sample pores. The measurement of filtration was done after hydraulic gradient regulation by means of overfall and stabilizing water surface in two apparatus chambers.

Afterwards the indicator of water permeability (K_t) was determined according to the following formula:

$$K_t = \frac{Q_{\text{mean}}}{ATi},$$

where:

K_t – water permeability indicator at the water temperature t [$^{\circ}\text{C}$] during measurement [cm/s],

Q_{mean} – water volume flowed through the sample during time T [cm^3], five-fold measurement,

A – sample surface perpendicular to water flow [cm^2],

T – filtration time [s]

i ($\Delta h/h$) – hydraulic gradient,

Δh – difference in water levels in two chambers [cm],

h – sample height, i.e. length of filtration way [cm].

Afterwards the reduced indicator of water permeability (K_{10}) was determined according to the formula:

$$K_{10} = \frac{K_t}{0.7 + 0.3t},$$

where:

K_{10} – reduced indicator of water permeability at the water temperature of 10 $^{\circ}\text{C}$,

t – water temperature during measurement [$^{\circ}\text{C}$].

4. RESULTS

The results of the analyses are presented in table 1 and in table 2.

Table 1

Chemical composition of by-products [%]

Component	Electrostatic precipitator			Right reactor			Fluidized bed boiler
	1EF	2EF	3EF	1R	2R	3R	
Humidity	0.098	0.176	0.092	11.08	7.54	14.51	0.33
Roasting losses	15.34	13.77	17.89	18.29	17.26	15.81	43.38
SiO ₂ + insoluble part	56.89	49.69	52.23	44.45	48.42	52.49	22.88
including SiO ₂	15.19	22.67	25.63	17.49	21.43	20.52	n.a.
Al ₂ O ₃	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7.60
CaO	7.80	12.90	12.20	12.40	11.40	9.34	9.28
including CaO _{free}	0.27	1.80	2.45	0.96	0.58	0.72	3.47
MgO	1.40	1.63	1.63	1.47	1.82	1.63	1.23
Na ₂ O	0.46	0.49	0.48	0.42	0.39	0.44	0.24
K ₂ O	0.49	0.43	0.45	0.53	0.42	0.44	0.52
Fe ₂ O ₃	3.18	3.66	2.73	3.44	3.87	3.71	4.74
SO ₃ with sulfate ion (VI)	2.97	4.66	3.22	4.22	4.55	5.99	3.49
SO ₂ with sulfate ion (IV)	3.56	4.78	5.03	2.17	2.46	2.36	3.84
Cl ⁻	1.01	0.81	1.00	0.91	0.91	1.01	0.35

n.a. - not analyzed.

The compositions of the by-products from the reactor and from the electrostatic precipitator are similar. They are characterized by great amounts of silica and insoluble parts. A distinct difference is observed in the content of sulfates (VI), which is

Table 2

Heavy metals' contents in the by-products [%]

Heavy metal	Electrostatic precipitator			Right reactor		
	1EF	2EF	3EF	1R	2R	3R
Cu	0.015	0.015	0.016	0.012	0.014	0.013
Cd	0.004	0.004	0.005	0.002	0.006	0.003
Pb	0.029	0.010	0.029	0.012	0.025	0.025
Hg	$4.82 \cdot 10^{-4}$	$4.89 \cdot 10^{-4}$	$5.55 \cdot 10^{-4}$	$4.66 \cdot 10^{-4}$	$3.65 \cdot 10^{-4}$	$3.54 \cdot 10^{-4}$
Zn	0.017	0.015	0.017	0.010	0.012	0.011
Cr	0.007	0.013	0.006	0.010	0.012	0.010
Ni	0.009	0.013	0.011	0.010	0.012	0.010
Mn	0.023	0.031	0.025	0.024	0.033	0.029

higher in ash from the reactor and the content of sulfates (IV), which is higher in ash from the electrostatic precipitator.

Comparing the by-products from WAWO method and from fluidized bed boiler, it can be reckoned that the latter shows bigger roasting losses and free CaO amount. The contents of other components of by-products are of the same order.

The indicator of by-products harmfulness is a toxicity of heavy metals' contents. The by-products analyzed contain trace amounts of these metals, in many cases close to analytical detection limit.

5. ANALYSIS OF WASHING OUT

Raw by-products were mixed with distilled water in one to ten proportion (100 g of deposit and 1 dm³ of distilled water), then they were shaken for 4 hours in a shaker

Table 3

Physical and chemical analyses of by-products' water extracts and filtrates

Indicator	3EF			3R			Fluidized bed boiler fly ash extract	Limit standard
	Raw by-product extract	Raw by-product filtrate	Solidified by-product extract	Raw by-product extract	Raw by-product filtrate	Solidified by-product extract		
Reaction pH	12.85*	12.07*	12.0*	10.1*	8.4	7.0	13.1*	6.5–9.0
Conductivity [$\mu\text{S}/\text{cm}$]	5950	5110	2140	2170	330	1400	3773	–
Alkalinity M [mole/m^3]	44.00	33.0	14.0	0.25	2.0	1.0	51.00	–
Alkalinity F [mole/m^3]	39.75	31.0	15.0	n.d.	n.d.	n.d.	–	–
g OH ⁻ /m ³	603.5	493.0	221	n.d.	n.d.	n.d.	833	–
g CO ₃ ²⁻ /m ³	255.0	120.0	60	n.d.	100	n.d.	60.0	–
g HCO ₃ ⁻ /m ³	n.d.	n.d.	n.d.	30.5	n.d.	61	n.d.	–
Nitrates [g NO ₃ ⁻ /m ³]	3.5	1.2	0.6	2.6	n.d.	0.8	0.58	6.0
Chlorides [g/m ³]	1000	520.0	700	1010*	150.0	400	280.0	1000
Fluorides [g/m ³]	27.0*	1.5	0.85	0.16	n.d.	0.80	18.0	15.0
Sulfates(VI) [g/m ³]	1230*	924*	143.2	859*	54.7	801.4*	744.0*	9500
Sulfates(IV) [g/m ³]	623.0	575.7	542.5	126.0	60.9	63.2	n.a.	–
Calcium [g/m ³]	1000	1075	560	580	40.5	640	1175	–
Magnesium g/m ³	0.20	0.05	n.d.	1.1	0.25	5.70	0.01	–
Sodium [g/m ³]	35.0	21.5	125	135.0	30.0	180	10.5	800
Potassium [g/m ³]	10.0	7.0	175*	105.0*	46.0	250*	4.0	80.0
Dissolved substances [g/m ³]	4165*	3577*	–	1519	234.0	–	3233*	2000
Solubility [%]	4.16	3.58	–	1.52	0.23	–	3.23	–

*Exceeded limit standards for wastewater discharged to water and soil, n.d. – not detected, n.a. – not analyzed.

and left for 24 hours. After that time they can be decanted and water extracts may be prepared. Physical and chemical analyses were done after filtering the solution. The results are presented in tables 3 and 4.

On the basis of the experiments carried out, it can be reckoned that the reaction of water extracts of raw by-products from electrostatic precipitator and from fluidized bed boilers is strongly alkaline. In the case of the reactor by-product, limiting standards of dissolved substances such as sulfates, chlorides, fluorides, and potassium are exceeded.

The reactor by-product filtrates and also the fluidized bed boiler fly ash filtrates are strongly alkaline. Limiting standards of dissolved substances are exceeded in wastewater discharged to water and soil. In the case of the electrostatic precipitator samples, the limiting standard of sulfates is exceeded.

After 28 days of binding by water, solidified samples were crushed, sieved and covered with water, then filtered and analyzed.

Water extracts of the electrostatic precipitator solidified by-product remain strongly alkaline. Potassium limiting standard is exceeded. Comparing the water extract of solidified by-products to raw by-products, it can be reckoned that the contents of chlorides and fluorides in the former are significantly smaller.

Table 4

Contents of heavy metals in by-products' water extracts and filtrates [g/m³]

Heavy metal	3EF			3R			Fluidized bed boiler	
	Raw by-product extract	Raw by-product filtrate	Solidified by-product extract	Raw by-product extract	Raw by-product filtrate	Solidified by-product extract	Raw by-product extract	Raw by-product filtrate
Cu	0.05	0.05	0.05	0.05	n.d.	0.06	0.032	0.05
Cd	0.02	0.02	n.d.	0.01	n.d.	0.01	0.01	0.02
Pb	n.d.	1.13	n.a.	0.09	n.d.	n.a.	0.02	0.34
Hg	0.0012	0.0019	n.a.	0.0163	0.0022	n.a.	n.a.	0.0021
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	0.30	0.20	0.20	0.20	n.d.	n.d.	0.02	0.10
Ni	0.10	0.10	0.02	0.10	0.05	0.06	0.15	0.15
Mn	0.04	0.04	0.02	0.04	0.02	0.03	0.01	0.04

n.d. – not detected, n.a. – not analyzed.

The examined filtrates and water extract solidified and raw by-products consist heavy metals in the amounts not exceeding the limiting standards due to alkaline reaction of the solutions.

6. WATER PERMEABILITY INDICATOR

The water-permeability indicator (table 5) of the electrostatic precipitator by-products from the reactor averages $1 \cdot 10^{-7}$ m/s and $2-5 \cdot 10^{-7}$ m/s (WAWO method). Unless the fine granulation, water flow through ash is proportionally fast due to a spherical shape of the WAWO by-product grains. The coefficient of the fluidized bed boiler by-products is one order bigger due to different fraction contents; the fluidized bed boiler ash particles are plate in shape. The particles of substitute diameter less than $20 \mu\text{m}$ are in a majority (50–70%).

Table 5

Reduced indicator of water permeability

Sample	Reduced indicator of water permeability K_{10} [m/s]
1R	$2.21 \cdot 10^{-7}$
3R	$5.19 \cdot 10^{-7}$
1EF	$1.29 \cdot 10^{-7}$
3EF	$1.01 \cdot 10^{-7}$
FB without sorbent	$2.37 \cdot 10^{-6}$
FB with sorbent	$2.14 \cdot 10^{-6}$

FB – fluidized bed boiler.

7. FINAL CONCLUSIONS

- The index of by-product hazard is the content of transition and heavy metals of toxic properties. The by-products tested and their water extracts contain metals in the amounts not exceeding limiting standards, which allows us to categorize them as the IV class of toxicity, thus to dispose them into environment.

- Water solubility as an assessment of the washout capability of substances contained in the by-products for the reactor amounts approx. to 1%, and for the electrostatic precipitator and fluidized bed boiler – approx. to 3%. Taking into account solubility, the by-products analyzed are categorized as moderately soluble.

- While characterizing the water extracts it can be stated that their reaction is strongly alkaline (11.3–12.85).

- The concentration of dissolved substances in the by-products' water extracts is higher than the limiting standards for wastewater discharged into water and soil. These excesses result from excessive concentrations of sulfates, fluorides and chlorides.

• Also filtrates show high pH and high contents of soluble substances when the filtrates were obtained under laboratory conditions from raw by-products. Due to the pozzolanic properties of the by-products and as a result of their slow contact with water under real conditions the by-product will be bound and its permeability as well as the amount of the washed out compounds will significantly decrease.

• The reduced coefficient of water permeability for the by-products from WAWO method ranges from 1 to $5 \cdot 10^{-7}$ m/s. The filtration coefficient of the materials used for disposal site sealing should be in the range of $1 \cdot 10^{-9}$ – 10^{-12} m/s. This value is enough for a safe waste disposal.

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ZESTALANIE ODPADÓW Z ODSIARCZANIA SPALIN SUCHĄ METODĄ WAWO I W KOTLE FLUIDALNYM JAKO SPOSÓB ICH ZAGOSPODAROWANIA LUB BEZPIECZNEGO SKŁADOWANIA

Zasadniczym problemem składowania odpadów z odsiarczania spalin jest alkaliczność odcieków. Na podstawie wstępnych badań prowadzonych w Instytucie Inżynierii Ochrony Środowiska Politechniki Wrocławskiej i danych literaturowych można stwierdzić, że odpady powstające podczas odsiarczania spalin metodą kondycjonowania (WAWO) i odpady z kotłów fluidalnych mają właściwości wiążące. Są one efektem reakcji pucolanowych zachodzących między składnikami popiołów (glinokrzemiany), nie-

przereagowanego sorbentu (wolny CaO) i produktów odsiarczania. Zbadano wyciągi wodne i filtry odpadów surowych i po związaniu w wyniku reakcji z wodą. Stwierdzono, że dopuszczalne wartości pH, substancji rozpuszczonych, w tym chlorków, fluorków i siarczanów (VI) zostały przekroczone. Zestalenie się popiołu pod wpływem wody znacznie zmniejsza przepuszczalność odpadu i ilość wymytych składników. Pozwoli to prawdopodobnie wykorzystać odpady z instalacji do odsiarczania spalin (WAWO) do budowy warstw uszczelniających wysypiska.