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**PROPERTIES OF THE STABILIZATE
AND POSSIBILITIES OF ITS UTILIZATION**

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The paper is devoted to production of the stabilizate as a procedure for utilization of wastes from coal burning and desulfurization process in heat power stations. This study completes the knowledge concerning the leachability of several metals (As, Al, Cr, V) and some properties of the stabilizate — pH and changes of conductance — in dependence on the method of stabilizate production and on the age of samples.

The composition of the stabilizate presenting the best properties has been suggested. Future studies should focus on verification of these results during the longer time period.

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Introduction

The aim of this study is to outline briefly some possibilities of utilization of wastes from coal-fired power generator units and their desulfurization. Additional installation of the desulfurization technologies in large power stations is a necessary measure for reaching the emission standards, but we do not intend to discuss many complicated problems connected with the production of electricity and also with saving of energy.

Technological and economical demands of the desulfurization lines are a consequence of the fact that enormous volumes of flue gases containing very low concentration of SO_2 to be separated must be processed.

Dust particles contained in gases are of the inorganic character. Their content causes the unfavourable effects like forming of deposits, contamination of outgoing flue gases stream and an undesirable catalytic activity. More than 180 methods are known at present and can be divided according to the process type into two categories:

- cyclic (a reagent is regenerated)
- uncyclic (a reagent is not regenerated).

According to ČEZ (i.e. Czech Energetical Plants) company's programme there are 30 desulfurized energetical blocks of coal power stations being tested or in continuous operation. A wet lime or limestone method is used in the majority of cases.

In the wet limestone method sulphur dioxide is absorbed into the aqueous suspension of the finely ground limestone. A gypsum slurry is the final product which can be dewatered and then used as a by-product or chemically stabilized to produce an inert matter (the stabilizate).

The wet lime process is based on the absorption of sulphur dioxide into the aqueous solution of calcium hydroxide or calcium carbonate.

The modern desulfurization methods operate in a closed circuit with addition of some reagents intensifying the absorption process. The gypsum slurry is the final product as well. The wet-dry desulfurization method is realized in a reaction vessel situated behind electrofilters. The aqueous suspension of lime with addition of a part of the recycled final product is sprayed into the cleaned flue gas. So called REA product results from this process.

It follows from this fact that great changes in amount and composition of wastes produced by coal-fired power stations are forthcoming. The fly ash and the rests of burning will be unambiguously dominating, but wastes from limestone desulfurization units and from fluidization technologies will be added to them. According to ČEZ information the production of ash in 1990 year was 11.79 mln.t. After putting the desulfurization facilities into operation the production of wastes is supposed to increase to 14.8 mln. t per year.

The ash from the coal power stations is preferably landfilled at present, only an insignificant amount is utilized. Unfortunately, this fact led to considerably negative impacts on the landscape around energy sources and ash pounds. The utilization of ash and wastes from desulfurization by other methods (for example in civil engineering) is of a greater importance. Likewise the properties of these materials should be more friendly to the environment. One of the possibilities is the production of the gypsum slurry or the stabilizate.

Utilization of Desulfurization Products

As noted above, one of the products of the wet desulfurization procedures is the gypsum slurry. It can be used in the Portland cement manufacturing as a solidification regulator or — after partial dehydration by calcination — utilized as a plaster of Paris for making of plaster slabs. According to the literature data, more than 3 billions m^2 of the plaster slabs are produced all over the world and only 1.34 bill. m^2 are produced in the USA and Canada per year. Consumption in the USA is $48.2 \text{ m}^2 \text{ year}^{-1}$ per caput, in Western Europe $53.4 \text{ m}^2 \text{ year}^{-1}$, while in Czechoslovakia (1988) only $0.03 \text{ m}^2 \text{ year}^{-1}$. There are, therefore, good conditions for utilization of gypsum in CR in a quality given by the production method. The production of plaster is insufficiently developed in CR owing to the deficiency in sources of natural gypsum. On the other hand, it must be supposed that the consumption of these wastes produced in the relatively pure form (as the gypsum slurry) does not exceed the amount of 1 mln. t year^{-1} . So it is evident that every coal-firing unit should have the possibility not only to utilize the produced “secondary row materials” but also to deposit them.

Properties and Utilization of Stabilizate

The term “stabilizate” means the product of mixing of slurry (i.e. the product of desulfurization of flue gases) with ash (the solid product of burning) leading to a decrease of moisture content and to an improvement in the possibilities of handling it.

The mixture prepared by this procedure solidifies owing to hydration and pozzolanic reactions. Originated hydrated oxides (SiO_2 , Al_2O_3 , Fe_2O_3), hydrated calciumsilicates and calciumaluminates react with calcium sulphite hemihydrate present in the mixture to give $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_3\cdot 7\text{H}_2\text{O}$ or with gypsum $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ (ettringite) and $3\text{CaO}\cdot 2\text{Al}_2\text{O}_3\cdot\text{CaSO}_4$ (monosulphate). Reactions of the mullite part of fly ash with lime, water and calcium sulphite or sulphate are principles of hardening. According to the studies worked out in USA calcium sulphite shows analogous properties as plaster.

Calcium sulphite is stabilized in a crystal lattice of hardened stabilizate by

building in to the crystalline phase which is similar to the stabilizate mentioned before. Chlorides are stabilized in the mineral structure as well. The process of forming the new stabilizate structure is long-lasting. The resulting material is hard and watertight. Toxic metals are immobilized, their leachability is minimized. This can be confirmed by comparing the leaches made from some kinds of ashes, desulfurization products and stabilizates prepared from them. The leaches from the stabilizates show lower values than those prepared from the other materials in the majority of investigated parameters. The final properties of the stabilizates depend on the ratio of inlet materials, on properties of these materials, on the water content and on the production method.

The ecological importance of the production of the mixture of fly ash, gypsum and waste water with occasional addition of lime is evident. The solubility of those heavy metals which can be extracted from fly ash to water is decreased owing to physical bonds formed in a fixed structure of the stabilizate and also by chemical effect of increased alkalinity (i.e. the residues of calcium hydroxide, carbonate and sulphite). Dustiness from the ash-ponds is reduced too.

The supplier of the desulfurization technology for Opatovice power station warrants the compression strength of $2 - 5 \text{ MN m}^{-2}$ and the water permeability of $1 \times 10^{-9} \text{ m s}^{-1}$ for the stabilizate. The stabilizates showing very low leachability can be produced by the use of suitable ratio of the components so it would be classified into the leach class I.

Experimental

A study explaining behaviour of arsenic and its compounds in the stabilizate formed by fly ash, several kinds of gypsum or cement was carried out. The process was evaluated by experimental measurement of arsenic leaching from prepared samples during the period of 0 – 300 days. The aim of the study was to find the optimum composition of the stabilizate with the minimum leachability of As. For the sake of comprehensiveness some other parameters as the leachability of Ca, Al, Cr and V, pH and conductance of the leach were also measured. One set of the samples was kept out of the laboratory in the open air to involve the influence of the climate. Two samples were prepared by also using gypsum.

The samples analyzed were prepared according to the following recipes:

- recipe 1 – 97 % of fly ash from Chvaletice power station (CHPS), 3 % of lime from Prachovice cement factory (PCF)
- recipe 2 – 97 % fly ash CHPS, 3 % dolomite lime
- recipe 3 – 97 % fly ash CHPS, 3 % Portland cement PCF
- recipe 4 – 94 % fly ash CHPS, 3 % lime PCF, 3 % gypsum
- recipe 5 – 94 % fly ash CHPS, 3 % Portland cement PCF, 3 % gypsum

Water from a well situated in the area of CHPS was used for preparation of the samples. The prepared mixtures were poured into glass bakers and then compacted. The bakers were broken after setting the material. As already mentioned, one set of the samples was deposited in the laboratory, the second one in the open air.

General Characteristics of the Samples

The samples prepared can be characterized qualitatively as follows:

recipe 1 – a homogenized block was formed already after 7 days. However, the block was not sufficiently compact to enable leaching. This was possible after 28 days.

The sample deposited in the atmosphere got fragile. It had to be dried before the leaching procedure.

recipe 2 – the sample prepared according to the recipe did not form a block, it remained in the loose form.

recipe 3 – the sample formed the compact homogenized block as early as after 7 days. It was not influenced by the weather.

recipe 4 – the sample showed the same properties as the sample 1.

recipe 5 – the sample showed the properties similar to those of the sample 3.

Analyzed Parameters, Analytical Methods

The samples prepared according to the recipes 1 – 5 were analyzed in a long-term stability programme (see Tables II – IV). Each analysis began by preparation of the leach according to the Ministry of Environment Intimation No. 338/97. The leach was also prepared from the cubes 4×4 cm cut from the solidificates (of course, in the cases where it was possible). Instead of these procedures, the leaches made by an acid extraction agent were performed to express the influence of acid rains. The following parameters were investigated:

pH — with a pH-meter OP 211/1, equipped with a glass combined electrode

conductivity — conductivity meter RADELKIS with conductivity cell

determination of Ca — by chelatometric titration

determination of As — by the atomic absorption spectrometry with electrothermic atomization of the sample. Instrumentation: AA spectrometer GBC 906 Elite, electrothermic atomization by the GF 300 with autosampler PAL 3000, discharge lamp with the hollow cathode Photron, pyrolytic graphite measuring cell. The detection limit: $0.01 \text{ mg As l}^{-1}$

determination of Al, V, Cr — by the ICP OES spectrometer GBC Integra

XLZ. The detection limit:

Al — 0004 mg l⁻¹; V — 0.001 mg l⁻¹; Cr — 0.001 mg l⁻¹.

Note: the accuracy of the methods used is currently verified by participation in tests organized by ASLAB organization.

Evaluation of Results

Physical properties of the samples were investigated. The leachability of some metals was also analysed and the measured values were compared with the standardized ones (see Table I).

Table I Limiting values according to the Ministry of Environment Public Notice No. 338/98

Leachability Class	I/I	I/II	II	III
pH	5.5 – 11.0	6.5 – 8.0	5.5 – 13.0	5.5 – 13.0
Conductivity, mS m ⁻¹	150	40	300	-
Al, mg l ⁻¹	2.0	0.2	10.0	-
As, mg l ⁻¹	0.1	0.05	1.0	5.0
Cr, mg l ⁻¹	0.1	0.05	1.0	50.0
V, mg l ⁻¹	0.2	0.05	0.2	20.0

- I. The recipe No. 2 is not useful (addition of dolomite lime) because the sample did not form the compact hard product to stand the 300 days stability test. So it strongly depends on the weather and cannot be accepted for deposition and commercial utilization.
- II. The best results were obtained with recipe No. 4.
- III. It follows from the comparison of materials produced according to the recipe No. 2 (the worst one) and No. 4 (the best one) with the limiting values in the leaches (see Table I):
 - (i) because of the facts mentioned in paragraph I, the samples made according to the recipe No. 2 deposited in the laboratory only were analyzed
 - pH: the values reach to the leachability class I/I
 - Al: the concentrations pertain to class I/I (excluding the first analysis)
 - As: class II
 - Cr: class II
 - V: the values oscillate around the limit for class I/I
 - (ii) the recipe No. 4

- pH: the values after 28 days belong to class I/I, but they successively reached class I/II
- Al: class I/I, but after the period of 210 days the concentrations belonged to class I/II
- As: throughout the investigation the values reached class I/I, but analyses of the compact block conform to class I/II
- Cr: class I/II
- V: class I/I, the analyses of the compact block oscillated between the classes I/I – I/II

IV. It can be concluded that there is not important difference in the leachability tests of the studied materials processed by water or diluted acid ($\text{pH} = 4.5$), i.e. the leachability will probably not be changed in the case of acid rains.

A slight dependence of amount of extracted arsenic on pH can be observed. The decrease of pH values from basic to neutral causes the increase of the extracted amount. This fact will be verified by further experiments.

V. According to the experiments reported, the best binding material is lime produced by the Prachovice cement factory.

Tables

In the following survey the results of analyses of the samples prepared according to the recipes Nos 2 and 4 are presented.

Table II Water leach, the sample deposited in the laboratory — recipe No. 2

Time, days	pH	Conductivity, mS m^{-1}	Ca, mg l^{-1}	Al, mg l^{-1}	As, mg l^{-1}	Cr, mg l^{-1}	V, mg l^{-1}
0	11.9	50	180	3.244	0.108	0.031	0.099
7	10.6	50	160	1.192	0.249	0.015	0.263
28	9.8	260	220	0.444	0.316	0.016	0.297
56	8.8	230	270	1.247	0.301	0.086	0.149
90	10.5	205	178	0.226	0.350	0.007	0.172
210	8.5	88	160	0.619	0.205	0.023	0.699
240	8.3	73	160	0.222	0.249	0.006	0.112
300	9.2	128	170	0.210	0.185	0.010	0.094

Table III Leaching at pH = 4.5 the cube, deposited in the laboratory — recipe No. 2

Time, days	pH	Conductivity, mS m ⁻¹	Ca, mg l ⁻¹	Al, mg l ⁻¹	As, mg l ⁻¹	Cr, mg l ⁻¹	V, mg l ⁻¹
0	11.7	50	200	2.665	0.865	0.032	0.217
7	9.1	45	200	0.511	0.033	0.016	0.206
28	10.3	195	190	0.300	0.310	0.017	0.277
56	8.8	250	270	1.512	0.328	0.101	0.137
300	7.8	82	160	0.200	0.180	0.009	0.090

Table IV Water leach, the sample deposited in the laboratory — recipe No. 4

Time, days	pH	Conductivity, mS m ⁻¹	Ca, mg l ⁻¹	Al, mg l ⁻¹	As, mg l ⁻¹	Cr, mg l ⁻¹	V, mg l ⁻¹
0	12.8	450	120	0.016	0.007	0.011	0.007
7	12.2	850	90	0.146	< 0.001	0.025	0.019
28	10.5	500	15	1.805	0.012	0.041	0.083
60	9.2	640	700	1.066	0.200	0.087	0.208
210	8.8	178	561	0.062	0.072	0.005	0.186
300	6.7	231	611	0.085	0.072	0.010	0.095

Table V Water leach, the sample in the open air — recipe No. 4

Time, days	pH	Conductivity, mS m ⁻¹	Ca, mg l ⁻¹	Al, mg l ⁻¹	As, mg l ⁻¹	Cr, mg l ⁻¹	V, mg l ⁻¹
60	9.3	520	562	0.139	0.040	< 0.010	0.071
300	7.7	143	441	< 0.010	0.043	0.008	0.071

Table VI Water leach, the cube, deposited in the laboratory — recipe No. 4

Time, days	pH	Conductivity, mS m ⁻¹	Ca, mg l ⁻¹	Al, mg l ⁻¹	As, mg l ⁻¹	Cr, mg l ⁻¹	V, mg l ⁻¹
0							
7							
28	10.1	110	10	1.002	0.016	0.044	0.053
60	9.2	205	176	0.240	0.028	0.010	0.042
300	7.9	98	190	< 0.010	0.051	0.004	0.036

Table VII Water leach, the cube, in the open air — recipe No. 4

Time, days	pH	Conductivity, mS m ⁻¹	Ca, mg l ⁻¹	Al, mg l ⁻¹	As, mg l ⁻¹	Cr, mg l ⁻¹	V, mg l ⁻¹
60	8.5	220	166	0.110	0.052	< 0.010	0.043
300	8.0	666	992	0.039	0.096	0.097	0.111

Table VIII Leaching at pH = 4.5 the cube, deposited in the laboratory — recipe No. 4

Time, days	pH	Conductivity, mS m ⁻¹	Ca, mg l ⁻¹	Al, mg l ⁻¹	As, mg l ⁻¹	Cr, mg l ⁻¹	V, mg l ⁻¹
0	12.8	440	118	0.015	0.006	0.013	0.006
7	12.3	845	91	0.132	< 0.001	0.023	0.023
28	10.5	490	140	1.800	0.120	0.042	0.079
60	6.4	490	120	0.950	0.036	0.027	0.079
300	8.5	684	530	< 0.010	0.088	0.007	0.070

Table IX Leaching at pH = 4.5 the cube, in the open air — recipe No. 4

Time, days	pH	Conductivity, mS m ⁻¹	Ca, mg l ⁻¹	Al, mg l ⁻¹	As, mg l ⁻¹	Cr, mg l ⁻¹	V, mg l ⁻¹
60	9.6	450	495	0.143	0.061	0.010	0.177
300	8.1	534	992	0.010	0.088	0.007	0.069

Conclusion

Evaluation of the long-term stability test (300 days) revealed that the best recipe for the production of the stabilizate is No. 4. The product of the recipe can be deposited on the ponds without further safety precautions. It can also be utilized in the field of civil engineering with regard to its obeying the leachability class I/II for the investigated metal elements. However, it should be verified for a longer time period.

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