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Part 3

ASH AND SLAG HANDLING

3.3. Ash and slag properties

3.3.2. Assessment of the degree of tpp ash-and-slag waste hazard for environment and human health

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ABSTRACT

The mineral part of coals with acid ash is approaching in its composition to the sedimentary rocks of Earth crust, which create the habitat for flora and fauna. Therefore the ash-and-slag waste after combustion of such coals must not be very hazardous both for environment and human health. It was established that the insignificant excess of potentially dangerous small elements in comparison with their content in sedimentary rock will not place in the TPP ash and slag in the category more hazardous for environment than in sedimentary rocks. Therefore the overwhelming majority of such ash and slag relates to the 5th class, i.e. to the practically safe waste.

The TPP ash-and-slag waste is classified abroad as not hazardous that is reflected in the main EU normative documents.

1. GENERAL POSITIONS

In our country the degree of waste gravity for environment (WGE) and human health is estimated by a few normative documents. The basic ones of them are: «Criteria of rating hazardous waste to the class of threat to environment» approved by Order of Ministry of Natural Resources (MNR) no.511 in June 15, 2001 and SanPiN 2.1.7.1386-03 «Sanitary rules for determination of hazard rating of toxic waste of production and consumption» approved by RF Ministry of Health in June 16, 2003. In accordance with these documents the assessment of waste hazard rating can be carried out by calculating and experimental methods. The priority is here given to the experimental methods, however the hazard rating can be approximately estimated by the method of calculating its component content.

The degree of waste gravity for environment subdivides into 5 classes, for human health – into 4 classes (Table 1). The essence of both calculating methods consists of the fact that the values of hazard rating coefficients for each component of waste W_i are determined by means of combination of a few hygienic, toxicological and other component characteristics; these coefficients allow to determine the hazard rating indicators K_i of these components; and the summary value of hazard rating of total waste K is found by the sum K_i. Then the accessory of waste to some or other hazard rating is determined by Table 1.

It should be noted here that the calculating methods demand a certain qualification, because, as a rule, the results of waste analyses are given by analytical laboratories in the form of elemental composition, while the calculation should be carried out by component content [1]. The recalculation of element composition in component content represents the certain difficulties.

A calculation of the degree of waste gravity on «Criteria…» of MNR and SanPiN 2.1.7.1386-03 is practically the same in its structure. But the experimental methods are substantially different. The experimental part for MNR "Criteria…" consists of determining the probability of survival in water draws from the waste of two test-organisms from the different taxon groups. The experimental investigations for SanPiN 2.1.7.1386-03 are more complicated and include the evaluation of waste components migration in air, water, soil, vegetative tests, impact on warm-blooded organisms etc.

Table 1. **Classification of waste hazard rating**

Hazard rating	1st class Extremely hazardous	2nd class Highly hazardous	3rd class Moderately hazardous	4th class Low-hazard	5th class Practically not hazardous
«Criteria…»	$10^6 \geq K \geq 10^4$	$10^4 \geq K \geq 10^3$	$10^3 \geq K \geq 10^2$	$10^2 \geq K \geq 10$	$10 \geq K$
Sanitary rules and standards (SanPiN)	$K > 5\ 10^4$	$5 \cdot 10^4 \geq K \geq 10^3$	$10^3 > K \geq 10^2$	$10^2 > K$	—

Taking into account the above described positions, we will consider the degree of TPP ash-and-slag waste (after coal combustion) gravity on the environment and human health.

2. DEGREE OF ASH AND SLAG GRAVITY FOR ENVIRONMENT

The coals are the same sedimentary substances, their composition includes the same minerals, which exist in sedimentary. The sedimentary rocks are the most widely-spread rocks, which form the habitat for flora and fauna including for human. The clay minerals are ones of the most widely-spread sedimentary rocks, and they cover more that 50 % area occupied by these rocks [2].

Accordingly to available data, the largest amount from the general content of mineral substances in coals is formed by clay minerals (first of all, hydromica, then by kaoline clays, montmorillonites) and then in descending degree – by quartz (SiO_2), limonite ($mFe_2O_3 \cdot nH_2O$), pyrite (FeS_2), feldspars, siderite ($FeCO_3$), calcite ($CaCO_3$), etc. [3].

By the data of pedologists, the loose sedimentary rocks are also the parent material, from which the soils are formed [4]. The mineral components of sedimentary rocks undergo some changes depending on the conditions of bedding. In particular, a part of aluminum containing in the clay minerals of soils, in which there is the subacid medium because of decay of plant residues (humic acid), is going to the water-soluble state and is migrating with underground waters. Therefore, as a rule, the aluminum content of soils is a little less than in the parent beds.

Thus, the mineral part both of coals and soils is geneticall-y connected with the sedimentary rocks. A mineral part in the coals with acid ash composition (the CaO content is less than 10 %, GOST 25818-91) consists by 2/3 of clay minerals. The variations of compositions for the most widespread clay types, the main types of soils and the average composi-

tion of acid sedimentary rocks (clays and oil shale [5] are presented in Table 2. The main types of soils (7 types of soils: tundra, light-grey podsolic, grey and dark-grey, chernozem, chestnut and brown, aerial, laterite soils) were taken accordingly to V.V.Dokuchaev [6], their compositions — from Geochemical Manual [5]. As it is seen from Table, the clay minerals, soils and sedimentary rocks have approximately the same chemistry (elemental composition).

Table 2. **Ranges of composition variations for clay minerals, main types of soils and average composition of sedimentary rocks, mass %**

Element	Clays	Soils	Sedimentary rocks
SiO_2	43.6…62.9	31.8…80.0	58.8
TiO_2	0.2…2.1	0.6…1.2	0.9
Al_2O_3	14.8…38.9	8.5…27.0	22.8
Fe_2O_3	1.0…9.2	1.7…9,8	5.5
CaO	0.2…4.1	0.3…4.7	4.1
MgO	0.2…5.4	0.6…2.0	2.6
K_2O	0.3…5.6	0.3…3.1	3.2
Na_2O	0.2…2.7	0.1…2.1	1.0
SO_3	0.01…0.6	<0.1…0.6	0.9
P_2O_5	—	0.1…0.3	0.2
MnO	0.0…0.05	0.0…0.1	0.1

It is pointed out in two mentioned procedures for assessment of waste hazard rating both for environment and population health that the waste components consisting of the chemical elements with the content not overwhelming their content in the main types of soils (correspondingly in the sedimentary rocks) are relating to the practically not hazardous components.

In VTI the component contents of ash-and-slag waste under investigation [7] were established, when ash-and-slag hazard rating for environment was determined by the results of chemical analysis. The component contents of ash-and-slag waste after combustion of coals of main deposits with the acid ash composition are presented below in Table 3.

Table 3. **Component contents of ash-and-slag waste for coals of main deposits, mass %**

Coal	$C_{ПО}$	C_S	C_{Fe}	C_c	$C_{МЭ}$
Kuznetsky [7]	83…95	< 2.7	< 0.8	1.2…17.0	0.2…0.3
Ekibastuzsky	91…97	< 2.2	—	5.8…7.7	0.2
Pechorsky	92…96	< 3.9	< 2.3	3.6…12,9	0.2
Irkutsky	86…98	< 3.9	< 5.0	0.8…9.1	0.1…0.3
Chelyabisky	92…98	< 2.2	< 4.3	1.6…3.8	0.2…0,3
Neriunguinsky	94…96	< 1.0	—	4.0…4.4	0.1…0.2
Background content in sedimentary rocks [5]					0.161

As seen from this Table, the ash-and-slag waste of TPP consists by 83-98% of the rockforming components (C_{RF}), i.e. from the same substances, which are typical for the sedimentary rocks. Therefore they can't create the considerable threat both for environment and population health. Another 2…17 % falls on the unburned carbon (C_c = 0.8…16.8 %), anhydrite $CaSO_4$ (C_S up to 4 %) and ferric oxide Fe_2O_3 (C_{Fe} up to 5 %). All these substances are also not hazardous. Only the small elements (C_{SE} — V, Cd, Mn, Cu, As, Ni, Hg, Pb, Sr, Cr, Zn), when their total content in ash and slag doesn't exceed 0.3 %, can be potentially hazardous for environment and population health. Actually the calculations show that in spite of so low their content in ash-and-slag waste the share of these elements in indicators of gravity can achieve 10 % in calculating the hazard rating for environment and 40…50 % — in calculating the hazard rating for a human. Taking into account the insignificant excess of these elements over the background content, their content is, as a rule, not enough for going the ash-and-slag waste to the more hazardous zone. It was also confirmed by biotesting. The biotesting of aqueous extracts from ahs-and-slag waste after combustion of coals with acid ash confirmed their accessory the 5th class, i.e. to the waste practically not hazardous for environment.

Thus, it is possible to consider as established that the TPP ash-and-slag waste after burning coals with acid ash composition doesn't present the threat for environment (of the 5th class).

3. DEGREE OF ASH-AND-SLAG IMPACT ON POPULATION HEALTH

The assessment of ash-and-slag hazard threat for human health is much more complicated. The special feature of calculating part of SanPiN 2.1.7.1386-03 is the fact that this procedure doesn't allow to calculate the accessory of the safest substances to the most hazardous ones. Even the components, which are by definition practically not hazardous (SanPiN, item 4.4.5) cover the 3rd hazard class, but not the 4th one. It overestimates substantially the hazard rating of waste for human health. In the same time the medical workers gathered in last years the sufficient amount of experimental material testifying the absence of hazardous properties of TPP ash-and-slag waste after coals combustion of coals with acid content of ash.

In 1992 the RF Government made a Decision «On approval of order in determining the payment and limits of its size for environmental contamination, waste disposal and other kinds of hazardous impact». This Decision installed the payment for storing 6 classes of waste - 4 toxic ones and 2 not toxic ones, to which the waste of processing and extractive industry were related. In this case the difference in storing the toxic and not toxic waste differs in ten's times. In connection with the originated disputed between nature-protective bodies (conservancies) and power engineers on the matter of being TPP ash-and-slag waste toxic or not, a series of medical agencies carried out the tests on evaluation of toxicity level of these waste. The following medical concentration centers took part in studying the ash-and-slag waste after combustion of Ekibastuze, Kuznetsky, Sverdlovsky, Chelyabinsky and other coals with acid ash composition:

- Medical scientific center of preventive health care and health protection of industrial enterprise workers, city Ekaterineburg;
- Regional toxilogical center in Kemerovo region;
- Moscow F.F.Eriksman Scientific-Research Hygienic Institute;
- Institute of toxicology, city Saint-Petersburg;
- SRI of hygienics, professional pathology and human ecology, city Saint-Petersburg;
- Kemerovskaya State Medical Academy, city Kemerovo.

The following toxicity levels have been investigated: acute toxicity, long-term effects (gonadotoxic and mutagenic effects), toxicity by biotesting methods for coaching the seed, on daphnids, with single and repeated impacts on mousse and rats, with impact on microorganisms, toxicity with the single intragastric introduction to animals, with intraperitoneal introduction. All investigations showed that the TPP ash-and-slag waste are not toxic or are related to the 4th class

of hazard rating in accordance with the vocabulary adopted in SnPiN 2.1.7.1386-03.

It should be noted here that the volume of tests for carrying out the hazard rating accordingly to SanPiN 2.1.7.1386-03 is extremely high as to the ash-and-slag waste. It complicates substantially the obtaining of sanitary epidemiologic conclusion for enabling to use the ash-and-slag waste in construction industry. Taking into account that the waste of coal-extracting and processing industry constitutes more than 50 % of all waste formed in Russia; it seems to be expedient to develop the procedure for hazard rating of waste of such type by abbreviated program.

Abroad the fact of hazardous properties absence for TPP ash-and-slag waste was installed a long time ago. The TPP ash-and-slag waste is considered as not hazardous in the total world (a term «toxic» is not used there with respect to ash-and-slag waste).

The convention on control over Tran boundary transportation of hazardous waste and their removal was passed in March 1989 in Basel. In March 1992 the countries-members of Organization on economic cooperation and development approved the system of control over the Tran boundary transportation of waste [8]. This document divides all the waste in three lists depending on their hazard: Red, Yellow and Green ones. The Red and Yellow lists include the waste possessing one or multiple hazardous properties. The waste included in Green list don't possess no one from the hazardous properties (toxicity, carcinogenicity, teratogenicity, mutagenicity, ecotoxicity) listed in Directive EC 91/689/EEC on hazardous waste [9]. The TPP ash-and-slag waste is included in Green list in this document The Basel convention was ratified by Federal Law of Russian Federation no. 49-ФЗ in November 25, 1994. Actually the ratification of convention is per se the admission of the fact that the TPP ash-and-slag waste relate to the safe waste.

A catalogue with pointing the waste, which is hazardous or safe, was put into action in EC in 2002 [10]. Ash and slag waste of coals are related in this catalogue to the safe ones, (items 0 01 01 and 10 01 02 of catalogue), oil ash – to the hazardous waste (item 10 01 04).

Each State of the USA has its own criteria for hazard rating of waste. There are the most rigid requirements to the hazard rating of substances and, in particular, of waste in State California [11]. The hazard rating in this state is primarily determined by the content of microelements, for which the maximum allowable concentrations (MAC) is established and above which the waste is related to the hazardous ones. It was installed that there is no one country in the world, where the content of microelements exceeds these MAC. So, at rates or standards of USA the ash-and-slag waste after combustion of coals with acid ash composition are also related to the safe one.

Thus, the absence of hazardous properties of TPP ash-and-slag waste was established by many works of scientists in different countries, and it was reflected in the series of normative documents.

Accordingly to data being available in VTI, the ash-and-slag waste of acid composition has been studied by some medical concentration centers already after publishing SanPiN 2.1.7.1386-03. The results of studying ash-and-slag waste after combustion of Ruznetsky coals at TPP's Kuzbassenergo, Novosybirskenergo are the same that were obtained in the end of XX century (see above), i.e. they have no toxic properties that allows by new classification to relate them to the 4th class. Nevertheless, the local bodies of Rospotrebnadzor (supervision bodies) demand to carry out the high-priced and now already not expedient tests of ash-and-slag waste from combustion of Kuznetsky coals once and once more. It is just a time for leading medical concentration center to rush these bodies to the established things

4. CONCLUSION

1. The ash and slag after combustion at TPP of pulverized coals with acid ash composition have the chemistry and component content approaching to the composition of sedimentary rocks; the summary content of potentially hazardous small elements in some ash-and-slag waste is a little higher, however not in such degree that allows going them to the category of more hazardous ones for environment.

2. The investigations carried out up to now showed that, as a rule, the ash and slag of acid compositions relate to the class of practically not hazardous for environment (the 5th class).

3. A few medical concentration center found the absence of toxic properties for ash-and-slag waste that allows relating them to those that are low-hazardous for human health (the 4th class). However the existing data is insufficient for the final conclusion. It is necessary to generalize the existing data and to create the program of further tests in this direction.

4. Taking into account the proximity of TPP ash-and-slag composition to that in sedimentary rocks, it is necessary to shorten the volume of their tests by SanPiN that will simplify the procedure of obtaining sanitary-epidemic conclusion and remove this barrier on the way to ash-and-slag utilization in construction industry.

5. As to the foreign normative documents (Classifier of waste of 2002 and Basel Convention on transboundary transportation of waste), the ash-and-slag waste after coals combustion at TPP are related by them to the safe ones.

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