CHARACTERISTICS OF THE FLY ASH AND SLAG RESULTED FROM PULVERIZED COAL COMBUSTION IN PAROSENI POWER PLANT

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The fly ash and corresponding slag, formed during pulverized combustion of Valea Jiului energetic bituminous coals and deposited in the close vicinity of power stationi, represent a bulky waste with a strong ecological impact including possible adverse health effects. The big fly ash and slag quantities are, primarily, a consequence of the high content of coal associated mineral matter, that influences the burnout structure and chemical composition.

This paper presents the chemical and energetical characteristics of some collected samples of fly ash and slag resulted from Valea Jiului coals combustion in Paroseni power plant.

Cenuşile zburătoare şi zgurile corespunzătoare rezultate din procesul de ardere prin pulverizare a huilelor energetice de Valea Jiului reprezintă un deşeu cu un puternic impact ecologic, cu efecte negative asupra stării de sănătate a locuitorilor din vecinatatea termocentraleii. Procentul ridicat de cenuşă este consecința cantității mari de material mineral asociat cărbunelui care influențează compoziția chimică şi structura reziduului solid.

În lucrare se prezintă caracteristicile chimice şi energetice ale unor probe de cenuşi şi zguri rezultate din arderea huilelor energetice de Valea Jiului în termocentrala Paroşeni

Keywords: pulverized coal combustion, burnout, fly ash, slag, oxidic composition, energetic bituminous coal

1. Introduction

The solid burnout quantity generated during pulverized coal combustion has a large variation in volume, chemistry and grain size, depending on parent coal characteristics – rank and petrographic composition – but also influenced by coal preparation and burning parameters [1.5.7.10.11].

From the pulverized fuel combustion process of Valea Jiului low rank bituminous coals (usually coal blends with a high mineral matter content, between

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40 – 70%), it results large fly ash quantities with a very fine grain sized proportion.[9.11] This involves adecquate technical measures to decrease the environment impact.[1.4]

In order to estabilish the proper possibilities of using these waste deposits or destroing them, it is necessary to find out their composition and characteristics.[1.5.6.9.11.15]

2. Experimental

Grouping the samples according to Table 1 in $\mathbf{P_1+P_2}$, $\mathbf{P_3+P_4}$, $\mathbf{P_5+P_6}$ was made because of their sampling possibility: electrofilter ashes and slag were taken from the collecting sacks and slag extinguishing line; hydraulic ash – slag blend, from the burnout deposits.

To determine the major- and microconstituents of the fly ash and slag collected samples, there were used analytical methods: plasma emission spectrometry and atomic absorbtion (ICP-AES) using the procedure described in national and international standards.

3. Results and discussion

The experimental results regarding chemical composition in oxides and microelements, and their energetical characteristics are given in Tables 1 – 4.

The variation of some interesting factors from scientific and practical viewpoints is presented in Figs. 1 – 6.

Table 1

Oxides composition of fly ash and slag, % wt

Nr crt	Sample	SiO_2	TiO_2	Al_2O_3	MnO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3
1.	**Electrofilter ash P1+P2**	53.99	1.03	25.64	0.09	8.70	2.05	2.78	1.42	2.88	0.38	0.71
2.	**Ash+slag P1+P2**	55.76	1.02	25.43	0.06	7.68	1.98	2.59	1.34	2.78	0.32	0.82
3.	**Slag P1+P2**	54.21	0.96	25.75	0.06	8.16	1.88	2.19	1.37	2.87	0.35	1.36
4.	**Electrofilter ash P3+P4**	54.28	0.94	25.33	0.08	9.24	1.88	3.29	1.05	2.68	0.36	0.48
5.	**Ash+slag P3+P4**	55.92	0.98	23.89	0.09	7.68	1.80	3.16	1.12	2.63	0.35	1.85
6.	**Slag P3+P4**	57.30	0.92	23.27	0.08	9.16	1.82	3.21	0.88	2.29	0.35	0.75
7.	**Electrofilter ash P5+P6**	54.07	0.97	26.40	0.07	8.22	1.82	2.23	1.15	2.97	0.33	1.33
8.	**Ash+slag P5+P6**	52.88	0.82	18.12	0.17	12.94	2.75	4.46	1.26	2.25	0.37	3.16
9.	**Slag P5+P6**	55.30	1.05	26.20	0.07	7.11	1.68	2.24	1.58	2.85	0.50	1.22

Tabel 1 presents oxides composition of the fly ash and slag for 9 types of samples which are representative for the collected material and were taken in three periods of time.

These values are used for their energetic characterization given in Tabel 2 and 3.

These main characteristics [8.11.12] are expressed by the corresponding (according to Romanian standards)

Basicity ratio (R_b):

$$R_b = (Fe_2O_3+CaO+MgO+Na_2O+K_2O) / (SiO_2+Al_2O_3) \quad (1)$$

Si content (Si):

$$Si = (SiO2) / (SiO_2+Fe_2O_3 +CaO+ MgO)x\ 100, [\%] \quad (2)$$

Fusion criterium expresed by the ratio (F_c):

$$F_c = (SiO_2+Al_2O_3) / (Fe_2O_3+CaO+MgO) \quad (3)$$

When F_c value is < 5, the ash is slightly fusible.

Ash fusion critical temperature (T_{cr}):

$$T_{cr} = 2990–1470SiO_2/Al_2O_3+360(SiO_2/Al_2O_3)^2–14,7(Fe_2O_3+CaO+MgO)+ 0,15(Fe_2O_3+CaO+MgO)^2, [K] \quad (4)$$

Ash characteristics depend on coal type (rank petrographic composition, associated mineral matter) and burning conditions. The ash resulted types may be grouped in four classes:

1) alumino-silicious, when SiO_2/Al_2O_3 > 2 and CaO < 15%;
2) silico – aluminous, when SiO_2/Al_2O_3 < 2 and CaO< 15%; 3) sulpho – calcic, when CaO >15% and SO_3 > 3%; and 4) calcic, when CaO > 15 % and
   SO_3 < 3%. [1.3]

According to the obtained values, all the fly ash and slag studied samples are classified as acid ones (subunitary basicity ratio) of alumino-silicious type.

Concerning the fusibility, expressed by the fusion criterium, it was observed a different behaviour, because of the fact that the oxides groups, that produce critical fusion temperature increase (ex. P_5+P_6 with SiO_2=52.88%; Al_2O_3=18.12%, SiO_2/ Al_2O_3 = 2.92). Its knowledge is very important to avoid burning residuum slagging, a process with negative economic effects: decrease of the heating transmission and boiler output as well as of the corresponding equipments safety exploatation.

Fig 1 presents Ca, Na, K, Mg, Al and Si oxides influence on ash melting temperature.

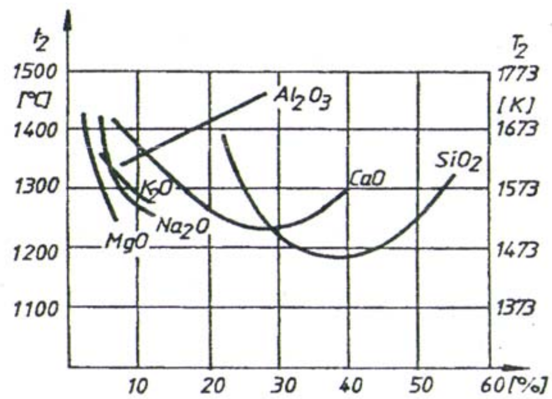


Fig 1 Influence of CaO, Na_2O, K_2O, MgO, Al_2O_3 and SiO_2 on the ash melting temperature, [12]

Table 2

The type of fly ash and slag resulted from Valea Jiului coals combustion

Nr crt	Sample	SiO_2	Al_2O_3	SiO_2/Al_2O_3	CaO	SO_3	T_{cr}	Ash and slag type
		%	%		%	%	K	
1.	**Electrofilter ash P1+P2**	53.99	25.64	2.11	2.78	0.71	1318	Alumino-silicious
2.	**Ash+slag P1+P2**	55.76	25.43	2.19	2.59	0.82	1488	
3.	**Slag P1+P2**	54.21	25.75	2.11	2.19	1.36	1332	
4.	**Electrofilter ash P3+P4**	54.28	25.33	2.18	3.29	0.48	1312	
5.	**Ash+slag P3+P4**	55.92	23.89	2.34	3.16	1.85	1361	
6.	**Slag P3+P4**	57.30	23.27	2.46	3.21	0.75	1373	
7.	**Electrofilter ash P5+P6**	54.07	26.40	2.05	2.23	1.33	1330	
8.	**Ash+slag P5+P6**	52.88	18.12	2.92	4.46	3.16	1530	
9.	**Slag P5+P6**	55.30	26.20	2.11	2.24	1.22	1334	

Table 3

Ash and slag characteristics resulted during combustion

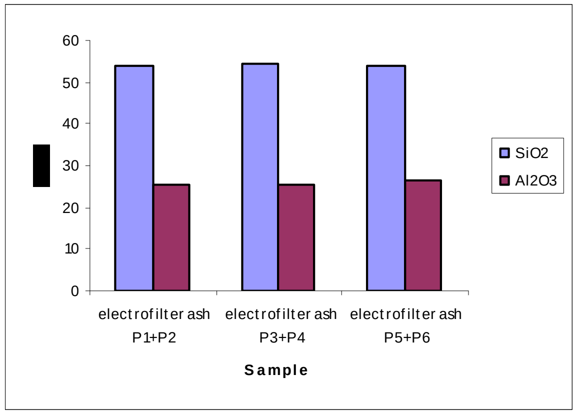
Nr crt	Sample	SiO_2/Al_2O_3	R_b	Si	F_c	T_{cr}
				%		K
1.	**Electrofilter ash P1+P2**	2.11	0.22	79.96	5.89	1318
2.	**Ash+slag P1+P2**	2.19	0.20	81.98	6.63	1488
3.	**Slag P1+P2**	2.11	0.21	81.59	6.54	1332
4.	**Electrofilter ash P3+P4**	2.18	0.23	79.02	5.52	1312
5.	**Ash+slag P3+P4**	2.34	0.21	81.56	6.31	1361
6.	**Slag P3+P4**	2.46	0.22	80.15	5.68	1373
7.	**Electrofilter ash P5+P6**	2.05	0.20	81.50	6.59	1330
8.	**Ash+slag P5+P6**	2.92	0.33	72.40	3.52	1530
9.	**Slag P5+P6**	2.11	0.19	83.37	7.39	1334

R_b = basicity ratio; Si = Si content; $F_c = (SiO_2+Al_2O_3)/(Fe_2O_3+CaO+MgO)$

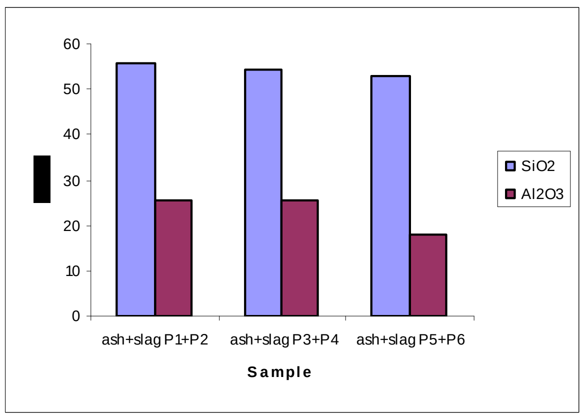
It is interesting to mention that for electrofilter ash and ash – slag P_3+P_4 blends, with Fe_2O_3 content of 9.24%, respectively 9.16%, T_{cr} have the lowest values: 1312 and 1573 K (Fe_2O_3 diminishing critical fusion temperature).

The gravity separation of particles produced same differences refering to their chemical composition. This aspect was observed to P_1+P_2 and P_3+P_4 (electrofilter ash and corresponding slag), that present similar values for Fe_2O_3 8.70% ÷ 8.16% and 9.24% ÷ 9.16%, while the values for samples set P_5+P_6 are different: % Fe_2O_3 is higher in the case of ash – slag hydraulic blend: 12.94% and 8.22% for ash, respectively 7.11% for slag.

Fig. 2 gives the homogeneous repartition of principale oxides (SiO_2 and Al_2O_3) for all samples, that confirm the classification criteria of ash chemical types (Table 2): all being of aluminosilica type.



a



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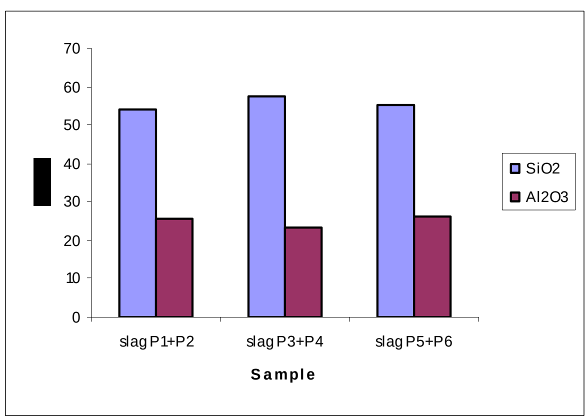

c

Fig. 2 The variation of Si and Al oxides for each sample type:
a- electrofilter ash;**b-** ash – slag blend: **c-** slag.

The variation of alkaline oxides composition, directly responsable for specific temperatures differences shown in Fig 3, presents narrow intervals for: Na_2O (0.88 – 1.58 %gr.), K_2O (2,25 – 2.97 %gr.), MgO (1.68 – 2.75 %gr.), excepting CaO (2.23 – 4.46 %). CaO is not so significant to modify the melting temperature, as shown in Fig.1 (only over 30% CaO can determine an important increase).

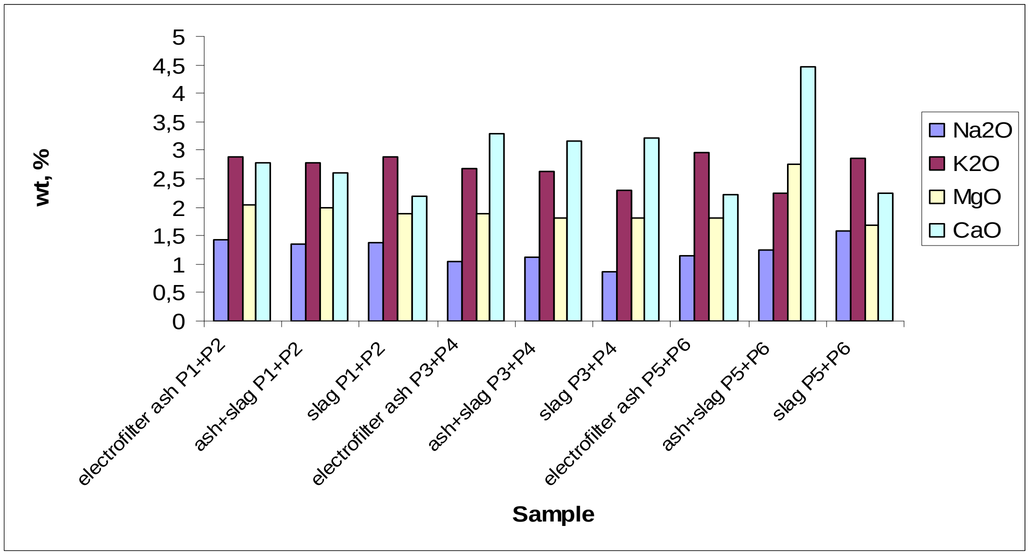

Fig. 3 The variation of alkaline oxides composition

Coals enrichment in some elements which are found in their burning residues, ash and slag, is, in most cases, due to the deposit conditions, especially to the percolated water that has transported both Mg, Ca, Fe salts and pyrite, marcasite, (ionic type reactions in the presence of humic acids).

The microelemental composition of fly ash and slag is presented in Table 4 and Fig 4 – 6.

From all determined microelements Ba content has the highest values for all six samples. The minimum value is for the ash+slag blend P_5+P_6 (450 ppm) and the maximum value, for P_1+P_2 slag (2438 ppm).

The high Ba content in Valea Jiului coals is an interesting fact from scientific and practical viewpoints (in respect with the special carbon products properties). Its variation for the studied samples is given in Fig 4.

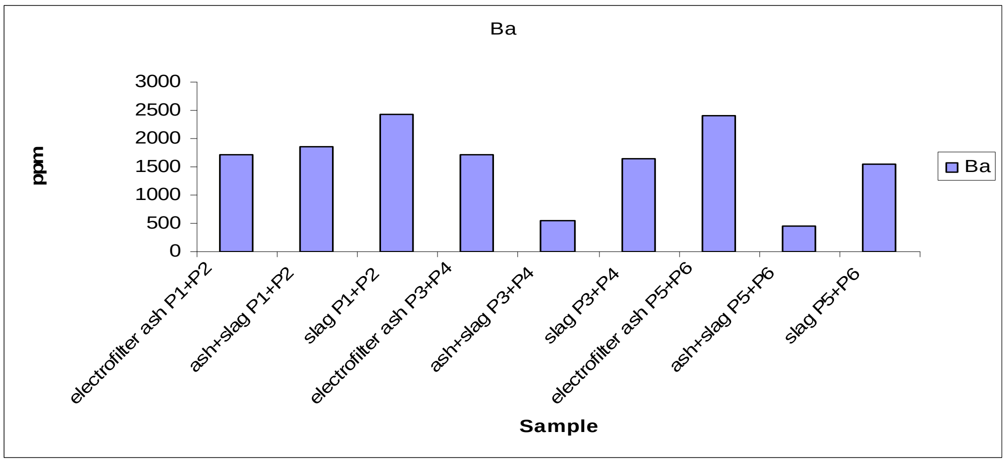

Fig.4 The variation Ba content of fly ash and slag samples

Another environmental problem is represented by their content of heavy metals (eliminated with the burning gases), waste water, slag and ash, which can produce adverse health effects. The main elements found in our samples and their content in the samples are given in Fig 5.

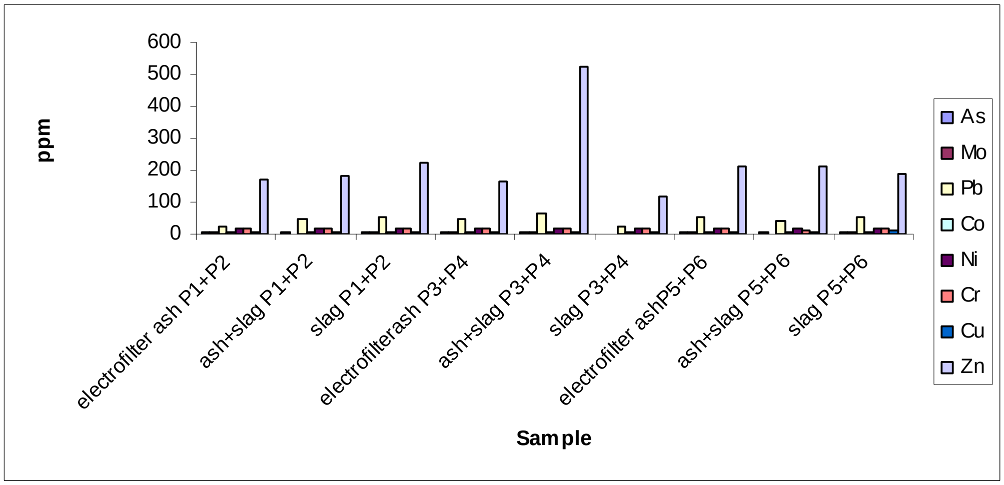

Fig. 5 Variation of fly ash and slag samples heavy metals content

It is observed a homogeneous content of these microelements with an exception for the ash+slag blend P_3+P_4, that has the highest values of Zn (521 ppm).

Coal as the all environmental elements, has a discreete radionuclides content: Th, U and their dezintegration products. By their distribution on the earth surface and their concentration in industrial areas, they may generate unbalanced fenomena of the natural radioactivity. As is showed in Fig 6, Th and U have limited variation intervals (13.97 – 22.37 ppm and 4.48 – 10.82 ppm respectively), but these values do not exceed the standards actually in use.

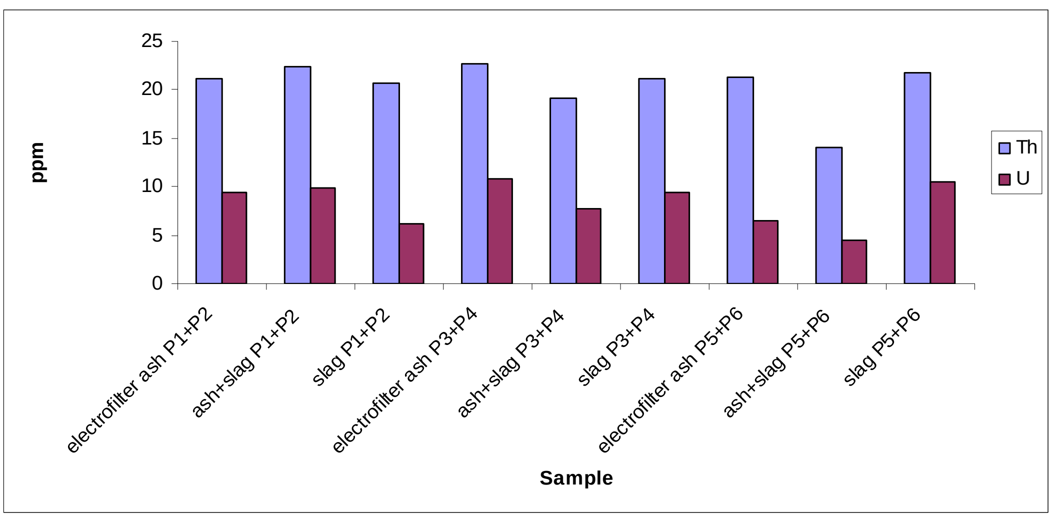

Fig. 6 Variation of radioactive microelements content, Th, U, ppm

4.Conclusions

- During pulverized coal combustion mineral matter is transformed – by a complex mechanism and associated fenomena specific to the burning system – into ash and slag, that have different chemical and mineralogical composition. The determination of the major– and microelements is very important for their use in different energetic processes.
- Six fly ash and slag samples, collected from Paroşeni power station (special arranged places for combustion residues deposits), have been studied from chemical and energetic viewpoints.
- The experimental study provided important information regarding the oxides composition of fly ash and slag generated during Valea Jiului coals pulverised combustion, giving the possibility to classify them from energetic criteria. Chemical oxides composition revealed a high content of SiO_2 and Al_2O_3, that classifies ash and slag samples in the aluminosilicious type, with acid character.
- The acid ashes can produce major problems to the equipment by chemical corrosion. In the same time the high quantity of very hard mineral matter increases its deterioration degree.
- Microelements concentration is, practically, the same for all samples, with the exception of Ba, V, Ni, Zn and Sr with higher values; but their recovery is not profitable.
- Because of the radioactive elements specific chemical character and discreet quantity, the resulted burnout from Valea Jiului coals pulverized combustion, can be used only in small quantity for the materials construction industry, limited to auxiliary buildings. Blended with sand, in suitable proportion, they are used sometimes for cement manufacturing.
- From the viewpoint of environmental protection it would be recomanded to take corresponding measures, by limiting the fly ashes fine in atmospheric emission, for instance by deposits covering.
- Chemical and energetical characteristics of the fly ashes and slag resulted during Valea Jiului pulverized combustion in Paroşeni power plant, do not rise special problems for the industrial processing.

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Table 4

Microelemental composition of fly ash and slag, ppm

Sample	Li	Be	V	Cr	Co	Ni	Cu	Zn	As	Sr	Y	Zr	Nb	Mo	Sn	Sb	Te	Ba	W	Pb	Bi	Th	U	Ce
Electrofilter ash P1+P2	138	4	19	20	4	18	7	171	7	227	35	131	57	4	1	5	0,1	1712	7	21	0,1	21	9	98
Ash+slag P1+P2	101	4	19	20	4	16	7	180	3	228	35	142	57	2	1	4	0,1	1859	9	48	0,67	22	10	104
Slag P1+P2	136	4	18	15	4	15	8	224	4	220	22	96	52	3	1	2	0	2438	9	53	0,3	21	6	99
Electrofilter ash P3+P4	96	3	17	18	4	16	7	167	3	219	39	186	60	3	1	3	0,1	1709	9	45	0,5	23	11	105
Ash+slag P3+P4	90	3	17	18	3	15	7	521	3	189	22	95	45	4	3	3	0,2	541	10	67	0,4	19	8	94
Slag P3+P4	92	3	17	19	3	17	6	116	2	201	36	175	58	2	1	2	0,1	1644	7	21	0,1	21	9	98
Electrofilter ash P5+P6	125	4	17	17	4	15	7	210	4	212	22	85	47	3	1	2	0,1	2396	8	51	0,1	21	6	99
Ash+slag P5+P6	62	2	14	13	4	18	7	212	5	164	21	74	28	2	1	2	0,2	450	6	43	0,5	14	4	77
Slag P5+P6	100	4	22	20	4	19	9	190	4	209	26	99	51	4	2	4	0,1	1556	10	51	0,2	22	11	98

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