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CHARACTERISATION OF COAL SAMPLES USED IN THE DEVELOPMENT OF NEW COMBUSTION TECHNOLOGY

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Coal is the most abundant source of fossil energy. However, its utilization poses several problems for society, among which are those associated with the formation of atmospheric pollutants during its combustion. Thus, inorganic matter in association with organic nitrogen and sulphur form during combustion complex particulates (fly ash), nitrogen oxides and sulphur oxides. The emission of such pollutants to the atmosphere is undesirable and can be avoided by removing the pollutants from the combustion products, preventing their formation, or removing the constituents which form pollutants from the coal.

In the work developed in the research project, the injection of hydrogen-reach gases (HRG) has been taken into consideration as a method to improve the coal burning process and to reduce the SOx level in burned gases.

In order to understand the factors influencing the pollutants evolution, a complete characterisation of coal utilised for experimental tests of coal burning with HRG injection need to be performed. This paper focused on those analysis methods that are able to highlight mainly the sulphur composition, but also the elemental analysis of organic and inorganic matters that can interfere in chemical pathways of volatile compounds combustion.

Keywords: HRG (hydrogen-reach gases); pollutant emission; clean energy; chemical and structural analysis of coal

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1. Introduction

Despite the fact that the use of fossil fuels is lately subjected to restricted policies, coals is still one of the most important sources of energy. As known, coal combustion emits pollutants such as SO_x, NO_x, CO_2 and CO, which affect the environment. During combustion over 95% of sulphur contained in fuels is oxidised to SO_2. In the atmosphere these compounds oxidise further with free radicals, such as HO and HO_2 to form sulphur trioxide (SO_3). SO_3 can react with water vapours or water drops in the clouds, thus forming sulphuric acid, and with dusts containing metal oxides, forming sulphites [1].

As a result, the proper use of fossil fuels is a high priority for European countries in order to reduce and keep a low level of energy dependency. This is confirmed by the statistics published by EURACOAL in 2011 (Fig. 1) that present the balance of production and imports of different coals by the EU27 https://euracoal.eu/info/euracoal-eu-statistics/.

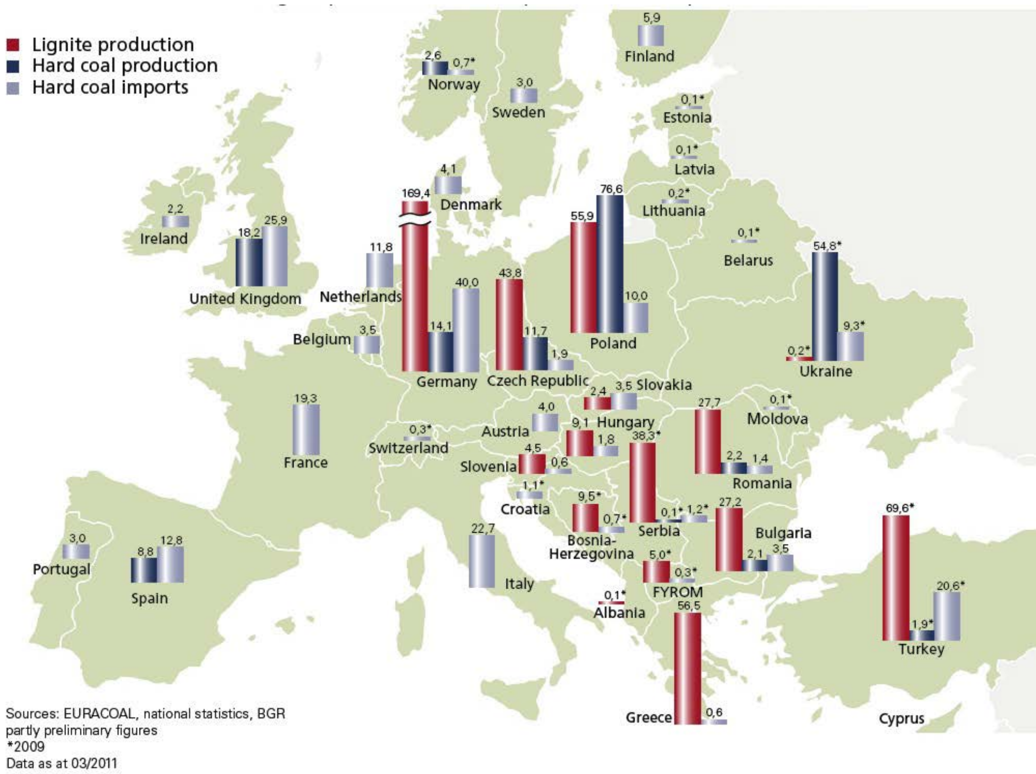

Fig. 1. Coal production and import in EU27

This paper aims the complex characterisation of Romanian lignite used for the development of new combustion technology involving injection of renewable hydrogen.

At present, the production of hydrogen is related to different technologies such as electrolysis of water, steam reforming of hydrocarbons, and biomass conversion into biogas or syngas. There are other methods of producing hydrogen, such as thermo-chemical decomposition of water and photo solar electrolysis. Also, non-conventional energy sources as hydro-energy, solar and wind energy are designed to produce hydrogen [2].

Such are the short and medium term programs designed to start building hydrogen economy also encouraged the effort to save fossil fuels and reduce greenhouse gas emissions.

HRG is a hydrogen enriched gas, obtained from water electrolysis into a generator and which is used in the energy sector and transport. Chemically HRG is a mixture of molecules and radicals (H, O, OH, HO_2, H_2O), H_2 being the main component.

Another remarkable characteristic is that the HRG type used in this work does not require supplementary oxygen for combustion because it contains within it all the oxygen necessary for this purpose. This is a major advantage compared to other fuels used for coal co-combustion, including pure hydrogen, where the supplementary oxygen is requires for combustion. This particularity allows a better pattern for sustainability assessment of HRG technology integrated in coal-based plant.

Current global hydrogen production [3]:

- 48% from natural gas
- 30% from oil
- 18% from coal
- 4% from electrolysis of water

HRG has a density of 0.503 kg/m^3, a molecular weight of 12.3 kg/kmol, an auto-ignition temperature of 591-605°C and a flammability limit concentration between 7.3 and 100% [4, 5]. These characteristics were considered in developing a new technology that aims on the one hand the improvement of coal burning behaviours, knowing that the lignite has low content of volatile matters and, on the other hand, the reduction of SO_2 emissions by changing the involved chemical mechanisms.

2. Experimental work

This paper presents complex characterisation of coal samples used from experiments performed on the 1 MWt pilot furnaces belonging to the University “Politehnica” of Bucharest - Thermal Research Center, using HRG injections at different concentration of hydrogen (30% and 60%) within the pulverized coal (lignite). The difference of gases is represented by O_2.

In this work three samples of coal, with and without treatment with HRG, are characterised. For these three samples the proximate and ultimate analyses have been performed and in *Table 1* the obtained results are presented. The elemental analysis (C, H, O, S, N) has been performed in a Thermo Electron Flash EA1112 elemental analyser. The water content (W) of the untreated coal was determined by drying at 105°C in a drying oven, while for the ash content (A) the samples have been burned in a laboratory bench heating oven at 850°C.

The higher heat value (HHV) of each sample was determined using a calorimetric bomb (Parr Calorimeter – Model 6200).

Table 1

Proximate and ultimate analysis of coal

Sample	H_2 in HRG, [%-vol]	C^i, [%-wt]	H^i, [%-wt]	O^i, [%-wt]	S^i, [%-wt]	N^i, [%-wt]	W^i, [%-wt]	A^i, [%-wt]	HHV^i [kJ/kg]
Coal (P1)	-	34.00	2.61	28.70	1.81	0.64	7.19	25.05	14895
Coal with HRG (P1H30)	30	36.32	3.52	27.63	1.85	0.72	-	25.43	15019
Coal with HRG (P1H60)	60	36.82	3.73	27.12	1.72	0.75	-	25.25	15184

The results presented in Table 1 show that by mixing the coal samples with HRG (67% of H_2 and 33% of O_2) there are very small differences in terms of total amounts of C, H, O, S and N. These differences appear most likely due to a slight loss of hygroscopic moisture during the mixing process.

The inorganic elemental compositions of the samples were analyzed by EDXRF Analysis using an EDX-720/800HS Energy Dispersive X-Ray Fluorescence Spectrometer.

By analyzing the spectrum, the mineral composition of the sample can be determined. This technique offers the advantage of being less expensive, non-destructive and does not require any prior sample preparation (except fine grinding of the sample). The results are presented graphically in Fig. 2 and show that Si, Al, Fe, Ca, K, S, Ti, Mg and Na are the main elements of inorganic matter, and low concentrations of P, Mn, Sr, V, Zr, Rb, Zn, Y and Rh are also identified.

With the aim of identifying changes in thermal behaviours of treated samples thermogravimetric analysis (TGA) of coal has been employed. The analyses were carried out in a SETSYS Evolution Setaram Instrument using SETSOFT2000 software. Thermogravimetric tests were performed on 60g of sample under 16 mL/min air-flow rate and 4 mL/min N2-flow rate. In order to establish the influence of process thermal parameter, in the temperature range of

25-800°C the analyses were run under three heating rates: 5°C/min, 10 °C/min and 15 °C/min.

In Fig. 3 representative curves of mass loss for the three tested coal samples can be observed. It appears that the mix of coal with HRG with 30% of H_2 induced a more intense degradation in thermal range of 100 – 350°C marked by a loop compared to untreated coal.

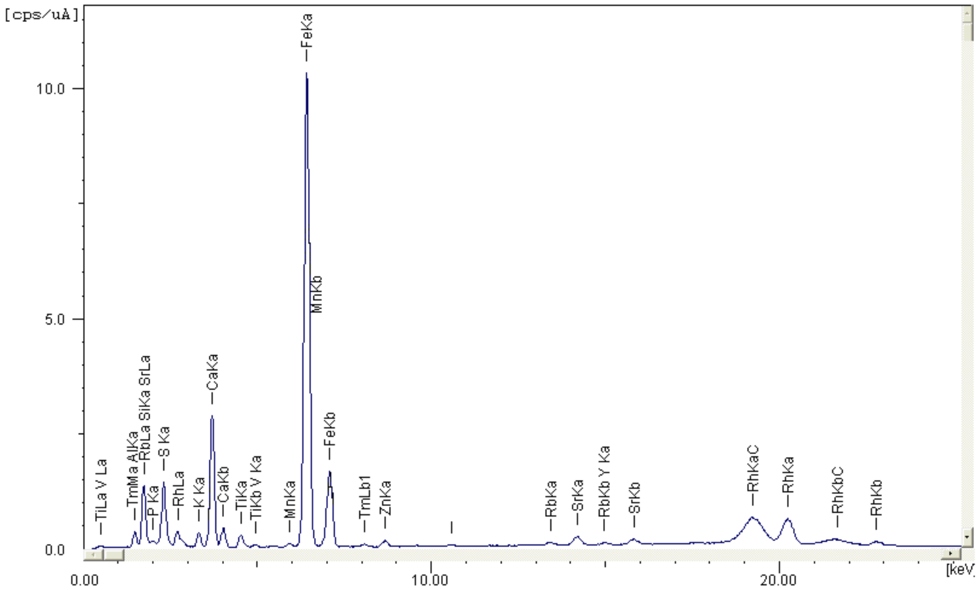

Fig. 2. Inorganic composition of used coal

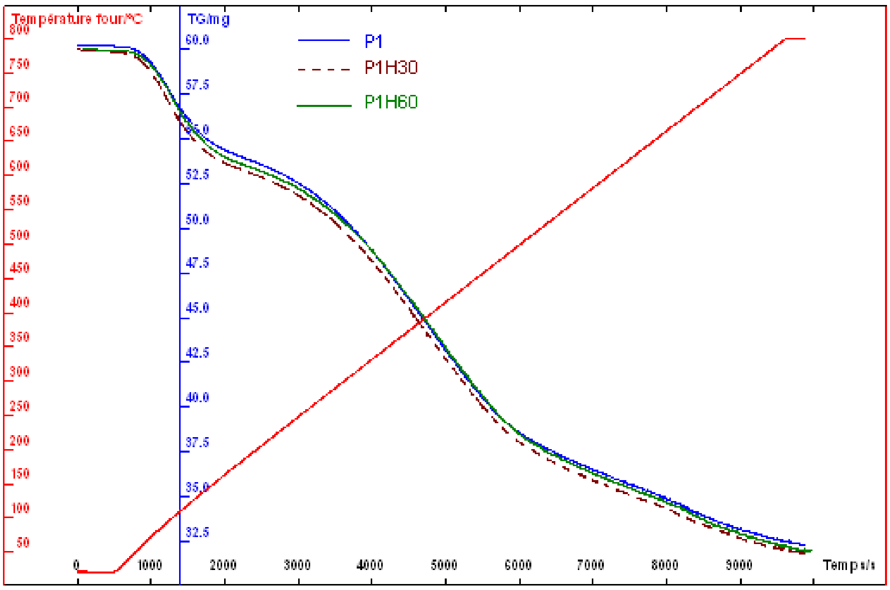

Fig. 3. Comparative curves of mass loss in TGA used coal samples

Thus, the measurement of mass loss in the main thermal range of thermochemical degradation (230 – 400 °C) proves that the increase of H_2 content in HRG lead to a continuous decrease of mass, from 13.5891 mg in coal sample (P1) to 13.3928 in P1H30 and 13.5484 mg in P1H60 (see Fig. 4-6).

The solid residue resulted after thermogravimetric analysis was analysed in order to identify the influence of HRG on the coal decomposition behaviour. The results are found in *Table 2*.

Table 2

The yield of solid residue and its proximate analysis

Fuel	Yield [%-wt]	C, [%-wt]	H, [%-wt]	O, [%-wt]	S, [%-wt]	N, [%-wt]	LHV*, [kJ/kg]
SR-P1	53.60	48.82	0.77	13.67	2.17	0.55	28017
SR-P1H30	53.10	47.18	0.83	6.93	1.45	0.65	28655
SR- P1H60	53.30	46.88	0.87	6.34	1.54	0.77	28752

* calculated with Dulong formula [6]

The solid residue yield of overall process exhibits small differences but confirms that the process is more intense for the sample P1H30.

The carbon content decreases slightly under HRG treatment, while the oxygen amount registered a significant contraction. As regarding the total sulphur content, the treatment with HRG induces 33.2 % loss in solid residue in P1H30 and 29% in P1H60.

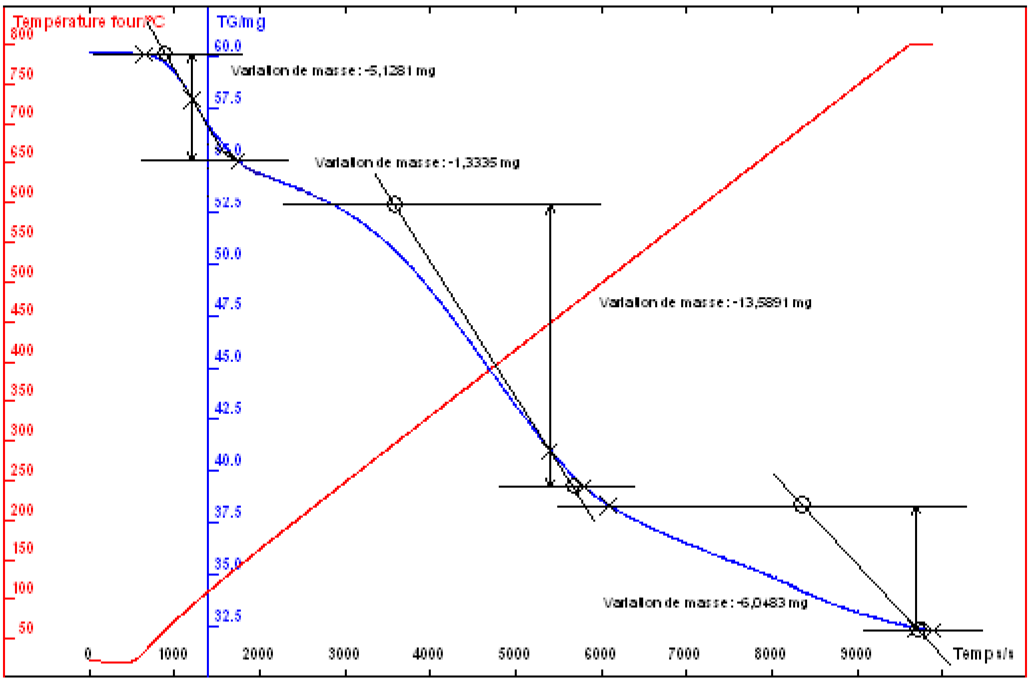

Fig. 4. Measurement of mass loss in TGA of P1 sample

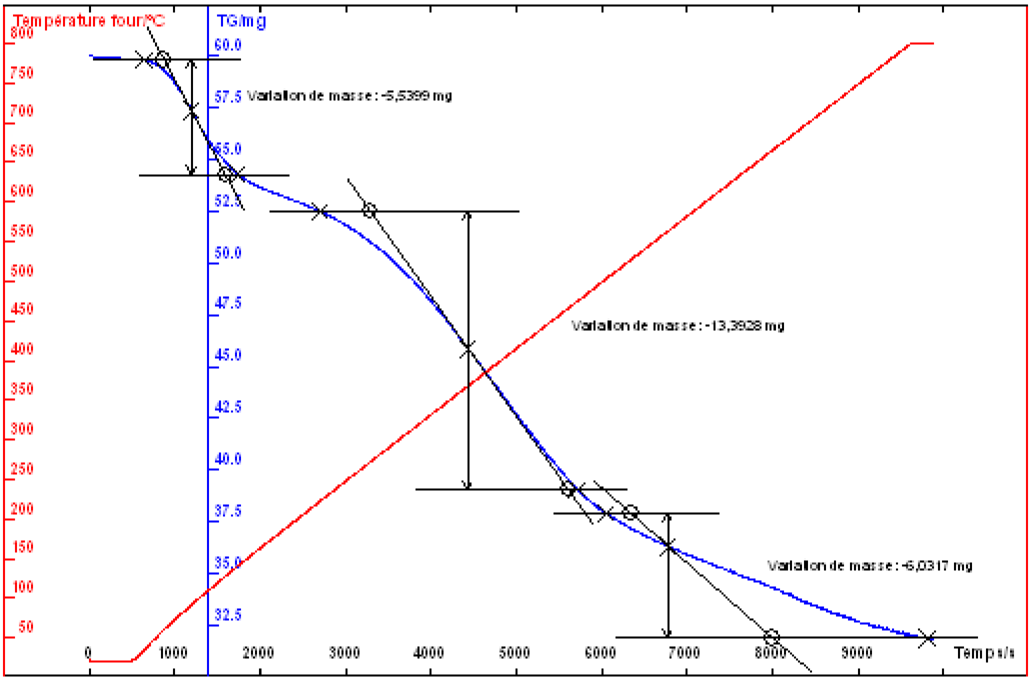

Fig. 5. Measurement of mass loss in TGA of P1H30 sample

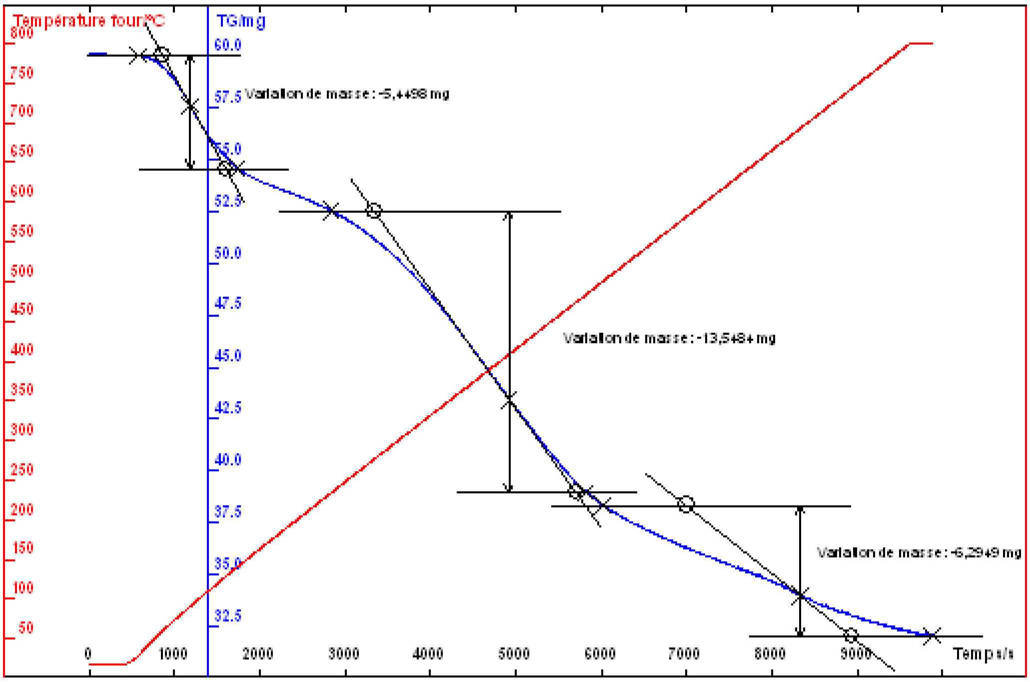

Fig. 6. Measurement of mass loss in TGA of P1H60 sample

Also, the Scanning Electron Microscopy coupled Energy Dispersive X-ray Spectroscopy (SEM/EDX) has been applied in order to investigate the surface of coal particles. In Fig. 7 the most representative SEM images are presented.

It can be seen that the carbonaceous matrix is rarely presenting cavities or pores larger then 10μm. On the other side, there are lots of straight fractures due probably to milling process. The inorganic matters is concentrated in small particles (1-7 μm) attached at the external surfaces of carbonaceous matrix.

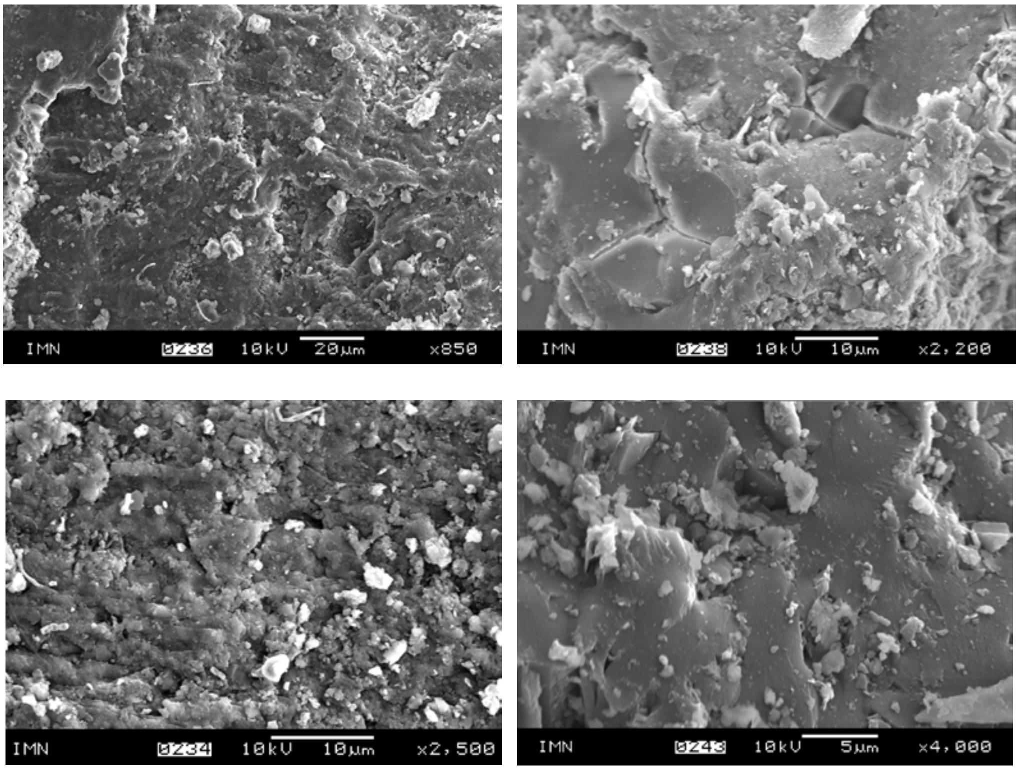

Fig. 7. SEM images for coal sample

The results of EDX analysis showed in *Table 3* represent average values for the mineral composition of used coal and in the solid products of its combustion (slag and flying ash).

Table 3

EDX analysis of coal and its slag and flying ash

Identified Element	Coal	Slag	Flying Ash
	%-wt		
O	50.32	39.18	36.34
Na	nd	0.64	0.14
Mg	1.51	1.33	2.04
Al	10.09	13.26	9.84

Si	22.21	31.53	23.14
S	4.09	0.63	2.00
K	1.92	3.21	2.27
Ca	3.92	2.66	11.94
Ti	nd	0.79	0.51
Fe	5.96	6.77	11.76

Table 3 provides valuable information on the distribution of mineral matter after burning in the pilot furnaces will be further coupled with the studies on burning performance in presence and absence of HRG injection. Since there are reasonable premises that alkaline and alkaline-earth oxides can be actively involved in sulphur cycle during combustion processes this information are even more important.

6. Conclusions

The paper focused on coal samples characterisation for the development of new cleaner technology of coal combustion. Related to the mass loss analysis during the thermal range of coal decomposition, the HRG treatment induced specific variation in the solid residue for the studied samples. Thus, the sample of coal treated with HRG containing 30% of H2 registered a more intense degradation curve all along the thermal range of decomposition, especially between 100 – 350°C and 420 – 600°C.

Moreover, analysing the ashes recovered after coal combustion, it was found that Ca and Fe oxides are concentrated more likely in the flying ash, which can contribute naturally to the SO_2 capture during the exhaust of the flue gases from the furnace.

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R E F E R E N C E S

[1]. *Krawczyk E., Zajemska M., Wylecial T.*, The chemical mechanism of SOx formation and elimination in coal combustion process, CHEMIK 2013, 67, 10, 856–862

[2]. *Balat H., Kırtay E.*, Hydrogen from biomass - Present scenario and future prospects, International Journal of Hydrogen Energy 35, 2010

[3]. *Balat M.*, Potential importance of hydrogen as a future solution to environmental and transportation problems, International Journal of Hydrogen Energy 33, 2008.
[4]. *Pisa I., Lazaroiu G., Prisecaru T.*, Influence of hydrogen enriched gas injection upon polluting emissions from pulverized coal combustion, International Journal of Hydrogen Energy 39, 2014.
[5]. *Demirbas A.*, Hydrogen rich gas from fruit shale via supercritical water extraction, International Journal of Hydrogen Energy 29, 2004.
[6]. *Speight G.J.*, The chemistry and technology of coal, 2nd Ed., Marcel Dekker Inc., 1994.
[7]. *Alaa Abou Harb, Ion Ciuca, Bilel Rahali*, Investigation the corrosion of heat transferring unit in hydrogen peroxide &sodium chloride solution using weight loss measurements, U.P.B. Sci. Bull., Series B, Vol. 79, Iss. 4, 2017, ISSN 1454-2331
[8]. *Dan Pascaru, Cristina Modrogan*, On the susceptibility of forest biomass for burning and combustion, U.P.B. Sci. Bull., Series B, Vol. **76**, Iss. 4, 2014, ISSN 1454 – 2331.