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Sulfur dioxide reactivity potential of different types of coal fly ash

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ABSTRACT

Fly ash (FA) collected in the electrostatic precipitators of the main Thermal Power Plants (TPP) in Bulgaria, burning different types of domestic (lignite and bituminous) and imported (anthracite) coals was studied with respect to its chemical composition and some physical properties. The potential for reaction with SO_2 of studied fly ashes in flue gas desulphurization systems was evaluated by empirical criteria, such as total and real alkaline and sulfur capture capacities. The reactivity of mixtures of FA with alkaline and alkaline-earth additives in conjunction with the available surface area was also calculated.

KEYWORDS

Fly ash;
SO_2 emission removal;
Sulfur capture capacity;
Fly ash chemistry.

INTRODUCTION

The incineration in the Thermal Power Plants of solid organic fuels, containing combustible (organic and pyrite) sulfur and incombustible sulfates, as well as of high-sulfur oil residues, sulfur oxides (SO_x) are generated[1]. The emissions of SO_x (SO_2 and SO_3) cause negative ecological impact and are of grave danges for human health, therefore a number of desulfurization technologies for their restriction have been developed. At present, more than one hundred methods for SO_x removal are known, which generally could be divided in two main groups – sorptional and conversional[2,3]. As reagents in the desulphurization systems different solutions, suspensions, and solid compounds are applied.

The classification of desulphurization technologies with respect to aggregate state of the applied reagent, the process type and the reaction products is presented in Figure 1 and Figure 2.

During the coal incineration, the mineral components in their composition are modified at the temperatures in the combustion cameras, generating ash residues. A part of the ash remains on the bottom of the incinerators in the shape of agglomerates with 0.15 - 20.00 mm in size, so called bottom ash, while the fine fraction is carried away with the flue gases due to the draught in the burning system, namely fly ash (FA). The composition and the quantity of FA vary in a broad interval depending on composition of the mineral mass of coals, the type of the incineration installation and the specifics of the burning process. Normally, at the dust burning systems FA reaches up to 90 % form the incombustible mineral constituents.

Generally, FA is composed of fine particles with a mixed amorphous-crystalline nature[4]. In its composition is presented macro-components, such as amorphous silicon dioxide (a-SiO_2), amorphous and crystalline alymosilicates, as well as a number of crystalline phases: quartz, brushite, hematite, magnetite, and oxides of alkaline and alkaline-earth metals. Microamunts of oxides of transitional metal oxides and a broad variety of trace elements are also observed[5,6].

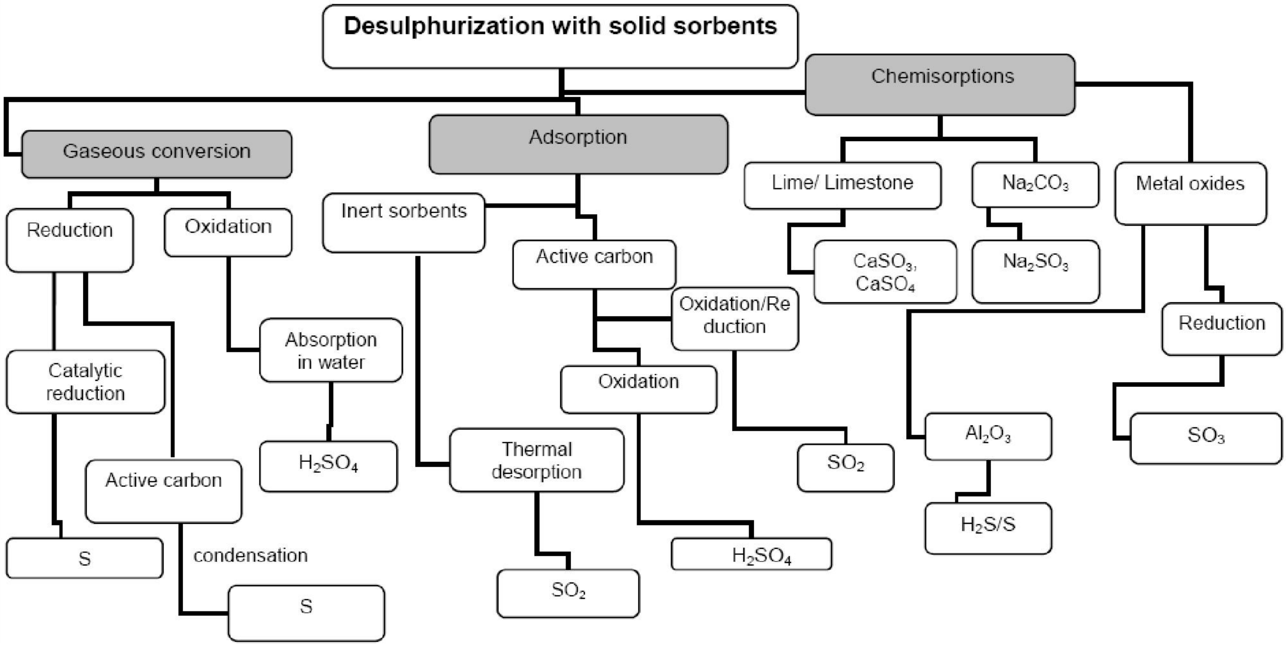

Figure 1 : Desulphurization with solid reagents.

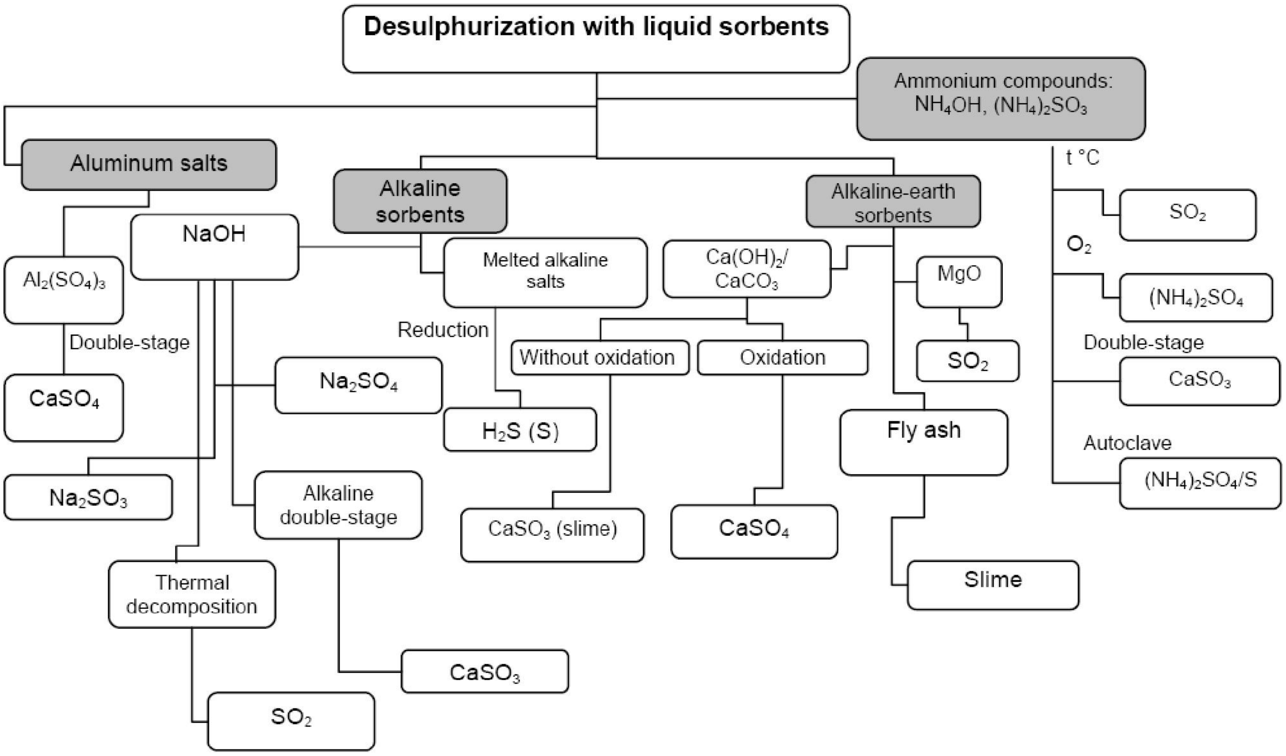

Figure 2 : Desulphurization with liquid sorbents.

FA disposal creates serious problems, because of its unfavorable pH value, the presence of heavy metals and radioactive traces, which can be infiltrated into the soil and the subsoil waters. In this reason different possibilities have been investigated for FA reuse[4]. In addition, it has been established that the amount of sulfur oxides captured by FA is closely related with the concentration of alkaline and alkaline-earth metal oxides (CaO, Na_2O, MgO, and K_2O) within the fly ash composition[7]. Related to this the reactivity potential with respect to sulfur dioxide of different types of coal fly ash generated all over the world has been studied[7-9] for its utilization as a reagent for flue gas desulphurization. Thus three severe ecological problems can be reduced to some extend, namely sulfur oxide removal, utilization of FA alkaline capacity and raw material economy.

In Figures 1 and 2 can be seen that different alkaline reagents are spended for SO_2 removal from flue gases, as the some processes leads to formation of additional solid residues. Due to its chemistry and physicochemical properties the FA has been found position in these diagrams, but in many countries this potential still is not utilized.

The present paper is emphasized on the evaluation of sulfur capture capacities of different FA obtained from lignite, bituminous and anthracite coals on the base of the investigated chemical composition and physicochemical properties.

FLY ASH CHARACTERIZATION

FA collected in the electrostatic precipitator of the main TPP in Bulgaria was subject to compositional and physicochemical analyses. The investigated FA was taken as average samples from the all fields of the dust collectors. Dust residues are generated from three ranks of coals - domestic lignite and bituminous and inported anthracite coals. The lignite coals from the "Maritza-East" basin are the basic Bulgarian domestic energy source, which unfortunately characterizes with unfavorable parameters: low caloricity (Q_r^i = 4600 – 7100 kJ/kg), high ash content (A^d=28-45 %), high humidity (W^r=49-55 %) and substantial sulfur concentration (S^r=2-2.5 %). For these reasons, their incineration creates serous ecological problems – emission of sulfur oxides and enormous amounts of ash residues. The bituminous coals from the "Bobov dol" basin possess much favorable caloricity, but containing significant ash ballast, i.e. Q_r^i = 11300-11750 kJ/kg, S^r=1.7 %, A^r=48 %. The imported anthracite coals are characterizes with Q_r^i = 23956 kJ/kg, A^r=18.4 % and Wr=8 %.

The chemical composition of the investigated FA generated from the incineration of three ranks of coals in different TPP has been studied by the standard classical and instrumental chemical analyses described in Ref.[10-13]. The obtained results are summarized in TABLE 1.

TABLE 1 : Chemical composition of FA from different TPP in R Bulgaria[10-13].

TPP	Composition, mass %			
	Maritza-East 2	AES Galabovo	Bobov dol	Varna
Installed Power	1546 MW	670 MW	630 MW	1260 MW
Type of coals Component	Lignite		Bituminous	Anthracite
SiO_2	52.66	23.40	50.90	46.70
Al_2O_3	23.37	13.54	20.81	23.50
Fe_2O_3	8.72	28.88	8.45	8.62
CaO	5.75	7.13	13.55	5.16
MgO	2.75	1.42	3.38	2.97
SO_3	2.40	9.00	0.70	0.20
MnO	0.06	-	-	-
ZnO	0.04	-	-	-
Na_2O	0.01	0.42	0.65	0.85
K_2O	0.01	1.11	2.07	2.91
Losses at 1273 K	-	22.88	1.00	9.83
pH	-	3.90	12.80	8.30

From the results presented in TABLE 1 it is evident that the investigated FA types are characterized with a total content of $SiO_2 + Al_2O_3 + Fe_2O_3$ = 70 mass %, Na_2O<1.5 mass % и MgO<5.0 mass % and could be referred to class F according to the international crystallographic standard ASTMC-618. An exception of this is the FA generated in AES Galabovo, which refers to class C. The last one also characterizes with strong acidity, which means significant quantity of the captured SO_2 during the contact of the FA and flue gases in the thermal system. Taking into account that the both TPP Maritza-East 2 and AES Galabovo are supplied by lignite coals from one and the same basin, it could be concluded that the substantial difference observed in the chemical composition of the FA is due to the peculiarities of the TPP systems and devices.

The FA reactivity and adsorption capacity is dependent not only on its chemical composition but also on a number physical parameters. Some physicochemical characteristics, such as specific weight (kg/m^3), density (kg/m^3), specific surface (m^2/g), dispersion composition (d_{50}, μm) and porous volume (cm^3/g), which are predictable for the reactivity of FA with SO_2 have been also studied. The applied procedures are described in details[10-12]. The obtained results ate summarized in TABLE 2.

The effect of particle sizes, density and available total and specific surface area on the SO_2 capture ability of FA is comprehensively examined[7].

TABLE 2 : Physicochemical parameters of different investigated FA[10-12].

Physicochemical parameter	TPP		
	AES Galabovo	Bobov dol	Varna
Specific weight, kg/m^3	2594	2177	2456
Fill density, kg/m^3	1960	1900	2000
Specific surface, m^2/g	12.70	1.90	3.00
Voids volume, cm^3/g	2.90	0.43	0.68
D_{50}, μm (number)	20.10	44.24	5.30
d_{50}, μm (volume)	0.56	0.58	0.59

ALKALINE AND SULFUR CAPTURE CAPACITY OF FA

For tentative prediction of FA reactivity potential to SO_2 on the base of chemical composition, the following empirical criteria could be applied[7,14]:

- *Total alkaline metal oxide capasity of FA, $TAMOC_{FA}$, % CaO*

$TAMOC_{FA}$ renders an account of the percentage of the all alkaline and alkaline-earth oxides, expressed as CaO by means of the corresponding stoichiometric coefficients:

$$\mathbf{TAMOC_{FA} = CaO + 1.4MgO + 0.9Na_2O + 0.6\,K_2O, \%\ CaO} \qquad (1)$$

where: CaO, MgO, Na_2O and K_2O are the content of the corresponding metal oxides in the FA composition, mass. %.

- *Real alkaline metal oxide capasity, $RAMOC_{FA}$*

$$\mathbf{RAMOC_{FA} = (TAMO_{FA})/(SiO_2+Al_2O_3)} \qquad (2)$$

where: SiO_2 and Al_2O_3 is the content of these oxides in the FA, mass. %.

The empirical equation (1) regards the separate alkaline and alkaline-earth oxides as discrete compounds, while $RAMOC_{FA}$ (eq.2) is a correction of $TAMOC_{FA}$ value, taking into account that in the real mixture oxides are not independent and their particles are combined in different alumosilicate modification, which could reduce their reactivity.

- *Sulfur capture capacity of FA, SCC_{FA}, gSO_2/100 g FA*

SCC_{FA} can be defined as a quantity of SO_2 (g) held by 100 g FA. The value of *SCC_{FA}* is determined by the reaction of the stoichiometric chemical interaction between SO_2 and the metal oxides in the composition of the FA, expressed as CaO:

$$\mathbf{CaO + SO_2 \rightarrow CaSO_3} \qquad (3)$$

For this calculation, the part of $TAMOC_{FA}$, which has not been consumed by the sulfatuzation of the FA in its route from the incineration camera to the dust collector system, has to be used. For tentative evaluations it is normally accepted that ~50 % of $TAMOC_{FA}$ remains after the contact of FA with SO_2-containing flue gases[14], but more precisely the quantity of the adsorbed SO_2(SO_3) can be measured experimentally.

Taking into account the measured content of SO_3 into the investigated FA samples (TABLE 3) collected from different TPP, the concentration of alkaline oxides as % CaO, which has not participated in the sulfatization reaction ($TAMOC_{FA}$*) was calculated – TABLE 3. The obtained values are input parameters for the estimation of the real sulfur capture capacity $RSCC_{FA}$ (g SO_2/100 g) according to the reaction (3). Thus, the obtained values exceed substantially the theoretical SCC_{FA}, as the real sulfatization ratio of the metal oxides for the time of passing of ash particles from the incineration camera to the electrostatic precipitator is тъй lower than 1 %.

The obtained results for total and real alkaline and sulfur capture capacities are summarized in TABLE 3.

TABLE 3 : $TAMOC_{FA}$, $RAMOC_{FA}$ and SCC_{FA} of FA from different coals.

TPP	$TAMOC_{FA}$, % CaO	$RAMOC_{FA}$	$RAMOC_{FA}$, %	SCC_{FA}, $gSO_2/100g$	$TAMOC_{FA}$*, % CaO	$RSCC_{FA}$, g SO_2/100 g
Maritza-East 2	9.62	0.13	8.37	5.50	7.94	9.07
AES Galabovo	10.16	0.28	7.32	5.81	3.86	4.41
Bobov dol	20.11	0.28	14.48	11.49	19.62	22.42
Varna	11.83	0.17	9.82	6.76	11.67	13.34

From the presented in TABLE 2 results, it could be concluded that the sulfatization of FA from the TPP AES Galabovo is with highest extend, which is related to the lowest measured content of SiO_2 and Al_2O_3. In this case, the real sulfur capture capacity $RSCC_{FA}$ is even lower than the theoretical. The highest value of $RSSC_{FA}$ is obtained for the FA from bituminous coals incinerated in the TPP “Bobov dol”. The theoretical calculations reveal that for a completely 100 %) desulphurization of 1 Nm^3 highly concentrated in SO_2 flue gas flow, for example containing 20 000 mg SO_2/Nm^3, FA in quantity of ~90 g generated from bituminous coals is necessary. For comparison quantitative calculations for the limestone, which is necessity for the chemical combining according to the most spread desulphurization limestone-gypsum wet process with intensive force oxidation of the same SO_2 concentration were made. The total chemical reaction can be expressed as:

$$2SO_2 + O_2 + 2CaCO_3 + 4H_2O \quad 2\,CaSO_4.2H_2O + 2CO_2 \qquad (4)$$

and the molar ratio between the compounds is:

$$nSO_2 = nCaCO_3 = \frac{m\,CaCO_3}{M\,CaCO_3} = \frac{m\,SO_2}{M\,SO_2} = 20/64 \qquad (5)$$

where: nSO_2 and $nCaCO_3$ are the molles of the corresponding reagents, m is their weight, g, and M – their molecular mass, g /mol.

It is calculated from the Eq. (5) that for the desulphurization of 1 Nm^3 flue gases with 100 % of efficiency roughly 31 g $CaCO_3$ is needed.

The made predictions shows that the utilization of the sulfur capture capacity of FA from bituminous colas before to be directed to disposal will result in substantial economy of raw material for flue gas desulphurization systems.

The other investigated FA possesses lower sulfur reactivity potential. The sulfur capture ability of FA from AES Galabovo is exhausted to a big extend in the course in the TPP due to the lower concentration of binding compounds (SiO_2 and Al_2O_3). FA obtained from the anthracite coals characterizes with a comparatively satisfying $RSCC_{FA}$ (TABLE 2), but the high content of SiO_2 and Al_2O_3 will make it inapplicable for direct addition into the incineration system because of the enhanced risk of the slag formation.

Taking into account the chemical composition of FA from lignite coals produced from TPP Maritza-East 2 (TABLE 1), it is obvious that it contains the most significant quantities of SiO_2 and Al_2O_3 which will make it an appropriate raw material for synthesis of zeolite material. An attempt of this direction already was performed[15]. Moreover, that the zeolites, possessing strongly developed internal surface, are very effective for SO_2 adsorption[16].

Besides of dry additives for direct desulphurization, FA is successfully utilized as slurry in wet and semi-wet FGD systems. Thus way, its alkalinity and reaction potential can be exceeded and managed by adding additional reagents, mostly lime and soluble carbonates and bicarbonates[17,18]. As a rule the surface available for the chemical reaction is a key factor, which it has been established influences the SCC_{FA} by a linear dependence[7]. For the case of FA based slurries, the following expression for SCC_{FA} have been drawn[14]:

$$SCC_{FA} = 0.0046.SS + 0.021\,TAMOC_{FA} + 45.65\,(OH^-) + 19.92\,(CO_3^{2-}) + 5.23\,(HCO_3^-) \qquad (6)$$

where SS is a surface parameter (specific surface); OH^-, CO_3^{2-} and HCO_3^- are the concentrations of the corresponding ions in the slurry.

The performed calculations according to the Eq. 6 indicate that small amounts of additional alkaline-earth component to the FA slurry will improved significantly its sulfur reactivity, not only in comparison with this of

FA but also of pure alkaline reagent. The obtained results show ten to twenty times higher SCC of the mixed slurry that that of the calcium compounds, which are normally used in the FGD systems (TABLE 4).

TABLE 4 : SCC of mixture slurry of FA from bituminous coals and calcium compounds.

Quantity of additive to 100 g FA, g	SCC ($Ca(OH)_2$ + FA), g SO_2/100 g	SCC ($Ca(OH)_2$) g SO_2/1 g	SCC ($CaCO_3$ + FA), g SO_2/100 g	SCC ($CaCO_3$), g SO_2/1 g
1	22.00	0. 86	12.38	0.64
2	43.34	-	24.33	-
3	64.81	-	36.29	-

The results presented in TABLE 4 shows that the positive effect of limestone and calcium bicarbonate additives on the mixed slurry reactivity is much slower than that of the hydrated lime and can be registered at ratios above 3 g/100 g FA.

CONCLUSIONS

Fly ash obtained from the incineration of three ranks of coals in different Thermal Power Plants was evaluated with respect to its reactivity potential to sulfur oxide emissions on the base of its chemistry and physical properties. Bituminous coal fly ash characterizes with significant sulfur capture potential and can be applied as a reagent for direct desulphurization in the incineration camera or above burning zone. A small additive of alkaline component (lime) drastically increases sulfur capture ability. Fly ash from lignite coals possess small reactivity to SO_2 but contain significant amounts of alumosilicates, which make it an appropriate raw material for zeolite synthesis. The utilization of fly ash total alkalinity will ensure raw material economy and cheap desulphurization technology.

REFERENCES

[1] A.K.Vnukov; Thermochemical Processes in Gaseous of Steam Generators, in B.S.Beloselskii, (Ed); Published by Energoizdat, Moskow, **(1981)**.

[2] S.Boycheva; Systems and Devices for Environmental Protection in Thermal Power Plants, Sofia, Publishing House of Thechnical University of Sofia, **(2011)**.

[3] M.Hokins; Advanced Chemical Technologies and Emission Control, University Publishing House St. Kl. Ohridsky, Sofia, **(2002)**.

[4] M.Ahmaruzzaman; Progress in Energy and Combustion Science, **36**, 327-363 **(2010)**.

[5] A.Shoumkova, V.Stoyanova; Trace Elements in Fly Ashes from Varna, Bobov dol, Maritza iztok I, Maritza III, Republika and Rousse iztok Power Plants, Bulgaria, Proceeding of the VIth International Scientific Conference – Modern Management of Mine Producting, Geology and Environmental Protection, Albena, Bulgaria, June 12-16, Section II, 348-357.

[6] L.C.Ram, N.K.Srivastava, R.C.Tripathi, S.K.Thakur, A.K.Sinha, S.K.Jha, R.E.Masto, S.Mitra; Environ.Geol., **51**, 1119-1132 **(2007)**.

[7] G.D.Reed, W.T.Davis, R.E.Pudelek; Environ.Sci. Technol., **18(7)**, 548-552 **(1984)**.

[8] K.T.Lee, S.Bhatia, A.R.Mohamed; J.Mater Cycles Waste Manag, **7**, 16-26 **(2005)**.

[9] Y.Wu, J.-P.Charland, E.J.Anthony, L.Jia; Energy &Fuels, **18**, 830-834 **(2004)**.

[10] A.Shoumkova; Journal of the University of Chemical Technology and Metallurgy, **41(2)**, 181-186 **(2006)**.

[11] A.Shoumkova, T.Tsacheva, V.Stoyanova, I.Grancharov, M.Marinov; XIII International Symposium Ecology 2004, 7-11 June 2004, Bourgas, Bulgaria, Proceeding Scientific Articles, N.Ribalski, V.Nenov, (Eds); **1**, 324-343 **(2004)**.

[12] A.Shoumkova, T.Tsacheva, V.Stoyanova, S.Shumkov, I.Grancharov, M.Marinov; Third International Conference on Ecological Chemistry, Chisinau, Republik of Moldova, Proceedings, 560-570, 20-21 May **(2005)**.

[13] S.Boycheva, V.Vassilev; Journal of the University of Chemical Technology and Metallurgy, **49**, **(2012)**.

[14] R.J.Ollerenshaw, K.Bull; SO_2 Emission Abatement from Industrial and Commercial Plant. Fly Ash as a Sorbent Desulfurizing Agent, Warren Spring Lab., **(1989)**.

[15] S.Boycheva, D.Zgureva; Ecological Engineering and Environment Protection, **1**, **(2012)**.

[16] T.T.Sucheski, T.Walek, M.Banasik; Polish Journal of Environmental Studies, **13(6)**, 723 **(2004)**.

[17] J.Fernandez et al.; Powder Technology, **94(2)**, 133 **(1997)**.

[18] Y.Wu, J.-P.Charland, E.J.Anthony, L.Jia; Energy & Fuels, **18(3)**, 830-834 **(2004)**.