

Utilisation of lignite fly ash in oil sorption and energy saving during clinker production

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Abstract

The present study aims at developing an environmental application of lignite fly ash, which constitutes the main by-product of power production by lignite combustion and whose greater amount remains unutilised. In particular, its application in oil spill cleanup and the further utilisation of the resultant oil-fly ash mixtures in energy saving during clinker production has been investigated. For the amelioration of the floating ability and the oil sorption capacity of lignite fly ash, the mixing with a cheap, light and porous agricultural by-product, such as sawdust, has been applied. The addition of 30-50% w/w sawdust results not only in amelioration of the behaviour of lignite fly ash when added to oil spill in marine environment, by contributing to better floating and total oil removal, but also in increase in its oil sorption capacity by up to 50-80%. The higher calorific value of the resultant oil-lignite fly ash-sawdust mixtures rising up to that of oil and bituminous coal encourages their utilisation as alternative fuels in cement industry. The remaining after their combustion ash varies from 18 to 58% w/w and its chemical and mineralogical composition differentiates slightly from the initial one. Analyses showed that it is enriched in Al_2O_3 , SiO_2 , reactive SiO_2 , Fe_2O_3 , CaO , CaO_f and SO_3 . An increase in phases, such as anhydrite, gehlenite, gismondine, portlandite, and a decrease in lime and calcite are observed. However, the change observed in its composition is not expected to change the composition of clinker produced.

Keywords: lignite fly ash, sawdust, oil, sorbent, energy, clinker

1 Introduction

The development of new fields of utilisation for waste materials constitutes an imperative need, since the European legislation [1] presupposes the certain further use of a waste material, so as to be

characterised as a by-product. Such a waste material, for whose characterisation as by-product great efforts are made, is lignite fly ash.

In Greece the power generation, being based by 52% on lignite, results in annual production of 56.5Mt lignite [2] and 11Mt lignite fly ash, of which only 8-11% is utilised in cement industry and 17-20% in subbase construction for mines' ground, the rest being landfilled [3]. Its low utilisation rate makes clear the necessity of finding out new application fields.

Except its successful utilisation in cement [4] and concrete production [5] and road construction [6], lignite fly ash can have application in the synthesis of new products, such as zeolites [7], geopolymers [8], glass and glass-ceramics [9], and in environmental fields, such as the adsorption of heavy metals [10, 11], dyes [12], chlorophenols [13], herbicides [14] from effluents and polluted soil.

An environmental field, where no research concerning the use of lignite fly ash has been carried out, is oil spill clean-up. According to previous studies of our laboratory, lignite fly ash has proved an attractive oil sorbent material [15-21]. The combination of lignite fly ash with an agricultural by-product of low cost, high availability, low specific gravity and high porosity, such as sawdust, has resulted in encouraging oil sorption behaviour [18, 21].

However, a crucial point in the use of oil sorbent materials is their further disposal, since they constitute an additional waste material burdening the environment. To this direction, the present study aims at investigating the further utilisation of oil-lignite fly ash-sawdust mixtures, resulting from oil sorption on lignite fly ash-sawdust mixtures, in clinker production. Especially, the energy saving achieved in clinker production by using oil-lignite fly ash-sawdust mixtures as fuel is determined and the remaining after their combustion ash is characterised, in order to investigate a potential effect on the structure of the resultant clinker.

2 Materials and Methods

2.1 Samples

The examined lignite fly ash (FA) originates from the electric power plant in Aghios Demetrios area, in Greece. It is a calcareous lignite fly ash, classified according to ASTM C 618 as class C. For its characterisation measurements of pH (ISO 6588), specific gravity (ASTM C 642-90), particle size distribution (DIN 4188 and laser diffraction by Malvern Mastersizer Micro Ver. 2.19) have been performed. Furthermore, X-Ray Diffraction Analysis (Siemens D-500), Thermogravimetric Analysis (Mettler TGA/STDA 851^C) and Scanning Electron Microscopy (FEI Quanta 200 SEM) have defined its structure, while its porosity and specific surface area have been measured by N₂-adsorption (NOVA-2200 Ver. 6.11). Its chemical composition is shown in Table 1, whereas its main mineralogical phases

are quartz (SiO_2), lime (CaO), anhydrite (CaSO_4), calcite (CaCO_3), gehlenite ($\text{Ca}_2\text{Al}(\text{Al},\text{Si})_2\text{O}_8$), gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$), anorthite ($(\text{Ca},\text{Na})(\text{Al},\text{Si})_4\text{O}_8$) and merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$).

In Table 2 its physical properties are shown. The N_2 -adsorption isotherms indicate the presence of macropores, which can contribute to the sorption of great organic molecules, such as oil molecules. Its hydrophobic index, determined by Thermogravimetric Analysis according to Giaya et al. [22], is close to 1, indicating its hydrophobic character.

Sawdust (S) in form of fine granules (60% less than $500\mu\text{m}$) has been used. Its specific gravity has been measured according to ASTM D 854-02. The water sorption capacity has been determined by the weight difference between the wet weight of the sawdust, after dipping it for 15min in water, and its dry weight. In Table 3 its basic characteristics are shown.

2.2 Oil sorption behaviour

The FA-S mixtures have been prepared by mixing of FA with S in dry state, in mass ratios 9:1, 7:3, 1:1 (addition of 10, 30, 50% w/w S to FA respectively).

For the evaluation of the oil sorption behaviour of the FA-S mixtures, an oil spill has been simulated in a 250mL beaker glass by adding 2mL of oil to 150mL of artificial ocean-water, prepared according to ASTM D 1141-90. Two different types of oil, especially heating oil (HO) and Iranian light crude oil (CO), have been used, in order to simulate all cases of transports. Their physicochemical characteristics, density (ASTM D 1298), kinematic viscosity (ASTM D 445) and S content, are shown in Table 4. For the sorption of the oil spill 1g of FA-S mixture has been added. The remaining on the surface oil-FA-S mixture has been collected after 4 days, in order to achieve a more cohesive semi-solid phase, and the settling down material, if any, has been determined. The amount of water adsorbed has been determined by distillation with toluene as carrier solvent according to ASTM D 4006-07.

The oil sorption capacity of FA-S mixtures has been determined in dry environment according to ASTM F 726-06. Oil retention by FA-S mixtures depending on time has also been investigated by letting the FA-S mixtures drain and weighing them after 1h, 3h, 6h, 12h, 24h, 3d, 7d, 14d, 21d, 28d, 30d.

2.3 Energy saving during clinker production

In order to investigate the contribution of the oil-FA-S mixtures in energy saving, when utilised as alternative fuels in cement industry, their higher calorific value (HCV) has been determined according to ASTM D 2015-00 (Adiabatic Bomb Calorimeter, Parr Instrument Company 6200). According to the required HCV for the production of clinker (3515kJ/kg clinker according to industry data), the energy saving by replacing the conventional fuel with oil-FA-S mixtures has been determined. The oil-FA-S

mixtures have then been combusted in 750°C for 12 hours and the remaining ash has been determined and characterised.

3 Results and Discussion

The lignite fly ash exhibits encouraging oil sorption behaviour, when added to thin oil spill layers (0.5mm), since it forms a semi-solid phase with oil, allowing its quite total removal from the water surface. Its oil sorption capacity, determined after draining, is at least 0.5g HO per g FA, rising up to 0.8g HO per g FA, immediately after sorption, and 0.9-1.0g CO per g FA respectively, as it is shown in Fig. 2.

The fact that the lignite fly ash is not firmly retained on the surface and settles down in form of granules and its low oil sorption capacity necessitate the amelioration of its oil sorption behaviour. To this direction, the mixing with a cheap and available agricultural by-product with low specific gravity and high porosity, such as sawdust, has been applied, resulting in encouraging performance of the mixture.

The FA-S mixture behaves better than each one of its constituents alone when added to oil spill, as it is obvious from Fig. 1. A much more cohesive semi-solid oil-FA-S phase is formed, floating on the surface and yielding total oil removal, whereas precipitation of FA-S mixture in form of granules is limited. Problems, such as the settling down of oil-FA mixture or the poor buoyancy of S, have not anymore been observed. Furthermore, the FA-S mixture adsorbs insignificant amount of water when added to oil spill, compared to S, which could be attributed to the mixing of FA with S, so that less S particles come in contact with water due to the presence of FA particles.

In Fig. 2 the oil retention by the FA-S mixtures depending on time is shown. The quantity of oil retained by the FA-S mixtures stabilises after 7 days. As it is obvious, their oil sorption capacity is greater than that of FA, as it is expected, since S has a greater porosity than FA. In particular, their oil sorption capacity is at least 0.5-0.9g HO per g FA-S, depending on FA:S mass ratio, rising up to 0.9-1.4g HO per g FA-S, immediately after sorption, and respectively at least 0.9-1.3g CO per g FA-S and 1.2-1.7g CO per g FA-S, immediately after sorption. In fact, an increase in HO sorption capacity for the FA-S mixtures by up to 80% and in CO sorption capacity by up to 50% is achieved.

The greater trouble when using oil sorbent materials is their treatment after oil sorption. To this direction, the possibility of utilisation of the resultant oil-FA-S mixtures in energy saving, especially in cement industry, is investigated. Their higher calorific value (HCV) and the remaining ash after their combustion have been determined and are shown in Fig. 3. In particular, the HCV and the remaining ash have been determined immediately after oil sorption, when the maximum oil sorption capacity is achieved, and after 7 days, when the quantity of oil retained by the FA-S mixtures is stabilised.

As it is obvious from Fig. 3, the HCV of all the oil-FA-S mixtures immediately after oil sorption is greater than that of bituminous coal and in the same order or greater than that of oil, whereas after 7 days, when the oil retention is stabilised, their HCV is in almost all cases in the same order or greater than that of bituminous coal. In any case, however, their HCV exceeds that of lignite. The remaining ash after their combustion, immediately after oil sorption, varies from 18 to 51% w/w, whereas if they are combusted after 7 days, when the oil retention is stabilised, the remaining ash is 20-58%, being 3-20% greater. Their remaining ash is 0.6-1.5 times that of lignite and 2.5-8.3 times greater than that of bituminous coal. In any case, the oil-FA-S mixtures have proved a better fuel than lignite and comparable to bituminous coal, having the disadvantage of higher amount of remaining ash.

In Table 5 the quantity of clinker is shown that can be produced by using oil-FA-S mixtures as alternative fuel, either immediately after oil sorption (2min) or when oil retention is stabilised (7d). The quantity of clinker produced is expressed in t per t oil sorbed on FA-S mixture. As it is obvious, if FA-S mixtures are used for the sorption of 1t HO, the resultant mixtures suffice for the production of 22-35t clinker, whereas FA-S mixtures after the sorption of 1t CO suffice for the production of 26-37t clinker, if all the fuel is replaced with oil-FA-S mixtures. However, in practice only 10% of the conventional fuel is replaced with alternative ones, so the oil-FA-S mixtures can be used for the production of about 200-370t clinker.

In Fig. 4 the clinker production achieved by replacing the conventional fuel with oil-FA-S mixtures, either immediately after oil sorption (2min) or when oil retention is stabilised (7d), is shown. As conventional fuel coke has been considered, whose HCV is maximum 31000kJ/kg. So, if the conventional fuel is replaced with oil-FA-S mixtures immediately after oil sorption the clinker production can be increased by 1.4-2.6 times, whereas if oil-FA-S mixtures are used, when oil retention is stabilised, the clinker production can be increased by up to 2.3 times. If only 10% of the conventional fuel is replaced with oil-FA-S mixtures, the clinker production can be increased by up to 16%.

In order to investigate the effect of using oil-FA-S mixtures as alternative fuels on the clinker composition, the remaining ash after their combustion has been characterised. In Table 6 and Fig. 5 its chemical and mineralogical composition is shown respectively. In Fig. 5 the remaining ash of oil-FA-S mixtures with the highest amount of S addition has been selected, since in this ratio the highest oil sorption capacity is achieved, so that the effect of oil and S on the composition of the remaining ash is greater.

As it is obvious from Table 6, the remaining ash of oil-FA-S mixtures is enriched in Al_2O_3 , SiO_2 , reactive SiO_2 , Fe_2O_3 , CaO , CaO_f , SO_3 . This is in accordance with a decrease observed in its mass after the combustion by up to 7-8% in case of HO and 3-6% in case of CO, which could be partially

attributed to the removal of unburned C. The greater enrichment observed in case of the remaining ash deriving from HO could be attributed to the greater decrease in its mass.

Concerning the mineral phases, the remaining ash is enriched in anhydrite, gehlenite, gismondine, portlandite, anorthite, whereas a decrease in lime and calcite and no change in quartz is observed. The decrease in lime and calcite can be attributed to their conversion in anhydrite, due to the S (sulphur) content of oil. The greater increase observed in the phase of anhydrite (CaSO_4), in case of the remaining ash deriving from the CO, could be attributed to the higher sulphur content of CO, as it is shown in Table 4. This can be confirmed by the SO_3 content of the remaining ash deriving from CO (Table 6), which is also increased.

Taking into account the quantity of oil-FA-S mixtures required for clinker production, if they replace the conventional fuel, their remaining after combustion ash constitutes only 1-8% w/w of the clinker produced. If the oil-FA-S mixtures replace only 10% of the conventional fuel, as it usually happens in practice, then the remaining ash constitutes only 0.2-0.7% w/w of the clinker produced. So, any change in the composition of their remaining ash is expected to be insignificant for the clinker structure.

4 Conclusions

In conclusion, the application of lignite fly ash in a new environmental field seems to be encouraging: its combination with sawdust, in order their mixture to be used as oil sorbent material, has proved efficient. Addition of 30-50% w/w sawdust to lignite fly ash results in increase in its oil sorption capacity by 50-80% and ameliorates its behaviour when added to oil spill, since the mixture floats on the surface, adsorbs almost no water and forms a more cohesive semi-solid phase, yielding total oil removal, in contrast to lignite fly ash and sawdust. The possibility of using the resultant oil-lignite fly ash-sawdust mixtures as alternative fuels in cement industry, since their higher calorific value exceeds that of bituminous coal, prevents from burdening the environment with another waste resulting from oil spill cleanup. In particular, the replacement of the fuel used in clinker production with oil-lignite fly ash-sawdust mixtures, resulting from 1t oil sorption, could support the production of 20-37t clinker, whereas its replacement with the same quantity of oil-lignite fly ash-sawdust can result in increase in clinker production by up to 2.6 times. In addition, the contribution of their remaining ash in clinker structure is expected to be insignificant.

5 Acknowledgements

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Table 1. Chemical composition of FA sample

Parameter	% (w/w)
SiO ₂	30.83
Al ₂ O ₃	9.05
Fe ₂ O ₃	6.49
CaO	34.74
CaO _f	10.28
MgO	3.56
SO ₃	3.59
Na ₂ O	1.12
K ₂ O	0.68
L.O.I.	4.03
Unburned C	2.87

Table 2. Physical properties of FA sample

Property	
Specific gravity (g/cm ³)	2.84
Specific area (m ² /g)	4.03
Mean pore diameter (Å)	160.2
Pore volume (cm ³ /g)	0.016
Hydrophobic index	0.72

Table 3. Sawdust characteristics

Parameter	
water content (% w/w)	8.3
ash (% w/w)	0.8
cellulose (% w/w)	37.4
semi-cellulose (% w/w)	23.8
lignine (% w/w)	24.7
specific gravity (g/cm ³)	1.38
specific area (m ² /g)	29.46
mean pore diameter (Å)	71.2
pore volume (cm ³ /g)	0.052
solubility (g per 100g H ₂ O) (20 °C)	0.003
solubility (g per 100g H ₂ O) (40 °C)	0.178
water adsorption (g H ₂ O per g dry S)	4.9
ocean-water adsorption (g H ₂ O per g dry S)	4.4

Table 4. Properties of heating oil (HO) and Iranian light crude oil (CO)

Property	HO	CO
density (g/cm ³) (20°C)	0.82	0.87
kinematic viscosity (cSt) (20°C)	3.27	13.84
S content (% w/w)	0.16	1.93

Table 5. Clinker produced by using oil-FA-S mixtures as alternative fuel, either immediately after oil sorption (2min) or when oil retention is stabilised (7d), expressed as t clinker per t oil sorbed on FA-S mixture

Oil-FA-S mixture			Clinker (t per t oil sorbed on FA-S mixture)
HO	FA	2min	23.0
		7d	20.2
	FA:S=9:1	2min	25.7
		7d	21.7
	FA:S=7:3	2min	28.5
		7d	25.3
	FA:S=1:1	2min	34.6
		7d	31.1
CO	FA	2min	25.4
		7d	24.6
	FA:S=9:1	2min	28.7
		7d	25.9
	FA:S=7:3	2min	30.8
		7d	29.1
	FA:S=1:1	2min	37.4
		7d	34.6

Table 6. Chemical composition of the remaining ash after the combustion of oil-FA-S mixtures

Parameter (% w/w)	FA	HO				CO			
		FA	FA:S=9:1	FA:S=7:3	FA:S=1:1	FA	FA:S=9:1	FA:S=7:3	FA:S=1:1
SiO ₂	30.8	32.4	32.0	32.0	32.5	32.3	31.0	31.5	29.7
SiO ₂ reactive	25.2	26.2	26.5	25.9	26.6	26.7	25.3	25.8	24.3
Al ₂ O ₃	9.1	10.1	8.8	9.7	9.7	8.8	9.7	9.2	8.3
Fe ₂ O ₃	6.5	8.6	10.7	8.5	6.8	7.8	6.2	6.4	6.0
CaO	34.7	39.4	37.5	40.3	39.9	38.0	37.3	35.6	32.2
CaO _f	10.3	16.1	16.2	16.0	16.3	14.8	14.6	13.6	12.7
SO ₃	3.6	4.1	4.3	4.4	4.2	6.0	6.3	7.1	8.3



FA

S

FA:S=3:1 w/w

HO



FA

S

FA:S=3:1 w/w

CO

Fig. 1 Oil sorption behaviour of lignite fly ash (FA), sawdust (S) and their mixture in a mass ratio FA:S=3:1 when added to heating (HO) and crude oil (CO) spill

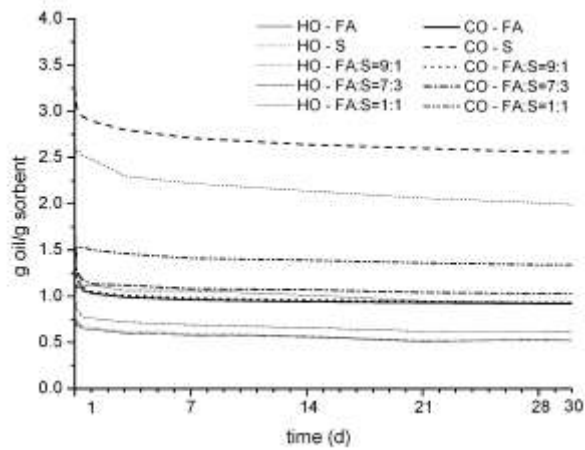


Fig. 2 Heating (HO) and crude oil (CO) retention by lignite fly ash (FA), sawdust (S) and their mixtures depending on time

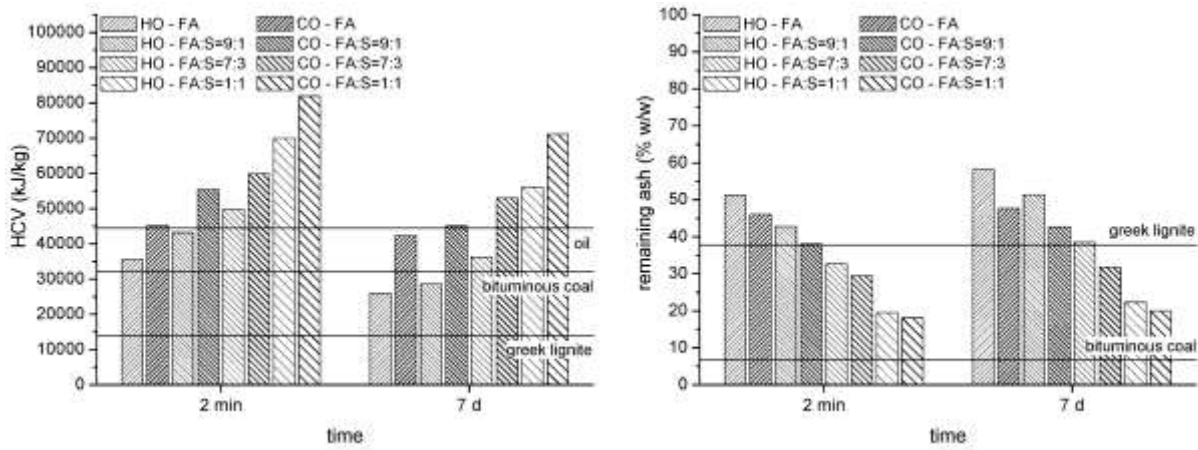


Fig. 3 Higher calorific value (HCV) and remaining ash of oil-FA-S mixtures depending on time

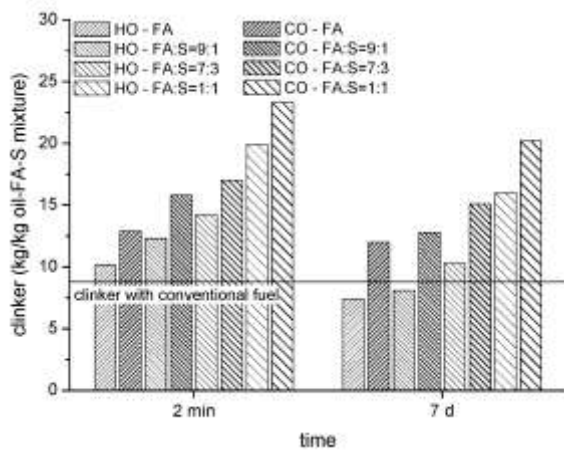


Fig. 4 Clinker production, if the conventional fuel is replaced with oil-FA-S mixtures, either immediately after oil sorption (2min) or when oil retention is stabilised (7d)

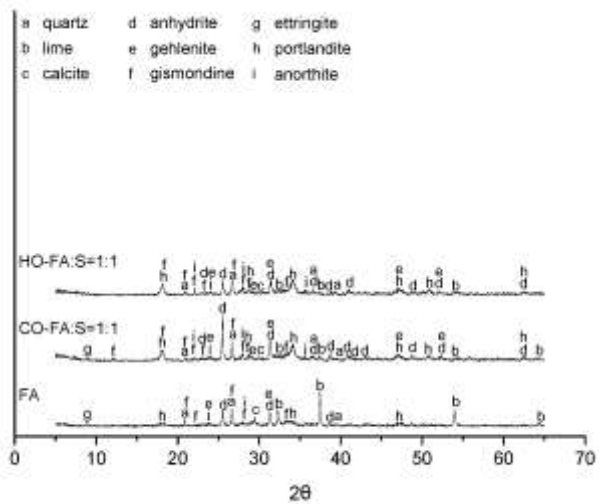


Fig. 5 XRD patterns of the remaining ash of oil-FA-S mixtures