

Recovery of unburned carbon by conventional flotation of bottom ashes from Tuncbilek Thermal Power Plant

by A. Yamik* and A. Dogruoz*

Transaction Paper

Synopsis

This research study includes studies carried out on the recovery of unburned carbon in the ashes of Tuncbilek Thermal Power Plant. Bottom ashes have been identified by X-ray diffraction and X-ray fluorescence. These samples are potentially of class F type and have significant amounts of unburned coal. According to the ash amount that units in the thermal power plant produce, and the analyses of the samples mixed, which used certain amounts in flotation tests, it was found that the bottom ash includes 91.47% ash in dry form and 8.53% combustible matter, and the lower calorific value is 491 kcal/kg. Optimum flotation conditions to get the unburned carbon were subsequently determined by examination of the optimum flotation grain size, pulp density, collector type and amount, depressant type and amount, frother type and amount, agitation speed, and froth-taking time.

While the lower calorific value of the thermal power plant bottom ashes of the 3rd , 4th and 5th units and the mixed bottom ash sample was, respectively, 959, 469, 279 and 491 kcal/kg in dry form, it increased to 2490, 1312, 786 and 1348 kcal/kg in the product obtained as a result of flotation in optimum conditions.

Key words: ash, conventional flotation, unburned carbon

Introduction

As is well known, energy sources fall into two categories: 'renewable' ones, such as water, wind, sun, tide, and geothermal, and unrenewable ones, such as petroleum, natural gas, uranium, and coal. The most evident characteristic of unrenewable energy sources (mainly coal) is that they can be used only once and cannot be replaced. Individuals and institutions, which have practised this one-way consumption, consequently have important responsibilities both towards the society to which they belong and to the generations that follow after.

The coal known as hard lignite, whose moisture content is less than 25%, keeps its grain hardness in open air, can be washed using wet methods and has a high calorific value; it is, however, in short supply, which makes it essential to use this coal in the optimal way. In Turkey, Tuncbilek coal has an important place among its peers as it has the properties mentioned above.

Total proven lignite reserves in Turkey amount to 8.4 billion tons, 90% of which have lower calorific value. Coal has an important share in power production and heating in Turkey. Almost half of the power is produced using coal. The thermal power plants (TPP) and lignite-using power plants are in the majority.

Approximately 38% of the electricity across the world is produced from coal (Helle *et al.*, 2003). Low quality lignites, which are in abundant supply in Turkey, are used in thermal power plants. Coal is burned after it is pulverized. During the combustion process, as a result of incomplete combustion, unburned carbon passing through the grizzly of the power plants is called bottom ash, while that which goes into the atmosphere through the plant's chimney is called fly ash (Vassilev *et al.*, 1997).

Moreover, some of the lignites burned in thermal power plants cannot be burned totally and go into ash, so the lignites obtained at high cost are wasted (Helle *et al.*, 2003,, Vassilev *et al.*, 1997). Research must therefore be done carefully before the building of thermal power plants to ensure they burn lignites with a high recovery. The better the lignites burn, the higher the energy produced.

Apart from energy production, too much waste ash is also released by thermal power plants. Whether a significant amount of ash is discharged from the power plants depends on the energy production rate (Rayalu *et al.*, 2001). This waste is used as filling material (Acosta *et al.*, 2001). The environmental benefits and economic feasibility of coal recovery were made clear from the results of a

* *DPU Mining Engineering Department, Kutahya, Turkey.*

© *The Southern African Institute of Mining and Metallurgy, 2008.* *SA ISSN 0038–223X/3.00 + 0.00. Paper received Jul. 2007; revised paper received Jan. 2008.*

study carried out in several coal preparation plants. The use of lignite in power plants has led to an increase in environmental problems related not only to gaseous emissions but also to the disposal of ash residues (Külatos *et al.*, 2004, Alonso *et al.*, 2002). In particular, the use of low-quality coals with high ash content produces huge quantities of bottom ash (Baba and Turkmen, 2001). The unburned carbon, which was treated in the combustion process and gained a hydrophobic characteristic, was obtained by flotation techniques.

The recovery and reburning of combustible matter in the ash (10%–20%) enabled the ash without carbon to be used in the ceramic and cement industries as raw material. Generally, fine material results from use of flotation methods (Guney *et al.*, 2002).

In the current reported study, bottom ash samples from a lignite-burning power plant have been identified by XRD, XRF and analytical techniques, and they have been subjected to upgrading tests of their unburned coal by means of a classical flotation set-up.

Experimental studies

Tuncbilek Power Plant is about 50 km away from Kutahya. The sample was taken from the 3rd, 4th and 5th unit bottom ash which passes through the grizzly in TPP on different days and periods in a systematic way. Results of the analysis of the mixed bottom ash samples used in the experiment are given in Table I.

Tuncbilek Power Plant produces about 2 000 tons of solid wastes annually. Currently, the total amount of bottom ash in Tuncbilek waste disposal area is 15 million tons. Particle sizes of fly ash and bottom ash depend on the type of the coal. Samples were taken under the grizzlies of the 3rd, 4th and 5th operating units. A large number of experiments were carried out using the bottom ash of samples blended in the ratio of 20%, 40% and 40%, respectively. Optimal experimental conditions from these series of tests were then applied to the bottom ash of samples from the 3rd, 4th and 5th operating units respectively.

Total carbon analysis of the bottom ash samples was carried out using a LECO instrument. The ash content of these samples was determined by burning 1 gram of representative samples in a furnace that could be heated up to 1200°C, with precise temperature control. The method of analysis was similar to the standard methods suggested by ASTM. The calorific values of the samples were determined using an IKA-4000 calorimeter device. Results of analyses obtained from the samples from the three units are reported in Table II.

Chemical analysis of the samples was carried out using an X-ray fluorescence (XRF) unit (119096/05 Spectro X-Lab 2000) and the results obtained are reported in Table III.

X-ray diffraction (XRD) analysis was carried out using a ZD 13113 Rigaku Miniflex unit. Results of the mineralogical analysis obtained are shown in Figure 1.

The ash sample taken from Tuncbilek was mixed in appropriate amounts according to the daily reserves obtained from these three units and brought to a size suitable for flotation experiments.

The flotation set-up and tests

The experimental studies were conducted in a one-litre capacity cell using a Denver-type conventional laboratory flotation machine.

Reagents used in the flotation experiments were kerosene as a collector, methyl isobutyl carbinol (MIBC) as a frother, and sodium metasilicate (Na_2SiO_3) as a potential dispersant and depressant for non-combustible matter. Tests were carried out at the natural pH of the slurry. Table IV shows the range of dosages for these reagents along with important operating parameters used in a series of experiments.

Results and discussion

Ash characteristics

Bottom ash samples from various units indicated a wide variation in combustible matter from 5.61% to 15.05%

Table I

Analysis of the mixed bottom ash samples used in TPP (dry basis)

Analysis	As received
Ash (%)	91.47
Combustible matter (%)	8.53
Calorific value (kcal/kg)	491

Table II

Carbon, ash and lower calorific value analysis of the ash samples

	Carbon (%)	Ash (%)	Lower calorific value (kcal/kg)
Unit III	15.05	84.95	959
Uni IV	8.21	91.79	469
Unit V	5.61	94.39	279
Mixed ash	8.53	91.47	491

Table III

Chemical analysis of the samples by XRF

Symbol	Unit III	Unit IV	Unit V
P_2O_5 (%)	0.2184	0.2083	0.2493
SiO_2 (%)	46.50	46.03	56.12
Fe_2O_3 (%)	9.540	9.606	10.85
Al_2O_3 (%)	14.44	14.25	15.20
TiO_2 (%)	0.6755	0.6540	0.6693
MgO (%)	2.629	2.600	4.331
CaO (%)	2.283	2.288	4.198
SO_3 (%)	1.847	1.785	1.283
Na_2O (%)	0.069	0.067	0.074
K_2O (%)	1.144	1.129	1.379
V_2O_5 (%)	0.0256	0.0218	0.0237
CuO (μg/g)	86.2	86.5	84.0
Ign-lpss	4.93	7.85	4.27

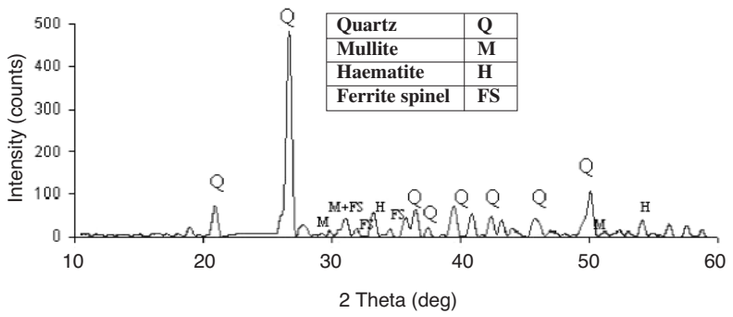

Figure 1—Mineralogical analysis of the ash sample by XRD

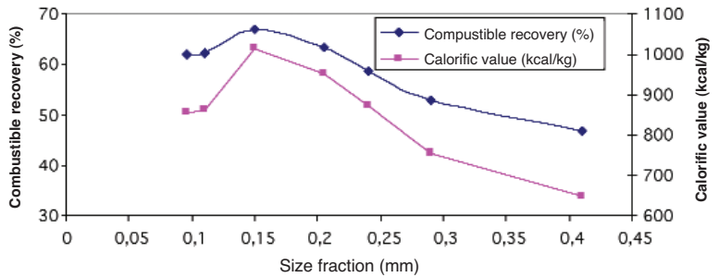

Figure 2—Flotation experiments conducted based on the grain size changes

(Table II). High values may reflect initiation of an operating unit for shutdown, which happens occasionally, if not a poor operating practice at the time of sampling. XRD results reported in Figure 1 indicated that the ash sample contained mainly quartz (Q, SiO_2), mullite (M), haematite (H, Fe_2O_3) and ferrite spinel (FS). Mullite is an alumininosilicate material ($3Al_2O_3.2SiO_2$) that forms at high temperatures by an interaction of silica and alumina-bearing minerals in the combustion environment. Ferrite spinel is generally a non-ferrous substitution phase of spinel structure $FeFe_2O_4$ or Fe_3O_4. Metal ions such as Mg (II), Al(III), Ti(IV), Ni(II) and Cr(III) can substitute for the Fe(II) and Fe(III) sites in this structure (McCarthy *et al.*, 1984).

The pozzolanic feature of ash material represents an important quality since it increases its value as an additive to cement. It is known that once hardened completely, a blend of the Portland cement with pozzolanic material is usually stronger than the Portland cement itself. According to characterization by ASTM C 618, a fly ash sample having $SiO_2+Al_2O_3+Fe_2O_3$ content greater than 70% and CaO less than 10% belongs to the F class (Kim and Prezzi, 2006).

As can be seen, the sample from unit IV is the only one that has this silicious mixture of oxides slightly lower than 70%. The weighted average value, however, obtained by mixing each type (3rd, 4th and 5th) on a 20%, 40% and 40% ratio respectively, meets this quality standard. Thus, it has a potential use in suitable combinations with fly ash that is already used by the cement industry in the surrounding areas (Demir *et al.*, 2007).

Flotation tests

Experimental conditions and the range of variables used in flotation tests are summarized in Table IV. For brevity, only one selected set of results will be presented here.

The optimum grain size of the sample was used in flotation experiments. Fixed conditions were: pulp density 20%, fuel oil 4000 g/t, Na_2SiO_3 500 g/t, pine oil 1600 g/t, agitation speed 1200 rpm, airflow rate 6 ℓ/min, froth-taking time 2.5 minutes.

The results of the experiment conducted according to the grain size are given in Figure 2.

As a result of the experiment conducted on different grain sizes, clean coal (in the size of –0.150 mm) with a 1 013 kcal/kg lower calorific value and 81.05% ash was produced with 67.10% combustible recovery.

Flotation experiments were carried out with a change to the solid ratio. Fixed conditions in flotation were: 80% of grain size -0.150 mm, fuel oil 4000 g/ton, Na_2SiO_3 500 g/ton, pine oil 1600 g/ton, solid-liquid mixing time 3 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time

Table IV

Experimental conditions used in flotation tests

Grain size (%80 ni mm)	-0.410, -0.290, -0,240, -0.150, -0.110, 0.096
MIBC (gt^{-1})	1200, 1400, 1600, 1800, 2000
Kerosene (gt^{-1})	1000, 3500, 4000, 4500, 5000, 5500, 6000, 6500, 7000
Na_2SiO_3 (gt^{-1})	400, 500, 600, 700, 800
Solid ratio (SR) (%)	10, 15, 20, 25, 30
Airflow rate (ℓ/min)	4, 6, 8, 10, 12, 14, 16
Agitation speed (rpm)	1100, 1200, 1300, 1400, 1500
Froth-taking time (min)	1, 1.5, 2, 2.5, 3, 3.5, 4
pH (natural range, not adjusted)	7.5–8

3 minutes, agitation speed 1200 rpm, airflow rate 6ℓ/min., froth-taking time 2.5 minutes.The results of the flotation experiment conducted according to the solid amounts in the pulp are shown in Figure 3.

As a result of the experiment based on the change in solid amount, clean coal, 25% of which was solid and 80.63% ash, was produced with 70.30% combustible recovery and with 1046 kcal/kg lower calorific value.

In the flotation experiments, kerosene, fuel oil and kerosene (50%) and fuel oil (50%) mixture were tried as collector reactives. Fixed conditions in the flotation were: 80% of the grain size -0.150 mm, pulp density 25%, Na_2SiO_3 500g/ton, pine oil 1600 g/t, solid-liquid mixing time 5 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time 3 minutes, agitation speed 1200 rpm, airflow rate 6ℓ/min, froth-taking time 2.5 minutes. The results of the flotation experiment to determine the collector reactive types are given in Figure 4.

As a result of the experiment carried out with different collector reactives, clean coal with 80.63% ash, 1046 kcal/kg lower calorific value and 70.30% combustible recovery was produced using kerosene. Kerosene was accordingly used as a collector reactive in flotation experiments.

Flotation experiments were carried out with different kerosene amounts. Fixed conditions in the flotation were: 80% of the grain size -0.150 mm, pulp density 25%, Na_2SiO_3 500g/t, pine oil 1600 g/t, solid-liquid mixing time 5 minutes, kerosene conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time 3 minutes, agitation speed 1200 rpm, airflow rate 6ℓ/min, froth-taking time 2.5 minutes.

The results of the flotation experiments to determine the amount of collector (kerosene) are given in Figure 5.

As a result of the experiment on changes in kerosene amounts, clean coal with 79.77% ash, 1108 kcal/kg lower calorific value and 74.40% combustible recovery was produced in 5500 g/t kerosene.

Na_2SiO_3 was used as a depressant in flotation experiments. Fixed conditions in the flotation were: 80% of the grain size -0.150 mm, pulp density 25%, Na_2SiO_3 5500g/t, pine oil 1600 g/t, solid-liquid mixing time 5 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time 3 minutes, agitation speed rpm, airflow rate 6ℓ/min, froth-taking time 2.5 minutes.

The results of the flotation experiments conducted to determine the Na_2SiO_3 amount are given in Figure 6.

As a result of the experiments conducted on the changes in Na_2SiO_3 amounts, clean coal with 79.21% ash, 1153 kcal/kg lower calorific value and 76.80 % combustible recovery in 600 g/t Na_2SiO_3 was produced.

In the flotation experiments MIBC, pine oil, flotol B, cresilic acid and resanol were used as frother reactives. Fixed conditions in the flotation were: 80% of the grain size 0.150 mm, pulp density 25%, fuel oil 5500 g/t, Na_2SiO_3 600 g/t, solid-liquid mixing time 5 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time 3 minutes, agitation speed 1200 rpm, airflow rate 6ℓ/min, froth-taking time 2.5 minutes.

The results of the flotation experiment to determine the frother reactive type are given in Figure 7.

The lowest ash amount in clean coal was found to be 78.78% and the highest combustible recovery 78.80% using MIBC.

Flotation experiments were conducted using MIBC. Fixed conditions in the flotation were: 80% of the grain size –0,150 mm, pulp density 25%, fuel oil 5500 g/t, Na_2SiO_3 600 g/t, solid-liquid mixing time 5 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, agitation speed 1200 rpm, airflow rate 6 ℓ/min., froth-taking time 2.5 minutes.

The results of the flotation experiments to determine the frother reactive amount (MIBC) are shown in Figure 8.

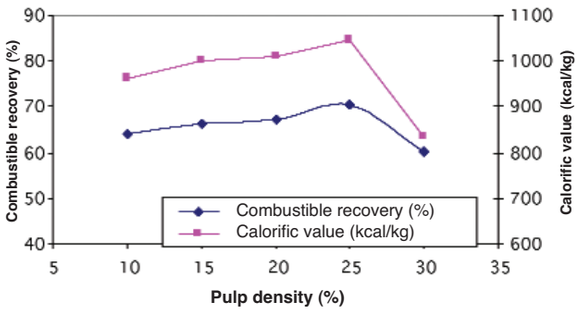

Figure 3—Flotation experiments carried out according to the changes in solid amount

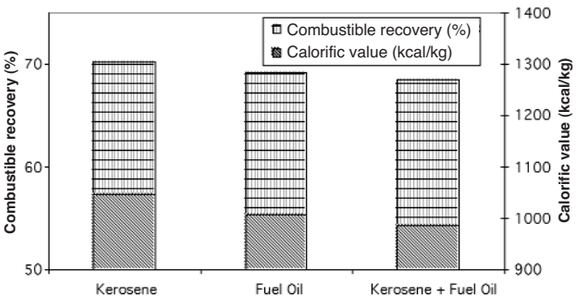

Figure 4—Combustible recovery and calorific values according to the collector types

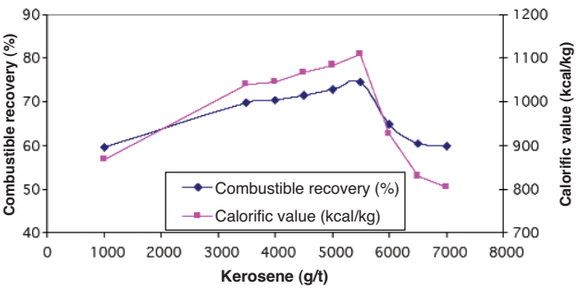

Figure 5—Flotation experiments conducted according to the kerosene changes

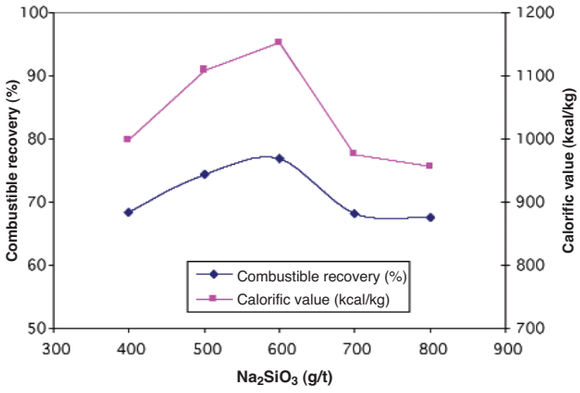

Figure 6—Flotation experiments conducted according to the changes in depressant amounts

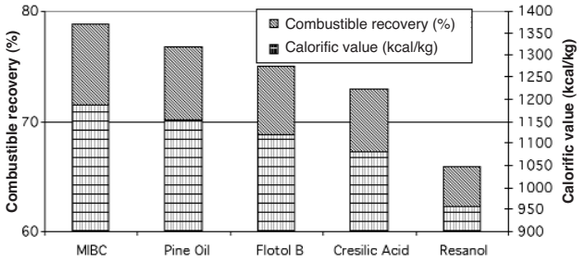

Figure 7—Effect of frother type on the combustible recovery and calorific value

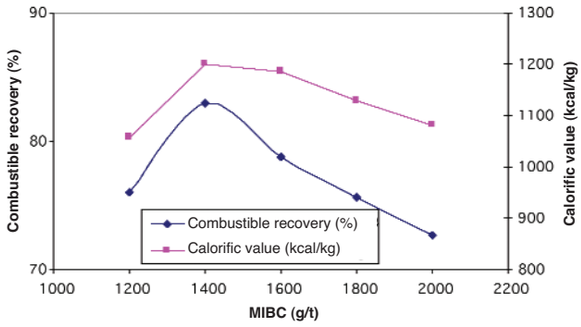

Figure 8—Flotation experiments conducted according to the frother amount changes

As a result of the experiment carried out on change in MIBC amounts, in 1400 g/t MIBC, clean coal with 78.57% ash and 200 kcal/kg lower calorific value was produced with 83% combustible recovery.

To determine in what way different froth-taking times affect the results of flotation, experiments were carried out independently and separately. Fixed conditions in the flotation experiment were: 80% of the grain size –0.150 mm, pulp density 25%, fuel oil 5500 g/t, Na_2SiO_3 600 g/t, pine oil 1400 g/t, solid-liquid mixing time 5 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time 3 minutes, agitation speed 1200 rpm, airflow rate 6 ℓ/min.

The results of flotation experiments to identify optimum froth-taking time are shown in Figure 9.

As a result of the experiment carried out that depends on the change in froth-taking time, clean coal with 77.81% ash and 1255 kcal/kg lower calorific value was produced with 84.40 % combustible recovery in two-minute froth-taking time.

To determine the optimum amount of air in flotation experiments, fixed conditions in the flotation were: 80% of the grain size –0.150 mm, pulp density 25%, fuel oil 5500 g/t, Na_2SiO_3 600 g/t, pine oil 1400 g/t, solid-liquid mixing time 5 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time 3 minutes, agitation speed 1200 rpm, froth-taking time 2 minutes.

The results of flotation experiments to determine optimum air amounts are shown in Figure 10.

As a result of the experiment conducted on the change in air amounts, clean coal with 77.29% ash and 1297 kcal/kg lower calorific value was produced with 87.70% combustible recovery in 12 ℓ/min. airflow rate.

Calculation of optimum agitation speed in the experiments was carried out as follows. Fixed conditions in the flotation experiment were: 80% of the grain size –0.150 mm, pulp density 25%, fuel oil 5500 g/t, Na_2SiO_3 600 g/t, pine oil 1400 g/t, solid-liquid mixing time 5 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time 3 minutes, air flow rate 12 ℓ/min., froth-taking time 2 minutes.

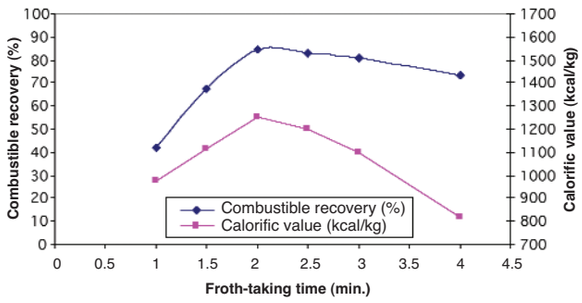

Figure 9—Flotation experiments conducted based on the changes in froth-taking time

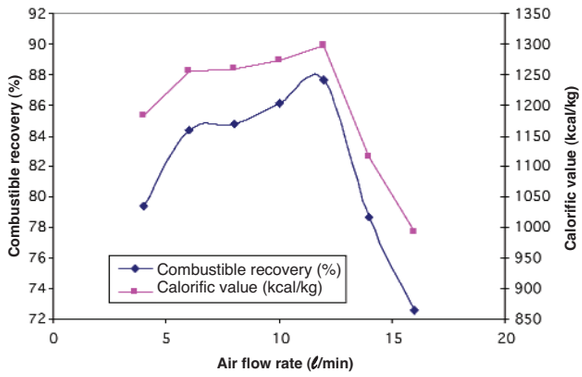

Figure 10—Flotation experiments conducted based on the changes in air amount

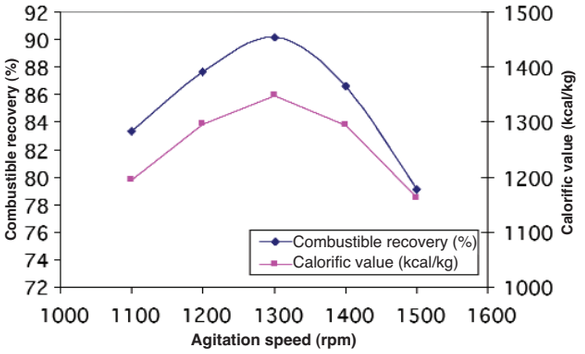

Figure 11—Flotation experiments carried out based on the changes in agitation speed

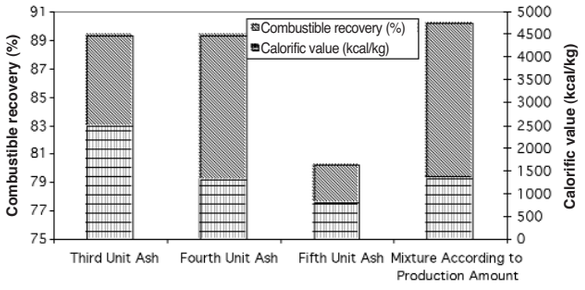

Figure 12—Flotation experiments of ash and mixture belonging to three units

The results of the flotation experiments to determine optimum agitation speed are shown in Figure 11.

As a result of the experiment conducted on the change in agitation speed, clean coal with 76.59% ash and 1348 kcal/kg lower calorific value was produced with 90.20% combustible recovery in 1300 rpm agitation speed.

Additional tests

The experiments applied to mixed ashes and the results obtained applied to the 3rd, 4th and 5th unit ashes separately; optimum flotation conditions were determined and the values of carbon, ash and efficiency and calorific value were compared.

Fixed conditions for the optimum flotation experiment (conditions of mixed ashes) were: 80% of the particle size -0.150 mm, pulp density 25%, fuel oil 5500 g/t, Na_2SiO_3 600 g/t, pine oil 1400 g/t, solid-liquid mixing time 5 minutes, fuel oil conditioning time 5 minutes, Na_2SiO_3 conditioning time 3 minutes, pine oil conditioning time 3 minutes, agitation speed 1200 rpm, air flow rate 6 ℓ/min, froth-taking time 2.5 minutes.

Total flotation experiment results of mixed ashes and ash samples belonging to the three units are shown in Figure 12.

As can be seen in Figure 12, the results listed below were obtained:

- The application of optimum flotation conditions to the 3rd unit ashes produced clean coal with 2490 kcal/kg lower calorific value and 60.91% ash with 89.30% combustible recovery
- The application of optimum flotation conditions to the 4th unit ashes produced clean coal with 1312 kcal/kg lower calorific value and 77.05% ash with 89.30% combustible recovery
- The application of optimum flotation conditions to the 5th unit ashes produced clean coal with 786 kcal/kg lower calorific value and 84.19% ash with 80.20% combustible recovery
- The application of optimum flotation conditions to the mixed ashes produced clean coal with 1348 kcal/kg lower calorific value and 76.59% ash with 90.20% combustible recovery.

Conclusions

Some of the pulverized coal used in the Tuncbilek Thermal Power Plant does not burn in burning units and passes through the grizzly to be wasted as ash.

Ash characterization has been made so various analytical techniques could be used. The characterization involved mineralogy by XRD and chemical analysis by XRF. The XRD analysis indicated that the ash samples consisted primarily of quartz (SiO_2), mullite ($3Al_2O_3.2SiO_2$) and haematite (Fe_2O_3) and had a low lime (CaO) content. The XRF analysis suggested that the samples can be placed in the class F ash type.

Bottom ash samples were taken from each of the three units in the TPP and detailed tests were applied to the samples, which were mixed in certain amounts. Tests carried out at the optimal condition are summarized in Table V.

Ash samples of three units and mixed in optimum conditions were exposed to separate flotation for comparison (see Table VI).

The lower calorific values of the 3rd, 4th, 5th units and the mixed ashes, which were 959, 469, 279, were increased to 2490, 1312, 786 and their lower calorific value was increased to 1348 kcal/kg from 491 kcal/kg in the clean coal after flotation.

According to the data above, in the cauldrons in 4th and 5th units in the Tuncbilek Thermal Power Plant, good burning was provided but in the 3rd unit, which was old, such was not the case. That is why the carbon losses in the ashes were high. That the third unit had effectively come to the end of its technological life so the feed-coal with high calorific value could not burn totally, is an evident reason for this.

The best set of results was obtained with the bottom ash sample from unit III, which brought the ash content from 84.95% down to 60.91% at a combustible recovery of 89.30%. The calorific value increased from 959 kcal/kg to 2490 kcal/kg. Further investigations are planned to improve the separation efficiencies.

Table V

Optimal experimental conditions used in flotation tests

80% of the grain size: –0.150 mm Pulp density: 25% Fuel oil: 5500 g/t Na_2SiO_3: 600 g/t	MIBC amount: 1400 g/t Froth-taking time: 2 min Airflow rate: 12 ℓ/min Agitation speed: 1300 rpm

Table VI

The analyses of the samples used in experimental and optimal test results obtained

Ash sample	Carbon (%)		Ash (%)		Calorific value (kJ/kg)	
	Before	After	Before	After	Before	After
3rd unit	15.05	39.09	84.95	60.91	959	2490
4th unit	8.21	22.95	91.79	77.05	469	1312
5th unit	5.61	15.81	94.39	84.19	279	786
Mixture	8.53	23.41	91.47	76.59	491	1348

In conclusion, the unburned carbon in the ashes of the Tuncbilek Thermal Power Plant will be regained to be burnt. Also, ash without carbon obtained as a slag will be used in the cement, brick and ceramic industries.

References

Helle, S., Gordon, A., Alfaro, G., Garcia, X., and Ullao, C. *Fuel Processing Technology,* vol. 80, 2003, pp. 209–223.

Vassilev, S.V, and Vassileva, C.G. *Fuel Processing Technology,* vol. 51, 1977, pp. 19–45.

Rayalu, S.S., Udhoji, J.S., Munshi, K.N., and Hasan, M.Z. *Journal of Hazardous Material,* 88, vol. 1, 2001, pp. 107–121

Acosta, A., Aineto, M., Iglesias, I., Romero, M., and Rincon, J.Ma. *Materials Letters,* vol. 50, 2001, pp. 246–250.

Külatos, I., Hurt, R.H., and Suuberg, E.M. *Fuel*, vol. 83, 2004, pp. 223–230.

Alonso, M.I., Valdes, A.F., Martinez-Tarazona, R.M., and Garcia A.B. Coal Recovery From Fines Cleaning Wastes by agglomeration with colza oil: a contribution to the environment and energy preservation, *Fuel Processing Technology*, vol. 75, 2002, pp. 85–95.

Baba, A. and Turkman, A. *Turkish Journal of Engineering and Environment Science*, vol. 25, no. 4, 2001, pp. 321–328.

Guney, A., Onal, G., and Ergut, O. *Fuel Processing Technology,* vol. 75, 2002, pp. 141–150.

McCarthy, G.J., Swanson, K.D., Keller, L.P., and Blatter, W.C. *Cement Concr. Res*., vol. 14, 1984, p. 471.

Kim, B. and Prezzi. Compaction characteristic and corrosivity of Indiana class-F fly and bottom ash mixtures. *Construction and Building Materials*, in press, 2006.

Demir, U., Yamik, A., Oteyaka, B., Kelebek, S., Ucar, A., and Sahbaz, O. Characterization and Column Flotation of Bottom Ashes from Tuncbilek Power Plant, *Fuel* in press, 2007. ◆

