Türkiye 14 Madencilik Kongresi / *14th Mining Congress of Turkey,* 1995 , ISBN 975-595-150-7

BENEFICIATION OF COAL-FIRED POWER PLANT FLY ASH

TERMİK SANTRAL UÇUCU KÜLÜNÜN DEĞERLENDİRİLMESİ

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ABSTRACT: Gale Common (UK) fly ash was investigated with the emphasis being on the recovery of cenospheres for use in PVC pastes. After mechanical screening and cyclosizing into various size fractions, each sub-sample was subjected to SEM, XRD and chemical analysis. No morphological, chemical or mineralogical differences were determined among the sized-samples of fly ash. Mineralogical analyses indicated that four major crystalline phases: quartz, mullite, ferrite spinel and hematite were evident in all sized-samples. Morphology studies showed that most of the particles from fly ash varying in size from sub-micron to about 100 lim appeared to be spherical. Selective flocculation results showed mat using optimum conditions and cleaning of the flocculated portion in a cationinc system, a product containing cenospheres was produced from Gale Common fly ash at a recovery of 0.62% by weight of feed. Preliminary investigations into the use of cenospheres as a filler in PVC resin indicated that they produce similar mechanical properties to those of talc and china clay fillers.

ÖZET: Gale Common (ingiltere) uçucu külünden küresel tane kazanımı ve bu ürünün PVÇ içinde katkı maddesi kullanımı incelenmiştir. Mekanik eleme ve siklon ile sınıflandırma sonrası her sınıflandırılmış, ürün, mikroskopi (scanning electron microscope), XRD (X-Ray diffractometry) ve kimyasal analiz işlemlerine tabi tutulmuştur. Ham uçucu kül ve sınıflandırılmış ürünler arasında morfoloji, mineraloji veya kimyasal bileşim açısından belirgin bir fark yoktur. Tüm numunelerde başlıca 4 kristal fazın; kuvars, mulit, ferro spinel ve hematit bulunduğu mineralojik inceleme sonucu saptanmıştır. Uçucu kül içindeki tane boyutları <mikron ve 100 um arasında değişen çoğu tanenin küresel yapıda olduğu gözlenmiştir. Seçimli saltamlaşürma optimal koşullarında çöken ürünün iki kere katyonik bir sistemde temizlenmesi sonucunda %0.62 (ağırlıkça) verimle küresel tane içeren bir ürün elde edilmiştir. Bu ürünün PVC içinde kullanıldığı ön incelemeler sonucunda elde edilen PVC kompozitin talk ve kaolen kulamlarak elde edilen PVC kompozitlere kıyasla aynı mekanik özellikleri gösterdiği tesbit edilmiştir.

1. INTRODUCTION

Conventional coal-fired power stations produce vast tonnages of residues, a high proportion of which is fly ash (Butler and Wearing, 1986). This material is essentially composed of amorphous alumino-silicate microspheres, together with small amounts of crystalline matter and unburnt coal granules (Elliot, 1981).

It has been known for a number of years that fly ash from coal combustion often contains a fraction of hollow particles (cenospheres) (Raask, 1968). Kaolinite decomposition, pyrite oxidation, calcium and magnesium sulphate decomposition, and calcium carbonate and dolomite decomposition may occur at 1 000 C or less and, thus, may provide gas pressure for cenosphere formation (Fisher and Natusch, 1979).

Fly ash is a unique material which can be considered as a resource rather than a waste. It is rich in a considerable number of elements, particularly iron and aluminium, and it also contains varying quantities of cenospheres and unburnt carbon. The processing of fly ash is highly dependent on its physical properties, such as particle size and density, as well as its chemical and mineralogical composition. Harvesting and processing of cenospheres is the major success story in fly ash beneficiation, with active processors in several countries, such as the UK, USA and Australia (Stamp and Smith, 1982). Simple sedimentation and froth flotation have been used for the recovery of cenospheres from fly ash (Alcalaetal., 1987).

.Although the potential value of fly ash has **been** recognised for many years, there has always **been a** substantial need for utilization. The most **widely used** disposal practices for fly ash are **settling ponds,** stockpiling and **land filling. Fly** ash also **finds** a market in grouting, lightweight aggregate, cement and concrete, bitumastic products and plastics. The use of cenospheres in industrial applications is relatively recent. They can be used in applications where manufactured glass microspheres are used at present, mainly as fillers in cement and concrete and polymer systems (O'Keeffe, 1982; Montgomery and Diamond, 1984; Plowman and Show, 1982; Pedlow, 1973).

2. PROPERTIES OF FLY ASH

2.1. Material

Representative sample of fly ash for this study was obtained from the Gale Common fly ash disposal site in North Yorkshire (England). Naturally floating cenospheres were also collected for use as a reference material.

2.2. Chemical composition

Chemical analyses of the sized products and raw fly ash (Table 1) showed that minor differences in chemical composition were evident in the sized fractions in comparison with the raw fly ash. Iron (Fe203), sulphur (SO3) and calcium (CaO) contents were found to be higher in the +250 ^m fraction (AI2O3 and SİO2 being correspondingly lower).

Table 1. Chemical analysis of fly ash and its size-classified products.

Element (% by weight)	Raw Fly Ash	Size Fractions (Um) +250	-250+22	-22
SiO_2	50.82	45.98	48.38	51.30
AI2O3	24.80	20.41	24.62	25.27
Fe2C>3	10.07	16.29	12.30	7.99
TiO_2	0.81	0.87	0.62	1.05
CaO	2.56	4.36	2.31	2.70
MgO	1.41	1.11	1.40	1.44
Na_2O	2.84	2.42	2.88	2.81
K_2O	3.09	1.97	3.47	2.66
MnO	0.04	0.09	0.02	0.07
SO3	0.31	0.83	0.34	0.25
P2O5	0.25	0.21	0.25	0.25
LOI	2.27	3.98	3.08	1.18
Total	99.27	98.52	99.67	96.97

2.3. Mineralogy

Mineralogical investigation (Fig. 1) showed that the raw fly ash, sized products and cenospheres all exhibited the four typical crystalline phases- quartz, mullite, ferrite spinel and hematite. A glassy phase was evident in the background of all sample's diffractograms and there was some indication of an increase in the glassiness as the particle size decreased (Poole and Bayat, 1993).

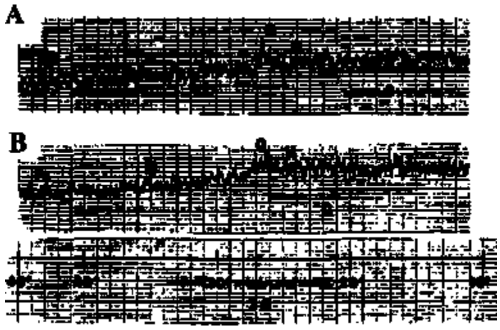


Fig. 1. X-ray diffractograms of fly ash (A) and cenospheres (B). Principal phases indicated as follows: H=hematite, Q=quartz, M=mullite, FS=ferrite spinel and G=glass phase

2.4. Microscopic investigation

Most of the particles examined appeared to be spherical and varied in size from sub-micron to about 100 \ua in diameter (Fig. 2). Irregularly shaped, lacy particles (Fig. 3) seen in the coarset (+250 ftm) fraction appeared to be incompletely combusted carbonaceous material.

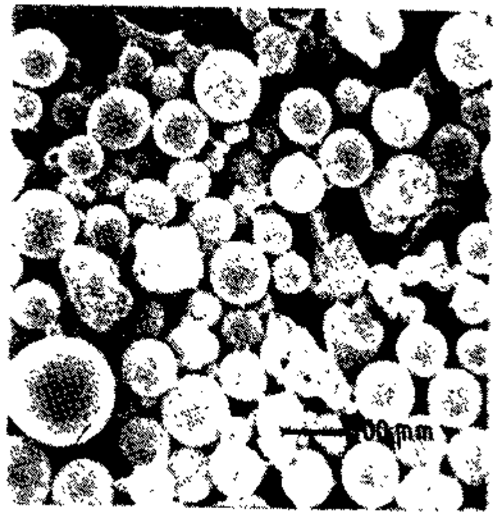


Fig. 2. Scanning electron microscope photograph of fly ash.

Fig. 3. Scanning electron microscope photograph of size-classified product (+250nm) of fly ash.

2.5. Particle size distribution

About 70% by weight of the fly ash was less than 53 \im, with 33.7% by weight less than 22 p.m. as indicated in Fig. 4.

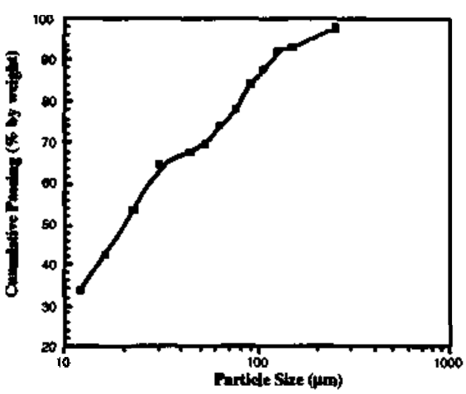


Fig. 4. Particle size distribution of fly ash.

2.6. Density determination

The bulk density of the samies ranged from 1.3 to 1.4 g/cm3, but as expected the true density was approximately 2.5 g/cm^ (Table 2). It was evident that both bulk and true density increased as particle size decreased. The major density differences were probably due to the inluence distributions in mean wall thickness, void volume and particle diameter. Therefore, it appears that the true density of the fly ash and sized products depends more on void structure than on the composition of each particle.

Table 2. Density values of fly ash and cenospheres.

Material	Bulk density (gem"^{3})	True density (gem"^{3})
Fly Ash (+250nm)	1.30	2.03
Fly Ash (-250+22um)	1.38	2.49
Fly Ash (-22mn)	1.42	2.61
Fly Ash (raw)	1.40	2.49
Cenospheres	0.50	0.73

2.7. Investigation of electrokinetic properties

Zeta potential data for fy ash and cenospheres reference material are shown in Fig. 5 as function of suspension pH. The point of zero charge (PZC) can be estimated at pH 6.5 for fly ash and pH 7.5 for cenospheres. Treating both materials with with an addition of dispersant (300 g/t, Dispex N40) produced significant changes in zeta potential and lowered to the PZC around pH 2.5 although the zeta potential behaviour of the cenospheres was relatively unchanged (Fig. 6). The reasons for this phenomenon are unclear, but mat be due to differences in surface area. However, it is clear that this difference in surface potential provides a possible means of separating cenospheres from fly ash by selective flocculation with a suitable selective dispersant

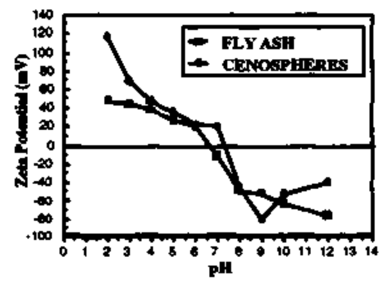


Fig. 5. Effect of pH on zeta potential

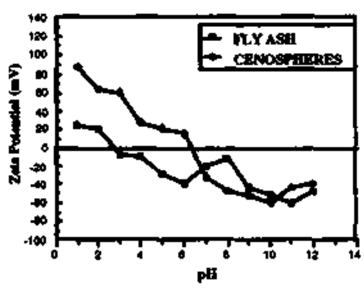


Fig. 6. Effect of dispersant on zeta potential

3. FLOCCULATION EXPERIMENTS

Cenospheres float without any reagent addition, owing to their low specific gravity. Therefore, the raw fly ash sample was prepared at 5% solids concentration and stirred at high shear rate (1200 rpm) for 10 minutes and allowed to stand for 24 hours. The "sinks" were cleaned twice by same procedure and results indicated that 0.32% by weight of fly ash reported as cenospheres. The selective flocculation experiments were performed under optimum effective parameters in the way shown in Fig. 7 (Bayat, 1992) and a final cenosphere product with a yield of 0.62% by weight was achieved using optimum conditions.

The properties of final cenosphere product obtained under optimum flocculation conditions is given in Table 3 and compared with the reference material and Armospheres-CN grade (commercial microsperes supplied by AML Int. Ltd., England). The results indicated that the cenosphere product have similar physical properties in terms of form, density and particle size to the reference materials. Chemical and mineralogical analyses indicated that the major components were silica, alumina and iron oxides and Fig. 8 confirms that product were spherical in form.

4. THE USE OF CENOSPHERES IN PVC RESIN

The filler used in this study were cenospheres, china clay (obtained from EEC bit Ltd) and talc (supplied by BDH Ltd.). Other chemical reagent used were:

(i) PVC polymer resin- Breon P. 130/3 (supplied by BP chemicals (UK) Ltd.)

(ii) Plasticiser- di-octyl-pthhalate (DOP), supplied by Aldrich chemicals Ltd.)

(iii) Heat stabiliser- Irgastab CZ59 (supplied by CibaGeigyLtd.)

The formulation used in all testwork was Tarpaulin grade PVC paste made as follows:

PVC polymer resin	100	parts by weight
Plasticiser	65	parts by weight
Heat stabiliser	2	parts by weight
Filler	0-10	parts by weight

All test methods used to determine mechanical properties were carried out according to BS 2782, Part 3: Method 320A-320F.

Tensile strength decreased with the introduction of all fillers, but cenospheres showed the largest decrease with Increasing loading (Table 4). This was almost certainly related to the larger particle size. It was observed that the cracks passed through the interface between the particle surface and matrix for all filled PVC specimens. Neither fractograph revealed any indication of bonding at the interface between spheres and resin matrix (Fig. 9). All of the filled specimens also exhibited reduced elongation and elastic modulus compared with unfilled PVC resin. However, with the exception of the 10 parts by weight cenosphere specimens, cenospheres showed similar results compared with talc and china clay composites (Poole and Bayat, 1992).

Table 3. Properties of cenospheres obtained by floculation in comparison with reference material and Annospheres (commercial cenospheres by AML International, England).

Ptapaty	Cenospheres (Gale Common)	Reference Material	Armospberes CN-Grade
Form	Hollow Balloons		
Colour	Off-white		
Bulkdensity*	0.50	0.43	0.4-0.5
True density*	0.73	0.70	0.7-0.8
Silica**	55.48	55.04	55.0-60.0
Alumina**	30.58	32.01	25.0-30.0
Iron oxides**	3.04	2.73	4.0-10.0
Calcium**	1.08	1.12	02-0.6
Magnesium**	1.25	1.31	1.0-2.0
Alkalis***	5.54	6.25	0.5-4 0
LOI**	1.99	0.10	-
Particle size**			
+125 urn	21.47	23.82	
-125+53 um	74.36	71.18	10 - 300 um
-53 um	4.17	500	

* (gem"3)
** *(%* by weight)
**• Na20andK20 (% by weight)

Table 4. Mechanical properties of filled PVC paste resin composites.

Huer	Loading (pbw)	Tensile Strength *m*	Elongation at break (100%)	Elastic modulus (pa)	Appâtent baldness (1RHD)
Unfilled		1969	340	1210	61
Cenosphaes	5	1540	310	1050	60
Cenosrjbaes	10	1390	245	910	66
Qmaday	5	1610	310	1035	68
China clay	10	1480	230	1020	67
laic	5	1640	270	1120	68
Tafc	10	1540	270	1065	66

5. CONCLUSIONS

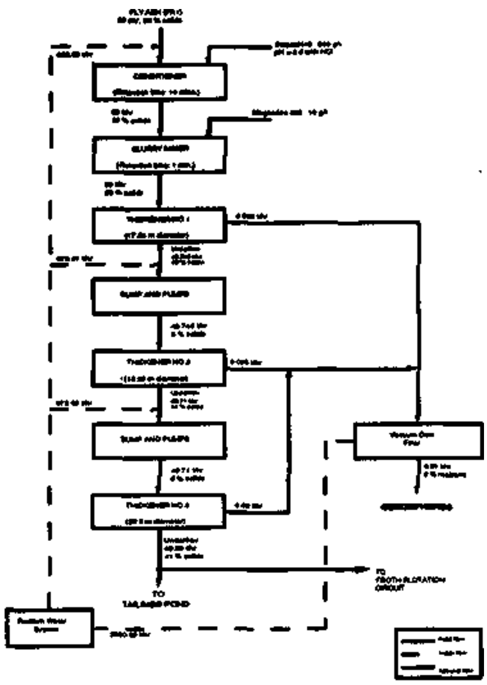
(i) No major morphological, chemical or mineralogical differences were revealed among the sub-samples of fly ash, although sizing was successfull in removing coarse non-spherical particles along with unbumt carbon and detrital quartz.

(ii) The amorphous silicate component of fly ash was predominantly in the form of cenospheres and may have been formed directly from clay minerals during coal combustion.

(iii) Using optimum flocculation conditions and floe cleaning, final weight recovery of cenospheres from Gale Common fly ash were significantly higher than achieved by conventional collection techniques.

(iv) Although the mechanism by which the selective flocculation process occurs is somewhat unclear, the fly ash particles are undoubtedly more negatively charged than cenospheres under acidic conditions in the presence of dispersant, so they will be more amenable to adsorption of a cationic flocculant by electrostatic bonding.

(v) When incorporated in PVC resin, cenospheres extracted from fly ash exhibit similar mechanical properties to those of talc and china clay fillers. However, since microspheres enjoy cost and other advantages over these two conventional fillers, it appears mat these spherical materials have a potential use in this field. Scanning electron microcopy showed that there was no indication of bonding between spheres and resin matrix, but a suitable surface treatment of spheres, such as coating with silanes, could improve the mechanical properties of filled PVC pastes.



Particle Size	100% of feed less than 300 µm
pH	3.0
Dispersant Type	Dispex N40
Dispersant Dosage (g/tonne)	500
Flocculant Type	MF 292 (cationic)
Flocculant Dosage (g/tonne)	10
Concentration of Solids (% by weight)	5
Conditioning Time (min.)	10 + 1
Agitation Speed (rpm)	1 200 then 350
Settling Time (min.)	
Rougher	7
Cleaning I	8.5
Cleaning II	12

Fig. 7. Proposed schematic representation of flocculation process flowsheet for fly ash

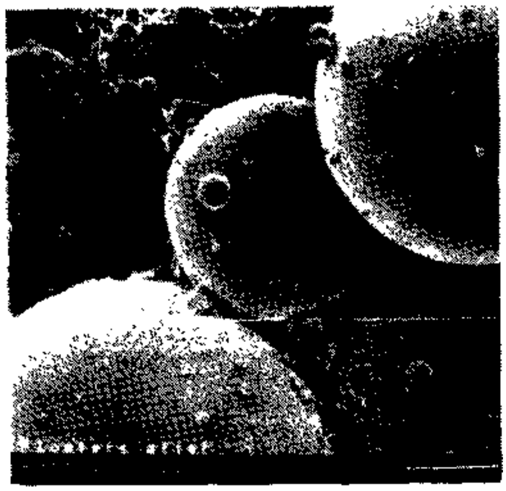


Fig. 8. Scanning electron microscope photographs of cenospheres recovered by flocculation

Fig. 9. Scanning electron microscope tensile fractographs of cenospheres (5 pbw) - PVC paste composites

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