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REPORT 82-17E

BENEFICIATED PRODUCTS FROM FLY ASH: MARKET RESEARCH

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MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES

SEPTEMBER 1982

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Catalogue No. M38–13/82–17E Canada: $2.50 ISBN 0-660-11587-5 Other countries: $3.00	N° de catalogue M38–13/82–17E Canada: $2.50 ISBN Hors Canada: $3.00
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BENEFICIATED PRODUCTS FROM FLY ASH: MARKET RESEARCH

by

H.S. Wilson* and J.S. Burns**

ABSTRACT

Research done in recent years shows that fly ash can be separated into size fractions and components, thus making it a valuable mineral resource.

This study examined the state-of-the-art on the beneficiation of fly ash to recover cenospheres, magnetic iron compounds, and carbon. Methods of beneficiation, applications for products and possible market prices are discussed.

RECHERCHE DE MARCHÉ SUR LES PRODUITS ENRICHIS PROVENANT DES CENDRES VOLANTES

par

H.S. Wilson* et J.S. Burns**

RÉSUMÉ

Selon des recherches effectuées récemment, on a pu démontrer que les cendres volantes peuvent être séparées en fractions granulométriques et en composés, et constituent ainsi une source précieuse de minéraux.

Lors de la présente étude, on a fait l'examen de l'état actuel des connaissances dans le domaine de l'enrichissement des cendres volantes dans le but de récupérer les cénosphères, les composés magnétiques du fer et le carbone. On y traite aussi des méthodes d'enrichissement, des mises en application du produit et des prix possibles sur le marché.

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INTRODUCTION

Since both metallic and nonmetallic mineral resources of the earth are being depleted at an ever increasing rate it is not only logical but prudent to examine the availability of resources from the byproducts of industry. The increasing use of coal for the generation of thermoelectric energy results in the accumulation of large amounts of fly ash and bottom ash. More than 80 Mt of fly ash was produced in 1980 of which less than 20% was utilized.

In 1981, Canadian utilities operated 21 coal-fired thermal generating stations at a total capacity of 16 600 MW. Thermal power generation in Canada in 1981 consumed about 29.5 Mt of coal and produced about 3.5 Mt of ash (1.2 Mt of bottom ash, 2.3 Mt of fly ash) (1). Table 1 gives details of ash production and consumption for plants located in the six producing provinces. Figures 1 and 2 show locations of coal mines and coal-fired thermal generating stations in Canada.

From 1982 to 1986 three additional generating stations are planned which will increase industry's capacity to produce electricity to 18 300 MW from burning of coal. After 1986, the situation is more uncertain. One plant at Genesee, Alberta, having a capacity of 2700 MW is expected to be in operation by 1996. A plant at Hat Creek, British Columbia is under consideration.

Table 1 - Ash production and utilization in Canada - 1980

Province	Total ash produced* (tonnes/a)	Ash used (tonnes/a)	Purpose
Nova Scotia	135 000	12 000	- Cyclone ash for blasting and roof grit
New Brunswick	105 000	none reported	
Ontario	930 000	40 00	- Cement replacement
		100 000	- Waste stabilization
		36 000	- Roads
		50 to 200 000**	- Special projects
Manitoba	30 000	none reported	
Saskatchewan	460 000	24 000	- Concrete
		6 000	- Oil well
Alberta	1 535 000	150 000	- Cement replacement
		70 000***	- Special project
Totals	3 195 000		

*Data include fly ash, bottom ash, boiler slag, and cyclone slag

**Irregular demand dependent upon construction activity

***Temporary supply to Revelstoke dam construction

Source: E.E. Berry & Associates

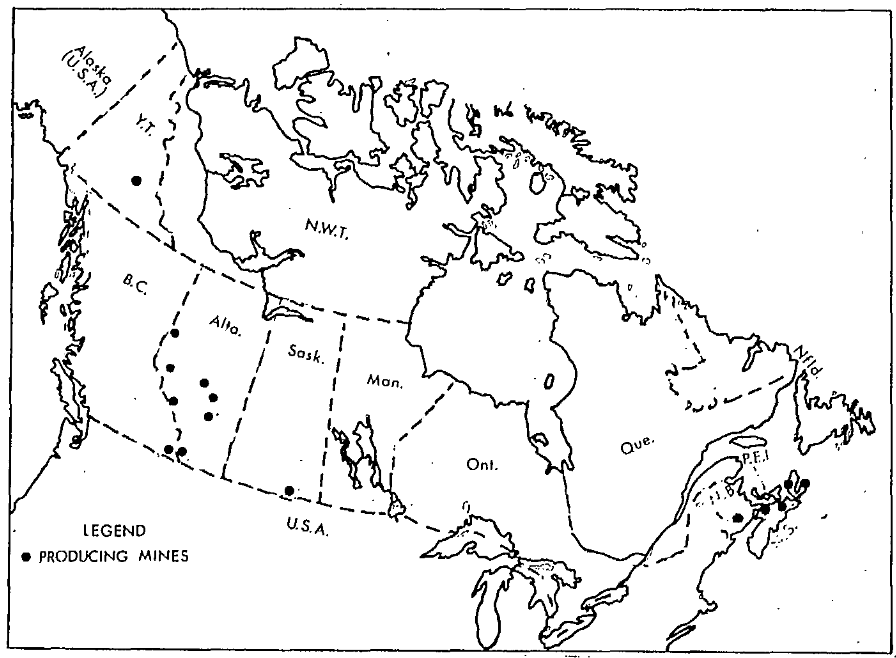

Fig. 1 - Principal coal mines in Canada, 1980

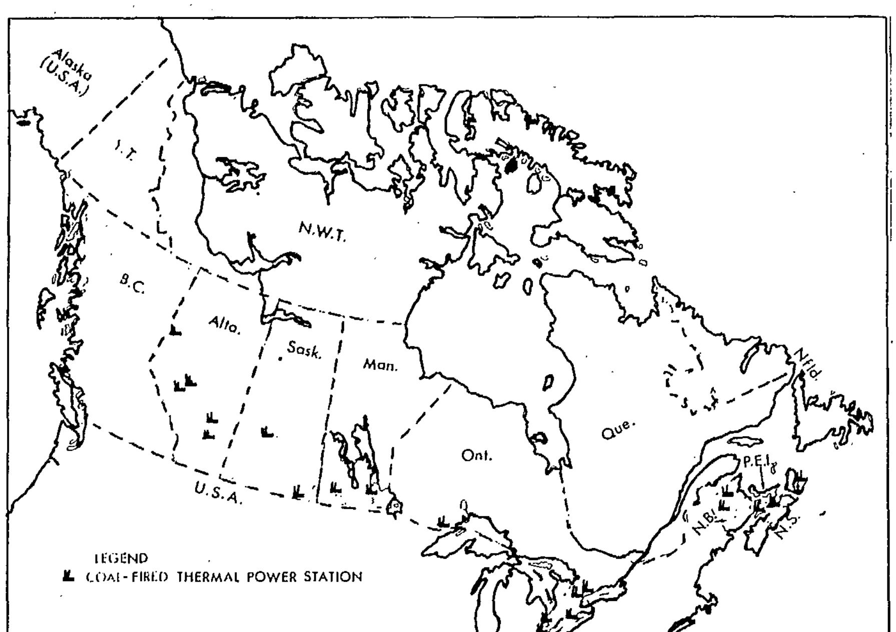

Fig. 2 - Principal coal-fired thermal power stations in Canada, 1980

The Canadian utilities predict that by 1986 coal consumption for power generation will increase by 30% over 1980. Total ash production will increase 45% during the same period, indicating a general decrease in the quality of coal being consumed. The largest increases in coal utilization and ash production will occur in Alberta, Nova Scotia, and Ontario. Proportionately, the most serious problems are likely to be faced in Nova Scotia where an increase of 125% in ash production is predicted by 1986. In magnitude, the largest increase will occur in Alberta where ash quantities will increase from approximately 1.5 to 2.5 Mt/a over the same period.

Fly ash is the particulate material discharged in the air stream from the burning of pulverized coals. In the past it was vented to the atmosphere. Today it is collected at most power plants by electrostatic precipitators and bag houses. Microscopic examinations show that fly ash is composed mainly of spherical particles of glass. Spheres inside spheres and hollow glass heads (cenospheres) are also found. Dark, magnetic spheres and crystalline particles, as well as carbon from incomplete coal combustion constitute important fractions in the ash.

The first major use of fly ash was as a pozzolan (a partial replacement for cement) in concrete, and is still the largest single use. Not all of the components of a specific fly ash contribute to its value as a pozzolan. Carbon and the large crystalline particles may be deleterious, and others may dilute the active fraction. Some fractions of fly ash with pozzolanic properties have greater potential value in other applications if they are separated from the bulk of the ash.

The value of a pozzolan is limited by its role as a partial replacement for cement, a relatively inexpensive bulk material. The market value of the total mixture of components comprising fly ash is less than the value of portland cement. Separation of fly ash into selected components, each with individual unit values determined by its own market role, could provide a better return.

Research carried out in recent years has shown that beneficiation of fly ash into a series of size fractions as well as of components makes it a valuable mineral resource.

The objective of this study was to examine the state-of-the-art on beneficiation of fly ash with regard to the recovery of cenospheres and other related fillers as well as of magnetite and carbon.

FLY ASH COMPONENTS

CENOSPHERES

Formation and General Characteristics

The cenosphere fraction has presented a problem during disposal of fly ash in settling lagoons. Being lighter than water, the hollow spheres float to the surface where they sometimes reach a depth of several metres. The surface of the material can become dry and the cenospheres are wind blown. They are also difficult to collect and transport for further processing. Most companies collect dry cenospheres after a storage lagoon has been filled. Elaborate skimmers have been developed for wet collection and efforts have been made to directly process the dry fly-ash stream from the power plant for the cenosphere fraction.

Cenospheres are formed by the evolution of carbon dioxide and nitrogen within particles of fused glass in the boiler, resulting in their expansion. The gas evolution is catalyzed by iron oxide. Raask states that the formation of cenospheres is determined by the mineral matter in the coal, the relationship between iron and mineral matter, the fineness of the coal and the temperature in the boiler (2).

Jan de Zeeuw and Abresch found that a large percentage of cenospheres are not truly floaters and remain below the surface of the lagoon (3). This was corroborated by Joshi. He found that about 2.5% of ash from Forestburg, Alberta, consisted of cenospheres having a specific gravity of less than 1.47, but only 0.6% had a specific gravity of less than 1.0. However, general practice in the market place is to refer to cenospheres as the "floaters". In some cases, researchers have found spheres inside of spheres and sometimes a third set. Fisher et al coined a term "plerospheres" to identify those spheres which were packed with other spheres (4). No effort has been made to report on the specific gravity of these spheres in relation to what might be the specific gravity of true cenospheres (single hollow glass spheres).

The spheres of glass are 20 to 200 µm in diameter with non-porous shells of 2 to 10 µm. The bulk density varies from 0.25 to 0.35 g/cm^3, the apparent density of the individual particles is between 0.4 and 0.6 g/cm^3.

O'Keefe, Li, Carpenter et al, Kubo and Hycner give additional information on the characteristics of cenospheres (5-9).

Figure 3 shows three scanning electron micrographs and an optical micrograph of cenospheres.

The general consensus is that the cenospheres are associated only with the fly ash, although various observers have noted that they also occur in the bottom ash.

Recovery Methods

Current methods of established marketing organizations involve recovery of cenospheres from the surface of filled fly ash lagoons. Although considered dry when recovered they may contain up to 20% water. From storage, the cenospheres are dried and then classified into various size fractions and specific gravities. A processor, Fillite (Runcorn) Ltd., in Cheshire, England and others in the USA use such methods.

A dry process for the treatment of fly ash has been announced recently by Zeelan Industries Ltd. in St. Paul, Minnesota. This company suggests that a more efficient process has been developed. Pilot plant and laboratory work on dry separation have been done elsewhere but to date no other commercial operation using dry separation is known. Most recovery methods involve the separation of various other components in the fly ash.

None of the commercial suppliers of cenospheres have made public the details of their process. One producer lists the following properties:

Chemical Composition:	Al_2O_3: 27 to 33%
	SiO_2 : 55 to 65%
	Fe_2O_3: 4% maximum
Density range:	0.3 to 0.8
Bulk density:	0.18 to 0.45
Hardness:	5 (Moh's scale)
Average wall thickness:	0.1 sphere diameter
Melting temperature:	1200 to 1250°C
Thermal conductivity:	0.09 W/mk
Coefficient of thermal expansion:	8×10^{-6} (°K)

Potential Markets

Cenospheres are used mainly as an industrial extender or filler which utilize the following inherent properties of the material: low specific gravity; inorganic and inert; good thermal resistance; good electrical resistance; and spherical shape.

Other competitive products are manufactured from glass compounds and therefore are expensive and highly energy intensive.

Cenospheres can be used in various applications, such as: (1) lightweight and thermal insulating concretes and inorganic cement products; (2) resin fillers; (3) paint fillers; (4) miscellaneous.

1. Lightweight and Thermal Insulating Concretes and Inorganic Cement Products - The most important application is in drilling cements. Harms and Lingenfelter state that the high strength microspheres (cenospheres) gave higher strengths than did other low density additives. They also used lower water-cement ratios. Excellent performance was demonstrated in high temperature applications such as deep wells and in geo-

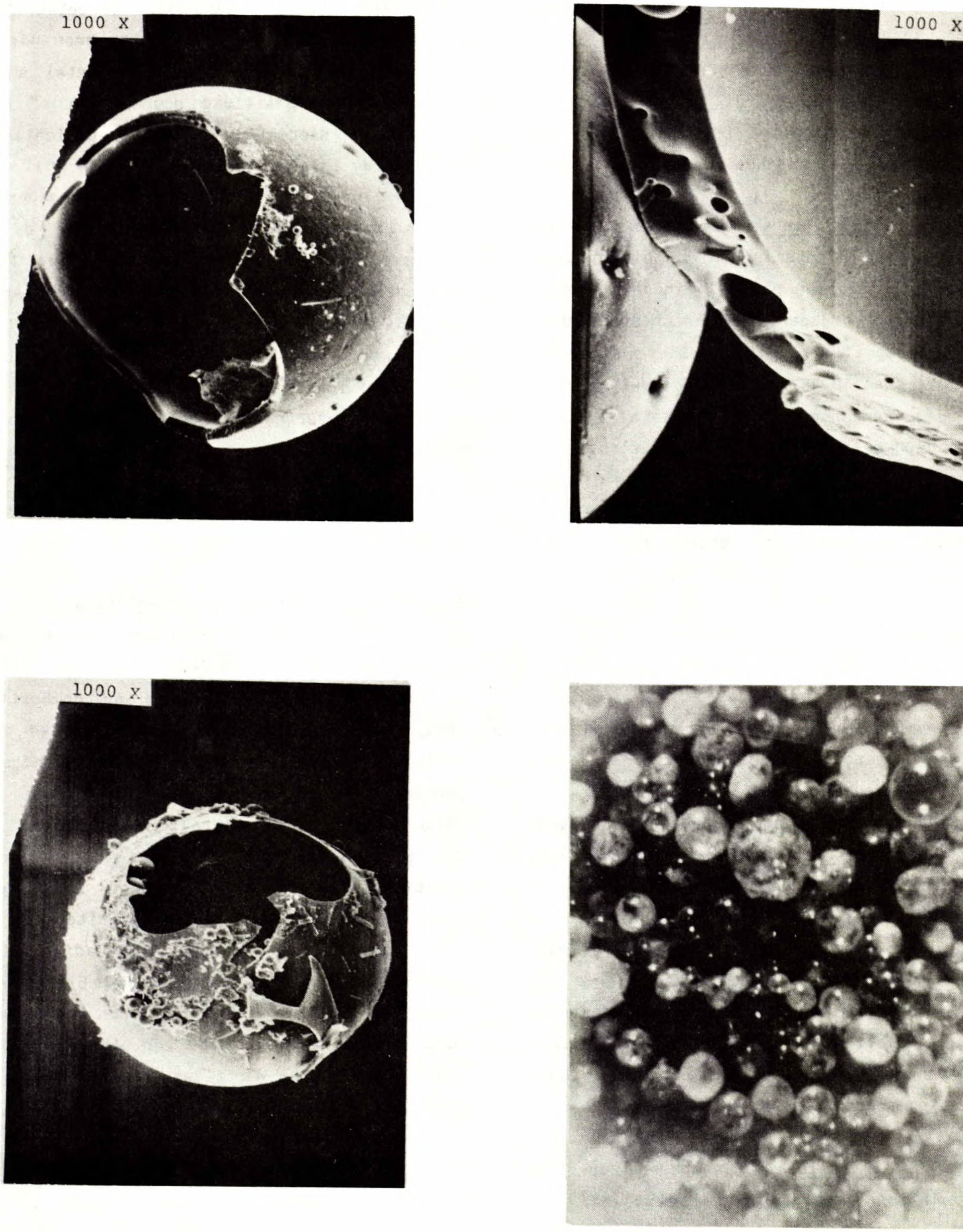

Fig. 3 - Micrographs of cenospheres

thermal applications. Likewise, equally effective performance was achieved in low temperature applications in the Arctic. The heat insulation properties were dramatically improved (10).

Other inorganic cement applications mentioned in the literature are: lightweight concrete; glass reinforced concrete; grouting; bricks; gunning mixes; and hot tops.

2. Resin Fillers - Extensive research has been done and patents issued on this application since it brings the highest financial return to the cenosphere producer. Depending upon particle size and specific gravity, prices range from \$0.10 to more than \$0.45/kg. The following advantages in using cenospheres have been claimed:

- High strength of the individual particles;
- Additional strength provided to the resin mix by better dispersibility;
- High loading potential and reduced shrinkage of the resin;
- Lightweight;
- Abrasion resistant;
- Inert and thermally stable; and
- Improved flow characteristics.

Cenosphere-filled resins have been used for deep sea buoyancy. These foams are being used on Canadian made submersibles.

Sandwich construction panels have been made with cenospheres for lightweight, decorative, rigid and impact-resistance fascia boards.

Cenospheres are also used in plastic fiberglass boat construction to provide lightweight construction and smooth surface.

The aircraft and automotive industries are making plastic parts utilizing the light weight of cenospheres and in some cases the thermal insulating properties.

3. Paint Fillers - Cenospheres used in paint formulations as a filler contribute to:

- Improved hiding power due to refraction from the paint-air interface;
- Low vehicle demand, (low oil absorption); and
- Scrubbability and burnish-resistance.

The annual North American consumption of fillers of all types is in excess of 9 Mt.

4. Miscellaneous - When cenospheres are used in brake linings, their insulating properties reduce heat transfer and result in better braking and longer brake life. They have been used as a dry insulating surface on molten metal and also in hydroponic, soil-less propagation of plants. Additional information on the applications of cenospheres is given elsewhere (11 to 25).

The market potential for cenospheres in Canada is currently being determined by tests underway on all the available Canadian fly ash sources. Canadian climatic conditions are not conducive to skimming operations from exposed lagoons, and dry separation of large quantities of fly ash for 1 or 2% of cenospheres may not be economic. Nevertheless, more research should be done on the separation of the cenospheres due to the variety of potential.

MAGNETITE

Formation and General Characteristics

Coal contains various percentages of iron, either as iron pyrites or as iron silicates of various compositions. During combustion of coal, these iron compounds are converted to magnetite, hematite, and magnetic glassy spheres, the percentage of each depending upon the coal composition and furnace and boiler conditions. Bituminous coals have a much higher iron content than sub-bituminous coals. The iron in bituminous coals is converted mainly to magnetite.

The iron content of Canadian fly ash varies. Western fly ash contains 5 ± 1% of iron calculated as Fe_2O_3. The ash from the bituminous coal used by Ontario Hydro contains approximately 16% Fe_2O_3. In the Maritimes, the fly ash contains from 16 to 50% Fe_2O_3.

Recovery Methods

Apparently the first production of magnetite from fly ash in North America was at the Lakeview plant of Ontario Hydro. According to Boux, magnetic separation of the iron was done with a permanent magnet drum separator, designed to yield a product of up to 65% iron (26). It was calculated that 14 000 t would result from a 180 000 t fly ash input.

Roy et al reported on a plant in Ohio which had produced 700 t per month of dry-separated magnetic fraction using three permanent magnet rotary separators (27). The plant is no longer in operation.

Aldrich reported that a company in Hatfield Ferry, West Virginia, produces commercial quantities of magnetite by a proprietary process (28). Nowak reported that a process in Poland uses a plate electro-magnetic separator to collect magnetite on a commercial scale (29). The Central Electricity Generating Board's laboratory in Leatherhead, England, apparently has a device for separating magnetite, involving a rotating tube incorporating a permanent magnet. Pilotec Inc. in Winona, Minnesota, apparently has conducted a feasibility study on the commercial separation of magnetite.

Other articles and patents on the separation of iron compounds from fly ash are given elsewhere (30 to 34).

A company in Ontario is doing a study on the removal of iron and alumina from fly ash. This study has shown that a large percentage of the iron in one fly ash is hematite and cannot be magnetically separated.

Recent work has been carried out at CANMET on fly ash from the power station at Grand Lake, New Brunswick, which has an iron content of 46%, the majority of which is magnetite (35). The fly ash produced by the coal-burning thermal stations in the Maritimes has sufficient iron content to warrant removal if successful separation techniques can be developed and tests for heavy media work can be completed.

Potential Markets

There is a large potential market for magnetite as an agent in the cleaning of metallurgical coal by heavy media separators. In Western Canada five coal companies in the Alberta and British Columbia coalfields in the Rocky Mountains have combined use for approximately 36 000 t/a of minus 45 µm magnetite for heavy media separation at $55 to $80/t, for the treatment of approximately 16 Mt of coal.

Magnetite is also used for coal washing in the Maritime provinces. One coal company uses 5000 to 6000 t/a of magnetite imported from the USA at a cost of approximately $70/t.

Saeuberlich and Richter discussed a method of using iron oxide from lignite fly ash in the production of pig iron (36). There is a Japanese patent on the use of iron oxide from fly ash in the manufacture of cement (37).

CARBON

Formation and General Characteristics

Unburnt or carbonized coal is carried into the fly ash as discrete particles when incomplete combustion takes place during the burning of coal. Electron microscope pictures show this material as being highly vesicular. Studies indicate that the carbon is 'activated' by the heat treatment and is reactive to a wide range of organic materials.

The percentage of carbon in the fly ash depends upon the type of coal; lignite and sub-bituminous coals usually produce less than 1% carbon. Bituminous coals on the other hand can leave a carbon residue in excess of 10%. The fineness of the ground coal as well as furnace conditions also can affect the percentage of residual carbon.

Recovery Methods

Carbon is not removed commercially from fly ash, however, pilot plant work has been done. The Lakeview, Ontario, separation plant was designed to remove carbon by dry screening. The plus 150 µm fly ash fraction has a high carbon content. Boux reported that 3000 t of plus 150 µm carbon could be collected from 200 000 t of fly ash feed (26).

Stemerowicz and Bruce studied flotation methods for carbon removal (38). This work indicated that it is possible to extract a carbon fraction by flotation, using kerosene.

Hurst and Styron reported a process for the separation of all components in fly ash (39). They used kerosene and pine oil in a flotation process yielding samples containing up to 75% carbon.

Inculet et al conducted pilot plant studies for the removal of carbon from fly ash by electrostatic separation (40). In this process the fly ash is fluidized and triboelectrically charged. The carbon particles become positively charged and the fly ash negatively charged. The carbon forms a deposit on the cathode.

Burns et al established that the carbon in fly ash is in the activated form (41). They found in previous studies that high-carbon fly ash has potential in the reduction of chemical and biological oxygen demand in sewage treatment and also in the cyanide extraction of gold.

Potential Markets

In the work reported by Boux, the carbon recovered was considered as a fuel (26). Hurst and Styron considered the use of carbon as a filler in rubber and as activated carbon.

Carbon extracted from fly ash should be considered for the 'activated' carbon market and not as a fuel. Pelletized carbon (2.36 mm to 850 µm) used for this purpose sells for approximately $2.00/kg FOB Vancouver. Most activated carbon used in Canada is imported. In 1981, 5 377 030 kg was imported into Canada at $7 489 000 or $1.39/kg; 83% of the total came from the USA and the balance from the Netherlands, West Germany, the UK, and Japan.

TOTAL SEPARATION TECHNIQUES

The only detailed techniques for separation of all fly ash components are those published by Boux (26) and Hurst and Styron (39). Jan de Zeeuw reported the initiation of research work in this area (3). Neither process is presently being utilized. Research on the efficiency of a wet-dry process should be done. In the work of Hurst and Styron, the value of fly ash was increased by a factor of 5 (39).

COST-BENEFIT ANALYSIS

A cost-benefit analysis implies knowledge of the plant location, size, component proportions, and methods of treatment, which are unique in each case. Therefore, in this study a cost-benefit estimate can be based only on the fly ash components at 1981 prices. It is assumed that the values of the components are; cenospheres at $0.77/kg, magnetite at $0.08/kg, activated carbon at $1.50/kg, classified fractions (fillers) at $0.55/kg and the balance as pozzolans at $0.02/kg.

The following is a hypothetical breakdown of the possible values of the components of ashes from three locations in Canada.

		Percentage of recoverable quantities		
Product	Unit price/kg	Ontario	Alberta	Nova Scotia
Carbon	$ 1.50	7.5	-	3.0
Magnetite	0.08	10.0	-	25.0
Cenospheres	0.77	0.5	2.0	1.0
Fillers	0.55	30.0	50.0	20.0
Pozzolan (balance)	0.02	52.0	48.0	51.0
Value per beneficiated		100.0	100.0	100.0
tonne		$299.75	$300.00	$192.90

The filler market represents a large percentage of the value of the beneficiated products where the use of fly ash is just now becoming established. Considerable marketing effort will be required before the above values can be realized.

As reported previously, 5.4 t of activated carbon valued at $7.5 million was imported in 1981. Magnetite imported for coal washing and other uses was about 20 000 t or $1.6 million. Importation of glass beads in 1980 amounted to almost $600 000. Other fillers are imported for a variety of uses and it is impossible to determine the percentages that might be replaced by fly ash. Many products incorporating fillers require a white filler; most fly ash would not be used in such products.

CONCLUSIONS

The need to re-evaluate our mineral resources has lead to studies on utilization of byproducts as source material for a variety of products. Fly ash, from coal-burning power plants, represents a possible source of fillers and additives to the oil-drilling, plastics and paint industries, a source of activated carbon for various purification problems, and a source of magnetite for heavy media cleaning of metallurgical and thermal coals.

Cenospheres, the very light component of fly ash, is becoming valuable as an ingredient of certain oil-drilling cements, insulating resins, and, in general, as a filler that is lightweight and inert. Other spherical components of fly ash, fractionated to narrow specifications, are beginning to be used in the manufacture of resins and paints as a filler with high loading factor.

Magnetite has been successfully removed from fly ash by both wet and dry processes and is reported to have been successfully used for heavy media washing of coal. An extensive market exists for this product.

Carbon has been removed by both wet and dry processes but there is no reported currently-operating process in North America. If the carbon can be shown to be 'activated', a large and growing market is available at a reasonably high return.

It is recommended that further study be made on beneficiation by wet-dry processes.

A theoretical cost-benefit analysis of the fly ash fractions indicates a six to tenfold increase in the fly ash market value based on selling price. Since there are no methods of separation available for study and factors such as transportation and plant equipment are not known, it is impossible to determine the net proceeds from beneficiation. Fly ash beneficiation could provide the materials currently being imported, therefore, contributing to improvement of the foreign trade balance.

ACKNOWLEDGEMENTS

This study was made by J.S. Burns, formerly Manager, Research and Development, Genstar Conservation Systems Ltd. in fulfillment of Department of Supply and Services Contract OSQ81-00117.

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