The Italian Approach to the Problem of Fly Ash

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ABSTRACT

The paper gives an overview of the activity carried out in Italy during the last three years in the frame of an applied research agreement involving ENEL, the Italian State-owned Company for electric energy, its subsidiary CESI, the Department of Geo-Engineering and Environmental Technologies of the University of Cagliari and the joint Research Centre of the National Research Council. After a general introduction regarding the Italian situation, the approach to the problem of fly ash beneficiation is dealt with, and results so far obtained both in the laboratory and at a pilot-plant scale are given and discussed. The research is directed to improve the capability to recover other useful products in addition to those traditionally used for concrete and cement applications, resulting in more outlets for fly ash and by-products.

INTRODUCTION TO FLY ASH

Fossil fuels are widely used in modern power stations throughout the world to produce electricity. Besides energy, a variety of by-products of different kind are also obtained from the combustion of coal, such as fly ash, bottom ash, flue gas desulfurisation sludge and so on. They are all inevitable at coal-fired boilers due to the presence of refractory mineral matter and of some components of the fuel, the combustion of which is slower and incomplete.
The inorganic powdery residue, made up of tiny sphere-shaped glassy particles that remain after the pulverised coal is burned, is called FLY ASH or Pulverised Fly Ash (PFA).
Ashes differ in characteristics depending upon the type of coal burned, the process undergone by the coal before combustion as well as the operating conditions of the boiler. Accordingly, fly ash composition and behaviour change widely from case to case.
Fly ash, entrained by the flue gas from the furnace to the dust collection system (filters and electrostatic precipitators), generally contains unburned coal in variable quantities.
The char particles that remain in the ash after the incomplete combustion of coal in the furnace essentially consist of carbon, free from volatile matter, often incorporating inorganic newly-formed components.
The LOI value (Loss On Ignition) is the parameter that gives an evaluation of residual quantity of carbon in fly ash.

FLY ASH, AN INCREASING PROBLEM

Every year huge quantities of potentially usable by-products of coal combustion are obtained in electric power stations. According to a crude estimation, more than 300 billion tonnes per year of fly ash are produced in the world. This figure has steadily increased over the last years and it is expected to grow up more rapidly in the future as a result of the pressing need to produce more energy. For this reason coal-fired plants larger than in the past are now required.

Older coal-fired power plants generally produce fly ash with a high percentage of unburned coal. However, although these plants are gradually being decommissioned, especially in industrialised countries, the quantity of low-LOI fly ash available in the market is always decreasing.

This is also due to the fact that more recent coal-fired plants are equipped with low-NOx burners in their boilers which are conducted at lower firing temperatures. This new approach, adopted for the sake of environmental protection, has however an adverse effect on the quality of fly ash produced and brings about an increase in the percentage of unburned coal (LOI).

Therefore it can be said that in the near future fly ash production will increase while at the same time ash quality will become worst.

FLY ASH USES

Fly ash can either be considered as a burdensome waste, if landfilled, or a tremendous resource for a wide range of uses, if employed as a raw material, from large-scale applications in the cement industry to some niche outlets like those of cenospheres and active carbon.

The importance of the LOI value is due to the fact that the most interesting use of fly ash, in terms of volume, is as a pozzolan-like material in Portland cement concrete.

Electric utilities have long recognised the necessity to reduce the high levels of residual unburned coal in fly ash, since a high carbon content could reduce and even prevent the possibility of placing fly ash in the concrete market. Moreover it represents an energy loss, albeit minor, of purchased fuel.

Fly ash sale is not, of course, the core business for electric companies; nevertheless it can be a significant economic concern capable of adding a certain income from ash sales to the cost savings related to landfilling.

STANDARD REQUIREMENTS FOR FLY ASH USES

Tests carried out by different organisations showed that carbon could be a deleterious substance in concrete because it adversely affects air entraining admixtures commonly used to impart desirable properties to concrete, including increased durability.

International standards (EN 450, fly ash for concrete) have established a 5% maximum content of unburned coal in fly ash usable for cement application, although some concrete producers set the maximum allowable LOI level at less than 4%.

Where there is such kind of market, higher prices for lower-LOI fly ash are generally recognised.

There are areas in the world where little or no fly ash is accepted because the residual carbon content of locally available ash is greater than that allowed by specifications while higher quality sources are remote, thus carrying unacceptable freight costs.

Fly ash that does not cover such requirement should be landfilled and thus either a disposal cost or an ecological problem or both will be incurred.

ENVIROMENTAL PROBLEM

Fly ash disposal is most of all an economic and environmental concern.
Costs of disposal have gradually been increasing in the last years, while the share volume of fly ash being disposed of swelled too. Consequently, the utilisation of a larger tonnage of such by-product in the future is highly desirable.
Nevertheless, since fly ash is known as a special waste, utility industries have been conservative about marketing this by-product in the fear for liability in face of existing environmental regulations. Accordingly, utility coal ash entails a disposal burden in presence of rising landfilling costs and more stringent environmental regulations.
Today modern community exerts an increasing pressure to reduce as much as possible the environmental impact due to by-products of working industrial processes.
In compliance with this, European Community instructions and rules are being developed aiming at:

- Minimisation of production of wastes;
- Waste recovering for use in different industrial processes;
- Thermal destruction of wastes with energy recovering;
- Waste dumping, as the last possibility.

It is clear that there is a sound indication for a policy aimed at making the re-utilisation of by-products feasible.
A beneficiationprocess capable of reducing the fly ash LOI could assist in eliminating/reducing the problems related to fly ash disposal; such as a land area needed for disposal and associated transportation costs.
That kind of treatment is becoming more and more compulsory.

THE ITALIAN SITUATION

The main goal of the environmental policy followed by ENEL is that of establishing an integrated management of its own by-products through which both a substantial reduction in the amount to be disposed of and the increase in energy and material recovery in any suitable form could be achieved. This in agreement with Italian law (1997, February) concerning the management of industrial by-products.
According to the most recent data available, about 775 million tonnes of fly ash have been produced in Italy in 1997, coming from 9 different sites. This is a quantity somewhat less than that achieved in the previous year (916 million tonnes in 1996) as a result of a better quality of imported coal accompanied by a reduction in the quantity burned.
Recovery in 1997 was 113% of the amount produced, owing to the fact that part of fly ash produced in 1996 and temporarily stockpiled has also been traded.
In compliance with its policy, ENEL is oriented to achieve the recovery of fly ash to be used as a raw material either in the same process (recovery of the residual heat value) or for other applications.
Fly ash recovery in cement offers also the benefit to overcome the need for alternative materials to be quarried in surface operations, thus avoiding an additional environmental damage.
In order to pursue the goal of adding new applications of fly ash in the cement sector (additive in concrete production, brick manufacturing and street flooring, which are the most common uses), research activity of ENEL has been addressed in various directions resulting in:

- tests concerning the use of fly ash in lighter structural aggregates for the manufacturing of poles and masts used in electric transmission lines or of prefabricated transformation cabinets [1, 2];
- experiments regarding the employment of fly ash either as a raw material in the mass production of ceramic-matrix elements or as an additive in the vitrification/inertisation of toxic/noxious wastes;
- investigations carried out in view of finding a cheap treatment process suitable to reduce the residual percentage of carbon in fly ash.

CESI was singled out by ENEL as the Partner Company for the development of such activities, while DIGITA and CSGM who had been working on the subject for a long time were later involved for their scientific knowledge and the know-how concerning separation technology. Their joint effort made it possible to obtain the results described in this paper.

CESI/DIGITA CO-OPERATION HISTORY

The achievement of the desired fly ash beneficiation process has been obtained through a step by step activity.

First of all a preliminary study has been carried out consisting in the analysis of physical and chemical characteristics of ash products from various sources. Later on, a number of candidate separation technologies, both dry and wet, were identified and tested on representative samples of fly ash, until the best flowsheet has been devised, taking into account both cost and performance.

As illustrated in some previous papers concerning the early stages of the research [3], the most advantageous process singled out for the beneficiation of fly ash essentially consists of a treatment including a stage of sieving, that by itself was found to be capable of providing a low LOI product in the fine undersize fraction, followed by a stage of electrostatic separation of the oversize fraction by means of which a coarser low-LOI product is separated from a carbon-rich material. Similar approaches are followed elsewhere [4, 5].

More recently the activity planned in the frame of the co-operation was directed to the optimisation of the treatment process, through a systematic study of the influence of operational variables and parameters, with particular focus on the electrostatic separation.

The main achievement of this activity was the development of different models of electric separators, which have been designed, built and tested at both the laboratory and pilot-plant scale. They are all based on the same principle, that was put into light in the course of the fundamental investigation made with a classic roll separator under carefully controlled environment.

The results of this experience showed that:

- Ash particles are non-conductor and exhibit a marked trend to take a negative polarity by contact charging;
- particles of unburned matter behave as conductor and thus always take a charge with the same polarity as that of a metal surface on which they get in contact;
- separation is very sensitive to temperature and humidity.

Therefore if a stream of fly ash is fed onto a grounded metal surface in presence of an electrostatic field generated by a negative electrode, ash particles are pinned while carbon-rich particles are extracted from the layered mixture carried through the separator.

The problem is that of freeing the unburned particles captured inside the mass of feed material for making the “lift” effect feasible. Since the concept of feeding the material in the form of a very thin layer (like in the roll separator) would decrease the throughput capacity to unacceptable

levels for a commercial application, a better cost-effective solution has been found to be that of imparting a suitable shaking action to the carrier surface in order to produce a periodic expansion of the bed.
The carrier device can be either a belt or a revolving cone or a still surface onto which the stream slides entrained by a drag force, like in a pneumatic cyclone.

WHY A FLY ASH TREATMENT IS NEEDED

The first aim for the treatment of fly ash is to increase the overall recovery of a low-LOI product, as well as to obtain a by-product rich in carbon (LOI > 40%) for different possible applications.
A second, not less important, requirement is the commercial development of a simple, low-cost process, due to the fact that fly ash has a low commercial value especially for the most common applications.
A high treatment cost would put fly ash in a not attractive position with respect to the cheaper alternative materials and, in such a way, out of the market.
The cost of processing should not be higher than the possible market value of beneficiated ash, whatever it will be, although in some cases a treatment can simply be justified by the possibility of avoiding the cost of disposal.
Moreover it should be taken in mind that one of the major problem preventing a large utilisation of fly ash is the difficulty of producing a quality-controlled fly ash material, which consistently meets market specifications. In addition to a better management of the process (selective collection of ash, blending of coal, product handling and storage, a more careful control of combustion), beneficiation could be very helpful is smoothing the variability of ash quality.

USES OTHER THAN CEMENT/CONCRETE

The diverse chemical, mineralogical and morphological properties of fly ash offer an opportunity to process it and recover various fractions with particular attributes.
Currently, fly ash is being utilised to an ever increasing extent in building and construction applications (cement additive, lightweight aggregate), environmental rehabilitation (mine spoil ameliorate), waste management (toxic element immobilisation) and polymers (functional filler).
However, the value of fly ash as a resource is still probably underestimated.
Another important application is to use unburned carbon as filter media, in place of activated carbon or as a substitute for industrial carbon.
In fact, the unburned coal particles are structurally modified while passing through the combustor resulting in the formation of macro-porous surfaces with presence of silica and alumina compounds, so that, after separation from the true ash, they may constitute a unique precursor for the production of bulk adsorbents. The recovery of cenospheres as a filler in plastics and other materials can yield a high-value product suitable for several commercial applications.
Cenospheres are essentially thin-walled glass spheres with a relative density less than 1.0. They float on water and can be recovered from the surface of ash disposal ponds or by means of wet gravity-sensitive mineral processing techniques. Their use imparts excellent flow properties to the product, enhancing the pliability of monolithic linings. Insulating refractors based on fly ash have remarkable strength-to-density ratios, excellent thermal shock resistance and improved thermal conductivity for a given bulk density. Most important, they are far more cost-attractive than competitive products.

In addition to this, unburned coal can be recycled as a fuel for its residual heat content. In fact, tests have shown that combustion kinetics of the carbon-rich fraction recovered from fly-sash is not greatly different from that of the original coal
Therefore utility coal ash may become an important resource as the market for this by-product of combustion will expand to include a wide variety of possible applications.

RESULTS OF EXPERIMENTAL TESTS

The results of the experiments carried out in the course of the development of the beneficiation process have been illustrated and discussed elsewhere [6].
It seems now interesting to give a short report on the results regarding the absorption potential of the carbon-rich fraction separated from fly ash in view to solve the problem of decontamination of waters polluted by metal elements or hydrocarbons.
A typical composition (ppm) and the results of a leaching test for the carbon-rich fraction recovered by electric separation is reported in Tables 1 and 2.

Table 1.Content of some heavy metals (ppm) in the entire carbo-rich fraction and in the non-magnetic residue of coarse fly ash

Elements	Entire fraction	Non-magnetic residue	Allowed limits *
As	100.17	93.80	100
Cd	0.29	0.37	100
Cr	96.06	80.25	100 (Cr VI)
Cu	77.06	88.10	5000
Ni	171.54	133.66	-
Pb	133.82	108.06	5000
Zn	142.00	90.00	-

** DPR 915/82 (Italian legislation)*

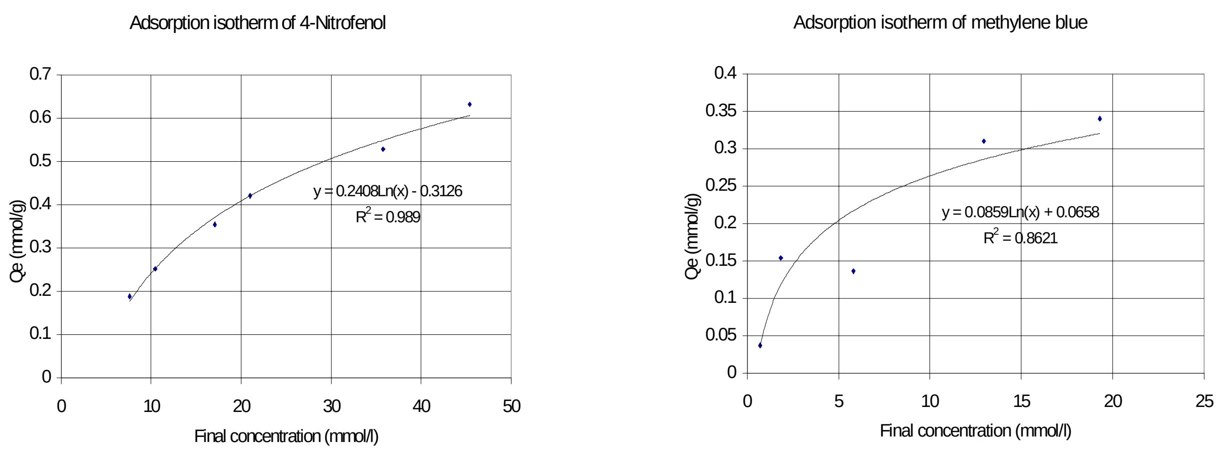
Table 2. Content of some heavy metals (mg\l) in the eluate of a leaching test with acetic acid on the carbon-rich fraction of coarse fly ash.

Elements	Entire fraction	Non-magnetic residue	Allowed limits *
As	< 0.08	< 0.08	0.5
Cd	< 0.005	< 0.005	0.02
Cr	< 0.002	< 0.002	0.2 (Cr VI)
Cu	0.015	0.12	0.1
Pb	< 0.02	< 0.02	0.2
Zn	0.8	1.4	0.5

** Tabella A Legge Merli (Italian legislation)*

It can be said that mobilisation of the metal elements contained in this by-product is not particularly high compared to the chemical analysis, due to the prominent buffer effect of the

matter, although for Zn and Cu the legislative limits are passed especially for the non-magnetic residue, posing some problems for its commercial utilisation.
Preliminary adsorption tests have been made with the high-carbon fraction as such, using a high molecular weight (4-nitrofenol) and a medium molecular weight adsorbate (methylene blue) with a dosage of 0.5 g per 100 ml of a solution at variable concentrations ranging from 3 to 50 mmoles/l for the nitrofenol and from 1 to 30 mmoles/l for the methylene blue.
Absorption isotherms from tests conducted in a reactor at constant temperature (25°C) and moderate agitation (90 strokes per minute) over a contact time of 24 hours are given in Figures 1 a and b.



a) b)

Figure 1. Adsorption isotherm of 4-nitrofenol (a) and of methylene blue (b) on the carbon-rich fraction of fly ash (Q_e = adsorbed concentration per gram of adsorbant)

The adsorption potential of the coarse carbon-rich fraction of electrostatic separation appears interesting in comparison with the corresponding data for three samples of active carbon (CA1, CA2, CA3) as shown in Table 3.

Table 3. Maximum adsorption capability of carbon-rich by product of treated fly ash compared with that of three samples of activated carbon from Moringa Oleifera at variable temperature and activation time.

Adsorbant	Maximum adsorption capability Qe (mmoles/g)
Coarse carbon-rich residue as such	0.56
Active carbon CA1 (750 °C, 30 minutes)	0.44
Active carbon CA2 (750 °C, 120 minutes)	0.99
Active carbon CA3 (800 °C, 30 minutes)	1.06

Adsorbate: Methylene blue

On the basis of these encouraging results two further series of tests have been carried out aiming at assessing the adsorption potential for metal elements and for bio-refractory organic molecules dissolved in water.

Results for Cu and Zn which are characterised by a higher mobility in the leaching test are reported in Figure 2. Similar curves have been obtained for the other metals: concentration first increases to a peak point and then decreases until reaching a value lower than the initial concentration after 4 hours.

The residual organic load of a liquid from a purging plant of urban sewage (measured in terms of COD, Chemical Oxygen Demand) was partially removed from an original level of 35 mg O_2/l due to the presence of some organic compounds difficult-to-remove with conventional biologic units. Final COD resulted to be a 23 mg/l (Figure 3).

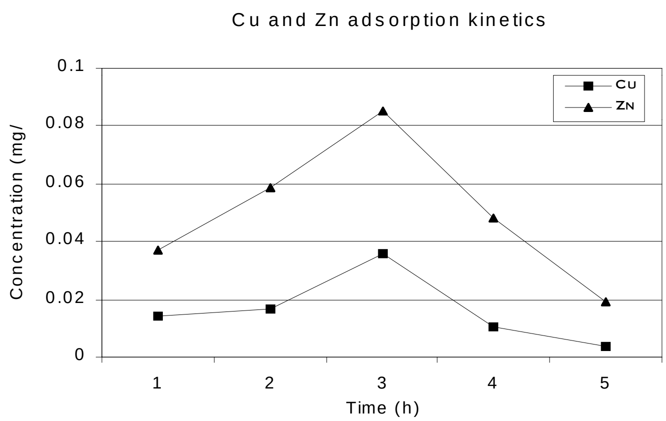


Figure 2. Adsorption kinetics of Cu and Zn on the coarse carbon-rich fraction of fly ash washed with a soda solution.

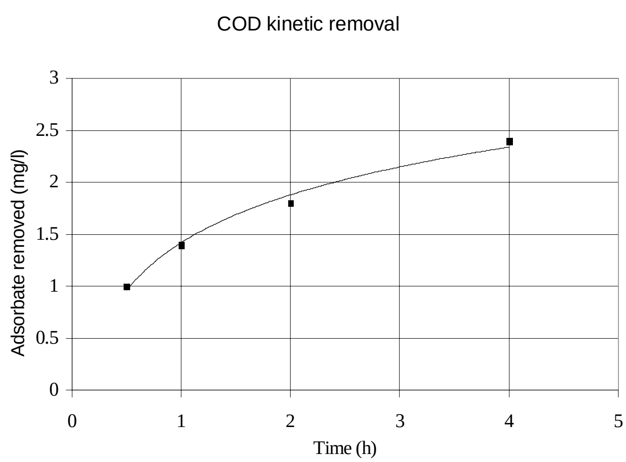


Figure 3.Removal kinetics of residual COD of a biologically treated urban effluent by means of the coarse carbon-rich fraction separated from fly ash.

INDUSTRIAL ASPECTS

As shown in previous papers, the flowsheet envisaged for the beneficiation of fly ash has been proved technically viable resulting in:

- The recovery by a screening stage of a low-LOI product meeting the requirements for cement applications, the quality of which can be controlled by the separation size depending on the mesh opening and on the setting of the screen;
- the electrostatic separation of the screen oversize into two products: again a low-LOI fraction (to be either blended with the sieve fines or possibly treated for the preparation of a cenosphere concentrate) and a carbon-rich fraction to be recycled to the boiler o used for other applications.

There is a great confidence that the laboratory results can be reproduced at a commercial scale on the grounds that the process is simple and reliable. This is confirmed by the results of some trials with a machine of industrial size as briefly discussed below.

A - Screening

Size classification tests have been carried out using a Vibrowest 36” circular screen with different mesh openings and variable setting of the counterweights in order to control the kind of movement of the fly ash mass flowing through the machine. The aim of the tests was that of identifying the optimum setting giving the highest yield of fines for a given quality of the product.

Taking into account that fly ash sieving is relatively simple, in spite of the fineness of the material, owing to the favourable shape and the high mobility of the particles, a too long residence time in the attempt to increase the yield of product would be detrimental concerning both the throughput capacity and the LOI content of beneficiated ash (more particles of unburned matter are likely to break into smaller fragments that would pass in the underflow).

Three sieving surfaces have been tested: 46, 76 and 89 μm. Of course both product yield and throughput capacity increase with the screen opening but LOI content of the undersize also increases as shown by the figures of Table 4.

Table 4. Typical screening results with the Vibrowest circular screen provided with ultrasound cleaning.

Mesh opening [μm]	Undersize [LOI %]	Oversize [LOI %]	Yield [%]	Capacity [kg/h]
76	2.98	9.31	68.1	612
89	3.14	9.18	82.2	750

The use of ultrasounds proved to be highly beneficial to the capacity of the machine which is increased by about 25 %.

Moreover a theoretical study based on a simple model has been carried out in order to predict the influence of the mesh opening on the throughput capacity of the screen and on the yield of product (beneficiated ash).

Throughput capacity was found to increase slowly from 200 to 400 kg/h in the range of screen opening smaller than 61 micrometres, more rapidly for larger openings reaching 1,500 kg/h at 125 micrometres.

Concening the yield of product the results are reported in Figure 4.

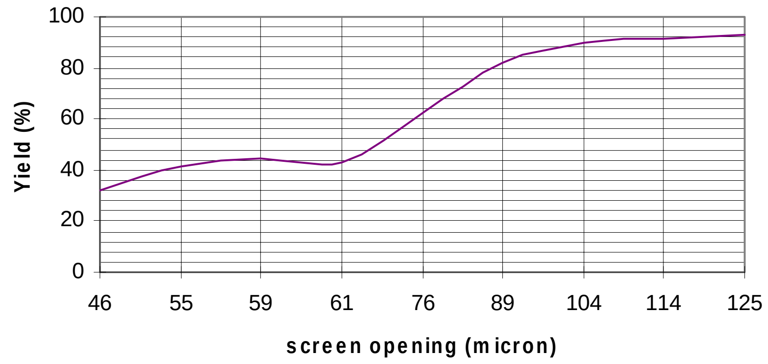
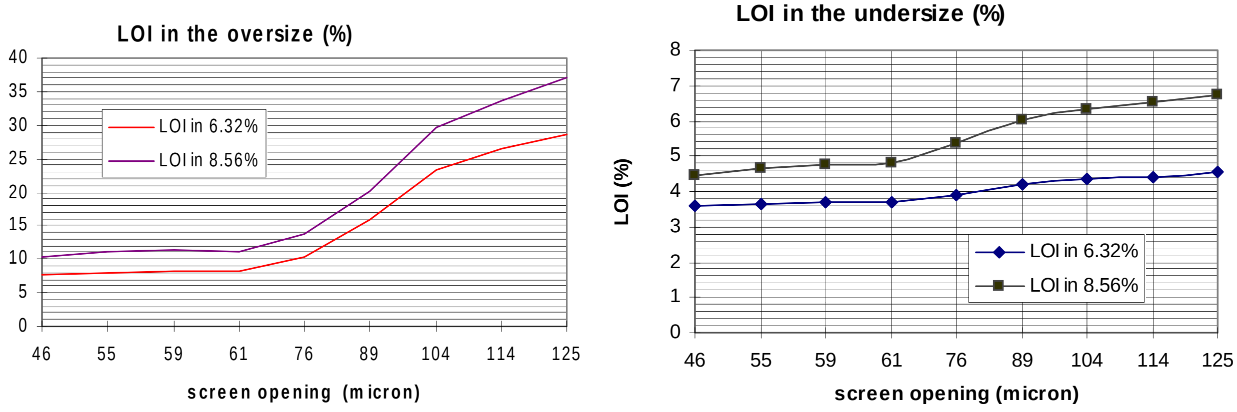


Figure 4. Yield of product as a function of the mesh opening.

The values are rather independent of the LOI in the feed.
Correspondingly, the quality of the product deteriorates as the mesh opening increases as shown by the curves of Figure 5 a and b for two different LOI content in the feed.



a b

Figure 5. Quality of ash screening products as a function of sieve opening for two different ash content in the feed.

Results put into evidence that:

- Screening at 89 µm represents the best trade-off between yield and quality of the undersize product (beneficiated ash); the throughput capacity of the screen is also interesting for an industrial application, approaching 1,000 kg/h.
- The quality of the product depends on the LOI in the feed; higher yield of product with acceptable quality (LOI < 5%) can be obtained from fly ash having lower LOI. This implies that the screen opening must be reduced in the case of unsuitable ash, rich in unburned particles, for obtaining the desired quality, although at the expense of yield and capacity.
- The ultrasound cleaning of the sieve mesh assures an increase in the throughput capacity of the screen by about 25% at 76 micrometres opening, slightly less (probably around 20 %) at 89 micrometres.

- The capacity, which is less than 1,000 kg/h for the 36” circular screen, can be expected to increase up to 2,700 kg/k for the 60” machine.
- The configuration of the counterweights must be carefully studied aiming at optimising the product quality and yield as well as the operational feed rate.
- Care must be taken in the design of the feed chute in order to assure the best distribution and movement of the material onto the screen.

B – Electrostatic separation

According to the devised flowsheet for the beneficiation of fly ash, the coarse fraction of screening is processed by electrostatic separation aiming at recovering a carbon-free product and a concentrate of unburned matter suitable for the uses pointed out in the above.

Separation results with different experimental machines based on the same principles are very interesting as shown in other papers.

Without entering in details concerning the separators which will be described in a paper accepted for presentation at the Rome 2000 XXI International Mineral Processing Congress, the following aspects are worth mentioning as regards the feasibility of the technology:

- Starting from a LOI level up to 20% typical of the screen oversize for most ash samples tested (at an effective classification size 45 μm), a product characterised by a LOI around 2.5% can be obtained in the most favourable cases with only one pass through the electrostatic separator. For difficult-to-treat materials two or three passes would be required for achieving a similar target.
- Correspondingly, the carbon-rich product of the separation has a typical LOI content in the range between 20 and 40%, according to the cases.
- The product yield of electrostatic separation (coarse beneficiated ash) is higher that 70% in the most favourable cases but drops down to 60% for difficult materials due to the necessity to resort to multiple steps of carbon extraction for reaching the desired quality.
- The throughput capacity of electrostatic separators is not as high as that of the screen although it can be assumed that a machine of commercial size can treat up to 1 tph, about 10 times larger than that achieved with the laboratory prototype.
- The electrostatic separation of the coarse fraction of screening is much easier than that of the fly ash as such including fines.

CONCLUSIONS

Coal-fired boilers for the generation of electric energy currently produce huge quantities of fly ash in the world. The largest part is disposed of in landfills, although a considerable portion is used as a component in the manufacturing of cement.

However more severe restrictions are now incurred regarding the quality of the cement and thence that of the raw materials employed in the production process. In agreement with this, the content of carbon in fly ash should be limited to at least 5%, in order to assure a satisfactory performance of structural concrete, or sometimes to less than 3%, as market requires for special application.

Again more severe approach concerning landfill is coming on and many restrictions keep up with it. Consequently, in order to reduce and prevent the landfilling burden, as well as to increase the use and value of fly ash related to the various applications, a beneficiation process becomes necessary.

To this end a project has been undertaken aimed at finding and developing a cheap and high-capacity technology for the achievement of this goal.
On the basis of the laboratory investigation results, the solution envisaged consists in a screening stage yielding a fine fraction already poor in carbon followed by the electrostatic separation of the coarse fraction.
That is in order to increase the overall recovery of beneficiated ash, as well as to obtain a by-product rich in carbon to be recycled to the boiler or suitable for other applications.

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