Different uses of CFB ash - EDF investigations

I. LECUYER*, S. GUERAUD**, J.M. BURSI***

* EDF R&D, 6 quai Watier - 78400 CHATOU - France.

** EDF R&D, Route de Sens - Ecuelles - 77250 MORET SUR LOING - France.

*** EDF Engineering & Service Division - 12-14 rue Dutriévoz - 69628 VILLEURBANNE - France.

INTRODUCTION

Within a fluidized bed boiler, coal is burned at 850°C, while limestone is added in the boiler to trap (sorb) the acidic SO2 gas before its atmospheric emission. This process has been developped to minimize emissions of pollutants such as SO2 and NOx. Two kinds of residues are produced : bed ash extracted from the bottom of the boiler, and fly ash resulting from dust filtration of the flue gas. Depending on coal sulfur content, ashes may have high sulfate content. In this case, ashes cannot be used in cement or concrete industry, which are the main use of conventional pulverized-coal ashes. Also, unreacted sorbent, such as calcium oxide (CaO), often causes high alcalinity in many of the ash produced.

EDF initiated specific research programs to identify the possible uses for CFB ashes and especially for those new kind of high sulfate content residues. Most of the studies have been achieved with ash samples coming from the Provence 250MWe Circulating Fluidized Bed Combustion (CFBC) unit, located at Gardanne, France. This unit has been in operation since April 1996 and happened to burn various types of fuels: a heavy-sulfured local coal, a French hard coal, imported coals (from South-Africa for instance), and, more recently, pet coke. This variability reflects the flexibility of CFB boilers, which allow to burn bad quality or high-sulfured fuels, or even residues from fuel processes (schlamms, pet coke...).

ASH CHARACTERIZATION

The amount of residues produced from CFB boilers depends mainly on coal ash and sulfur contents and also on sorbent reactivity for desulfuration. This amount increases with the coal sulfur and ash contents at a given SO2 removal [1]. For a given CFB boiler design, bottom ash and fly ash output flows shall be influenced by coal range : relative quantities of fly ash have been recorded at the Provence 4 CFBC unit between 60 to 90%.

The ash chemical composition (for both bed ash and fly ash from the particulate control device) directly arises from the fuel characteristics : it results 1) from the chemical composition of the inorganic fraction of the fuel and 2) from the fuel sulfur content and the SO2 removal rate.

Figure 1 shows some examples of the composition of Provence 4 CFBC ashes : the variability is high, even for a given unit, according to the various fuels used. This variability can also hinder the ash management, because the producer cannot guarantee a constant quality of a potential commercial by-product.

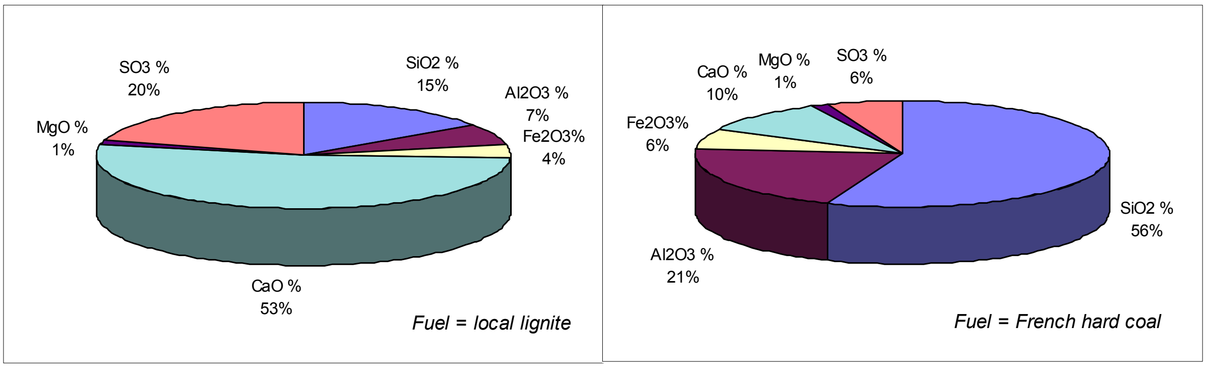

Figure 1 : Examples of chemical composition of fly ash from Provence 4 CFBC unit.

Depending on ash use, main features (or constraints) of the chemical composition are usually the high calcium and high sulfate contents resulting in a high alcalinity (pH = 12 to 12.7) (not suitable in civil works engineering), also {SiO2+Al2O3+Fe2O3} content.

The granulometry has also been characterized : whereas bed ash is a rough, sand-like material (particle size from 0.1 to 20 mm, with a median diameter of 0.35 ± 0.1 mm), fly ash extracted under the ESP is a silt-sized material (particle size from 0.5 to 100 µm, with a median diameter of 21 ± 3 µm, depending on cyclone design).

Heavy metal are in trace concentrations, like in conventional pulverized-coal ash. These concentrations only depends on the fuel characteristics, as the limestone has usually no or very low heavy metal content. The following table gives the observed ranges of heavy metal concentrations in the ash produced from Provence 4 LFC :

	range in mg/kg
Arsenic	7.6-135
Cadmium	0.03-2.0
Chromium	4.0-92
Copper	4.4-66
Nickel	16-79
Mercury	0.18-1.4
Lead	0.2-74
Zinc	19-155

Table 1 : Ranges of trace elements (heavy metals) concentrations in the ash produced from Provence 4 LFC (bed ash and fly ash).

STUDIES ON SULFO-CALCIC CFB ASH UTILIZATION

1. AGRICULTURE :

As already shown in litterature, sulfo-calcic CFB ash have potential benefits for soils which may include modification of soil pH, supply of essential plant nutrients for crop production, increasing water infiltration, soil aggregation and modification of the texture of clay soils to promote root growth. The high free lime content of a CFB ash makes it an effective agricultural limestone substitute. The neutralising value (equivalent to CaO and MgO content) of this potential liming agent should be at least 30% : some CFB ash meet indeed this criterion, others should be studied case by case to assess their possible benefits.

A complete three years' study have been achieved on this issue, combining laboratory and field scale experiments, and focussing on the possible burden arising from the heavy metals (which are the only potential contaminants in the CFBC ash).

When the aim of the amendment is to correct an acidic soil pH, the ash input rate is determined by preliminary tests in laboratory : this rate depends strongly on the soil characteristics and on the ash neutralising value, varying from 0.05 to 0.4% (i.e. 2 to 17 t/ha) in the studied cases.

The crop yield is exactly the same with the CFB fly ash as with a traditionnal liming (limestone).

The concentrations of extractable (bioavailable) heavy metals (soil sample extractions with CaCl2 solution) have been shown to decrease for cadmium and zinc in the treated samples, due to increasing pH values.

The heavy metal input fluxes into the soil are far lower than the european limits for spreading residues (sewage sludges).

The heavy metal uptake by edible part of crops (8 vegetables and 2 cereals) has been carefully checked. It has been proved that :

- no significant increase of heavy metal contents has been observed in the edible fraction of plants grown with the CFBC ash treatment, except a slight increase for cadmium in lettuce, which is a very sensitive vegetable as for heavy metal uptake,

- all heavy metal contents in edible products are lower than the official recommended values.

Lastly, ecotoxicological bioassays on micro-organisms and worms have proved no detectable effect on these soil faunas, within the experimented conditions (CFB ash input rate < 1%).

Figure 2 : Field experiments on sandy soils in south-west of France : vegetable crops.

As a conclusion, sulfo-calcic CFBC ash have been successfully used as a agricultural liming agent, with no observable effect on crop quality neither on soil mesofauna, at the studied rates. Any large-scale application should anyway induce feasability study, because of the wide ranges of soil and ash characteristics ;

successive limings using ashes (or other by-products) should be carefully recorded in order to control the total heavy metals inputs to the soil.

Considering a preliminar technical study based on soils and ash caracteristics to insure a rational use, sulfo-calcic CFB ash have proven their benefits with regard to agricultural liming application, without environmental impact.

2. SOIL REMEDIATION

Current remediation methods applicable to soil highly contaminated with heavy metals are most often expensive, environmentally invasive and labour intensive. There is a clear need for remediation alternatives which are cost-effective, environmentally sound and equally protective of human health and environment.

Addition of alkaline fly ash to acidic contaminated soils can, as a first step, neutralise acidity, and hence reduce the « bioavailability » of metals in the soil, bioavaibility being defined as the fraction of metal content which can interact with a biological target. For highly polluted bare or scarcely vegetated areas, a combination of pollutant immobilization and revegetation can be proposed to limit the environmental wrong impact of the areas, preventing especially lateral wind erosion and downwards metal percolation.

Field experiments have been started on heavily polluted soils of former metallurgic sites in Belgium [2] and in France [3]. The amount of added ash has been fitted according to the soil characteristics (usually with a pH target value of 8). It has been shown that zinc and cadmium mobilities can be reduced from 28% to respectively 1% or 5%. Simultaneaous bioassays assessed a decrease of the capacity of stress enzymes in the plant leaves.

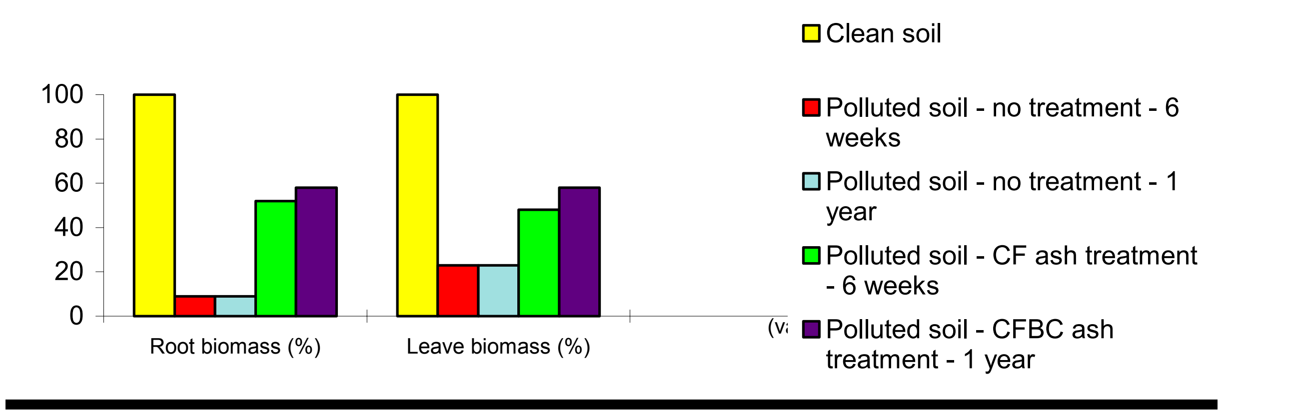

Figure 3 : Comparison of biomass yields on clean, polluted, and treated soils.

Former and current studies seem to assess that a single ash treatment would be enough to definitely stabilize heavy metals within the soil : as a matter of fact, the pH effect may last only one year, but as a second stage, adsorption of heavy metals on ash particles [4] or even locking of these pollutants within the evoluting mineralogic structure of the ash [5] will provide a long-term remediation effect.

A 1-ha metallurgic site contaminated with lead (800-1000 mg/kg), cadmium, zinc and antimony in the north of France has been treated at the beginning of year 2000 with two types of CFBC fly ash, with very distinct chemical compositions. After grass has been seeded and young trees (5 species) have been planted, this site is going to be monitored for 5 years, in order to check the long term effects of the treatment : soil characteristics (pH, heavy metal mobility and speciation), growth of vegetation and concentrations of heavy metal in plants.

3. SLUDGE STABILIZATION

Another way to take advantage of the high lime content of CFB sulfo-calcic ash is to substitute the usual lime utilizations. We have thus studied the ability to use these ash to significantly reduce pathogens and stabilize urban sludges from wastewater treatment plant. The exothermic reaction of free lime with water allows to cut down the sludge fermentation, hence controlling odours, as recommended by the regulation. However during the first experiments the microbiological criteria were not completely met, possibly because of a lack of efficiency when homogenizing the sludge+CFB ash mixture.

The stabilized sludge can then be used as an agricultural fertilizer : field experiments have been achieved on a calcareous soil with wheat culture. One parcel of the field was treated with the raw sludge, as a reference, and the other one with the mixture sludge+CFB ash. No change could be observed between both collected samples, nor for the crop yield neither for the crop heavy metals contents. The soil agronomic parameters have also shown to be the same as with a traditionnal treatment (sludge + calcium oxide CaO).

This experiment began in spring 1999 (when sludge+CFB ash treatment was realised) and will be going on until 2002 (for specific observations in soil and crops), in order to check the possible long term effects of the amendments, and also to assess the influence of the sulfur input, resulting from the high calcium sulfate content in the ash.

The following pictures show some aspects of the on-site implementation.

Figure 4 : On-site implementation of ash treatment to the soil.

CONCLUSION

Two aims were looked for :

- to find possible and valuable uses for sulfo-calcic CFB ash.
- to assess the status of CFB ashes as a non-hazardous waste, which fits with environment-friendly uses such as agriculture, soil remediation or sludge stabilization.

These valorization ways require only low volumes of ash but allow to scan carefully the real « on-site » impact of CFB ash and their low ecotoxicity.

These results demonstrate by-product CFB ash status in environmental fields. Other investigations are also in progress in EDF to find high-volume uses in civil engineering fields.

References :

[1] L. SLOSS, « Residues from advanced coal-use technologies », IEA Coal Research, Nov. 1996.

[2] J. VANGRONSVELD, A. RUTTENS, « Evaluation of the use of coal fly ashes for the remediation of metal cpntaminated soils », Convention B04510/AEE2591/E35L85, Final Report.

[3] F. DOUAY, « Intérêt des cendres de LFC pour le phytomanagement des sols contaminés par les métaux lourds », in « La lettre du Pôle », n° spécial oct.2000 Pôle de Compétences sur les sites et sols Pollués/Nord Pas de Calais, France.

[4] P. RICOU-HOFFER, I. LECUYER, P. LE CLOIREC, « Experimental design methodology applied to adsorption of metallic ions onto fly ash », Wat. Res. Vol. 35 n°4, pp965-976, 2001.

[5] J. VANGRONSVELD, S. CUNNINGHAM, N. LEPP, M. MENCH, « Physico-chemical aspects and efficiency of trace element immobilization by soil amendments », in « Metal-Contaminated soils : in situ inactivation and phytorestoration », R.G. Landes Company, 1998.