PFBC ashes – a material with commercial potential

Further development of the pressurized fluidized bed combustion (PFBC) process over the past two decades has resulted in a technology with important ecological benefits that include low emissions and solid residues with commercial potential. PFBC ashes can be transformed into a concrete-like material with excellent technical properties simply by adding water and vibro-compacting the mixture. Several pilot projects have been carried out with this material, which has several uses in road construction.

Extensive leachability studies, including column tests, tank tests and batch tests, have shown that PFBC ashes have only a minimal impact on the environment.

As the hydraulic conductivity of hardened ash mixes is very low, the leachability depends more on the diffusion velocity of the elements than on the convective water-flow.

PFBC technology

PFBC technology makes use of a combined cycle in which electricity is generated by both a gas turbine and a steam turbine **1** [1, 2]. The result is higher efficiency and reduced fuel consumption, the latter being approximately 15 % lower than with conventional technologies. Combustion takes place in a fluidized bed at an elevated pressure of 500 to 1,200 kPa (5–12 bar), depending on the load. The combustion temperature is about 820–880 °C, resulting in lower nitrogen oxide emissions since thermal NO_x is only formed at higher temperatures.

Prior to combustion, the coal is crushed to a maximum size of about 5 mm and then mixed with a sorbent (limestone or dolomite). During combustion, the sorbent captures released sulfur to form harmless calcium sulfate.

PFBC plants can utilize a very wide range of solid fuel, from poor quality sub-bituminous coal to high-quality hard coal. Plants burning brown coal and petroleum coke - a fossil fuel similar to oil – are under construction or at the planning stage.

The residues produced by a PFBC plant are of three types:

- Granular bed ash
- Fly ash captured by the cyclones
- Filter catch from the final back-end filter

In terms of grain size distribution, fly ash can be characterized as sandy silt and the bed material as coarse sand. The amounts of ash from the back-end filter are very small (less than 1 to 2 %) and are normally added to the fly ash from the cyclones.

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Mechanical properties of PFBC ashes

A comprehensive study was carried out in 1988/89 to investigate the properties of ashes from the pilot plant at ABB Carbon in Finspong. The laboratory investigations were complemented by field tests performed on ashes from the commercial Värtan PFBC plant in Stockholm **1**. In these tests, the sorbent was mainly limestone, although dolomite ashes were also investigated.

It was seen at an early stage that, even though spent bed ash and fly ash can be used separately, a mix of the two has most benefits. By mixing these ashes, adding water and vibro-compacting the mixture, a concrete-like material with high bearing capacity and compressive strength is obtained.

For the described tests, bed ash and fly ash were mixed mainly in the ratio of 50/50 or 30/70, with fly ash dominating. In most cases, the bed material and fly ash were mixed in the dry state, before water was added. The amount of water was varied to obtain either a paste or a slurry. The samples were then vibro-compacted. Curing normally took place at a high relative humidity (about 90 %) and a temperature near to +20 °C. Some test series were carried out under other conditions, for example with curing under water or at a high (+50 °C) or low (–18 °C) temperature.

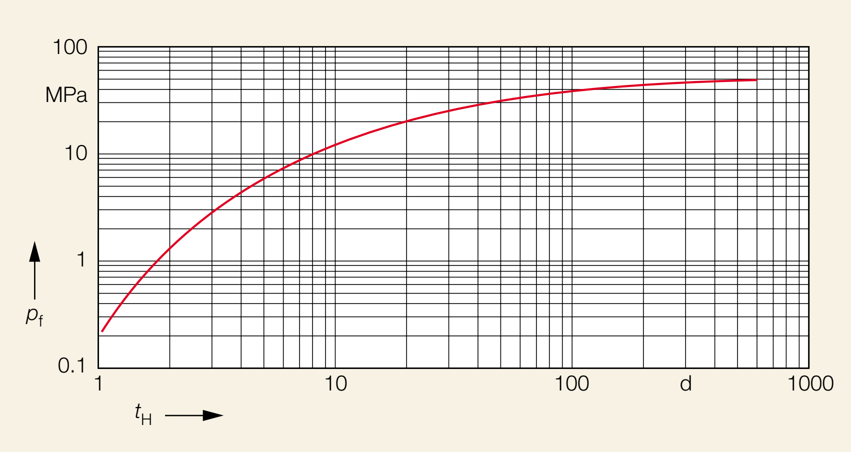
An important factor in any estimation of the potential utilization of fine-grained combustion residues is their strength properties. In the case of ashes, the

Värtan PFBC combined cycle power plant, Stockholm, with an electrical rating of 135 MW and a thermal rating of 224 MW **1**

strength is usually given by the unconfined compressive strength. This is normally assessed from samples with different curing times, for example 7, 14, 28, 56, 90 and 360 days. The growth of compressive strength in PFBC ash mixes is fast and values of over 5 MPa are achieved within a few days. The final strength is normally between 20 and 45 MPa, although values above 50 MPa have also been measured.

2 presents examples of the development of strength of ash mixtures obtained from Polish coal with limestone as sorbent. Other results have shown that when dolomite is used as the sorbent the compression strength may decrease. Maximum values so far for dolomite-based bed material vary between 15 and 25 MPa. However, the test series are too small to be statistically significant.

To clarify the long-term durability of the compression strength, one test series based on limestone as sorbent was cured for 28 days and then placed in pressurized cell permeameters. Water under high pressure (170 kPa) was forced through the samples for up to 8 months, this corresponding to several hundred years of constant water percolation at a pressure equal to a 1m water column. Afterwards, the unconfined compression strength was determined. The results indicated no reduc-



Development of strength of PFBC ash mixtures comprising 70% fly ash and 30% bed material from Polish coal, with limestone as sorbent **2**

p_f *Compressive strength*

t_H *Curing time*

tion in strength compared with samples cured in the normal way.

However, it should be noted that the strength properties depend very much on the mixture being cured at a temperature above freezing until the hardening process is completed or at least has progressed for a certain time. In some laboratories, and even with some full-scale tests, the ash mixture was exposed to temperatures below 0 °C from the beginning or after only a few days of curing, resulting in almost no increase in strength.

As the test results show, the permeability of the ash mixtures is very low, with values of less than 10^{-10} m/s exhibited by the samples after curing for 28 days **3**.

A large number of laboratory tests were also carried out to clarify the properties of synthetic aggregates produced from PFBC residues. These looked at the compacting characteristics, aggregate degradation, flakiness index and impact value, etc. In general, the results showed that, after curing and crushing, PFBC ash mixtures are well suited for use as synthetic aggregates in fills and road building.

Leaching characteristics

Like all other coal ashes, PFBC ash mostly consists of a mixture of amorphous glass and crystalline phases as well as some unburnt material. The main components of the ash are compounds of silicon (Si), calcium (Ca), aluminium (Al) and iron (Fe). The desulfurization process results in the capture of sulfur as calcium sulfate ($CaSO_4$), while surplus calcium is captured as calcium carbonate ($CaCO_3$). The chemical composition of the ashes may vary to a certain extent, depending on the type of fuel and whether limestone or dolomite is used as sorbent.

If dolomite is used as sorbent, the ash will also contain a certain amount of magnesium. In general, the results of analyses of ash mixtures from the Värtan plant have shown that the amount of trace elements is normally less than 200 mg/kg, and for most of the elements even less than 50 mg/kg.

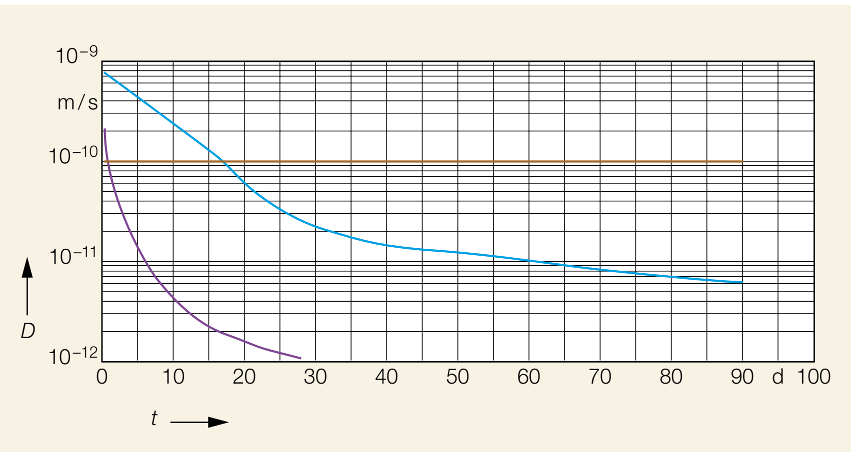
In general, the main environmental consequences of utilizing such residues are that contaminants can be released with percolating water. The possible release of contaminants from PFBC ashes has been evaluated by means of leaching tests based on Sweden's ENA method. This involves a serial batch test with four leachings at the L/S ratio 4 (accumulated L/S ratio 16) and with 24 h agitation by horizontal oscillation. The L/S 1 ratio was also determined.

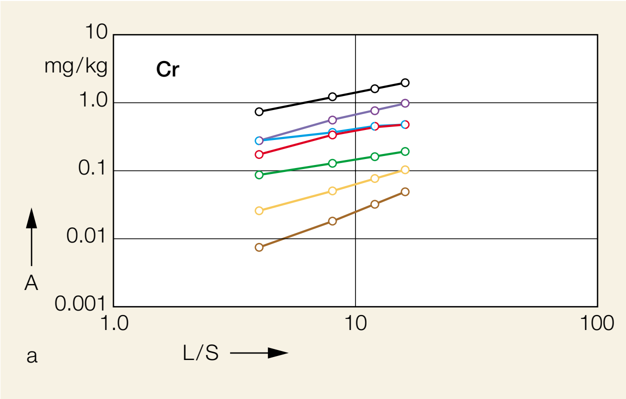
In an extensive study during 1988/89, leaching tests were performed on mixtures of PFBC fly ash and bed ash with the ratio 70/30 (samples no

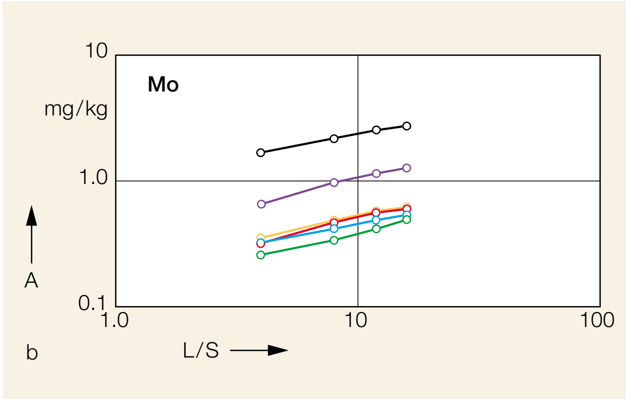
Permeability of PFBC ash mixtures (Polish coal, limestone as sorbent, curing time 28 days). The permeability of Swedish clay is shown for comparison. **3**

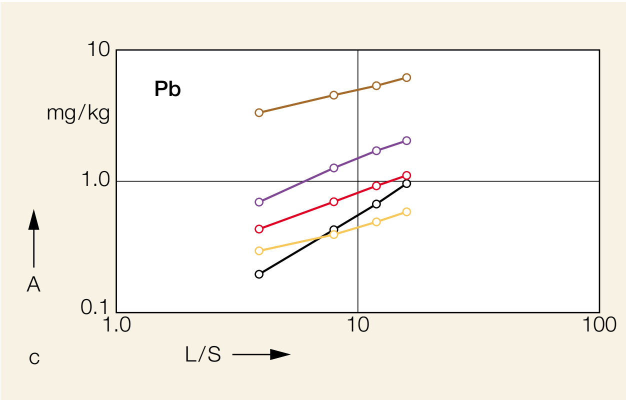
D *Permeability*
t *Time*

Blue *50/50 bed ash/cyclone ash*
Purple *30/70 bed ash/cyclone ash*
Brown *Swedish clay*









Accumulated leaching of chromium (Cr), molybdenum (Mo) and lead (Pb) as a function of the L/S ratio for PFBC ashes, a PFA ash and normal Swedish moraine **4**

A	*Accumulated leachout*
L/S	*Liquid/solid ratio*
Light-brown	*PFBC ash 1*
Red	*PFBC ash 2*
Purple	*PFBC ash 3*
Blue	*PFBC ash 4*
Green	*PFBC ash 5*
Black	*PFA ash*
Brown	*Moraine*

1–3) and 50/50. For the 70/30 mixture, tests were performed both on untreated samples and samples that had been cured and afterwards crushed to a gravel-like material (synthetic agglomerates).

The ash showed a high buffering capacity and the pH was high in all of the leachings (between 10 and 13), the lower value being in the leachates with higher L/S ratios.

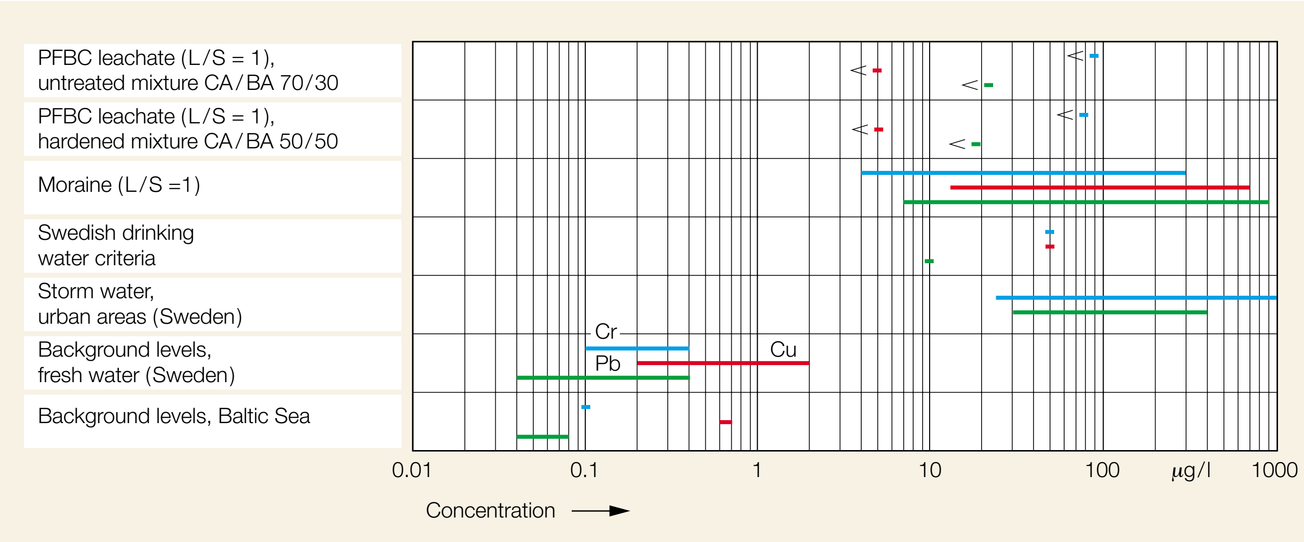
4 shows the accumulated leaching of Cr, Mo and Pb as a function of the L/S ratio, and compares the figures with results from identical leaching tests with ordinary pulverized fly ash and normal Swedish moraine. From the results, it appears that leaching from the synthetic agglomerates and from the untreated sample lay in the same range. Neither were any significant divergences observed between samples with different mixing ratios.

It is possible that the leaching from sample no 3 **4**, which originated from combustion with ammonia (to reduce the emissions of nitrogen oxides), was slightly greater than from the other samples. However, it is difficult to draw any firm conclusions as many elements in the leachates lay below the detection limits.

It was concluded that leaching of chromium and molybdenum was greater than for other trace elements.

From **4**, it can be seen that more chromium is leached from PFBC ashes than from a normal moraine, but less than from PFA fly ash. Leaching of lead from PFBC ashes was in the same range as from PFA, but the amount was considerably lower than for the moraine. The reason for the high figure for leaching of Pb from the moraine is not clear, but has been noticed in several samples from different places in southern Sweden.

In Sweden, leachate levels from the L/S 1 test have in the past often been used to estimate the environmental impact of disposal or utilization of different residues. In **5**, maximum levels of chromium, copper and lead in leachate from PFBC ashes are compared with results from identical tests involving moraine. Limits for Swedish drinking water, storm-water from urban areas, normal background levels in unaffected fresh water, and water from the Baltic Sea are also shown. From an environmental standpoint, the leaching levels of Cr, Cu and Pb from PFBC ashes are considered to be the most critical, compared with the background levels. As shown, the leachate levels from PFBC ashes are more or less comparable with the Swedish drinking water criteria. For other elements, the leachate levels have been generally low, and in many cases even below the adopted detection limits.



Leaching levels (L/S = 1) from PFBC ash mixes compared with other background levels in Sweden **5**

CA *Cyclone ash*
BA *Bed ash*

Blue *Chromium (Cr)*
Red *Copper (Cu)*

Green *Lead (Pb)*

Potential uses are numerous

The residues from PFBC, in particular hardened mixtures of spent bed ash and fly ash, have proved to be one of the important competitive edges of this valuable technology **6**, **7**. Mechanical properties such as high strength, high bearing capacity and low permeability, combined with a low environmental impact, make PFBC residues well suited for a range of uses, for example as:

- structural fill
- road construction materials
- stabilizing agents
- sealing layers on waste disposal sites

Structural fill

Due to their mechanical properties, residues from PFBC are well suited for different fill applications. Adding water to a mixture of spent bed ash and fly ash, followed by vibro-compaction, results in a monolithic fill material of high strength. Half-scale tests have demonstrated that this is possible even

PFBC ash being cast into a large slab by means of vibro-compaction **6**

Manufacture of paving stones from PFBC ash mixes **7**

directly into water; this could be useful, for example, for extending harbour areas.

In the tests, a mixture of spent bed ash and fly ash was mixed in a dry state and poured into a basin filled with fresh water. The mixture was then vibro-compacted under water. After one week of curing, a standard penetration test (SPT) was performed on the fill. The results showed a coefficient of elasticity modulus of more than 300 MPa.

Another way of using PFBC ash mixtures as fill material is to produce synthetic aggregates from the material. This can be done by casting large slabs and then curing them for a certain time. After being cured, the slabs are used directly as fill material or crushed in a conventional rock crushing plant and used as synthetic gravel.

Synthetic gravel produced from PFBC ash **8**

Road construction material

Using a method similar to the one described above, synthetic aggregates can be produced from PFBC ash mixtures for use as road construction material. Various full-scale tests have already been performed. In one case, a mixture of spent bed ash and fly ash was cast into a homogeneous slab which, after curing, was crushed to a coarse gravel **8**. This was then used for an embankment and as sub-base for an industrial road. The road was built in 1989 and results so far have been good **9**.

In a similar half-scale test, synthetic aggregates were used as road-base material on an industrial site at ABB Carbon in Finspong **10**. Above the road-base, a mixture of fly ash and conventional crushed bedrock was used as a sealing layer. The sealing layer was allowed to cure for about six weeks. All of the goods transports in the area were then re-routed across the test area. Here, too, results are still good even after several years, and no damage has yet been observed on the surface.

Stabilizing agent

Due to their self-binding properties, PFBC residues, and especially fly ash, are well suited for use as stabilizing agents. A project financed by the Swedish National Road Administration has shown that fly ash from the PFBC process can confidently be used as a stabilizing agent. In the project, different stabilizing agents were mixed with natural silt. The results showed that when 15 weight-% of pure PFBC fly ash is added to silt, the shear strength increases to more than 10 times the figure for natural silt.

Consequently, using PFBC fly ash as a stabilizing agent in embankments either increases the quality of the road or allows the thickness of the sub-base and/or road-base layers to be reduced. Similarly, PFBC fly ash can be used as a stabilizing agent for pile foundations. In this application, it can be added to lime or cement to reduce costs.

Tests have also been performed to investigate the possibilities of using PFBC fly ash as a stabilizing agent in mining with back filling. Since a short hardening time is important for this application, the fly ash was mixed with small amounts of cement.

The results showed that, once again, PFBC fly ash increased the shear strength. Consequently, less cement has to be added, resulting in lower costs for the back filling. The laboratory investigations also showed that with PFBC fly ash used as additive, the shear failure is more plastic than with conventional cement admixtures. The fill can absorb rock movements better, thereby reducing the risk of cracks.

These self-hardening properties make PFBC ashes interesting for the manufacture of cement and concrete. One limiting factor when using ordinary coal fly ash as an additive in concrete is the amount of unburnt carbon it contains. A comprehensive analysis of PFBC ash from the Värtan plant indicates that during normal operation the unburnt carbon content is less than 3 %, which is well below the Swedish requirements for such additives. A limiting factor of greater significance is the relatively high content of sulfate in PFBC ash, which normally easily exceeds the specifications for raw material used by most cement clinker manufacturers.

Investigations into the possibility of producing a material based on cement-stabilized PFBC ash have still only been carried out a small scale. A construction material known as *Cefyll* is marketed in Sweden by *Cementa*. This product is based on PFA ash, FGD residues and about 5–20 % of cement. It sets to form a hard, tight, durable material that is similar to concrete.

Initial tests on PFBC residue-based mixtures containing free lime (0.4–2.3 %) and MgO (3.9–14.1 %) showed that they could be used as concrete under certain circumstances. Before this can be done on a commercial basis, however, complementary laboratory tests have to be performed to investigate long-term durability, swelling and frost resistance.

Waste disposal applications

Another interesting application for PFBC ash is in the waste disposal sector, where it can be used as a sealing and stabilizing agent. Leachability is reduced considerably by the high bearing capacity and low permeability. PFBC fly ash generated at the Värtan plant in Stockholm is used in this way. It replaces cement as a stabilizing agent for flue gas cleaning products from a nearby waste incineration plant.

Synthetic gravel used for an embankment and as sub-base material in road construction **9**

Conditioned and compacted PFBC residues will set to a concrete-like material with a permeability which is lower than that required by most landfill directives (10^{-9} m/s). It should be possible to use ash mixes both as basal layers, which prevent leachates from reaching groundwater, and as surface capping layers to prevent the percolation of rainwater.

Environmental aspects

If PFBC ash is to be used in aggregates such as gravel, the results from the leaching tests mentioned above can be used for environmental impact assessments. From the leaching tests it can be concluded that the leaching of trace elements from PFBC ash is generally low. However, the results in relation to the background levels indicate that leaching of chromium could be a problem. This is illustrated by an environmental impact assessment performed for a planned fill for a harbour reclamation project in Stockholm. The fill is small, being about 10,000 m^3. For environmental reasons, the leaching was calculated under the assumption of a relatively high permeability, such as for silt, although the hardening could result in a much lower figure. Calculations of the leaching from the fill, based on the leachate levels from the L/S 1 tests, showed that the leaching of chromium should be in the same range as the wet deposition on the surface of the close recipient (7 square kilometers) or 5–20 % of the direct local urban run-off into the recipient.

A more probable scenario was also calculated on the assumption of a hardened fill of low permeability. To estimate the leaching, tank tests were performed with ash from the Värtan PFBC plant. These determined the leaching by diffusion from a monofill. An environmental assessment based on these assumptions showed a considerably lower leaching of chromium, namely about

PFBC ash used as base material and as a sealing layer on the site of ABB Carbon in Finspong, Sweden **10**

5 % of the wet deposition on the close recipient and less than 1% of the urban run-off in the area.

The relatively high leaching of chromium calculated for the first case is a consequence of the high permeability of an unhardened fill in combination with changing water levels, causing frequent pore water exchanges in the fill. This effect would be even more pronounced if the fill were constructed with synthetic gravel because of the higher permeability of such a fill. A permeable fill constructed on land would leach much less, since the amount of water flowing through the fill decreases and the release of chromium would consequently be less important in relation to other sources. Recent leaching tests also indicate that leaching of chromium may not be the same for all ashes, but can vary. The leaching properties may depend, for instance, on the type of coal burned and/or on the combustion conditions.

Finally, it should be emphasized that leachate levels measured in laboratory leaching tests should be used with caution when predicting leachate levels and the environmental impact of real fills. For example, leaching tests carried out on conventional filling materials such as moraine result in leachate levels which are in the same range or are higher (except for chromium) than with the tested PFBC ashes.

Other tests have shown that the leachate level of PFBC ash fills most closely resembles that of conventional concrete.

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