



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

The Uses and Morphology of Atmospheric Fluidized Bed
Combustion Wastes from Canada's First Industrial AFBC Boilers.

E.E. Berry, E.J. Anthony and D.P. Kalmanovitch

January 1987

Presented to the Tenth Annual ASME Energy-Sources Technology
Conference and Exhibition, Dallas, Texas.

February 15-18, 1987

Energy Research Program
Energy Research Laboratories
Division Report ERP/ERL 87-09-OPJ

MLV

THE USES AND MORPHOLOGY OF ATMOSPHERIC FLUIDIZED BED
COMBUSTION WASTES FROM CANADA'S FIRST INDUSTRIAL AFBC BOILERS

E.E. Berry*, E.J. Anthony**, and D.P. Kalmanovitch***

* E.E. Berry and Associates, P.O. Box 7261, Oakville, Ontario

** CANMET, Energy, Mines and Resources Canada, Ottawa

*** University of North Dakota, Energy Research Center, Grand Forks, North Dakota

ABSTRACT

The literature on FBC solid wastes has been critically evaluated and solid wastes from Canada's first atmospheric fluidized bed combustion (AFBC) boilers at the Canadian Forces Base (CFB) Summerside, Prince Edward Island have been investigated in order to determine possible uses for AFBC wastes. Scanning electron microscopy (SEM), electron microprobe and chemical and physical tests were employed to determine the suitability of the material for pollution control, construction and other uses. SEM and ancillary techniques have shown that the chemical and physical properties of the bed material and the elutriated streams are significantly different. Agricultural use, pollution control, soil stabilization (where freezing and thawing are not significant problems), asphaltic concrete, and specialized construction applications such as low strength backfill appear to be potential uses for FBC solid wastes.

INTRODUCTION

Fluidized bed combustion (FBC) is being developed to produce steam efficiently with reduced acidic gaseous emissions for space heating for large buildings, industrial use or for thermal power. For high sulphur fuels, limestone is an appropriate bed material and sulphur sorbent for atmospheric pressure fluidized bed combustion (AFBC).

For optimum sulphur capture, AFBC combustion systems are typically controlled between 815° and 870°C. At these temperatures the calcium carbonate in the limestone fed to the bed, first calcines to calcium oxide and then reacts with the oxides of sulphur formed during combustion to produce calcium sulphate. Spent bed material is removed at a controlled rate by a bed drain and fine particles are removed from the exhaust gases by dust collecting devices such as cyclones or baghouses or electrostatic precipitators.

Under some circumstances the disposal of the solid residues may cause pollution of soil and water. The principal concerns are as follows:

- generation of high pH levels in soils and water courses;
- discharge of dissolved solids (TDS) to water courses;
- leaching of calcium and sulphate to ground waters;
- trace element leaching to ground waters;
- thermal activity of the quicklime component on exposure to water;
- release of trace organic components to the environment.

To help fully commercialize FBC burning high sulphur fuels, it is necessary to establish environmentally acceptable means to dispose of the sulphated solid residues. In this respect it would be valuable if AFBC wastes could be used as secondary resources in the construction or manufacturing industries.

The departments of Energy, Mines and Resources Canada (EMR) and National Defence co-sponsored the installation of two 18 t/h steam boilers at CFB Summerside, Prince Edward Island. The installation has been designed to burn high sulphur (5%) maritime coals using New Brunswick limestone as a bed material (1).

This paper summarizes the findings of a study of the potential uses of AFBC residues from the plant at Summerside and reviews the current knowledge of the uses for AFBC residues to provide information for similarly planned AFBC installations.

The Portland Cement Association recommends that for adequate field durability, a soil-cement specimen should not lose more than 14% of material during 12 cycles of freezing and thawing in standard tests. Unfortunately, this criterion was not met by the soil-cement mixes containing silo ash. These observations are consistent with those reported by Minnick (4) on work using AFBC residues as a lime substitute for stabilization of two soils: silty loam and a silty clay soil.

However Nebgen et al (6) who studied soils ranging from non-plastic silts to highly plastic clays have reported that except for montmorillonitic clay other types of soil respond well to the use of AFBC residues as a stabilizing aid. Thus AFBC residues may be acceptable for stabilization or cementing of some soils.

Dimensional Stability. Two series of tests were carried out using a free swell method for the determination of expansion. Table 7 shows the results from expansion measurements up to 30 h for four soil-cement-residue mixes and Table 8 shows the data for tests up to 3 days long using different mixes.

Compatibility of AFBC Wastes with Asphaltic/Concretes

To evaluate the performance of AFBC wastes as fillers in asphaltic concrete mixes, a series of Marshall Mix Design experiments were conducted using local materials. Acceptable asphaltic concretes were produced using AFBC residues from Summerside.

The mixes produced with bed drain resulted in an increased use of imported sand and did not appear economic. However, the use of silo ash was more encouraging. Thus using 5% silo ash enabled 26% of the imported sand to be replaced using a 19% increase in local sand and 2% of imported sand. The resulting increase in surface area by the addition of silo ash increased the asphalt demand to 6.5% (compared with 6% for the normal mix).

Compatibility with Portland Cement Systems

To see whether Summerside AFBC residues have value as components of construction materials based upon Portland cement binders, the following criteria must be observed:

- The material must be a pozzolan, reducing the requirements for Portland cement, or it must be an aggregate so that less sand is needed. Failing this, it must bring some other performance value to the product.
- It must do one or more of the above without adversely influencing any of the desired properties of the normal Portland cement system.

The following were examined:

- pozzolanic activity
- set time
- strength development
- dimensional stability

Pozzolanic properties. Standard tests found the Summerside residues were not pozzolanic which is consistent with both the literature and the conclusions drawn on the basis of chemical properties. AFBC residues must be clearly distinguished from coal residues in pulverized fuel boilers which are often highly pozzolanic glasses.

Setting time. Mortars made using the Summerside residues showed some decrease in set time compared with control mortars. No retardation or false-setting was observed.

Strength development and dimensional stability of test mortars. To evaluate strength development of Portland cement systems in the presence of AFBC residues, tests were conducted on mortars made in accordance with the ASTM C 109 procedure. It was noted that the incorporation of AFBC residues caused an increase in the water demand for equivalent workability.

Figure 2(a) shows the strength development of mortars containing bed drain as sand replacement and indicates that bed drain had an adverse influence on compressive strength. The reduction in strength must be attributed to one or more of the following:

- the bed drain residue is significantly weaker than sand;
- it causes expansion and micro-cracking;
- the increased water demand causes excessive porosity in the cured mortars.

All three effects probably contributed to the observed poor strength development. However, the loss of strength is much less severe than that observed with soil systems and therefore cannot be due to interference with the hydration of the Portland cement.

Figure 2 (b) shows the strength development of mortars containing baghouse residue as cement replacement. It indicates that though there is no apparent disruptive activity, the residue acts only as a diluent and contributes no cementing value.

As anticipated, the behaviour [Figure 2 (c)] of the silo ash as part aggregate / part cement replacement is intermediate between the bed drain and the baghouse ash that are its component parts.

The expansion data are consistent with these findings. Although expansion was observed with all of the materials, the mortars made with baghouse ash showed a little more expansion behaviour than the controls. Major dimensional changes were found for mortars incorporating bed drain material and silo ash which likely resulted from the substantial volume change that occurs upon hydration of CaO and the lesser volume change associated with the formation of gypsum from anhydrite. This would be expected to be particularly destructive when the CaO is present in large particles. Some expansion may also originate with the formation of sulpho-aluminates in the mortars.

CONCLUSIONS AND RECOMMENDATIONS FOR UTILIZING AFBC WASTES

AFBC residues are unique among the solid products of coal combustion. Unlike pulverized fuel ash (fly ash) they are not solely composed of the elements contained in the coal, nor are they pozzolanic glassy particulates. They resemble the wastes produced by FGD systems except that they are dry and contain lime and calcium sulphate in anhydrous forms. The particles are primarily a heterogeneous mix of CaO and CaSO₄, with minor and trace inclusions of the elements normally found in coal ashes and limestone.

From the point of view of disposal, they present dust problems similar to fly ashes, potential for water pollution similar to FGD wastes and are additionally somewhat more caustic as they contain unhydrated lime.

For utilization they present three classes of exploitable properties, being:

- potential sources of low grade lime;
- granular;
- somewhat cementitious (non-hydraulic).

Many uses have been proposed for AFBC residues in such industries as:

- agriculture - as a source of lime;
- pollution control - to neutralize and stabilize acidic and other liquid wastes

Their heterogeneous nature, lack of pozzolanic properties and the elevated sulphate content clearly limit their application (especially in construction) to a few very specific potential uses. The most promising are:

- agriculture
- lime substitute in acidic waste naturalization
- waste stabilizing agent in lime/pozzolan systems
- low strength backfill applications (with or without Portland cement);
- soil stabilization and soil cementing
- asphaltic concrete aggregate

Agriculture

This is the most potentially attractive application for AFBC wastes providing environmental, health and plant growth requirements are met.

Pollution Control

AFBC residues offer two uses in pollution control. First the lime content, though less than chemical lime, could be used to neutralize acidic wastes. Second the cementitious and water absorbing capacities of the residues could be used in the stabilization of sludges. However, like agricultural applications their use in pollution control must be subject to environmental acceptability.

Aggregate

As aggregate for structural fill, AFBC residues have the advantage that they are moderately cementitious. However, they are also potential sources of soluble sulphate, limiting their use to circumstances where ground water pollution or sulphate attack on surrounding structures are not at issue.

Cementitious Applications

Previous investigators have sought to use AFBC residues in construction materials based on Portland cement such as structural concrete and masonry block. The present authors consider such applications to be very limited by the chemical and physical properties of the materials. The cement manufacturers take great care to limit the quantity of free lime to prevent the dimensional instability and cracking that occurs after the hardening of the mass if the hydration of CaO is still occurring. Similarly the sulphate content is limited in cement to prevent interference with setting.

Experimental examination of the Summerside residues and reported investigations by others confirm that Portland cement-based materials containing AFBC residues are subject to severe dimensional instability and lack of structural integrity. Thus only under exception circumstances would AFBC residue be used as a concrete component. Such circumstances might be where expansion of the material was desirable (e.g. in a grout) or where dimensional stability was not important, such as in low strength backfill applications.

Soil Modification and Stabilization

In soil modification and soil cementing applications the same dimensional instability has been noted when unconditioned AFBC residues are used. In general applications this behaviour would preclude their use, however, under circumstances where soil shrinkage is a problem AFBC wastes may be used to advantage. The major disadvantage in this application is the poor performance under freezing and thawing conditions of soils stabilized with AFBC residues.

Asphaltic Concrete

The objections that limit applications in cement based systems do not apply to the use of AFBC residue in asphaltic paving. Expansion of the residue on aging should be less destructive than in applications such as concrete where a brittle solid is formed. Leaching to the immediate surroundings is unlikely to occur and sulphate attack on the binder matrix will not be an issue as it is for cementitious applications.

Experimental examinations of a limited range of asphaltic concrete materials using Summerside residues indicated no particular technical advantages or disadvantages. Their selection as asphaltic concrete aggregate will depend largely on the economics of transportation. It is worth noting that a 100 m test section of road at CFB Summerside was covered with asphalt employing a 3% silo ash mix in 1983 and at the time of writing (August 1986) the section is still in good condition and shows no sign of deterioration. (23,24)

ACKNOWLEDGEMENT

We wish to acknowledge the financial support of the Coal Division, Conservation and Alternative Energy Branch for the funding for two studies on AFBC Waste Evaluation upon which much of this paper is based and the award of a visiting fellowship to D.P. Kalmanovitch during the course of this work from the Natural Science and Engineering Council of Canada.

REFERENCES

1. Taylor, M.E.D. and Friedrich, F.D. "The CFB Summerside Project, Canadian state of the art in AFBC boilers", Division Report ERP/ERL 82-10(TR), CANMET, Energy, Mines and Resources Canada, 1982.
2. Berry, E.E. "An evaluation of uses for AFBC solid wastes", Final Report DSS Contract OSQ83-00077, 1984.
3. Berry, E.E. "An evaluation of uses for AFBC solid wastes": Phase II, Final Report DSS Contract OSQ84-00037, Sept. 1984.

4. Minnick, L.J. Reports under contract No. EF-77-C-01-2549. "Development of potential uses for the residue from fluidized bed combustion processes"; Final Report, DOE/ET/10415-T6, Dec. 1982.
5. Minnick, L.J. Reports under contract No. DE-AC21-77-ET10415. "Development of potential uses for the residue from fluidized bed combustion processes"; Final Report, DOE/ET/10415-T6, Dec. 1982.
6. Nebgen, J.W., Edwards, J.G. and Conway, D. "Evaluation of sulphate-bearing material from fluidized bed combustion of coals for soil stabilization", Final Report, September 1977. Contract No. EX-67-A-01-2491. Report No. FHWA-RD-77-136, 69 pp, Available from NTIS.
7. Sun, C.C., Peterson, C.H. and Keairns, D.L. "Experimental/engineering support for EPA's FBC program: Final Report, Vol. III. Solid Residue Study", EPA-600/7-80-015c, January 1980.
8. Stone, R. and Kahle, R.L. "Environmental assessment of solid residues from fluidized bed fuel processing", Final Report EPA 600/7-78-107, June 1978.
9. Hern, J.L., Stout, W.L., Sidle, R.C. and Bennett, O.L. "Characterization of fluidized bed combustion waste composition and variability as they relate to disposal on agricultural lands", Proc 5th Int Conf fluidized bed combustion, Vol II, pp 833-839, 1977.
10. Stout, W.L., Sidle, R.C., Hern, J.L. and Bennett, O.L. "Effects of fluidized bed combustion waste on the Ca, Mg, S, and Zn levels in red clover, tall fescue, oat and buckwheat", J. Agronomy 71:662-665, July-Aug. 1979.
11. Bennett, O.L., Stout, W.L., Hern, J.L. and Reid, R.L. "Status of research on agricultural uses of fluidized bed combustion residue", Proc 6th Int Conf Fluidized Bed Combustion, Vol III, pp 885-891, 1980.
12. Bennett, O.L., Stout, W.L. and Hern, J.L. "Fluidized bed combustion fuel ash disposal", Proc DOE/WVU Conf Fluidized-bed Combustion System Design and Operation, Morgantown, West Virginia, Oct. 27-29, 1980, pp 402-427.
13. Bennett, O.L., Hern, J.L. and Stout, W.L. "Fluidized bed combustion waste, a potential agricultural soil amendment", Proc Gov Conf Expanding Use of Coal in N.Y. State: Probl. Issues. 1981, pp 43-48.
14. CH2M Hill Canada Ltd. "Characteristics of coal fueled fluidized bed combustion wastes", Environmental Canada, March 1982.
15. INTEG - Intercontinental Engineering Limited. "Investigation of the utilization and disposal of boiler ash from C.F.B. Summerside, P.E.I.", Interim Report, CANMET/EMR CONTRACT 78-9037-1, Sept. 1979.
16. Dearborn Environmental Consulting Services. "Preliminary evaluation of AFBC solid waste properties, 1982/83", Report EPS 3/P9/2, Sept. 1985.
17. Collins, R.J. "Utilization of fluidized bed combustion wastes", J. Testing and Evaluation 8:5:259-264, Sept. 1980.
18. Minnick, L.J. "Development of potential uses for the residue from fluidized bed combustion processes"; Final Report DOE/ET/10415-T6, Dec. 1982.
19. Johnson, I. "Sorbent utilization, enhancement and regeneration", Proc DOE/WVU Conf Fluidized-bed Combustion System Design and Operation, Morgantown, West Virginia, Oct. 27-29, 1980. pp 333-360.
20. McLaren, J. and Williams, D.F. "Combustion efficiency, sulphur retention and heat transfer in pilot-plant fluidized-bed combustors", J Institute of Fuel, 303-308, Aug. 1969.
21. Constable, T.W. Canada Centre for Inland Waters. Personal Communication, 1984.
22. Kalmanovitch, D.P., Razbin, V.V., Anthony, E.J., Desai, D.L. and Friedrich, F.D., "The Microstructural Characteristics of AFBC Limestone Sorbent Particles", Proc 8th Int. Conf. Fluidized Bed Combustion, Vol. I., pp 53-64, 1985.
23. Yurkiw, P. and Brown, M.T.G., Hardy Associates (1978) Ltd. Personal Communication, 1985.
24. Razbin, V.V. Energy, Mines and Resources. Personal Communication, 1986.

TABLE 1 - Chemical Analyses of Summerside AFBC Residues

Element	Concentration (ppm)	
	Bed drain	Baghouse Ash
Aluminum	14200	30900
Arsenic	310	220
Barium	154	213
Beryllium	0.10	2.09
Boron	24.6	63.1
Cadmium	1	15
Calcium	448000	299000
Chromium	10	23
Cobalt	5	5
Copper	7.7	29.4
Iron	16500	75900
Lead	45	140
Lithium	8	30
Magnesium	5350	9030
Manganese	849	635
Molybdenum	20	20
Nickel	27	47
Phosphorus	290	650
Potassium	2800	5500
Silicon	30900	54800
Silver	5	5
Sodium	1300	2100
Strontium	123	60.1
Titanium	574	1090
Vanadium	8.8	37.5
Zinc	209	343
Zirconium	20	24

From reference 22

TABLE 2 - Total Sulphur Content and Calculated Anhydrite Contents of Summerside AFBC Residues

Material	Total S (%)	Approx. % CaSO ₄
Bed drain	11.46	48.7
Baghouse ash	6.89	29.3

TABLE 3 - Relative alkali activity of lime and Summerside AFBC residues

Type of alkali	Equivalent weight of sulphuric acid 100 g of alkali	Per cent activity relative to CaO
CaO	175.0	100.0
Bed drain*	15.8	9.0
Baghouse ash*	16.9	9.6
Bed drain**	71.1	40.6
Baghouse ash**	59.3	33.9

* Determined by ASTM C 400-64 (Hardy Associates)

** Data from reference 21

TABLE 4 - Calculated phase composition of Summerside AFBC residues

Material	CaO	CaSO ₄	Other
Bed drain	40.6	48.7	10.7
Baghouse	33.6	29.3	37.1

TABLE 5 - Strength development of soil cements based on AFBC residues

Material	Age (days)	Unconfined compressive strength (MPa)
Series 1:		
Soil	7	0.13
	28	0.09
Soil + 10% PC	7	4.03
	28	4.19
Soil + 10% SA	7	0.32
	28	0.41
Soil + 10% BD	7	0.26
	28	0.30
Soil + 7.5% PC	7	2.28
	28	2.04
Soil + 7.5% PC + 7.5% SA	7	.80
	28	1.46
Soil + 7.5% PC + 7.5% BD	7	0.70
	28	0.53
Soil + 10% PC + 10% SA	7	0.85
	28	1.75
Soil + 10% PC + 10% BD	7	0.74
	28	1.13

PC = Portland cement; SA = Silo ash;

TABLE 6 - Strength development of soil/cement/silo ash mixes with adequate moisture during curing

Material	Age (days)	Unconfined compressive strength (MPa)
Series 2:		
Soil + 7.5% PC	28	2.25
Soil + 7.5% PC + 7.5% SA	28	2.12
Soil + 7.5% SA	28	0.30

PC = Portland cement; SA = Silo ash

TABLE 7 - Dimensional changes of soil cements up to 30 h

Material	Expansion (%)
Soil + 5% SA + 5% PC	0.8
Soil + 10% SA + 10% PC	-2.5
Soil + 5% BD + 5% PC	1.1
Soil + 10% BD + 10% PC	2.1

PC = Portland cement; SA = Silo ash; BD = Bed drain

TABLE 8 - Dimensional stability of soil cements up to 3 d

Time (mins)	1	2	4	8	15	30	60	120	240	4320
	Per cent expansion (+) or contraction (-)									
Mix No.					(+)	(+)	(+)	(+)	(+)	(+)
1	0	0	0	0	0.02	0.05	0.05	0.08	0.09	0.12
2	0	(-) 0.02	0	0	0	(+) 0.04	(+) 0.08	(+) 0.10	(+) 0.40	(+) 0.30
3	(-) 0.05	(-) 0.07	(-) 0.08	(-) 0.10	(-) 0.03	(-) 0.10	(+) 0.25	(+) 0.32	-	(+) 1.8
4	0	0	(+) 0.02	(+) 0.08	(+) 0.10	(+) 0.20	(+) 0.25	(+) 0.40	-	(+) 2.17

Key: Materials

Soil + 7.5% PC

Soil + 7.5% SA

Soil + 7.5% SA + 7.5% PC

Soil + 7.5% BD + 7.5% PC

Mix No.

1

2

3

4

PC = Portland cement; SA = Silo ash; BD = Bed drain

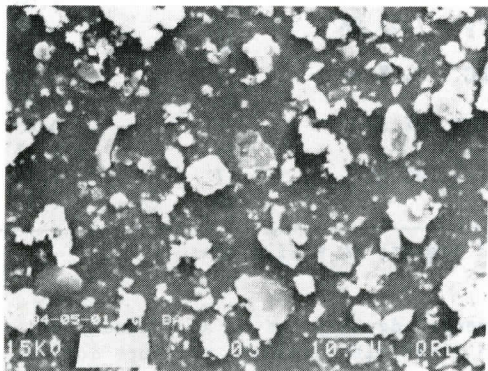
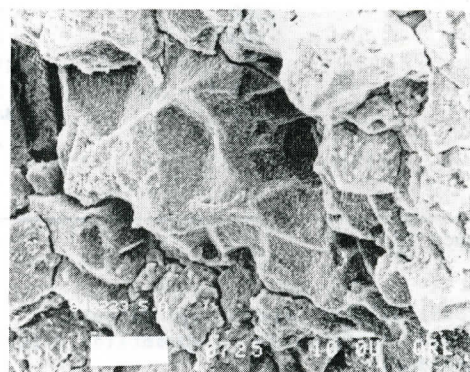
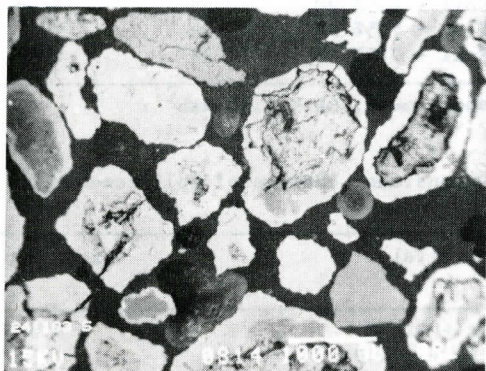
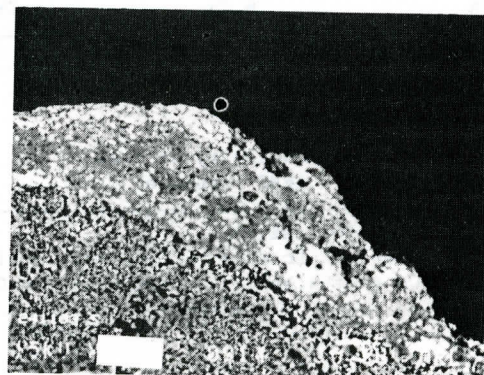
Plate 1 - Baghouse material. Bar = 10 μ m.Plate 2 - Relatively non-porous sulphated region of limestone bed samples. Cracks were probably due to fracturing of particle for topographical observation. Ca and S only present. Bar = 10 μ m.

Plate 3 - Overall view of bed material from the Summerside boiler. Large coal mineral particles (dark grey) can be seen. The inner calcined region was "picked out" during polishing leaving the sulphate rim. Note the relatively symmetric rim and cracks in the particle. Bar = 1 mm.

Plate 4 - Details of ash rich skin or limestone particles about 15-20 μ m thick. The skin is rich in Fe, Al, Si and Ca but relatively low in S. Apart from Fe inclusions the skin appears homogeneous indicating a phase had formed as a product of reaction. Bar = 10 μ m.

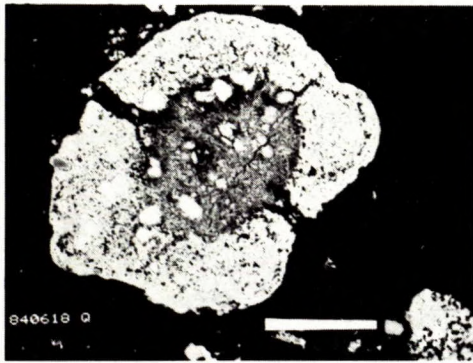


Plate 5 - Particle exposed to the atmosphere for a sufficiently long time to observe hydration effects. The structure clearly indicates hydration of CaO and an increase of volume leading to cracking and fragmentation of the bed particle. Bar = 1 mm.

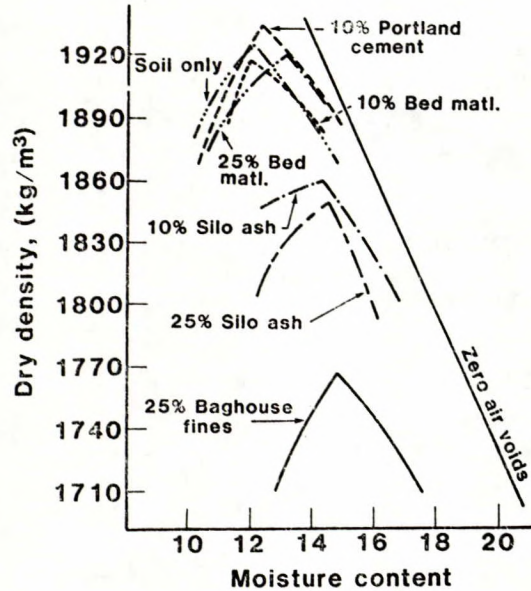


Fig. 1 - Moisture-density relationship of soil/AFBC residue/Portland cement combinations.

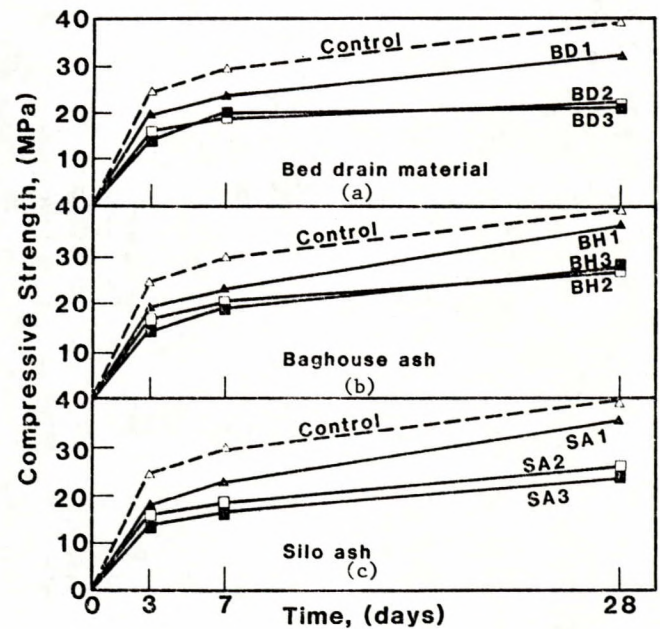


Fig. 2 - Strength development of Portland cement mortars containing AFBC residues.