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PROPERTIES AND DISPOSAL CHARACTERISTICS OF SOLID WASTES FROM CIRCULATING FLUIDIZED BED COMBUSTION OF HIGH SULPHUR COAL

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by

E.J. Anthony[1], C.C. Doiron[2], R.K. Kissel[3] and G. Ross[4]

ABSTRACT

Wastes from circulating fluidized bed combustors (CFBC) are quite unlike those discharged from conventional pulverized fuel (PF) furnaces. They consist of a heterogeneous mixture of CaO, $CaSO_4$, fly ash and some unreacted $CaCO_3$. Consequently they have quite different properties and handling problems from those of the glassy silicates produced by PF combustors. This report describes a number of research programs supported by Energy, Mines and Resources Canada, Environment Canada and the New Brunswick Electric Power Commission to characterize these wastes, develop safe disposal procedures and investigate potential uses. In order to accomplish these objectives wastes from a number of pilot scale CFBC units and a 22 MW_e demonstration unit have been examined from the point of view of sulphides formation, disposal and utilization. A peripheral issue that has been addressed is whether pilot scale units can be used to predict the behaviour of full scale units.

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INTRODUCTION

Fluidized bed combustion (FBC) is a method for burning low grade and high sulphur fuels efficiently while meeting strict air emission requirements. The sulphur is retained in the bed during combustion by means of a sorbent which is usually limestone or occasionally dolomite. In the bed, the limestone calcines and sulphates following the global reactions:

$$CaCO_3 = CaO + CO_2 \quad (1)$$

$$CaO + 1/2O_2 + SO_2 = CaSO_4 \quad (2)$$

Limestone utilization is quite low, varying from about 25% to 45%. Experience with pilot scale units indicates that circulating beds have higher utilization than bubbling beds, but it is still unclear whether full scale units will live up to expectations in this respect. Large volumes of waste are produced particularly when high sulphur coal is burnt and limestone utilization is low. This material is quite unlike that discharged from conventional pulverized fuel (PF) furnaces burning coal. It consists of a heterogeneous mixture of CaO, $CaSO_4$, fly ash and some unreacted $CaCO_3$ rather than the glassy mixture of fused silicates obtained from PF systems. It is exothermic in nature due to the presence of CaO and unhydrated $CaSO_4$ and can produce a highly alkaline leachate, with a pH between 11 and 12, which can present some problems for disposal.

The quantity of residues for disposal and their chemical characteristics have been identified as a significant potential problem that may impede the introduction of the technology (1). In consequence both Energy, Mines and Resources Canada (EMR) and Environment Canada have been carrying out research on FBC solid wastes for the last six years. More recently the New Brunswick Electric Power Commission (NBP) has also become involved with research efforts in this area. NBP is co-sponsoring with EMR a demonstration program in which a 22 MW_e circulating FBC boiler was erected at Chatham, New Brunswick and is currently being used to carry out combustion trials on a number of high sulphur fuels.

SULPHUR STATES IN FBC ASH

The Canadian Electrical Association recently sponsored a study (2) of solid wastes from a circulating FBC, this unit plus several other fluidized bed combustors, which have been used to generate wastes discussed in this report, are identified in Table 1. A startling result was the detection of up to 6% CaS in residues from a pilot scale CFBC operated by the New Brunswick Research and Productivity Council (RPC). The presence of sulphides in waste solids at concentrations of several per cent would be undesirable because they can lead to the production of hydrogen sulphide. Subsequent analytical work carried out for Environment Canada on residues from a pilot scale bubbling FBC at Queens's University indicated that CaS concentrations of up to 3% could occur, even though combustion occurred under overall oxidizing conditions. This suggested either a partial sulphidization of the limestone rather than sulphation or alternatively the reduction of sulphates to suphides within the combustor. The most likely reactions for producing sulphides in fluidized beds are:

$$CaO + H_2S = CaS + H_2O \qquad (3)$$

$$CaSO_4 + 4CO/H_2 = CaS + 4CO_2/H_2O \qquad (4)$$

$$CaSO_3 = 1/4\ CaS + 3/4\ CaSO_4 \qquad (5)$$

Analytical work did not reveal any traces of other reduced sulphur forms such as sulphites or elemental sulphur. It did, however, identify the presence of other sulphides besides CaS (by up to 50% by weight of sulphide sulphur), since digestion with hot H_2SO_4, which is appropriate for water soluble sulphides, gave results significantly different from those obtained by treatment with hot HCl, which dissolves sulphides other than CaS (3).

A detailed examination of solid residues from other units showed that the sulphide levels from the RPC rig were atypically high. Samples from a pilot scale circulating FBC at the University of British Columbia (UBC) yielded sulphides levels of less than 1%. Examination of residues from the full scale bubbling FBC boilers at Summerside and more recently the circulating FBC boiler at Chatham indicate that pilot scale units overpredict sulphide levels. For the two full scale plants, CaS levels range from parts per thousand to below the limits of detection. Table 2 gives some typical results.

The mechanisms by which sulphides are formed remain of interest. Currently EMR supports ongoing work on residues taken from different locations in the combustor and hot cyclone of the pilot scale unit at UBC. The preliminary conclusion is that high sulphide levels always seem to be associated with solid streams having high carbon loading. This supports the

Table 1 - Description of FBC Test Rigs used to generate solid residues for this study

Rig	Size	Return Leg	Heat Exchanger	Baghouse
MSL	100 mm diam. 2.8 m high	L valve	Yes	Yes
RPC[1]	130 mm diam. 5.8 m high	J valve	Yes	Yes
UBC	152 x 152 mm 7.3 m high	L valve	Yes	Yes for part of the study
HA	600 mm diam. 8.5 m high	L valve	Yes	Yes
Queen's[2]	380 x 400 mm 4.8 m high	-	Yes	Yes
Point Tupper[2]	1 x 1 m 10 m high	-	Yes	Yes
Chatham	Industrial scale, 22 MW_e or 95,240 kg/h of steam, the unit was designed by Lurgi and is equipped with an external bubbling bed heat exchanger.			
Summerside[1]	Industrial scale, two beds, a preferential and a secondary bed, of dimensions 1.23 x 2.88 m and 1.39 x 2.88 m respectively. Each of the two FBC boilers, at CFB Summerside, is rated at 18,150 kg/h of steam.			

(1) Unit used in the CEA study

(2) Conventional bubbling bed units, with cyclones for fly ash recycle, included for the purpose of comparison.

results of previous work with the RPC combustor which showed that CaS concentrations in the return leg of the combustor increased with increasing carbon loading. Similar studies were carried out at CANMET's Mineral Sciences Laboratories (MSL), also with a pilot scale circulating bed combustor (4). This has shown that sulphides increase with decreasing sulphur capture and with decreasing cyclone performance i.e. increasing elutriation losses.

All of this work supports the conclusion that sulphides are not likely to be a major problem for CFB technology and during normal operation are only likely to be a concern if solids are collected under reducing conditions.

GEOTECHNICAL PROPERTIES

Following the CEA study, Environment Canada undertook a two year study on waste disposal from circulating FBC with the cooperation of EMR and NBP. The study was divided into two phases, the first involving scoping trials with residues from the UBC pilot scale circulating FBC and the second involving field trials of disposal alternatives for residues generated from the Chatham full-scale unit.

Material for the first phase scoping work was obtained from three extended runs burning Minto coal (fuel sulphur 7.2%) with Elmtree limestone (containing 96% $CaCO_3$) as the sulphur sorbent at Ca/S molar ratios of 1.5, 2.0 and 3.0. Table 3 summarizes typical combustor operating conditions during the sampling periods.

The heat release of the samples was measured by a modification of the test procedure described in ASTM C110-76, which requires that a liquid to solid ratio of 5:1 be used and that the temperature of the well stirred mixture be monitored for at least 30 minutes or until a change of less than 0.5°C is detected among three consecutive temperature readings. The heat release values during hydration were 71.5, 83.4 and 95.3 kJ/kg for samples corresponding to Ca/S molar ratios of 1.5, 2.0 and 3.0 respectively. These values are about a third of what might be expected on the basis of the chemical and crystalline composition of the residues. However, they can produce temperatures over 100°C on hydration of the waste and hence hydration prior to disposal would be advisable.

Laboratory leachate tests indicated that leachate pH was typically about 12 which is similar to results obtained from other studies on FBC residues. Total disolved concentrations were around 4700 mg/L, with the principal constituents being sulphate (about 1700 mg/L), calcium (about 1700 mg/L) and strontium (about 3 mg/L). Concentrations of other contaminants such as heavy metals of environmental concern were below the detection limits. This indicates that, as in the case of wastes from bubbling FBC, the high pH of the leachate effectively negates the concern of leachates with high heavy metal contents.

Table 2 - Sulphide formation in circulating beds

Unit	Fuel[4]	Sorbent	Sulphide Concen. Range (expressed as wt % CaS)
MSL	Syncrude Coke	Athabasca	0.7 to 1.3
MSL	Minto	Elmtree	0.3 to 0.6
Lurgi[1]	Minto	Sauerlaender/ Oil Shale	0.0
UBC	Minto	Elmtree	0.3 to 0.7
HA	Syncrude Coke	Athabasca	0.0 to 0.1, 1.2[2]
Chatham	Minto	Elmtree	0.4
Summerside[3]	Devco	Havelock	0.0 to 0.1

(1) Large pilot scale unit with feed rates over 100 kg/h

(2) Solids withdrawn from return leg, into which the fuel is fed

(3) Bubbling bed boiler included for comparison

(4) All fuels had 7% sulphur except Devco which has around 5% sulphur.

Samples from the UBC rig which were wetted and compacted following the standard Proctor procedure (ASTM D698-78) had very low unconfined compressive strength and showed poor freeze-thaw behaviour making them unsuitable for any load-bearing purposes. The residues also showed high permeability (ranging from 1.6 x 10^{-3} cm/s for the loose material to 5.0 x 10^{-4} cm/s for compacted material). In general they did not perform as well as expected based on experience with other FBC residues.

It was thought one possible reason for this rather disappointing performance was the absence of a baghouse with the UBC rig. This gave rise to a rather coarse waste with a mean size, D_{50}, of about 0.2 mm compared to 0.04 mm for residue generated from the Chatham unit.

A baghouse was subsequently retro-fitted to the UBC rig and additional samples were taken from a test run at a Ca/S molar ratio of 2.0 under conditions as nearly identical to the earlier runs as possible. The size of the particles from these samples were much more narrowly distributed, with a D_{50} close to 0.04 mm. The geotechnical properties of these samples were then compared with those of previous UBC samples (without a baghouse) and those of residues from full scale equipment. Hydraulic conductivity (ASTM D2434-68) and unconfined compressive strength (ASTM D2166-66) were determined on samples prepared at optimum water content according to the Standard Proctor procedure and cured for varying periods of time or subjected to freeze thaw testing.

On hydration, temperatures up to 110°C were achieved, which were similar to those for earlier samples taken from the UBC rig and comparable to temperature rises seen with residues from the full scale Chatham boiler when hydrated under the same laboratory procedure. The specific gravity of the material was 2.58 as determined by ASTM D-854-83, which was lower than that for previous UBC samples (which varied from 2.83 to 3.07). In comparison, the Chatham material had a specific gravity of 2.95. The optimum water content, as determined by a Standard Proctor test was 32% (almost twice that of earlier samples, which varied from 14.5 to 17.5%). This is in the same range, of 13.7 to 30.5%, obtained with the Chatham samples.

More importantly, the hydraulic conductivity of the new samples from the UBC rig with a baghouse were comparable to previous cured samples obtained from the UBC pilot scale rig, after 8 and 12 days and both sets of residues, gave higher hydraulic conductivities than those seen with the Chatham samples. The permeabilities after six freeze thaw cycles were comparable to those from earlier pilot scale results but lower than those of the Chatham samples.

Unconfined compressive strength reached a level of 461 kPa as compared with 415 kPa which was the maximum strength achieved on curing with earlier UBC samples. After four freeze thaw cycles, the compressive strength was reduced to 200 kPa compared with increases ranging from 544 to 1018 kPa following six freeze thaw cycles with the earlier pilot scale UBC samples. Both sets of samples, however, compare unfavorably to a strength of 4,660 kPa which was the best achieved with Chatham samples in laboratory testing.

All of this suggests, that in terms of their geotechnical properties at least, the samples taken from the UBC rig with a baghouse were more typical of the previous UBC samples than the residues obtained from Chatham. This work clearly indicates the danger of trying to simulate the behaviour of waste residues from full scale units by using pilot scale residues and suggests that although such wastes may be quite similar chemically they may not be similar in terms of geotechnical properties. Why such large differences occur is not fully clear at this stage and will be the subject of further study.

FIELD PERFORMANCE OF WASTE FROM THE CHATHAM BOILER

Samples of solid wastes were taken from the Chatham unit for a confirmatory laboratory test program on September 19, 1987 and subsequently several tons of similar material were used to fill a number of disposal test cells (TC) to study the field performance. Mean combustor conditions for the two periods when samples were collected are given in Table 4 and the mean composition of the samples are given in Table 5. As the residue was highly exothermic, a two stage conditioning procedure was adopted, in order to prevent the high temperatures and expansion that would likely result if attempts were made to consolidate unhydrated material. The residues were first conditioned with approximately 15% by weight of water and the material was then allowed to cure until most of the heat of hydration had dissipated. The samples were then hydrated again while the materials were being landfilled in three 20 m x 5 m x 1 m test cells. Attempts were then made to achieve design compaction and hydration targets as indicated by Table 6.

Table 3 - Operating conditions for the UBC CFB Pilot Plant

	Test Run		
Parameter	One	Two	Three
Bed Temp °C	860	840	870
Ca/S Molar Ratio	1.5	2.0	2.5
Superficial Velocity m/s	7.1	6.8	7.9
Sulphur Capture %	74	80	88
NO_x ppm vol	113	134	149
SO_2 ppm vol	1576	1205	770
CO_2 vol %	18.3	18.8	18.4
O_2 vol %	3.4	3.4	3.4
Calcium Utilization %	49	40	35

Table 4 - Combustor conditions in the Chatham demonstration unit

Parameter	Laboratory Tests	Field Test
Power Output; MW_e	19.9	21.6
Fuel Sulphur %	7.37	6.59
Ca/S Molar Ratio	2.2	2.2
Bed Temp °C	841	831
NO_x ppm vol	74	74
SO_2 ppm vol	1275	1884
CO_2 vol %	13.2	14.9
Baghouse O_2 vol %	5.9	8.3

Table 5 - Major chemical components of the Chatham CFBC residue

Component	Concentration (wt %)
$CaSO_4$	26.1
CaS	0.45
$CaCO_3$	4.57
Free CaO	23.5
Fe_2O_3	15.9
Other, mainly SiO_2	24.2
LOI, corrected	4.3
Total	99.0

Table 6 - Target ash conditioning and placement conditions

Cell	Moisture Content %	Compaction
TC1	15	Six passes with a small bulldozer
TC2	30	Six passes with a small bulldozer
TC3	20	Six passes with smooth drum vibrating compactor

Analysis of samples taken from the Chatham unit in the second phase of the study indicated, as discussed previously, that the solids had a similar chemical composition and behaviour to those obtained from the pilot scale study, but that the geotechnical and physical properties were significantly different. The permeability of the loose material was comparable to that seen in the UBC samples but on conditioning and compaction the waste residue in the test cells showed significant reductions in permeability. At this point values as low as 1.1×10^{-6} cm/s have been achieved with only moderate degrees of compaction. The strength development achieved with cured field samples was an order of magnitude greater than that of the UBC samples (Table 7).

The full-scale residues samples have much more desirable characteristics from the point of view of disposal than the pilot scale residues. The ash can be easily worked and compacted with standard construction equipment providing it is properly conditioned, i.e. wetted, prior to disposal. It is also apparent that appropriate conditioning and compaction improves disposal properties. Thus the disposal site material is almost three orders of magnitude more permeable than the material in TC3 and less densely compacted, (see DS1, Table 7, which denotes the active disposal site with no specific procedures for moisture addition and compaction).

Table 7 - In-situ characteristics of residues in test cells and active disposal area

Test Cell Sample	Moisture Content	Dry Density	Coefficient of Permeability	Unconfined Compressive Strength
	%	Mg/m^3	cm/s	kPa
TC1	13.8 - 26.3	1.01	3.32×10^{-5}	1800
TC2	19.1 - 28.4	0.993	4.42×10^{-5}	1720
TC3	17.2 - 27.8	1.112	1.14×10^{-6}	2540
DS1	16.9	1.025	8.32×10^{-4}	*

FBC WASTE UTILIZATION

A desirable alternative to waste disposal is utilization. However, apart from the preliminary CEA study there has as yet been no work on finding applications for wastes from circulating beds. Possible applications determined for waste solids from bubbling bed facilities include use in agriculture; lime substitutes in acidic waste neutralization; waste stabilization agents in lime/pozzolan systems; low strength concretes; soil stabilization and soil cementing; and asphaltic concrete aggregate. Recent work by Rose (5) using material from the 20 MW_e TVA bubbling bed demonstration plant has shown that it is possible to make "no cement" concretes with strength development equivalent to conventional concrete.

This cement uses FBC bed material and fly ash in place of portland cement to supply the pozzolanic component. EMR is now carrying out work by contract to investigate the possibility of using waste solids from Chatham to make such concretes.

Preliminary results indicate that unlike wastes from bubbling beds complete hydration cannot be easily achieved with waste from circulating beds, presumably because of the much smaller size of the resulting ash. Currently the best that has been achieved with Chatham baghouse waste is 76% hydration compared with 95% hydration for wastes from the TVA unit. This is important as subsequent hydration, heat release and swelling can adversely affect the concrete's integrity. At the time of writing the best strength development that has been achieved is 18.9 MPa which is about half of that obtained from bubbling bed wastes. Work is continuing to improve the performance achieved.

Environment Canada and EMR are currently supporting continued studies of disposal of combustion residues from Chatham and will be participating in continued studies on the potential for utilization of circulating FBC wastes.

CONCLUSIONS

Work on circulating FBC wastes has shown that high concentrations of sulphides are always associated with high carbon loading in the solid streams, which suggests that reduction of sulphate, rather than direct reaction of CaO with reducing sulphur gases, may be an important method of formation. However, evidence suggests that under normal operation sulphide production is not likely to be a problem for the technology unless solids are withdrawn under reducing conditions. Landfill with prehydrated and suitably compacted wastes can produce solids which are easily worked, and have low permeabilities (1×10^{-6} cm/s) and relatively high unconfined compressive strengths (2540 kPa). Comparison with materials generated by a pilot scale unit burning the same fuel and limestone combination under conditions meant to simulate the Chatham unit have indicated that although the residues are very similar chemically their geotechnical properties are sufficiently different that it would be unwise, at least at the present time to make predictions for full scale units based on results from pilot scale equipment.

Work on residue utilization is currently concentrating on "no cement" concretes similar to those developed with residues from the TVA bubbling FBC. The smaller particle size of the circulating FBC residues make it more difficult to hydrate the residues completely and currently the strength development is less than that achieved with bubbling bed wastes. Should the calcium utilization of CFBCs remain comparable to bubbling bed units the use of these materials to treat acidic wastes would warrant further investigation . Utilization work for these materials is still in its infancy and will require a great deal of development work.

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