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

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ABSTRACT

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

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Wastes from circulating fluidized beds are quite unlike those discharged from conventional pulverized fuel (PF) fired equipment. They consist of a hetrogeneous mixture of CaO, $CaSO_4$, ash and some unreacted $CaCO_3$. As such they have quite different properties and handling problems from those of the glassy mixture of silicates obtained from PF systems. This report describes various research programs supported by Energy, Mines and Resources, Environment Canada and New Brunswick Power to characterise these wastes, develop safe disposal procedure and investigate potential uses for these solid wastes.

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INTRODUCTION

Fluidized bed combustion (FBC) is a method for burning low grade and high sulphur fuels efficiently while achieving strict air emission requirements. The sulphur is removed 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:

$$CaCO_3 = CaO + CO_2 \tag{1}$$

$$CaO + 1/2O_2 + SO_2 = CaSO_4 \tag{2}$$

Limestone utilization is quite low, varying from 25% to about 45%. Experience with pilot scale units indicates that circulating beds have higher limestone 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. The resulting combustion waste is quite unlike that discharged from conventional pulverized fuel (PF) coal burning equipment. 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 produces a highly alkaline leachate, with a pH between 11 and 12, which presents some problems for disposal.

The quantity of residues for disposal and their chemical characteristics have been identified as significant problems that may impede the introduction of the technology. Consequently both Energy, Mines and Resources Canada (EMR) and Environment Canada have been carrying out research on FBC waste solids 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 the Chatham 22 MW_e Circulating FBC Demonstration Program together with EMR and Combustion Engineering. Under this program a circulating FBC boiler facility was established at Chatham, New Brunswick and is being used to carry out combustion trials on a number of high sulphur fuels.

SULPHUR STATES IN FBC ASH

In a recent Canadian Electrical Association study (1) of waste samples generated in a pilot scale circulating bed unit operated by the New Brunswick Research and Productivity Council (RPC) the presence of significant amounts of CaS was detected (up to 6%). Subsequent analytical work carried out for Environment Canada on residues from a pilot scale bubbling bed at Queen's University indicated that CaS concentrations of up to 3% could be found in the waste solids, even though combustion occurred under overall oxidizing conditions. This suggested that at least part of the sulphation process might proceed through the sulphidization of the limestone rather than sulphation or alternatively that the sulphides produced result from the reduction of sulphates in reducing zones within the combustor. Analytical work did not, however, reveal any traces of other reduced sulphur forms such as sulphites or elemental sulphur. The presence of sulphides in waste solids at such concentrations would be undesirable because they can lead to the production of hydrogen sulphide.

A detailed examination was made of solid residues from other units and this showed that the sulphide levels from the RPC rig were atypically high. Test work, which is discussed below, from a pilot scale circulating FBC of cross sectional area 152 x 152 mm at the University of British Columbia (UBC) gave levels of sulphides of less than 1 %. Examination of residues from the full scale bubbling bed boilers at Summerside and more recently from the Chatham circulating bed, burning high sulphur coal, indicates that pilot scale units over-predict sulphide levels. For the two full scale units CaS is present at levels which are either below the limits of detection or are present at levels of parts per thousand or less. The mechanisms by which sulphides are formed remain of interest, however, and under an EMR contract work is currently being carried out on residues obtained from the pilot scale unit at UBC, taken at different positions around the primary combustion circuit, i.e. combustor and hot cyclone. Work is also being carried out at CANMET's Mineral Science Laboratories using a 100 mm diameter circulating bed unit (2).

FBC WASTE DISPOSAL

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 compared 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 unit. Material for the first phase scoping work was obtained from an extended pilot scale test run burning Minto coal and using Elmtree limestone as the sulphur sorbent at three different Ca/S molar ratios of 1.5, 2.0 and 3.0. The heat release during hydration of the samples was 71.5, 83.4 and 95.3 kJ/kg respectively and was measured by a modification of the test procedure described in ASTM C110-76. These values are about one third of that which might be expected on the basis of the chemical and crystalline composition of the residues but are sufficiently high that hydration would be advisable prior to disposal. Leachate tests indicated that leachate pH was typically about 12; similar to results obtained from other studies on FBC residues. Total dissolved solids were about 4700 mg/L, with the principal constituents being sulphate (about 1700 mg/L), calcium (about 1700 mg/L) and strontium (about 3 mg/L). Other components such as heavy metals were present in negligible quantities.

Samples from the UBC rig, which were wetted and compacted by the standard Proctor procedure, had very low compressive strength and showed poor freeze-thaw behaviour making them unsuitable for any load-bearing purposes. The residues also showed high permeability (from 1.6×10^{-3} cm/s for loose material to 5.0×10^{-4} cm/s for compacted material) and in general did not perform as well as expected based on experience with other FBC residues. One possible reason for this rather disappointing performance may have been the absence of a baghouse with the UBC rig, giving rise to rather coarse waste having with a mean size, D_{50}, of about 0.2 mm compared with 0.04 mm for residue generated from the Chatham unit. Tests are now underway with samples generated from the UBC rig with a fully operational baghouse to see if their behaviour differs substantially from the earlier residues. At this point it is not clear whether the geotechnical evaluation of residues generated by pilot scale units can be used to simulate the behaviour of residues from full scale units.

Analysis of samples taken from the Chatham unit in the second phase of the study indicates that the solids have a chemical composition and behaviour similar to those obtained from the pilot scale study. However, the geotechnical and physical properties are significantly different. The permeability of the loose material is comparable to that obtained from the UBC sample but on compaction the waste residue in the test cells show significant reductions in permeability and at this point levels as low as 1.1×10^{-6} cm/s have been achieved for only moderate degrees of compaction. The strength development achieved with cured samples is up to an order of magnitude greater than the UBC samples.

These results indicate that the Chatham residues differ substantially from those obtained from the pilot plant without a baghouse in terms of their physical and geotechnical behaviour and in fact seem to have much more desirable characteristics from the point of view of disposal. The ash can be easily worked and compacted with standard construction equipment providing it is properly conditioned, i.e., wetted prior to disposal.

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 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 (3) using material from the 20 MW_e TVA bubbling bed demonstration plant has shown that it is possible to make "no cement" concretes whose strength development is equivalent to that of 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. Environment Canada is supporting continued studies of disposal of combustion residues from Chatham and will be participating in studies on the potential for utilization of circulating FBC wastes.

REFERENCES

1. "Characterization of circulating AFBC wastes"; CEA Report No. 432 G 494; Dec. 1986.

2. Liang, D.T. and Hamer, C.A. Report MSL 88-41; April 1986.

3. Rose, J.G., Bland, A.E. and Jones, C.E. "Production of no-cement concrete using fluid bed combustion waste and power plant fly ash"; TVA Contract No. TV-60433A; Sept. 1986.