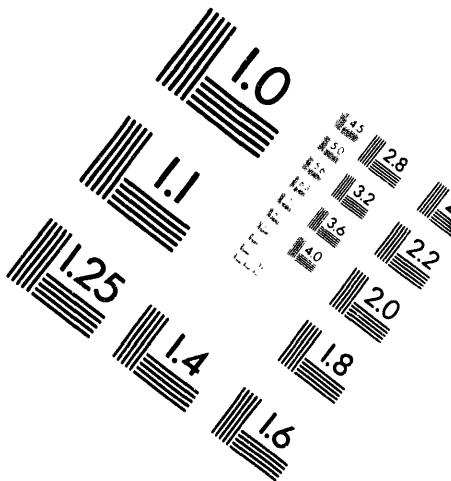
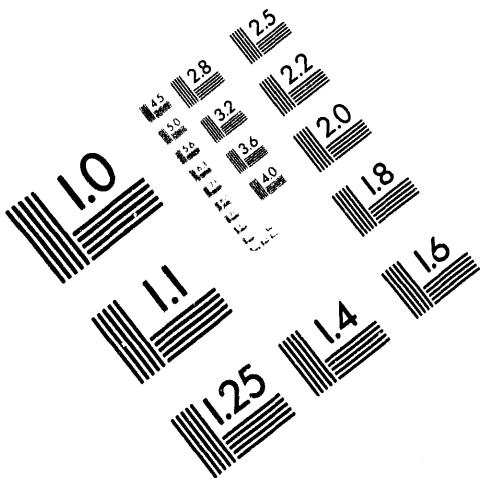




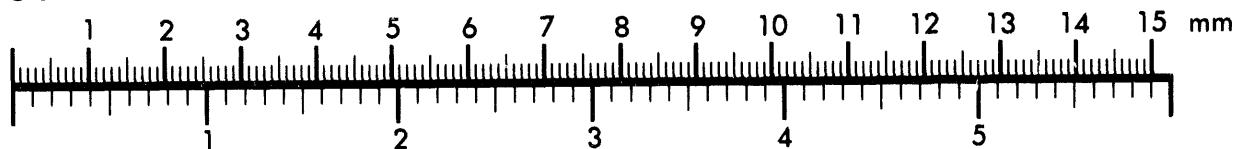
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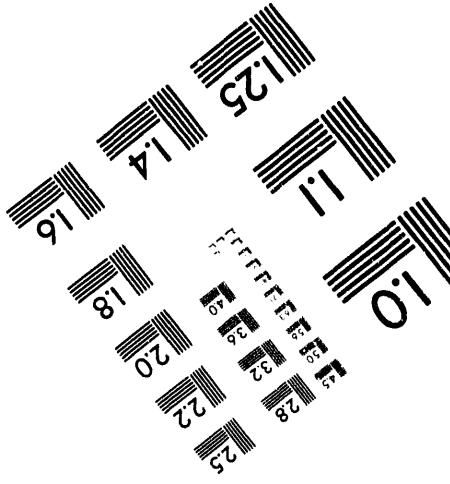
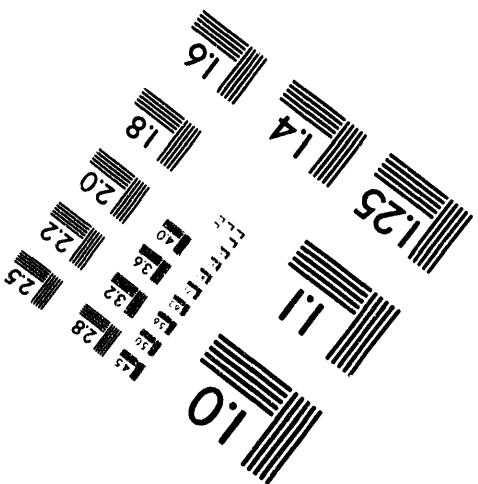
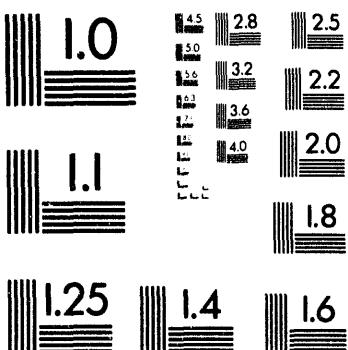
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**Evaluation of Cement Production Using A  
Pressurized Fluidized-Bed Combustor**

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**Topical Report**

**Michael DeLallo  
Robert Eshbach**

**January 1994**

**Work Performed Under Contract No.: DE-AC21-89MC25177**

**For  
U.S. Department of Energy  
Office of Fossil Energy  
Morgantown Energy Technology Center  
Morgantown, West Virginia**

**By  
Gilbert/Commonwealth, Inc.  
Engineers and Consultants  
Reading, Pennsylvania**

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## 1.0 BACKGROUND

Considerable effort has been made to find ways of using solid wastes from fluidized bed combustors as a productive feedstock. If FBC wastes can be economically utilized to support structural material manufacture instead of being landfilled this can improve the commercial attractiveness of FBC plants. One possibility is the conversion of FBC ash into portland cement feedstock. This report provides background and discussion on the potential use of FBC ash as a cement feedstock.

The fact that FBC ash contains high proportions of unreacted lime, an essential ingredient in the production of portland cement, has attracted considerable attention and has been addressed in the literature. Dawson and others (1987<sup>(1)</sup>) ranked the use of FBC ashes in the production of cement as having a moderate market potential, primarily because FBC ash represents a source of the raw material, lime, used in the production of cement. Almost half of the energy requirement for the production of portland cement is associated with the calcination of the limestone (conversion of  $\text{CaCO}_3$  to  $\text{CaO}$ ) and, therefore, this use of FBC ash is an attractive option if the technical and economic considerations can be resolved. The technical concerns are these:

- Calcium sulfate in the feed stock will melt when exposed to the temperatures in the preheater which precedes the kiln in many plants. The resultant pre-kiln plugging is obviously disruptive to plant operations.
- The high clinker temperatures in the kiln (1400 to 1600 degrees Centigrade/2500 to 3000 degrees Fahrenheit) will result in the decomposition of any  $\text{CaSO}_4$  existing in the kiln feed and the consequent release of  $\text{SO}_x$ . Such a release is not an emissions problem but is a cement production problem since kiln exhaust must be recycled back to the kiln rather than discharged to the atmosphere. This complicates production of cement conforming to required standards which limit the sulfur content in the cement.
- The ratio of silica to alumina is different in the FBC ash than in the requirements for cement clinker. For example, the typical silica to alumina ratio in FBC ash is approximately 2.5 to 1, while that required in cement production is approximately 4 to 1. This is, of course, only a problem if blending of the FBC residue with other raw materials is not permitted.

The amount of iron, particularly in the FBC fly ash, is also too high, thereby requiring high additional limestone and silica or resulting in the allowance of smaller amounts of FBC ash in the cement.

- The use of dolomite as a sorbent in FBC can result in excess  $\text{MgO}$ , a compound which causes volume instability in the cement. It is considered to be detrimental and is, therefore, limited in the ASTM specification for portland cement (ASTM C 150).
- Finally, FBC ash, especially if formed from the combustion of waste materials, has the potential for containing many materials and compounds which cannot be permitted to be included in portland cement. Heavy metal content is limited both by regulatory requirements and because it adversely affects the properties of cement.

One solution to these problems is to limit the ash content in the kiln feed sufficiently to dilute the concentration of the objectionable materials to the required degree. Doing so, of course, minimizes the significance of this means of ash utilization.

Another solution is to remove objectionable materials prior to their introduction to the kiln. One option to do so is the implementation of various beneficiation processes to remove appropriate

materials, as discussed later. However, the appropriate beneficiation technology may or may not exist in all cases.

A third option, applicable only to the reduction of the sulfur content of the potential kiln feed would be to integrate the cement clinker production with sulfur recovery in the form of sulfuric acid. TVA performed a feasibility study of this option in 1986-87 (Harness and others, 1986, 1987<sup>(2)</sup>; Salladay and others, 1986<sup>(3)</sup>; Finch and others, 1987<sup>(4)</sup>). Clinker tests using FBC ash from the TVA Shawnee 20 MWe bubbling FBC plant in Paducah, Kentucky were conducted at the Portland Cement Association (Construction Technology Laboratory) facilities in Skokie, Illinois. Successful clinkers were produced using proper proportions of limestone, white clay, coal, ferric oxide, and sand. The best mixes used between 10.5 and 13.9% of FBC ash.

An additional technical problem was encountered in the TVA studies and involved the use of FBC fly ash and char in the clinkers. The high carbon in these fractions resulted in the production of CaS, formed from the chemical reaction with carbon under reducing conditions (Finch and others, 1987<sup>(4)</sup>). However, in a properly operated kiln carbon should be burned off and reducing conditions should not exist.

An economic evaluation of the integrated industrial complex of a 500 MWe FBC electric power plant coupled with a cement plant and a sulfuric acid production facility was also performed by TVA. An estimated 500,000 tons per year of FBC ash would be produced at the electric power station. This ash, plus 30,000 tons per year of  $Al_2O_3$ , 40,000 tons/year of sand and 764,000 tons/year of limestone, would produce 992,000 tons/year of portland cement. The sulfuric acid production facility would use the  $SO_2$  gas, along with 106,000 tons/year of sulfur to produce 532,000 tons of 93%  $H_2SO_4$ . The study concluded that the integrated concept was indeed feasible.

A commercial example of the use of CFBC residue in the production of portland cement is the 25 MWe California Portland Cement Cogeneration Facility. The facility produces power from the combustion of low sulfur coal and uses all of the ash, along with additional cement ingredients, in the manufacture of portland cement.

## 2.0 CEMENT TECHNOLOGY

Portland cement is a finely pulverized material comprised primarily of various compounds, including calcium oxide, silica, alumina and ferric oxide, all in combined form. The raw materials to form these oxides may include:

- Calcareous materials - Limestone, chalk, marl and marine shells for the calcium oxide (CaO)
- Argillaceous materials - Clay, slate, shale and sand for the silica,  $SiO_2$  and alumina,  $Al_2O_3$ .
- Iron ore for the ferric oxide,  $Fe_2O_3$
- Aluminum ore for alumina
- Gypsum,  $CaSO_4 \cdot 2H_2O$  - Added at final grinding of the clinker to neutralize the affects of tricalcium aluminate and, thereby, control setting time and obtain optimum strength.

The chemical composition of the raw materials available to a given cement manufacturing facility determines the number of such materials and the relative amount of each. In any case the materials, when blended together in proportions specified by the cement chemist, must be capable of producing a clinker with about 65% lime, 22% silica and 8% alumina and ferric oxide. Usually two to five separate materials are blended together. Any number of materials containing the

required compounds could conceivably be used, although practical considerations generally limit the number of individual materials which can be economically handled.

The calcium, silicon and aluminum oxides formed in the manufacturing process exist primarily in the form of four major compounds in portland cement:

- $\text{C}_3\text{S}$   $3\text{CaO}\cdot\text{SiO}_2$   
Tricalcium Silicate (alite)  
Contributes to strength development and higher heats of hydration.
- $\beta\text{C}_2\text{S}$   $\beta_2\text{CaO}\cdot\text{SiO}_2$   
Beta Dicalcium Silicate
- $\text{C}_3\text{A}$   $3\text{CaO}\cdot\text{Al}_2\text{O}_3$   
Tricalcium Aluminate
- $\text{C}_4\text{AF}$   $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$   
Tetracalcium Aluminoferrite

Note that  $\text{C}_3\text{S}$  and  $\beta\text{C}_2\text{S}$  are the primary cementitious compounds in cement. Minor compounds, characteristically in the form of oxides of magnesium, sodium, potassium, sulfur, titanium, phosphorus, and manganese are also present.

## 2.1. Manufacture Of Cement

The process for producing portland cement is relatively standard and consists of the following activities:

- Mine/excavate the raw materials, lime and clay.
- Transport the raw materials to storage silos.
- Perform chemical analyses of the raw materials in order to determine blending proportions.
- Feed the raw materials in the proportions determined by the cement chemist to be appropriate for forming the required clinker to the grinding mill where they are dried and ground to a powder (raw meal) having a fineness approaching Portland cement. Where FBC ash is used in the kiln feed it is reasonable to expect that all component materials would be ground together in one mill.
- Sample the mixture and conduct a chemical analysis to determine if the raw mix will produce the required clinker.
- Transfer the raw meal to a blending bin, blend and test for chemical composition.  
Is a granulator generally used to make pellets?
- Combine the raw meal batch with other raw meal batches having slightly different compositions to obtain the desired blend for the kiln feed.

- Feed the finely ground and blended raw materials into the upper end of the inclined rotary kiln (kiln is fired at the lower end).
- As the mixture moves through the kiln the moisture is driven off, the limestone is converted to calcium oxide, the mixture fuses into small lumps called clinker which has the chemical composition of Portland cement
- Control the rate of cooling on discharge from kiln since cement properties relate to the thermal history of burning and cooling.
- Grind the clinker, adding gypsum or a blend of gypsum and anhydrite, to yield Portland cement.

Were PFBC residue to be used as a feedstock a number of these steps would require some modification. For instance:

- Storage silos would have to be provided for another raw material, the PFBC residue. The size and number of storage silos for the residue would depend on the rate at which the residue is produced and the rate at which it can be utilized for cement production. The latter rate would be a function of the extent to which other materials must be blended with the PFBC residue in order to produce a clinker with the desired chemical composition.
- Additional chemical analyses of the residue would be required because the PFBC residue has the potential for containing undesirable substances and because it will be variable in composition, especially if it is produced from burning waste. The undesirable materials include heavy metals, calcium sulfate and various compounds known to deleteriously affect the properties of the cement. The calcium sulfate and the various deleterious materials must be removed prior to entering the kiln.

The extent and variety of testing would be entirely dependent on the variability in composition of the feed stock. That variability is, in turn, primarily a function of the variability of the fuel entering the PFBC and, possibly, the plant power levels.

- If the residue does contain unacceptable levels of undesirable materials, they would have to be removed using one or more beneficiation processes appropriate for the materials being removed or by tying in a sulfur recovery system.

Note that all substances entering the kiln will, inevitably, be included in the portland cement produced. This is because the exhaust from the kiln is no longer fed to a stack but, because of environmental regulations, must be collected and returned to the kiln. Unfortunately, substances not contributing to the formation of the primary calcium silicates generally adversely affect the properties of the cement, particularly with respect to strength development or setting characteristics. Also, kiln exhaust is generally very high in alkalies of sodium and potassium, materials which have been shown to have undesirable reactions with certain aggregates in concrete. This exhaust is also recycled.

One such material is the calcium sulfate which is contained in the PFBC residue and which may represent a major problem in the development of this technology. In a cement mill the  $\text{CaSO}_4$  must be added in the final grinding process, following formation of the clinker in the kiln. It cannot be included in the kiln feed since it will either liquify and plug preheaters or it will decompose into  $\text{SO}_x$  in the kiln. In the latter event the unwanted sulfur will stay in the clinker and limit the amount of gypsum or anhydrite which can be added during final grinding to control setting characteristics.

For this reason the  $\text{CaSO}_4$  contained in the raw materials must be severely limited. One issue of a research program will be to determine if any processes are available for removing calcium sulfate, if they are available for use (they are probably patented) and if their utilization would be cost-effective.

## 2.2 Cement Types

The ASTM in designation C 150-92, "Standard Specification for Portland Cement"<sup>(5)</sup> has characterized portland cement into eight types, described as follows:

- **Type I:** General concrete construction  
**Type IA:** Air-Entrained Type I.
- **Type II:** General construction where moderate resistance to sulfate attack and/or a moderate heat of hydration are desired.  
**Type IIA** Air-Entrained Type II.
- **Type III:** High early-strength concrete.  
**Type IIIA:** Air-Entrained Type III.
- **Type IV:** Low heat of hydration concrete.
- **Type V:** High sulfate-resistance concrete.

### Primary Hydration Reactions For Cement

- $2 \text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{Ca}(\text{OH})_2$
- $2 \text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{Ca}(\text{OH})_2$

The standard chemical composition of the eight types of portland cement as specified by the ASTM is shown in Table 1. Additionally the ASTM has established optional chemical requirements, standard physical requirements, and optional physical requirements.

## 3.0 ASH CHARACTERISTICS

The constituents in ash that are needed to produce cement are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{CaSO}_4$ . These compounds, however, must be present in correct proportions and ratios. In general the following is required:

- High levels of lime, carbonated lime or calcium sulfate, materials required for production of Portland cement.
- No entrapped water or waters of crystallization, resulting in low processing energy requirements.
- No fluorine which would poison catalyst beds in a sulfuric acid plant.
- No phosphate which would reduce cement strength.
- Contains sulfur, iron and carbon, as required for the catalytic reduction and liberation of  $\text{SO}_2$  gas.

**Table 1**  
**ASTM Standard Chemical Requirements**

<b>Cement Constituents</b>	<b>Chemical Requirements for Cement Types</b>				
	<b>I,IA</b>	<b>II,IIA</b>	<b>III,IIIA</b>	<b>IV</b>	<b>V</b>
<b>SiO<sub>2</sub></b>	min, % =	20.00%			
<b>Al<sub>2</sub>O<sub>3</sub></b>	max, % =	6.00%			
<b>Fe<sub>2</sub>O<sub>3</sub></b>	max, % =	6.00%			
<b>MgO</b>	max, % =	6.00%	6.00%	6.00%	6.00%
<b>SO<sub>3</sub></b>	max, % =	3.50%		4.50%	
<b>C<sub>3</sub>S</b>	max, % =				35.00%
<b>C<sub>2</sub>S</b>	min, % =				40.00%
<b>C<sub>3</sub>A</b>	max, % =	8.00%	15.00%	7.00%	5.00%
<b>(C<sub>4</sub>AF + 2 (C<sub>3</sub>A))</b>	max, % =				25.00%
<b>(C<sub>4</sub>AF + C<sub>2</sub>F)</b>	max, % =				n/a

N/A = not applicable

There is no data on circulating PFBC ash compositions, but AFBC and PFBC ashes have been analyzed. The fact that AFBC ash contains high amounts of unreacted lime, an essential ingredient in the production of portland cement, has prompted investigations into the practicality of this process<sup>(6,4)</sup>. Technical problems were encountered such as uncontrolled SO<sub>2</sub> emissions during the production of clinker, pre-kiln plugging, formation of CaS and unfavorable silica to alumina ratio; however, a suitable cement was made from FBC ash.

At the Grimethorpe PFBC test facility data was obtained on the constituents of the ash<sup>(7)</sup>. Various coals and sorbents were combined and "ashed" in order to obtain analyses and ash fusion temperatures. Table 2 gives the ash analyses for four combinations of combusted Kiveton coal and Middleton limestone, which is a low magnesium limestone. The data indicates that the PFBC ash composition is high in unreacted lime as calcium oxide (CaO) and high in silica (SiO<sub>2</sub>), however it also shows significant amounts of alumina (Al<sub>2</sub>O<sub>3</sub>) and ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) which may present a problem.

#### 4.0 PFBC CASE ANALYSIS

For this study the small remote 4 MW PFBC case has been selected for investigation to determine the potential of producing Portland cement feedstock from the ash wastes. In this investigation it was assumed that the 4 MW PFBC uses Beluga coal and Lowelville limestone as the sorbent. Tables 3 and 4 show as-received analyses of the coal and limestone used in this analysis. Table 5 is an analysis of the Beluga coal ash. Using a 5.0 Ca/S ratio and assuming all the CaCO<sub>3</sub> is calcined

to CaO, a simulation was performed to determine the ash analysis that would result from combustion in the 4 MW PFBC. The effects of the co-firing of sewage sludge, RDF and tires were not included in the simulation.

**Table 2**  
**Ash Composition Analysis**

	80	90	95	98
% Coal (Kiveton)				
<u>Composition</u>				
SiO <sub>2</sub>	39.4	46.6	51.1	54.4
Fe <sub>2</sub> O <sub>3</sub>	6.2	7.7	8.4	8.6
MgO	2.3	2.9	2.8	3.1
CaO	31.0	18.5	11.0	6.4
Al <sub>2</sub> O <sub>3</sub>	14.0	16.5	18.4	19.1
TiO <sub>2</sub>	0.7	0.8	0.9	0.9
Na <sub>2</sub> O	0.4	0.5	0.5	0.5
K <sub>2</sub> O	1.6	2.0	2.2	2.3
SO <sub>3</sub>	4.0	4.3	4.5	4.5
CO <sub>2</sub>	<u>0.4</u> 100.0	<u>0.2</u> 100.0	<u>0.2</u> 100.0	<u>0.2</u> 100.0

Table 6 shows the eight cement types and the compounds that are present in the simulated PFBC ash. The percentages of constituents define each type, therefore, if PFBC ash and sorbent are combined such that the cement type composition limits can be met, the process could be considered feasible. The blank areas under the columns for the cement types indicate that there are no requirements for meeting ASTM C150 standards. For each cement constituent, such as SiO<sub>2</sub>, there is shown a percentage contained in the ash from the 4 MW simulated case (e.g., SiO<sub>2</sub> is 14.037%). For certain cement types there are minimum/maximum amounts for these compounds. Cements II and IIA, as an example, require a minimum of 20% of SiO<sub>2</sub>. Since the 4 MW ash has only 14.037% it does not meet the C150 requirements, so SiO<sub>2</sub> would have to be added to reach the 20% minimum, however this would not be considered a problem.

The table shows that requirements for types I, IA, III and IIIA can be met with little to no modification, so the ash from the 4 MW combustor has the potential to meet the criteria for those cement types. Type II and IIA would require the addition of SiO<sub>2</sub> and a reduction in Al<sub>2</sub>O<sub>3</sub> and C<sub>3</sub>A. Type IV has too much C<sub>3</sub>A and not enough C<sub>2</sub>S. Type V has too much C<sub>3</sub>A and too much (C<sub>4</sub>AF+2(C<sub>3</sub>A)). In order to meet the ASTM cement standards some chemical compounds would have to be added or removed either before or after PFBC combustion.

**Table 3**  
**Beluga Coal Analysis**  
**(Hot Water Dried)**

<u>Proximate Analysis</u> (% AF)	<u>%</u>
Moisture	15.0%
Volatile Matter	38.5
Fixed Carbon	40.5
Ash	6.0
<u>Ultimate Analysis</u> (% Air Dried Basis)	
Carbon	57.4
Hydrogen	5.8
Oxygen (by diff.)	29.8
Nitrogen	0.9
Sulphur	0.1
Chlorine	-
Carbon Dioxide	-
Calorific Value (Btu/lb.)	8,150

**Table 4**  
**Lowellville Sorbent Analysis**

Component	<u>%</u>
CO <sub>2</sub>	39.8
K <sub>2</sub> O	0.24
Na <sub>2</sub> O	0.01
MgO	0.48
CaO	49.1
Fe <sub>2</sub> O <sub>3</sub>	1.2
Al <sub>2</sub> O <sub>3</sub>	1.9
SiO <sub>2</sub>	6.4
TiO <sub>2</sub>	0.09

**Table 5**  
**Beluga Coal Ash Analysis**

<u>Ash Composition</u>	<u>%</u>
SiO <sub>2</sub>	36.6
Al <sub>2</sub> O <sub>3</sub>	28.4
Fe <sub>2</sub> O <sub>3</sub>	10.4
TiO <sub>2</sub>	1.2
P <sub>2</sub> O <sub>5</sub>	1.9
CaO	13.2
MnO	0.2
MgO	1.8
Na <sub>2</sub> O	0.4
K <sub>2</sub> O	1.3
SO <sub>3</sub>	4.2

While these results are encouraging, the assumptions made and the lack of real PFBC ash composition data (including effects of RDF, sludge, and tires) emphasize the need for further analyses based on reliable data. For example, data from Grimethorpe<sup>(8)</sup> which investigated the relationship between CO<sub>2</sub> partial pressure and percent calcination of the bed show percent calcination ranging from 13% to 91%. The above analysis assumed 100% calcination. Calcination is affected by temperature, pressure, and excess air which determine the partial pressure of CO<sub>2</sub> in the combustor flue gas. Conditions needed to achieve 100% calcination were not considered in the analysis used to predict compound percentages.

## 5.0 DEVELOPMENT NEEDS

There is a definite potential for utilizing CPFBC wastes for portland cement production. Although AFBC wastes may have differences compared to CPFBC wastes, there are enough similarities such that the successful production of clinker using AFBC wastes could be expected with CPFBC wastes. Cement made with TVA AFBC ash that was reported by the Portland Cement Association indicate CPFBC ash would react the same.

The following provides issues and development needs required to further this investigation.

**Table 6**  
**PFBC Ash Comparison to Cement Composition Requirements**

<b>Cement Constituents</b>	<b>PFBC Ash Weight Percent</b>	<b>Chemical Requirements for Cement Types</b>				
		<b>I,IA</b>	<b>II,IIA</b>	<b>III,IIIA</b>	<b>IV</b>	<b>V</b>
<b>SiO<sub>2</sub></b>	14.037% min, % =		o.k. 20.00%			
<b>Al<sub>2</sub>O<sub>3</sub></b>	8.189% max, % =		*PROBLEM* 6.00%			
<b>Fe<sub>2</sub>O<sub>3</sub></b>	3.304% max, % =		o.k. 6.00%			
<b>MgO</b>	0.911% max, % =	o.k. 6.00%	o.k. 6.00%	o.k. 6.00%	o.k 6.00%	o.k. 6.00%
<b>SO<sub>3</sub></b>	1.086% max, % =	o.k. 3.50%		o.k. 4.50%		
<b>C<sub>3</sub>S</b>	18.933% max, % =				o.k. 35.00%	
<b>C<sub>2</sub>S</b>	25.961% min, % =				*PROBLEM* 40.00%	
<b>C<sub>3</sub>A</b>	16.111 max, % =		*PROBLEM* 8.00%	*PROBLEM* 15.00%	*PROBLEM* 7.00%	*PROBLEM* 5.00%
<b>(C<sub>4</sub>AF + 2 (C<sub>3</sub>A))</b>	58.403% max, % =					*PROBLEM* 25.00%
<b>(C<sub>4</sub>AF + C<sub>2</sub>F)</b>	0.000% max, % =					o.k. n/a

### **5.1 Data to Define PFBC Performance and Ash Production**

1. Develop data defining the magnitude of the following variables which affect the quality and the quantity of the PFBC residue with respect to its use as an ingredient in kiln feed:
  - a. Chemical characterization of PFBC residue as a function of the full range of potential fuels and of time (instantaneous vs. long-term average), coal, waste (derived from both organic and inorganic materials), and coal/waste combinations.
  - b. Variability over time of ash chemical characteristics
  - c. Ash production rate
  - d. Variability of ash production rate
  - e. Maximum and minimum waste content in a typical PFBC ash.

2. What criteria exists for characterizing the nature of the fuel used in a PFBC, especially when waste is used as a fuel?
3. Can the materials used as PFBC fuel be screened in order to ensure that such substances will not be present in the fuel entering the PFBC?
4. Can limits be placed on the anticipated variability on the chemical composition of the residue and the amount of waste being burned in a PFBC at any given time?
5. What waste materials detrimental to the production of cement (such as heavy metals) could appear in the residue as the result of burning waste and in what concentration?
6. Develop means for disposing of materials and substances not traditionally a component of kiln feed, and potentially requiring removal prior to use in a cement plant. The following specific issues should be studied:
  - a. Determine the need for a conditioning procedure (including hydration) for ash used as cement kiln feed. Define the duration of the conditioning process and the conditions under which it will be carried out (ash temperature, ash composition, etc.)
  - b. Evaluate in greater detail the concept proposed by TVA for the integration of the cement production with sulfuric production. Proposed is a two-part evaluation to (1) establish the performance and economic characteristics for a PFBC ash with additional sorbent for portland cement production, and (2) perform a series of clinker formation studies to assess the technical viability of portland cement production and the relative amount of PFBC ash which can stoichiometrically be incorporated into the clinker composition.

The technical and economic feasibility from these evaluations will be used to assess the economics of the portland cement production. Associated with these assessments is a proposed investigation of the technical feasibility and economics of the sulfuric acid (or other potential sulfur recovery process). The overall preliminary economics will be used to determine if additional engineering and design studies are warranted for this application.

- c. Define the nature and allowable concentration of those apparently undesirable materials which can, nevertheless, be tolerated in the clinker and which, therefore, do not require extraction from the raw materials.
- d. Define and evaluate the available beneficiation processes (most of which are probably patented) required to separate undesirable materials from the PFBC residue prior to its introduction to the kiln should be defined. Such materials would include, as a minimum:
  - (1) Calcium sulfate (processes developed by Fuller or Dragon Cement have apparently been under development but may not be fully developed as yet).

- (2) Compounds of magnesium
- (3) Heavy metals (methods used in the refining industry may be appropriate)
- (4) Trace elements

7. Consider the potential need to impose temperature controls to control the rate of cooling of the PFBC residue should be evaluated. Will cooling or an inappropriate rate of cooling change the physical or chemical properties of the PFBC residue?
8. Evaluate the extent to which the chemical composition of the residue is affected by the design and operation of the PFBC. The effect of operating pressures, operating temperatures and plant load on the physical and chemical characteristics of the residue should be determined.
9. Conduct those tests (See Section II.C.4) required for conformance to ASTM C 150 of cement made from various PFBC ashes.

## 5.2 Cement Issues

1. Determine the need for temperature controls of the feedstock. Can the residue be allowed to cool down before being used as a feedstock? Will doing so change its physical or chemical properties?
2. The minimum kiln times, kiln temperatures and amount of coal required to form the appropriate calcium silicate crystals is a characteristic of the composition of the kiln feed. The relationships among these variables should be determined for various PFBC ashes. This defines much of the energy requirement. Microscopic examinations of the clinker produced using these ashes should be used to define the time limits for adequate burning and clinker formation.
3. What substances must be limited in a kiln feedstock because they adversely affect one or more properties of the cement produced? Such materials may have a deleterious affect primarily on setting times, strength, and volume stability. This is especially a concern if waste materials are to comprise part of the fuel.
4. To what extent are the trace chemicals in residue different from those found in normal cement feedstock? Will these chemicals form oxides which will affect atomic arrangements, crystal forms and hydraulic properties of the silicates in the cement?
5. What will be the alkali content of the cement produced using PFBC?
6. What compounds would have to be retained in the cement in lieu of discharge to the environment as the result of using this feedstock?
7. Is it possible to produce a relatively low-grade, low-cost portland cement intended for use in non-structural applications where properties of the cement such as compressive strength and volume stability may be much less critical? Such a cement could conceivably contain impurities in quantities unacceptable for inclusion in a cement which is required to conform to ASTM C 150. Production of such a material could hopefully be carried out without use of the beneficiation processes required to remove trace elements, heavy metals and similar substances.

### 5.3 Cost Issues

#### 1. Potential Capital Costs:

- a. Develop a quality control/quality assurance program to control the content of the residue and the variability of the component substances. The requirements of such a program could have a significant impact on PFBC plant costs.
- b. Determine the size and number of storage silos for holding PFBC residue prior to introduction into the kiln.
- c. Assess the adequacy of available process equipment for extracting CaSO<sub>4</sub>, potentially using a process similar to that reportedly being developed by either Dragon Cement or Fuller.
- d. Precise amounts of gypsum are added to the clinker in the final grinding in order to react with C<sub>3</sub>A which causes rapid setting. The result is insoluble calcium sulfoaluminate. The gypsum requirement increases with the C<sub>3</sub>A content and with increased fineness. However, gypsum cannot be permitted in the feedstock since it will either liquify and cause pre-kiln plugging or it will increase sulfur content of the kiln feed to unacceptably high levels. The CaSO<sub>4</sub> content in the feedstock is, therefore, a detriment rather than an advantage.
- e. Equipment for extracting undesirable materials. This could involve a large variety of equipment such that the extent and variety of such materials would be the determinant of the amount of beneficiation equipment needed and of the associated costs. See also Section IV.A.6.
- f. Determine the need for additional blending tanks.

The PFBC residue alone probably cannot be used to create cement. However, it can be supplemented by blending in additional materials of known composition in appropriate proportions. Such blending of materials of known compositions to provide the appropriate composition for the feedstock is typical of cement plant operation where separate storage facilities are provided for various feedstock materials, each of which has a known chemical composition.

- g. Additional laboratory testing facilities.

#### 2. Operating Costs:

- a. Amount of testing of feedstock testing to determine chemical composition prior to introduction into the kiln, as well as increased testing efforts reflecting the variability of the feed stock.
- b. The time required to form a clinker, and the amount of coal required to fuel the kiln, is dependent on the nature of the feedstock materials. Typically, about 100 tons of coal per hour are required to produce 65 tons of clinker. Energy costs can vary significantly with corresponding variations in the character of the kiln feed.
- c. In a cement plant/PFBC plant combined facility the coal handling and waste disposal facilities could be combined to realize some operating efficiencies.

- d. Evaluate costs, primarily for energy, incurred for additional grinding, blending, burning and processing.

## 6.0 CONCLUSIONS

There are several primary conclusions which can be reached and used to define research required in establishing the feasibility of using PFBC-derived materials as cement feedstock.

1. With appropriate blending almost any material containing the required cement-making materials can be utilized to manufacture cement. However, extensive blending with multiple materials or the use of ash in relatively small quantities would compromise the worth of this concept.
2. The composition of a potential feedstock must be considered not only with respect to the presence of required materials, but just as significantly, with respect to the presence and concentration of known deleterious materials.
3. The processing costs for rendering the feedstock into an acceptable composition and the energy costs associated with both processing and burning must be considered. It should be noted that the cost of energy to produce cement, expressed as a percentage of the price of the product is higher than for any other major industrial product. Energy consumption is, therefore, a major issue.
4. The need for conformance to environmental regulations has a profound effect on the cement industry since waste materials can neither be discharged to the atmosphere or be shipped to a landfill. Rather, they must be included in the cement itself, invariably with adverse affects on the desired properties of the cement. Obviously, the composition of the materials going into the kiln must be closely regulated if a process meeting required specifications is to be produced.
5. Fifth, the need for achieving uniformity in the composition of the cement is critical to controlling its quality. Unfortunately, certain materials in very small concentrations have the capability to affect the rate and extent to which the cementitious compound in portland cement are able to form. Particularly critical are variations in the ash, the sulfur content of the coal or the amount and composition of the stack dust returned to the kiln.

Therefore, the composition of the materials comprising potential feedstock must be determined in detail and closely controlled. This includes PFBC residue, both for the typical situation when coal is burned and also for the situation involving the combustion of refuse. Using that information, and any established tolerances levels for the offending substances, the need for post-PFBC processing must be established. If required, methods must be established for extracting deleterious materials before the residue is used as a component of kiln feed. Only then can realistic cost analyses be conducted to establish the overall cost-effectiveness of implementing the various steps required to utilize the residue as feedstock.

The final report for the research effort should contain recommendations for establishment, qualification and operation, of any PFBC which is intended to provide feedstock for cement production. Such recommendations might:

- a. Specify restrictions on the type or basic design of the PFBC.
- b. Limit the characteristics of the fuels or sorbents used in the PFBC (for instance, dolomite is not an acceptable sorbent because it contains magnesium which produces an expansive cement).

- c. Provide guidance on the need for and cost of owning any processing facilities for removing undesirable substances from the PFBC residue before it is fed into the kilns.

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