

Fly Ash – Production, Variability and Possible Complete Utilization

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ABSTRACT

Presently over 300 million tonnes of Fly ash is produced worldwide. Only about 10-30 percent of fly ash is used worldwide mainly as an additive in cement concrete and structural fill etc. The rest has to be stored in ponds or deposited in old mines, and remains a source of air, water and soil pollution. The ash results mostly from the non-combustible inorganic matter in the coal, which is generally composed of clay, calcite and pyrite. Similar minerals, calcite and clay, are used to produce Portland cement. Similarity of thermal treatment of similar minerals in varying proportions in the cement plants and power plants suggests that fly ash produced in power plants can be converted into cement like material by adding appropriate minerals to coal. Such a process should obviously result in energy saving and significant reduction of greenhouse gas emissions. This paper describes such a process.

1. INTRODUCTION

The industrial revolution in Europe and the United States increased the use of energy and cementing materials for construction particularly in early nineteenth century. Coal was the main fuel in early stages for energy as well as for cement production. Increased economic development in the rest of the world in the last 50 years has created greater need for energy as well as cement. China and India now utilize more coal and use more cement than many countries in the world. One coal fired power plant is reported to be commissioned every month in China. Although India is far behind China in the production and use of coal and cement, but the day is not far when more energy will have to be produced to meet the needs due to increasing economic activities and also the population. Coal accounts of about four fifth of the total fuel used for energy production. Above all the use of coal as fuel in power plants and calcining of limestone in cement account for more greenhouse gas emissions than any other industrial activity including transportation.

Initially, coal in lumps of 70 to 100 mm was fed into stationary or travelling-grate furnaces. The majority of the residue was collected from the furnace bottom and contained large amounts of unburned coal. About 10% of the ash escaped with the flue gases and caused extensive air pollution.

In late 1920s and early 1930s, pulverized coal was fed into cylindrical vertical furnaces, termed as suspension fired furnaces. Coal combustion residue in such furnaces was much finer. Bottom ash accounted for less than 20% to 30% of total ash. Since fine ash particles, carried with flue gases could not be captured by cyclone separators, escaped through smokestacks into the atmosphere. In Europe and the United Kingdom the ash was always referred to as pulverized fuel ash. But in the United States the ash was termed fly ash because it escaped with the flue gases and “flew” into the atmosphere.

Several methods including electrostatic precipitators and bag houses have been used to capture the fly ash from the flue gases. The majority of the bottom ash and fly ash were invariably sluiced into storage ponds. As land costs soared and water and air pollution problems were recognized, better storage and transportation methods had to be devised which added cost to the utility companies as well as the consumers.

Coal combustion residue in such furnaces was much finer and very similar to the ash produced naturally in volcanic eruptions. Volcanic ash around Vesuvius close to the village Pozzuoli in Italy was used by Romans to make concrete. The dome of the Pantheon, still standing after about 2000 years, is made with such concrete containing lime and volcanic ash as the cementing material.

Ash was used as a fill and pozzolan even before scientific studies proved that the fly ash portion of the coal combustion residue is a true pozzolan and can be used to produce economical and durable concrete. In the published literature, the credit goes to R. E. Davis (1937) and his team at Berkeley, California, USA, for suggesting the similarity between volcanic ash and fly ash and its use as a pozzolanic or mineral additive to cement concrete.

It has been an uphill battle for fly-ash marketers and others to find increased uses for the ash. Many universities, the U.S. Bureau of Mines, American Coal Ash Association (ASAA) formerly known as National Ash Association, Electric Power Research Institute (EPRI), Canadian Centre for Mineral and Energy Technology (CANMET), American Concrete Institute and other government agencies have participated in finding new uses for coal ash. Iowa State University, my Alma matter, was one of the pioneers in fundamental and applied research on fly ash, not only for use in concrete but also in soil stabilization and sand-fly ash brick production in 1950s. Many individuals and institutions have also been involved in metal and other elemental extraction like aluminum, gold, vanadium, etc.

During the last three decades, the use and production of fly ash has increased manifold. Many new uses have been developed for fly ash in producing new materials; however, the largest single use of fly ash to economize construction costs is in cement concrete. Unless all the ash can be converted into a cementitious material, transportation costs involved in different uses will not allow its increased use in construction.

Fly Ash Source and Variability

Coal

Coal deposits or seams contain inherent and extraneous inorganic or mineral matter in the coal which was added by natural processes in the cracks in the seams or on the plants before they were converted to coal. Almost all the elements on the face of the earth are present in coal in varying proportions. Nelson (1959) in a study of coals from various mines in the USA analyzed the mineral matter and reported that non combustible inorganic portion accounted for about 3% to 30 % coal deposits. The results of the study also concluded that kaolinite, pyrite and calcite account for 95% of the mineral in American coals. Kaolinite, pyrite and calcite accounted for about 70-95, 5-35, and 0-20 percent respectively. Since the study was conducted in late 1950s the western sub bituminous and lignite coals were not included in that study. The lignite and sub coals

always have much larger percentage of calcite and reduced amounts of kaolinite and other associated minerals. Therefore SiO_2 , Al_2O_3 , Fe_2O_3 contents of the lignite ashes is much lower than that of the Bituminous coal ashes.

Combustion Process and Products

Coal is converted to combustion gases, mainly CO_2 and also some SO_x and NO_x . The inorganic non-combustible, inherent and extraneous, matter associated with coal and mostly present as clay, calcite and pyrite slags and gives rise to bottom ash and fly ash. The bottom ash or boiler slag is a combination of heavier ash particulates, and molten slag that forms on the internal surfaces of the boiler. The fly ash is composed of fine particulates, which are carried from the furnace with the flue gases. Some carbon particles in coal pass through the flame zone unburned particularly in the bituminous coals and negatively affecting its properties.

The type, amount and proportion of different minerals as well as other complex organic compounds in the coal, which give rise to ash, vary with the coal type. The physical, chemical and engineering properties of fly ash from a particular plant or utility are contingent upon the inorganic chemical composition of the source coal, degree of coal pulverization, combustion conditions, and the ash collection, handling and disposal methods employed at each plant. Because no two power plants have all of these factors in common, coal ash and particularly fly ash from each plant is unique and may vary with time. Fly ash is not a product which is produced under strict or prescribed manner. It is why the fly ash properties from the same plant may vary from hour to hour depending on the coal as well as the fuel loading to meet the energy production.

Fly Ash a Pozzolan

Although the initial studies by Davis et al 1937 established the use of Fly ash as pozzolanic admixture to cement, such use was not universally accepted until the cooperative study on the use of fly ash in cement concrete was conducted by the C-9 Committee of the ASTM in 1962. Only the Ashes produced from Bituminous coals of the United States were included in this study. The use of high calcium ashes produced by Lignite or Western coals did not become prevalent until 1970s when the private industry started using such ashes which were not only pozzolanic but also self cementitious and allowed replacement of greater amount of cement in cement concrete mixes.

According to ASTM C618-93 specification (1993) for "Fly Ash and Raw or Calcined Natural Pozzolan for use as Mineral Admixture in Portland Cement

Concrete,” pozzolans are defined as “silicious and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.”

When fly ash is used in combination with Portland cement, calcium hydroxide liberated from the hydration of Portland cement reacts with the alumino-silicates present in the fly ash to form cementitious compounds possessing cohesive and adhesive properties. These calcium alumino-silicate hydrates so formed are termed as pozzolanic reaction products. However, pozzolanic reactions are much slower than cement hydration reactions.

ASTM C618-93 categorizes natural pozzolans and fly ashes into three categories, Class N, Class F, and Class C. The class C fly ashes were recognized as sub bituminous and or lignite ashes with varying degree of self hardening or self cementitious value and containing more than 15% CaO.

Joshi and Lohtia (1997) have suggested that the classification of the ashes should possibly be changed to two types only, pozzolanic but not self cementitious containing 2% unburned carbon and pozzolanic as well as cementitious and containing less than 1% unburned carbon. The bituminous ashes generally contain much higher carbon varying from 2% to 10% measured as loss on ignition where as the sub bituminous and lignite ashes generally contain very little carbon.

2. PRODUCING FLY ASH SIMILAR TO CEMENT

Background and Rational

Thermal power plants are of-course exclusively designed for electric power generation. But fly ash, a powdery material like Portland cement accounting for about 80% of the total ash, is a necessary, although unwanted, by-product of thermal power plants using pulverized coal as fuel. The coal ash is generated mostly from inorganic minerals in the coal, which are similar to raw materials used to produce cement. Nonetheless, very little effort is made to control ash quality for use as construction material, particularly as a partial substitute for cement. Power industry simply wants to get rid of coal as economically as it can.

Cement plants, on the other hand, require mineral resources and processing as well as enormous amounts of energy for calcination and clinker pulverization to produce a cementitious but ash like product. Cement plants also generate substantial quantity of CO₂ and other gaseous emissions along with some kiln dust. Of-

course proper quality control is exercised in cement plants for proportioning of clay and limestone, as well as clinker formation and subsequent pulverization and addition of gypsum, etc.

The author while working on his Ph.D. thesis in late 1960s noted that the fly ashes produced from a mixture of kaolinite and calcite minerals in a bench scale suspension fired furnace exhibited higher degree of pozzolanic activity than the ashes produce just from kaolinite or a mixture of kaolinite and pyrite minerals separately (Joshi and Roasauer 1973).

Again in 1970s while the author was working in the consulting industry in the USA came across many fly ashes in the middle west possessed varying degree and rate of self-hardening. Some of the power plants produced fly ash which looked and behaved some what like ordinary Portland cement. Furthermore it was observed that higher the self hardening or self cementitious value for an ash the higher the pozzolanic activity.

It therefore makes sense to develop technology to produce cementitious or cement like by-product in power plants by modifying or altering the proportion of minerals in pulverized coal feed and exercising some other quality control. High volatile sub-bituminous Alberta coals seemed to be well suited for the development of the proposed technology.

Studies on Conversion of Fly Ash into Hydraulic Cement

Two different studies were, therefore, conducted to see if the self cementitious value of the Alberta fly ashes could be enhanced so that more of the ash could be used in cement and concrete products. First study of this type by Joshi and Ward (1980) was conducted at the Grand Forks Energy Research Centre, Grand Forks ND, USA, using a 750 mm diameter refractory furnace. Study results suggested that the non self cementitious class F fly ash from a plant in the USA could be made self cementitious by adding as little as 5% calcite to coal. The second study was conducted by Chambers *et al.* (1991) at the Alberta Research Council Laboratory using a 3kg/h combustor to find if addition of limestone to the Alberta fly ashes would enhance the self hardening or self cementitious value. The results did indicate that lime injection enhanced the self cementitious properties of the Highvale and Sundance ashes used by power plants in Alberta.

In both the studies described above calcite mineral or limestone was pulverized to the same fineness as the coal. Both the studies were conducted using relatively small or bench scale combustors which allowed full

control of feed rates, coal fineness, and other related furnace conditions similar to the industrial furnaces.

All these bench scale studies confirmed that it should be possible to produce cement like ashes in the power plants if controlled quantities of calcite or limestone are added to the pulverized coal before it is pumped in to the furnace. These findings prompted to undertake a larger research project for developing the technology for producing cementitious or cement like ashes in the existing power plants using pulverized coal as fuel.

It was at this stage that the idea of cogeneration of electricity and cement in a power plant using suspension fired furnace and coal as fuel was developed since CO₂ emissions and climate change became the urgent topics of concern in the society and scientific community at large.

Fly ash and cement are produced by thermal treatment of pulverized minerals. Cement production requires large quantities of minerals similar to the inorganic impurities in coal although in different proportions. Processing and calcination of the minerals and subsequent pulverization of clinker requires enormous amounts of energy in cement production. As a result, substantial quantities of CO₂ are produced besides SO_x, NO_x, other gaseous emissions and kiln dust in cement plants. Additionally, the cement kiln dust collection, storage and subsequent disposal require special environmental safe guards.

The costs and environmental problems associated with both coal combustion residue and cement kiln dust disposal should also be mitigated, if not entirely eliminated by the co-generation technology. The industry as well as the provincial agencies agreed to conduct studies on a larger scale to evaluate the possibility of co-generation of power and cement like material in electricity generating plants in Alberta. Since the emphasis on reduction of greenhouse gas emissions also became equally important it was termed as CO₂ reduction by using coal for producing power and cement.

3. CO₂ REDUCTION USING COAL FOR CO-PRODUCTION OF POWER AND CEMENT

Project Planning – Phase I

The objectives of the project were to include all possible aspects of the process requiring production of cementitious ashes in a power plant using suspension fired furnaces.

Before the coal source could be decided an in depth study of the various cementitious fly ashes was required to establish the rationale for selecting parameters for the

combustion experiments. Samples of various fly ashes which exhibited varying degree of self hardening characteristics were selected for the study from USA as well as Canada and also from previous studies. Physical and chemical properties along with mineralogical composition using X-ray and scanning electron microscopic analyses and other relevant engineering properties including pozzolanic activity, and setting time, if any, were determined. The source and test data on the selected fly ashes are given in Tables 1 - 3.

Table 1: Sources of Fly Ash and Coal Samples

Ash #	Designation	Utility	Coal Type	Coal Source
1	Western Ash Henderson	Public Service Company of Colorado	Low sulphur sub-bituminous	Amax's Blayer & Eagle Butte Mines, Powder River Basin, Wyoming
2	Minnesota Ash	Minnesota Power & Light Company	Low sulphur sub-bituminous	Montana
3	White Bluff Steam	Arkansas Power & Light Company	Low sulphur sub-bituminous	Jacobs Ranch Mine, Wyoming
4	National Minerals	Wisconsin Electric Power Company	Low sulphur sub-bituminous	Powder River Basin, Wyoming
5	Basin Electric Power	Basin Electric Power Cooperative	Low sulphur sub-bituminous	Cordero Mine, Powder River Basin Gillitte, Wyoming
6	Cooperative Power	United Power Association	Low sulphur lignite	Mine Mouth Underwood, North Dakota
7	Sundance	TransAlta Utilities Corporation	Low sulphur sub-bituminous	Highvale Coal Mine
8	Wabamun	TransAlta Utilities Corporation	Low sulphur sub-bituminous	Whitewood Coal Mines
9	Modified Fly Ash with Limestone Injection	Alberta Research Council	Low sulphur sub-bituminous	Highvale Coal Mine

Table 2: Setting Time and Compressive Strength of Ashes

Ash #	Setting Time (min)		Compressive Strength (MPa)			
	Initial	Final	1 - Day	3 - Day	7 - Day	28 - Day
1	5.5	8.0	5.3	6.4	8.4	12.0
2	390.0	715.0	-	-	-	-
3	6.5	17.0	0.6	1.0	1.0	1.4
4	19.0	40.0	6.4	8.9	14.3	15.7
5	5.5	8.0	2.8	3.6	3.8	4.7
6	100.0	185.0	0.2	0.3	0.4	0.5
7	-	-	-	-	0.08	0.09
8	-	-	-	-	0.075	0.08
Portland Cement	180.0*	390.0*	-	-	16.0*	-

Table 3: Results of Chemical analysis of Fly Ashes

Parameter	Ash #1	Ash #3	Ash #4	Ash #5	Ash #6	Ash #7	Ash #8	Portland Cement	Range
Color	Biege	Biege	Biege	Biege	Biege	Biege	Grey	Grey	
Base / Acid	0.97	0.7	0.74	0.83	0.58	0.23	0.23		0.23 - 0.97
Loss on Ignition, LOI	0.27	0.06	0.34	0.48	0.00	0.94	0.47		0.00 - 0.94
Sp. Gravity	2.58	2.42	2.66	2.61	2.59	2.07	2.05	3.1 - 3.15	2.05 - 2.66
Sp. Surface (m ² /kg)	562	540	579	484	384	487	673	280 - 350	384 - 673
Free Lime, %	0.90	0.18	0.87	0.51	1.08	0.60	0.36	0.3 - 1.3	0.18 - 1.08
Silica, %	29.08	35.46	32.67	32.88	45.41	55.57	57.51	17 - 25	29.08 - 57.57
Alumina, %	15.57	19.25	18.70	16.01	14.45	24.30	21.82	3 - 8	14.45 - 24.30
Titania, %	0.92	1.28	1.44	0.94	0.53	0.59	0.68		0.53 - 1.44
Ferric Oxide, %	5.66	7.74	5.52	6.26	7.68	3.51	3.86	0.5 - 6.0	3.51 - 7.68
Calcium Oxide CaO %	29.21	24.43	26.87	26.78	19.80	10.77	11.52	60 - 67	10.77 - 29.21
Magnesia, %	7.87	4.99	4.93	6.25	5.55	1.19	1.56	0.1 - 4.0	1.19 - 7.87
Pot. Oxide, %	0.25	0.57	0.40	0.39	1.64	0.51	0.82	0.4 - 1.3	0.25 - 1.64
Sodium Oxide, %	1.30	1.63	1.59	1.49	0.57	2.55	0.98		0.57 - 2.55
Sulfur trioxide, %	4.11	1.78	3.13	3.29	1.39	0.17	0.24	1.0 - 3.0	0.17 - 4.11
Phos. pentoxide, %	1.10	1.23	1.26	0.90	0.15	0.12	0.08		0.08 - 1.26
Strontium Oxide, %	0.46	0.29	0.41	0.41	0.22	0.12	0.11		0.11 - 0.46

Results and Discussion - Phase I Studies

Table 1-3 include laboratory test data on chemical and physical properties of the selected fly ashes from various power plants burning coal in Alberta as well as from Powder River Basin and adjoining coal fields in the U.S.A. The data on coals is not presented for space limitations. The fly ash #2 contained large amount of carbon and exhibited little self cementing property and, therefore, was excluded from the study and analysis of the data.

The striking features of the two highly self cementitious ashes, #1 and #4, are that they are very fine and the CaO content of both the ashes is between about 27-29% as compared to 60-70% for Portland cement. It is, therefore, evident that the CaO content of Alberta ashes or for that matter any other ash does not have to be in the 60-70% range to exhibit highly cementitious properties but somewhere around 28%.

Alberta coals, like the tested American coals are low rank sub-bituminous coals with low sulphur content.

However, Alberta coals and their corresponding ashes are acidic in nature with high silica content. Base/Acid ratio, $(Fe_2O_3 + CaO + Na_2O + K_2O + MgO)/(SiO_2 + Al_2O_3 + TiO_2)$, of both the Alberta ashes is 0.23 as compared to 0.58 - 0.97 of the ashes from Powder River Basin coals, which are generally self hardening. The CaO content of Alberta coal ash samples varies between 10.77 - 11.52% in comparison to 19.8 - 29.21% for the American coal ash samples. Likewise, the SO₃ content of Alberta ashes is low because of the low CaO content. Therefore, it was concluded that the calcium content in the Alberta ash needs to be increased to alter and/or increase the self-cementing as well as pozzolanic characteristics of the ash.

Therefore, as part of analytical studies, a computer program, "Quick Basic", was developed to calculate the

amount of additives, including lime stone, required to be mixed with feed coal for producing a fly ash with targeted chemical composition. The program also allowed computation of base/acid ratio of the resultant ash.

Specialists in coal combustion in suspension fired furnaces, retained to evaluate the potential for slagging or fouling of furnace walls and boiler tubes as well as other maintenance and operational problems in full size utility boiler by use of additives in the pulverized coal, concluded that no fouling is likely to occur because of the addition of the planned additives. It was also revealed that all coal power plants in Canada and the USA are designed to handle additional 40% ash. The extra ash to be produced by the proposed additives is not likely to be even close to that limit for the plants.

An analysis of test data in Tables 2 and 3 on the fly ashes listed in Table 1 indicated that fly ashes # 1, 3, 4, 5 and 6 of the Western American low rank coals possessing high specific surface and base/acid ratio between about 0.6-1.0 also exhibit high self cementing properties. Based on the analysis of the data from X-ray diffraction, strength tests, specific surface area determination and also the setting time etc, it was concluded that the base/acid ratio of 0.75 to 0.8 should be targeted for the resultant modified ashes.

Analytical studies related to coal combustion in power plants, the resulting particulate, CO₂ and other gaseous emissions were undertaken. Raw material and energy requirements, fine particulate residues and CO₂ emissions in cement plants were also evaluated.

Computations indicated that about 2.6 tonnes of CO₂ are produced on combustion of every tonne of coal containing about 12% moisture and 13 % mineral matter in a power plant. Likewise, about 1 tonne of CO₂ is generated in producing one tonne of cement using coal for

calcination in a cement kiln. Even when gas is used as a fuel for calcination in a cement kiln about 0.8 tonne of CO₂ is generated for every tonne of cement produced. Calcination of limestone accounts for more than 50% of the CO₂ generation in cement production. The development of co-production technology will require addition of only about 5% to 7% limestone by weight of coal feed. Therefore, only about 0.27 tonnes of CO₂ will be generated in producing one tonne of cement-like ash. The co-generation technology of power and cement-like or cementitious ash in an existing power plant should result in net reduction of CO₂ emissions as compared to the emissions from a Portland cement plant. The reduction in CO₂ emissions will be about 66% and 74% for the cement plants using gas and coal as fuel, respectively.

Production/Testing of Modified Ashes – Phase II

The objectives of the project were to evaluate all possible aspects of the process requiring production of cementitious ashes in a power plant using suspension fired furnaces. As a result, the materials and parameters to be studied were investigated in detail in Phase I. The selection of coal, additive type, amount, feed rate, combustion, furnace fouling, if any, and ash testing for suitability for use in concrete were the main objectives of Phase II studies. Since such a study can not be conducted in a full scale furnace because of costs involved and also for fear of fouling of furnace and other combustion and ash collection related problems, it was decided to use the semi industrial furnace with a 0.7 MW pilot-scale research boiler (PSRB) at the Coal Combustion Research laboratory (CCRL) of CANMET at Ottawa. This boiler-furnace is also used by the industry to evaluate their coals and by the department for coal combustion research.

The Quick Basic program developed in Phase I was used to compute the additives to produce modified ashes with a base/acid ratio between 0.75 and 0.8. The resultant ashes so produced were tested as in Phase I for assessing both quantitatively and qualitatively for their cementing value as well as chemical, mineralogical and self cementing characteristics. The Phase II study also included determination of the frequency of soot blowing, fouling/slugging of furnace walls and boiler tubes, erosion problems etc. The possibility of re-injecting the fly ash along with coal feed and calcite was also considered during test burns and assessment of the ash collection capacity required under these conditions. But it was abandoned due to time constraints.

Crushed limestone and a mixture of 89% limestone, 9.76% gypsum and 0.84% calcium fluoride in varying quantities were used as additives to coal fuel to produce modified ashes in 5 test burns. The purpose of adding

gypsum and fluoride was to increase the possibility of base/acid ratio and thus self hardening of the modified ash.

Highvale coal from Alberta used by TransAlta Utilities Corporation, one of the sponsors of the program, was selected for producing the base line ash for comparison purposes.

It was observed that the coal quality was different in different bins at the CCRL laboratory and it was a matter of concern. The limestone was crushed at the CANMET facilities but unfortunately the fineness similar to coal used in the burns could not be achieved and that did affect the properties of modified ashes adversely as discussed further. The mixes selected for the burns are listed in Table 4.

Table 4: Mix Proportion for Test Burns

Mix/Test Burn No.	Fuel Type
1	Coal Only (Highvale Coal)
2	Coal+ 9.66% Modified Limestone (MLS)
3	Coal+ 7.7% Limestone (LS)
4	Coal+ 5.0% Limestone (LS)
5	Coal+ 7.7% Modified Limestone (MLS)
6	Coal+ 5.0% Modified Limestone (MLS)

Results and Discussion - Phase II Studies

Space considerations do not allow including all the data on combustion conditions, fineness, and chemical composition of fuel and limestone. The main constituents of lime expressed as oxides, CaO and MgO, were 51.29% and 2.47%, respectively. The coal was pulverized to the fineness as used in the large industrial furnaces. But the limestone could not be pulverized as fine as the coal fuel and contained over 50% particles coarser than 75 microns as against only 7% for the coal. The mineral matter in coal was, therefore, always finer than the additive and this was reflected in the coarse CaO particles in the ashes produced.

The ashes were sent to Finland where Mr. Bob Talling, a Cement Specialist, conducted or supervised all the related tests on the modified ashes. All the relevant tests including strength, chemical, X-ray fluorescence etc were conducted at Partek cement Laboratories and at the Abo Akademi University in Finland.

All the fly ashes produced were very fine and had almost similar particle size distribution.

The CaO content in six ashes #1, #2, #3, #4, #5 and #6 was measured to be 11.57%, 28.14%, 25.22%, 22.01%, 28.18% and 22.1%, respectively. The SO₃ content for the same ashes was found to be 1.96%, 3.7%, 2.01%, 2.34%, 3.67% and 3.95%, respectively. It is obvious that additives did increase the CaO content in each of the modified ash. Further chemical tests indicated that majority of the CaO was free lime and did not seem to have reacted with the

glassy fly ash particles. Even some spherical particles of CaO were detected in the modified ashes.

Detailed analysis and testing indicated that the free lime or CaO was rather a hard burned lime and not dead burned. As a result it was likely to react slowly with the glass and not be very efficient in producing self cementing or pozzolanic properties to the modified ashes.

Compressive Strength Tests

The strength tests were conducted on paste samples measuring 25×25×250 mm using water/fly ash ratio of 0.4. It was observed that the samples expanded and cracked and the strength could not be measured accurately for the first 7 days. But after a curing period of another 7 days the samples could be tested and retained their cracked state.

Tests were also conducted to determine if the samples made with rapid hardening cement could provide some early strength to suppress the expansion noticed in samples of pastes of fly ashes with 0.4 water/fly ash ratio. Rapid hardening cement and gypsum also could not suppress the expansion sufficiently in the modified ashes, which was caused by free hard burned lime.

Tests were, therefore, conducted to evaluate if the hard burned free lime could be activated by pre-hydrating them and adding some gypsum to activate the glassy fraction in the ashes and also eliminate expansion of samples. Tests were also conducted to see if heat of hydration, as observed in the ashes produced from Western American fly ashes from Powder River basin coals, was produced by pre-hydration of modified ashes. Tests indicated that there was some heat of hydration but since the lime or CaO was hard burned it did not react as much as did the lime or other compounds in the Western American fly ashes. But it provided a clue as to how the free lime in modified ashes could possibly be pre-hydrated to allow its use as hydraulic or latent cement.

Therefore, samples with modified ashes were prepared by pre-hydrating them with the addition of water heated to 35°C. Gypsum, 10% by wt. of ash, was also added to mixes to activate the hard burned lime in the ash and eliminate the expansion of the samples. It was also anticipated that adding gypsum will possibly increase development of early strength in the samples made with such ashes.

The strength test data on samples, in Series P, made with 70% sand and 30% pre-hydrated modified ash from Test Burns #2 and #4 are presented in Figure 1. The Codal values for 70% sand and 30% cement are also included in Figure 1. It is evident that early strength did not improve much but the samples did not expand and 28 day strength of samples using modified ashes exceeded the Codal strength for the samples made with sand and cement.

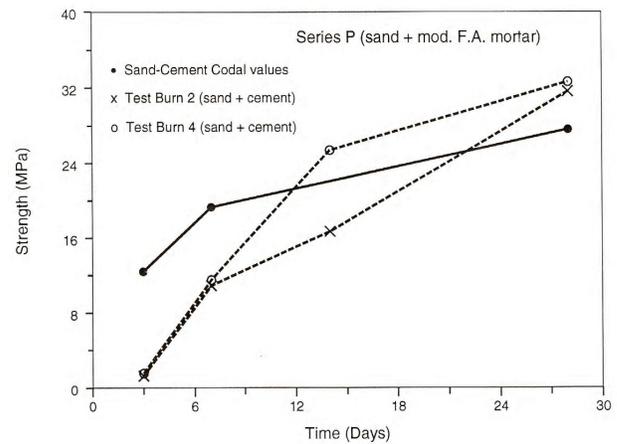


Fig. 1: Compressive Strength of Mortars Containing 70% Sand and 30% Modified Ashes (Series P)

Additional compressive strength tests in Series Q were conducted on samples containing 70% sand and 30% pre-hydrated ashes from all the test burns. Gypsum and super plasticizer were also added to enhance the early strength and improve workability of the paste, respectively. The data are presented in Figures 2.

An examination of data in Figure 2 indicates that only the samples made with ash from Test Burn #2 exceeded the Codal strength and that too at the age of 14 days. The early strength was still lower even for the ash from Test burn #2 and sand mortars. Yet all the modified ashes exhibited significant self cementing value and thus potential for use in construction to replace cement.

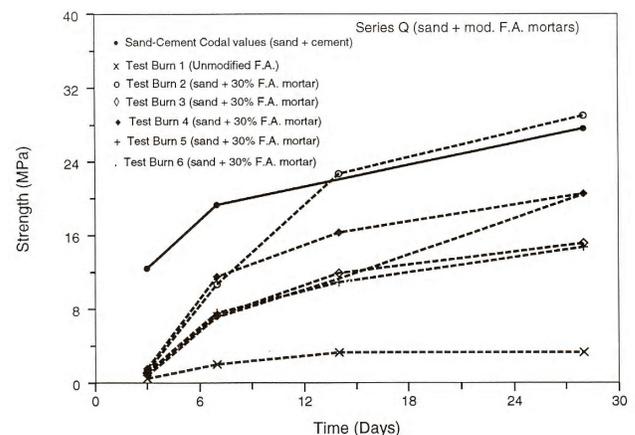


Fig. 2: Compressive Strength of Mortars Containing 70% sand and 30% Modified Ashes (Series Q)

Further tests were conducted to evaluate if addition of small amount of Portland cement to the mixes containing modified ashes could increase the 3 and 7 day strength. The strength test data are presented in Figure 3 for Series R samples containing 70% sand, 27% modified ash and 3% Portland cement.

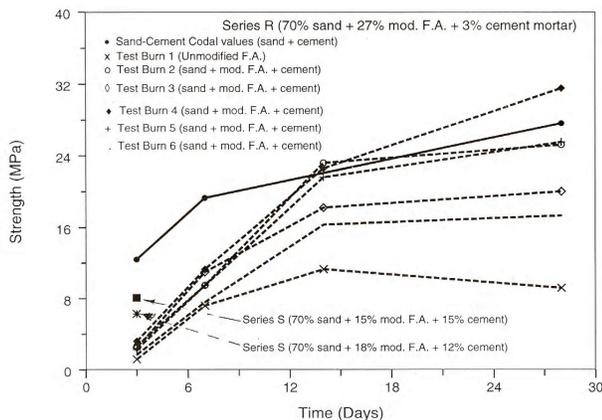


Fig. 3: Compressive Strength of Mortars Containing Sand, Modified Ashes and Cement (Series R and S)

It is noticed that modified ash from Test burn #4 containing just 5% limestone showed the most improvement particularly in the 28 day strength. The early strength gains were not very impressive. The modified Ash from Test burn #2 consistently showed highest 7 and 14 day strength in both the series.

The two data points for 3 day strength for two separate mixes of S series made with ash from Test burn #3 are also shown in Figure 3. It is evident adding increasing amounts of Portland cement increases the early strength. Although data are not included here the long term strength also increased in all such mixes containing 20% cement. Thus up to 80% cement could be easily replaced by the modified ashes in concrete.

Some Other Results/Observations and Discussion

It is important to note that even the semi industrial scale furnace used in this study did not resemble the industrial furnaces. The CCRL furnace produced 80% bottom ash and only 20% fly ash, which is just the opposite of the conditions in the power plant furnaces.

The coal and limestone could not be pulverized to the same fineness as a result majority of the lime stone was possibly lost in the bottom ash since coarse particles tend to fall before they exit flame zone. The fly ash samples collected from different locations such as Super Heater and Electrostatic precipitators were somewhat different. So the results in a full scale furnace will be more conducive to producing the types of cementitious ashes produced in the Western USA.

Although limited data could be obtained on the mixes made by pre-hydrating the modified ashes it is evident that the modified ashes behave like latent cements and can be used to replace Portland cement entirely on many projects. The expansion can be completely eliminated in samples by using pre-hydration and adding some gypsum to the mix. Additional tests in Series S indicated that even early

strength can be improved significantly by adding 12 – 15% cement as can be seen in Figure 3.

It appears that only 5% limestone addition would have been sufficient to produce highly cementitious ashes. This observation is based on the results of the earlier study (Joshi and Ward, 1980).

No doubt better quality control will ensure production of highly cementitious modified ash which can be used to replace all or most of the Portland cement in concrete for different types of construction.

The X-ray diffraction and scanning electron microscopic analyses of the ashes confirmed the observation that CaO was possibly hard burned and did not react with the glassy matter in the ash particles.

The data on fouling and ash handling and collection indicated that no problem is likely to be encountered in a full scale furnace of the power plant if limestone and other additives as used in this study are used to produce latent cement.

4. CONCLUSIONS

The results and data from the studies conducted for CO₂ reduction using coal for co-production of power and cement, and previous studies on converting fly ashes into hydraulic cements, prove that it is possible to produce highly cementitious fly ashes in suspension fired furnaces burning coal as fuel. Use of such ashes may allow almost complete utilization of fly ash and also reduce greenhouse gas emissions and conserve resources besides cost of construction and elimination of air, water and soil pollution.

Full scale tests in an industrial furnace need to be conducted with appropriate quality controls on fineness of the additives and also evaluation of all fly ash properties.

ACKNOWLEDGMENTS

Funds for the project were provided by TransAlta Utilities Corporation of Calgary, Alberta; Alberta Office of Coal Research and Technology (Alberta Energy), and Joshi Consultants Ltd. of Calgary, Alberta, Canada. Mr. Bob Talling of Finland, Dr. S. Chatterji of Denmark and Mr. Horace Whaley of CRRL, CANMET, Ottawa, Canada, were of immense help at different stages of the project.

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