

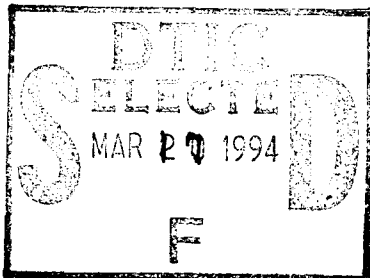
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PHOSPHATE-BONDED FLY ASH

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BACKGROUND OF THE INVENTION

Ash in the form of coal fly ash and of municipal solid waste (MSW) fly ash is a significant environment problem. It is estimated that power plants in the United States generate 80,000,000 tons of fly ash by burning coal. Only about 20% of this amount is utilized and the rest is
10 landfilled. Coal fly ash has complex chemical composition containing up to 80 weight percent of SiO_2 and Al_2O_3 , with Fe_2O_3 , CaO , MgO , Na_2O , K_2O , SO_3 and other oxides as the remainder. It may also contain traces of hazardous elements such as arsenic, lead, barium, and mercury. the chemical composition significantly varies depending on coal deposits and power plant operating parameters. In addition to coal fly ash, large quantities of municipal solid waste (MSW) fly ash
15 are being produced by the incineration of municipal trash, garbage, and even sewage solids.

Fly ash has been used in cement as a substitute for shale; in concrete as a substitute for cement and sand, and as aggregates; in road construction as a filler to bitumen, and as a substitute for sand in the foundation layer; in bricks as a substitute for clay; for soil stabilization; etc. These prior art uses do not lead to massive consumption of fly ash because the ash is
20 usually only a minor component in these composites. It would be desirable to provide processes and products that would use fly ash as the major component.

The fly ash products should be of good quality as judged by appearance and color and physical properties such as compressive strength, bending strength, impact strength, modulus of

elasticity, abrasion resistance, thermal conductivity (R-value), thermal expansion coefficient, water stability/leachability, freeze/thaw resistance, etc.

SUMMARY OF THE INVENTION

The present invention is directed to ceramic materials made from coal fly ash and from
5 municipal solid waste (MSW) fly ash and to processes for producing these ceramic materials. The fly ash is preferably used as it comes from the power plant or the municipal incinerator without any costly cleaning or separation steps.

The ceramic material is formed by the process of

- A. mixing the coal fly ash or MSW fly ash with aqueous H_3PO_4 (phosphoric acid);
- 10 B. forming the mixture into a green body; and
- C. heating the green body to cause the H_3PO_4 to react with oxides in the fly ash to form chemical bonds which bond the fly ash particles together to form the ceramic material.

The ceramic material is useful in forms such as aggregates, bricks, block, tiles, etc.

BRIEF DESCRIPTION OF THE FIGURE

- 15 The figure is a bar chart which illustrates the effect of the sintering temperature on the strength and the water resistance of a ceramic material made from H_3PO_4 and a class C coal fly ash and a ceramic material made from H_3PO_4 and a class F coal fly ash.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

- The present invention provides methods of producing new ceramic materials and structures
20 from ash which includes coal fly ash and municipal solid waste (MSW) fly ash. The coal fly ash is produced by the burning of coal in power and heating plants. The coal fly ash includes class C coal fly ash which comes from high sulfur lignite coal and the Class F coal fly ash which

comes from low sulfur bituminous coal. The class C fly ashes contain significant amounts of CaO resulting from the lime that is used to trap the sulfur during combustion. Table 1 gives the compositions of 7 typical fly ashes which were used to demonstrate the present process. These include a class C coal fly ash from the Coal Creek Station in North Dakota as well as various
5 sources of class F coal fly ashes including Rivesville with approximately 28 weight percent carbon. The MSW fly ash is produced by the burning of trash, garbage, and even sewage sludge in municipal incinerators. Like coal fly ash, MSW fly ash is made of fine solid particles of ash which are carried away by draft or by waste gases and then deposited in flues or trapped in filters or precipitators, etc.

10 The term phosphoric acid or the formula H_3PO_4 when used alone refers to the compound. The term aqueous phosphoric acid or aqueous H_3PO_4 are used to refer to a solution of the compound in water. This is the form that the acid is available commercially. When a simple percentage is given before the term phosphoric acid or H_3PO_4 , it refers to the weight percentage of phosphoric acid (H_3PO_4) in an aqueous solution. Thus 85 percent concentration phosphoric
15 acid or 85% H_3PO_4 refers to a solution of 85 weight percent H_3PO_4 and 15 weight percent water. The weight percentage ranges given for phosphoric acid (H_3PO_4) in the aqueous H_3PO_4 /fly ash mixtures are based on the actual weight of the compound H_3PO_4 present in the mixtures. The weight of any water is excluded from the calculation.

The raw coal fly ash or raw MSW fly ash is made up of loss on ignition components (LOI)
20 and ignition residue components. The LOI components include those components which are driven off or which are burned to form gaseous waste products when the raw fly ash is heated at 900°C. Carbon comprises the largest portion of the LOI material. The ignition residue

components are the portion of the raw fly ash that remains after the LOI components have been removed. The ignition residue components include SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , etc. (see table 1). These oxides react with the H_3PO_4 in the process of this invention. The LOI can be determined by heating a weighed sample of the raw fly ash at 900°C until a steady weight is achieved. The weight loss is the weight of the LOI components and the final weight of the sample is the weight of the ignition residue components. Thus, the weight percentages or fraction of the LOI components and ignition residue components can be calculated from the initial and final weights of the fly ash sample. For the present process, the loss on ignition (LOI) components will comprise preferably 15 or less, more preferably less than 11, still more preferably less than 7, and even more preferably less than 4 weight percent of the raw fly ash. If the loss on ignition components (LOI) components comprise more than 15 weight percent of the raw fly ash, they will preferably comprise from more than 15 to less than 30 weight percent of the raw fly ash.

TABLE 1

CHEMICAL COMPOSITION OF VARIOUS FLY ASH SAMPLES

(WEIGHT PERCENT)

FLY ASH ORIGIN							
OXIDE	Coal Creek Station, ND	Albright Station, Allegheny Power	Hatfield Station, Allegheny Power	Baldwin Power Station, IL	Pleasants, Allegheny Power	Rivesville, Allegheny Power	Spurlock Station, OH
SiO ₂	46.0	56.58	50.09	49.0	45.32	58.79	53.00
Al ₂ O ₃	14.5	27.45	21.57	19.0	20.38	27.91	31.80
Fe ₂ O ₃	6.73	10.64	15.24	15.0	19.60	8.41	6.50
CaO	17.9	1.70	4.95	5.0	9.45	1.20	3.07
SO ₃	1.36	0.90	0.88	4.3	0.56	1.01	0.39
MgO	5.08	0.79	-	0.9	1.07	0.46	0.50
Na ₂ O	1.16	0.29	0.45	0.9	0.44	0.47	0.87
K ₂ O	1.86	2.45	-	2.0	1.92	2.07	-
P ₂ O ₅	0.17	0.41	-	-	0.16	0.23	-
LOI, %	0.3	3.1	1.7	2.3	10.5	28.3	2.0

In the first step of the process, the aqueous solution of H_3PO_4 and the raw coal fly ash or raw MSW fly ash are thoroughly mixed together. In calculating the amounts of aqueous H_3PO_4 and raw fly ash needed, the weight of the water and the weight of loss on ignition (LOI) components of the fly ash are excluded. Thus 100 gms of 85% H_3PO_4 counts as 85 gms H_3PO_4 .
5 Similarly, 100 gms of raw Pleasants coal fly ash which has a LOI of 10.5 percent counts as 89.5 grams ($100-10.5=89.5$) of ignition residue fly ash. This is true even though much of the LOI material may not be removed during the process. The weight percentage of the compound H_3PO_4 will preferably be from about 10 to about 50, more preferably from about 10 to 30, still more preferably from about 10 to 25, even more preferably from 10 to 20, and most preferably
10 from 15 to 20 weight percent based on the total weight of the compound H_3PO_4 and the ignition residue (non-LOI) components of the fly ash. Again note that the ignition residue portion of the fly ash is made up of oxides such as SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , etc. with which the H_3PO_4 reacts to form the polymer-like phosphate bonds which hold the fly ash particles together.

In the second step of the process, the mixture of aqueous H_3PO_4 and raw coal fly ash or
15 MSW fly ash is formed into a green body of the desired shape. Conventional semidry pressing is the preferred method of forming the green body. The pressing may be done by die pressing, isostatic pressing, or other suitable conventional means. The moisture (water) content of the aqueous H_3PO_4 /fly ash mixture is preferably from about 3 to about 5 weight percent for semidry pressing. Sufficient pressure is used to produce a green body that is strong enough for handling
20 without breakage. The amount of pressure required will vary according to the particular raw fly ash chosen. In one test pressing at 10 MPa produced an unsuitable green body whereas the same mixture pressed at 50 MPa produced a good green body and final ceramic product. The green

bodies in the examples were semidry pressed using pressures of from 20 MPa to 100 MPa. However, these examples are merely a general guide and are not intended to limit the pressures that may be used to form green bodies. A person of ordinary skill in the brick or ceramic arts can easily try different pressures to arrive at the optimum pressure to economically form a suitable green body from a given fly ash.

The moisture content of the aqueous H_3PO_4 /raw fly ash mixture should be about 3 to about 5 percent for semidry pressing. If the mixture is too dry it will lack the cohesion necessary to form the strong green bodies. When the moisture content is too high, the mixture will have a waxy consistency which is unsuitable for semidry pressing. However, by allowing water to evaporate from the mixture at preferably from ambient temperature to less than $100^\circ C$ and more preferably from ambient temperature to $60^\circ C$, the moisture content can be reduced to the range of about 3 to about 5 percent where the aqueous H_3PO_4 /raw fly ash mixture has a powder consistency suitable for semidry pressing. During the evaporation process some of the H_3PO_4 may react with raw fly ash to produce agglomerates. This is more likely to happen with class C fly ashes which contain significant amounts of CaO and MgO which react with H_3PO_4 at ambient temperature. The agglomerates can be eliminated by conventional grinding and screening procedures and the resulting smooth powdery mixture can then be semidry pressed into green bodies. It is preferable to use aqueous H_3PO_4 of a concentration that will produce an aqueous H_3PO_4 /raw fly ash mixture having a moisture content suitable for semidry pressing as well as the right weight percentage of H_3PO_4 compound. Generally, about a 65 to 85 or preferably a 70 to 85 weight percent H_3PO_4 aqueous solution is used. For example, merchant grade phosphoric acid (75 weight percent H_3PO_4) will work well in the process. More dilute

aqueous H_3PO_4 solutions may be used, but evaporation at preferably from ambient temperature to less than 100°C . more preferably from ambient temperature to 60°C , and still more preferably at ambient temperature is then needed to reach a moisture content suitable for semidry pressing. Any agglomerates of fly ash particles formed during the evaporation process are broken up by grinding and screening prior to semi-dry pressing. The aqueous H_3PO_4 solutions need not be of commercial grade purity for this process. Wet process, or green, fertilizer grade aqueous H_3PO_4 , which is made by the acidulation of phosphate rock with dilute solutions of strong mineral acids (H_2SO_4 , HNO_3 , HCl , etc.), may be used in the processes of this invention without expensive purification. The wet process acid has an initial concentration of about 40 percent H_3PO_4 which may be use as is or preferably may be raised to a preferred range of 65 to 85 percent H_3PO_4 by removing water in a conventional rubber lined evaporator. Organic materials and other impurities are left in aqueous H_3PO_4 solution. Thus expensive purification procedures such as urea phosphate crystallization, ion-exchange processes, and calcination of the phosphate rock prior to acidulation are avoided. For some class C coal fly ashes excess water may be needed to prevent a vigorous reaction between the fly ash and H_3PO_4 at room temperature. When small laboratory samples of Coal Creek fly ash and 85% H_3PO_4 were mixed, a vigorous reaction occurred at room temperature. Yet, where Coal Creek fly ash and 85% H_3PO_4 were mixed in brick sized samples, no reaction was noticed and the resulting bricks had good properties. If reactions between a particular fly ash and aqueous H_3PO_4 is a problem, the H_3PO_4 concentration of the solution can be reduced until the reaction does not occur. Preferably the H_3PO_4 concentration will be from about 40 to about 65 and more preferably from 50 to 60 weight percent when this is done. In one case, a 50% H_3PO_4 solution was used with Coal Creek

fly ash. No reaction occurred but the aqueous H_3PO_4 /fly ash mixture was waxy. The mixture became powdery with lumps after it had stood at ambient temperature for several days. Grinding and screening produced a uniform, powdery mixture suitable for semidry pressing. The mixture was semidry pressed into a green body which was fired to produce a good ceramic product.

The third process step is the firing of the green body until the H_3PO_4 has condensed and reacted with oxides in the fly ash and formed polymer-like phosphate bonds which bind the fly ash particles together to form a ceramic material. The minimum firing temperature for coal fly ash and municipal solid waste (MSW) fly ash is preferably about $250^{\circ}C$, more preferably $275^{\circ}C$, still more preferably $290^{\circ}C$, and even preferably $300^{\circ}C$. The maximum temperature for fly ash having a loss on ignition (LOI) of 15 weight percent or less (or preferably less than 11 weight percent) is preferably about $1100^{\circ}C$, more preferably $1000^{\circ}C$, still more preferably $900^{\circ}C$, and even more preferably $800^{\circ}C$. When fly ash having a LOI of greater than 15 weight percent is used, the maximum firing temperature is preferably about $400^{\circ}C$, more preferably $390^{\circ}C$, still more preferably $375^{\circ}C$, and even more preferably $350^{\circ}C$. The purpose is to avoid or minimize the loss of LOI material during this firing process. Significant loss of LOI material begins somewhat above $400^{\circ}C$. On this point, when a green body based on H_3PO_4 and Rivesville coal fly ash (28.30 weight percent LOI) was fired at $700^{\circ}C$, the resulting ceramic structure was too porous and weak to be useful. In contrast, when a green body based on H_3PO_4 and Pleasants coal fly ash (10.50 weight percent LOI) was fired at $700^{\circ}C$, the resulting ceramic structure was strong and useful. Further, firing a green body based on H_3PO_4 and Rivesville coal fly ash (28.30 weight percent LOI) at $300^{\circ}C$ produced a strong and useful ceramic structure. Whatever

the firing temperature, conventional precautions are taken to heat the green body from room temperature to the firing temperature at a rate that allows water and other volatile materials to escape without the build up of pressure that would damage the green bodies. For instance, in the examples the temperature was ramped up to the firing temperature at a rate of from about 1 to 5 3°C per minute. The firing times used are on the order of about 12 to 15 hours as compared to 20 to 30 hours for conventional clay bricks. The firing time can be varied and optimized for the particular fly ash used and weight of phosphoric acid used. During the firing step, chemical reactions of H_3PO_4 with SiO_2 , Al_2O_3 , and Fe_2O_3 (predominate components in fly ash) occur which produce strong polymer-like phosphate bonds between fly ash particles.

10 The figure illustrates the importance of the firing temperature in achieving good strength and water stability. The data was obtained from samples made from class C coal fly ash from Coal Creek Station, ND (CC) and from Class F coal fly ash from Hatfield Station Allegheny Power (HF). Chemical compositions for these fly ashes are given in table 1. The H_3PO_4 /Coal Creek fly ash mixture contained 20 weight percent H_3PO_4 compound and the H_3PO_4 /Hatfield fly 15 ash mixture contain 15 weight percent H_3PO_4 compound. The mixtures were pressed into green bars for the test. Sample green bars were fire in air at temperatures of 150°C, 300°C, and 700°C to produce ceramic bars. The as-fired strength of ceramic bars was determined. Other ceramic bars were then boiled in water for 1 hour and the strength of the bars after boiling was measured. Placing a bar in boiling water for 1 hour is deemed to be equivalent to exposing it to water at 20 ambient temperature for about a month. Referring now to the figure, the bars represent average flexural strength (MPa) values of several samples with lines added to show plus or minus one standard deviation for the samples. The Hatfield (HF), class F, coal fly ash samples fired at

150°C initially had good strength but then disintegrated upon being boil in water for 1 hour. The Coal Creek (CC), class C, coal fly ash samples fired at 150°C had very poor strength even before boiling in water. The Hatfield (HF) samples fired at 300°C had good strengths before and after boiling. Boiling resulted in only a slight decrease in strength. The Coal Creek (CC) samples fired at 300°C had good strengths which were actually increased by boiling in water. Both the Hatfield (HF) and Coal Creek (CC) samples fired at 700°C had excellent strengths which were increased by boiling in water. The poor results for samples fired at 150°C but good results for samples fired at 300°C can be explained by the reaction between H_3PO_4 and SiO_2 requiring a temperature of at least about 250°C. As shown by table 1, SiO_2 is the major constituent in the various fly ashes.

The basic process may be modified by replacing from more than zero to less than 50, more preferably from 10 to 40, and still more preferably from 20 to 30 weight percent of the ignition residual (after LOI) portion of the coal fly ash with ground coal bottom ash. The coal bottom ash is ground and screened to a particle size of less than 2000, more preferably less than 500, still more preferably less than 125, and even more preferably less than 37 microns. The process steps will be the same for the fly ash/ground bottom ash mixture as it would be for the fly ash alone except that the maximum firing temperature is preferably 800°C, more preferably 750°C, still more preferably 700°C for raw coal fly ash containing 15 weight percent or less of LOI material. When the fly ash/ground bottom ash mixture includes fly ash containing more than 15 weight percent LOI material, the maximum firing temperature is preferably about 400°C, more preferably 390°C, still more preferably 375°C, and even more preferably 350°C. The remaining

process steps and parameters are the same for coal fly ash/ground bottom ash mixtures as they would be for the coal fly ash alone.

The general nature of the invention having been set forth, the following examples are presented as additional specific illustrations thereof. It will be understood that the invention is not limited to these specific examples but is susceptible to various modifications that will be recognized by one of ordinary skill in the art.

The weight percentage of H_3PO_4 given in tables 2 through 3 are based on the weight 100% H_3PO_4 present as a percentage of the total weight of 100% H_3PO_4 plus the dry weight of the fly ash present. Thus, the weight of water present is excluded in the calculations. The H_3PO_4 is not added as pure 100% H_3PO_4 but rather a more dilute form such as 85% H_3PO_4 . For purposes of calculating the amounts needed, 100 grams of 85% H_3PO_4 is 85 grams of H_3PO_4 compound and 15 grams of water. The concentration of the H_3PO_4 is important because the lower the concentration the greater the volume need and the greater the amount of water added. The amount of water added determines the moisture content and this affects the processability of the mixture.

The chemical compositions of the fly ashes used in the examples are given in table 1.

Table 2 presents the results of using the basic process with fly ashes from 6 different plants which were mixed with 85% H_3PO_4 . The ingredients were added in amounts necessary to produce a mixture containing 80 weight percent of fly ash and 20 weight percent of H_3PO_4 compound (100%) based on dry fly ash and H_3PO_4 compound. Water was present from the 85% H_3PO_4 . Samples of the 6 mixtures were fired at 300°C, 500°C, and 700°C and the results are

summarized in Table 2. The flexural strengths (σ_f), open (o.) porosities (%), and bulk density (ρ) for the resulting phosphate bonded fly ash ceramic materials are given.

Table 3 presents the results of using the basic process with fly ashes from 5 different plants which were mixed with 85% H_3PO_4 . In this case, the ingredients were added in amounts
5 necessary to produce a mixture containing 85 weight percent of fly ash and 15 weight percent of H_3PO_4 compound based on the H_3PO_4 compound and the ignition residue portion of the fly ash. Again, the ignition residue is that portion of the fly ash that would remain after all driven off. The loss on ignition (LOI) material has been driven off. Samples of the 5 mixtures were fired at 300°C, 500°C, and 700°C and the results are summarized in table 3. The flexural strengths (σ_f),
10 open (o.) porosities (%), and bulk densities (ρ) for the resulting phosphate bonded fly ash ceramic materials are given.

TABLE 2
Physical Properties of Ceramic Materials Made From
80 wt% fly ash + 20% wt H_3PO_4

Fly Ash	700°C			500°C			300°C		
	σ_f (MPa)	o. porosity, %	ρ , g/cm ³	σ_f (MPa)	o. porosity, %	ρ , g/cm ³	σ_f (MPa)	o. porosity, %	ρ , g/cm ³
Coal Creek	22.0	21.4	2.03	18.4	17.2	2.06	15.5	15.9	2.09
Baldwin	31.0	21.1	1.95	22.0	19.1	1.95	27.3	18.0	1.96
Hatfield	24.6	23.1	1.97	21.7	18.6	2.04	21.2	17.0	2.07
Rivesville	5.4	50.5	1.15	-	-	-	-	-	-
Spurlock	24.4	24.8	1.72	17.7	26.4	1.69	21.1	19.3	1.86
Albright	26.4	23.6	1.77	21.4	24.3	1.71	26.7	22.2	1.81

Table 3

Physical Properties of Ceramic Materials Made From

85 Wt% Fly Ash + 15% H_3PO_4

Fly Ash	700°C			500°C			300°C		
	σ_r (MPa)	o. porosity, %	ρ , g/cm ³	σ_r (MPa)	o. porosity, %	ρ , g/cm ³	σ_r (MPa)	o. porosity %	ρ , g/cm ³
Coal Creek	12.9	21.0	2.07	10.1	21.1	2.03	6.3	18.7	
Baldwin	23.2	25.7	1.85	17.3	21.6	1.92	19.3	19.2	
Hatfield	25.8	25.4	1.94	20.2	19.5	2.05	16.9	18.8	
Spurlock	18.3	28.2	1.67	13.1	28.6	1.64	13.7	26.7	
Albright	22.7	27.5	1.71	17.5	26.2	1.72	16.6	25.1	

Obviously, other modifications and variations of the present invention may be possible in light of the foregoing teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described.

PHOSPHATE-BONDED FLY ASH

ABSTRACT OF THE DISCLOSURE

A ceramic material made from raw coal fly ash or raw municipal solid waste fly ash and
5 phosphoric acid (H_3PO_4) and a process for making it.

NCH # 75-27

Effect of 1 Hour Boil on Strength of Phosphate Bonded Fly Ash Ceramics

