POTENTIAL WASTE PAPER SLUDGE ASH AS CEMENT REPLACEMENT IN CHEMICAL ASPECTS

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ABSTRACT

Cement or some form of binding agent is an important element in all types of construction and in recent years the cement market has been dominated by one product, Ordinary Portland Cement (OPC). In many countries of the active construction works, OPC is an expensive and sometimes scarce commodity. Thus, Pozzolanas has been an important ingredient in the production of an alternative cementing material to ordinary Portland cement (OPC). Pozzolanas or cement replacement are materials containing reactive silica and/or alumina which on their own have little or no binding property but, when mixed with lime in the presence of water, will set and harden like a cement. The Greeks and the Romans were the first civilisations known to use pozzolanas in lime mortars. The Romans used not only crushed pottery, bricks and tiles which formed the first artificial pozzolanas but also, found that some volcanic soils or ashes were excellent for producing a hydraulic mortar. Nowadays, a wide variety of siliceous or aluminous materials are used for producing pozzolanas, the common materials being calcined clays, pulverised fly ash, volcanic ash and ash from agricultural residues such as rice husks. This paper presents a study of the potential of Waste Paper Sludge Ash (WPSA) as a partial or fully cements replacement in different percentages. WPSA is a waste material taken from Malaysian Newsprint Industries sludge incinerator. Various tests were carried out to evaluate the potential of WPSA as cement replacement and compared with other cementitious materials or waste material like Silica Fume, Ground Granulated Blastfurnace Slag (GGBS) and rice husk ash. The WPSA will be checked the component of chemical inside it by using chemical analysis like Inductively Coupled Plasma (ICP) and Loss of Ignition (LOI). All results lead to the conclusion that WPSA is highly recommended to be a partial or fully cement replacement in concrete.

INTRODUCTION

The dust collection systems or the waste paper factory removes the ash from the combustion gases before they are discharged into the atmosphere. These waste materials in ash condition are known as waste paper sludge ash (WPSA). Cement production is an activity that consumes large quantities of raw materials and energy and emits large amount of CO_2 which is thought to be a major contributor to the greenhouse effect and the global warming of the planet. A large percentage of energy is spent decomposing calcium carbonates ($CaCO_3$) to lime (CaO) and for each tonne of cement produced, approximately the same quantity of CO_2 is emitted. If the fly ash or WPSA is used as source of lime, a reduction in CO_2 emissions could be achieved, thus, contributing to minimizing global effect warming. Therefore, with its ability to enhance the performance of the concrete with the right mix portion and cheaply available, the application of waste paper sludge ash (WPSA) in concrete is an alternative for a cost reduction and avoids air pollution.

When compared to composition and properties of cement, the chemical composition of cement influences the characteristics of cement. In producing cement, the chemical composition of cement is controlled by the content of silica (SiO_2), lime (CaO), alumina (Al_2O_3) and iron oxide (Fe_2O_3). These oxides become characteristically clinker minerals, which during the addition of gypsum, will be ground to cement. Portland cement is made up of four main clinker compounds, Tricalcium silicate (allite, C_3S), Dicalcium silicate (belite, C_2S), Tricalcium aluminate (C_3A) and tetra-calcium aluminoferrite (C_4AF), where C stands for calcium oxide, S for silica, A for alumina and F for iron oxide. Besides that, small amounts of uncombined lime, magnesia, alkalis and minor amounts of other elements (titanium, magnesium and etc) are also present. There are 5 types of Portland cement standardized in the U.S : 1) ordinary (Type I); 2)modified (Type II), 3) high-early-strength (Type III); 4) low heat (Type IV); and 5) sulfate-resisting (Type V).

Cement replacement materials can be also known as:

- Cementing materials
- Pozzolanic materials

- Alternative Cementing material
- Cement substitutes
- Supplementary cementing materials
- Cementitious materials
- Natural pozzolans/ Artificial pozzolans

There are five major cement replacement materials :

1. Industrial waste ashes
    - Fly ash
    - Pulverised-fuel ash (pfa)
    - Bottom Ash
2. Slag
    - Ground granulated iron blast-furnace
    - Steel slag
    - Non-ferrous slag
3. Silica
    - Silica fume
    - Silica flour
    - Silica Dust
    - Amorphous silica
    - Microsilica
    - Condensed silica fume
4. Agricultural Ashes
    - Rice husk Ash
    - Palm oil fuel ash
    - Ashes from other plants
5. Miscelleneous
    - Sludge
    - By-product gypsum

POZZOLANIC MATERIAL

Pozzolana describes pozzolanas as siliceous and aluminous materials which possess little or no cementitious value in them but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compound possessing cementitious properties. The Greeks and the Romans were the first civilisations known to use pozzolanas in lime mortars. The Romans used not only crushed pottery, bricks and tiles that formed the first artificial pozzolanas but also found that some volcanic soils were excellent for producing a hydraulic mortar.

Pozzolans can be divided into two groups, natural and artificial. The natural pozzolans are for the most part of the materials of volcanic origin but include certain diatomaceous earths. The artificial pozzolans are mainly products obtained by the heat treatment of the natural materials such as clay and shells, certain siliceous rocks and fly ashes. It is also generally agreed that although the chemical content of a raw material will determine whether or not it is pozzolanic and will react when mixed with lime or OPC, the degree of reaction and subsequent strength of the hydrated mixture cannot be accurately deduced from just the chemical composition. In most cases no direct correlation can be found between chemical content and reactivity. Other characteristics of the pozzolana also affect its reactivity, such as fineness and crystalline structure (Mahlhotra 1996).

CHEMICAL PROPERTIES

The chemical composition of the fly ashes depends on the characteristics and composition of the material burned either in coal burned power stations or waste materials in municipal incinerator. From the Inductively Coupled Plasma (ICP) techniques, it is shown the main chemical component of the fly ashes is SiO_2, Al_2O_3, Fe_2O_3 and CaO are the major constituents. Other elements are MgO, Na_2O, K_2O, SO_3, MnO, TiO_2 and C.

Loss on ignition (LOI), the weight loss of the fly ashes burned at temperature $\leq 1000^0C$, is related to the presence of the carbonates, combined in residual clay minerals and combustion free carbon. Carbon is the most important component of LOI. The water required for the workability of mortar and concrete depend on carbon content of fly ashes. The higher the carbon content of a fly ash, the more water is needed to produce a paste of normal consistency.

Table 1 : Chemical Analysis Of Cement and Fly Ashes (% by weight) Zhang, Sun and Shang (2003)

	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
Normal Cement	21.17	5.19	4.97	64.52	1.08	-	-	2.30	1.19
High Calcium Fly Ash	45	11.03	13.87	12.65	1.20	1.33	4.25	5.71	0.25
Low Calcium Fly Ash	45.47	7.76	31.11	2.74	1.10	0.64	0.35	1.49	5.04

Loss on Ignition

This test determines the loss in weight of cement when heated to approximately 1,000°C. The loss in weight occurs due to the liberation of absorbed moisture and carbon dioxide. All cements exhibit a loss on ignition (due to their gypsum content) so it is the relative value of the loss and its variability which should be noted. Loss on ignition is the loss of weight due to release of volatiles on ignition. A sample is ignited in a furnace under controlled conditions and the weight loss measured. This applies to pozzolanas which have to be calcined for use. LOI is given as a weight percentage loss. The accuracy of this test is ±0.1%.

Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. The primary goal of ICP is to get elements to emit characteristic wavelength specific light which can then be measured. The technology for the ICP method was first employed in the early 1960's with the intention of improving upon crystal growing techniques. Since then, ICP has been refined and used in conjunction with other procedures for quantitative analysis. The following is a cursory look at the driving forces behind this analytical tool, its use in series with other analytical tools, and environmental applications of ICP. The ICP analysis of the WPSA was carried out at Forest Research Institute Malaysia (FRIM) laboratory Kepong and SIRIM Berhad laboratory Shah Alam.

HYDRATION REACTIONS AND POZZOLANIC ACTIVITY

Portland cements are hydraulic cements composed of hydraulic calcium silicates. Hydraulic cements set and hardened by reacting chemically with water. This process is called hydration whereby the cement combines and reacts with water to form a hydrated cement paste. The products of cement are chemically the same as individual compound under similar condition. When the paste is added to aggregates, it acts as an adhesive and binds the aggregate together to form and in the presence of moisture, will chemically reacts with calcium hydroxide at ordinary temperature to form compound processing cementitious properties.

Property	Compound
Setting behavior	C_3S, C_3A
Temperature rise during hydration	C_3S, C_3A
Strength development	C_3S, C_2S
Creep and Shrinkage	C_3S, C_2S, C_3A, C_4AF
Durability	C_3S, C_3A

The hydration and reaction mechanism of fly ashes and cement compound such as C_3S and C_3A are more complicated than fly ash reaction with lime.

EXAMPLES OF CEMENT REPLACEMENT MATERIAL

Ground Granulated Blastfurnace Slag (GGBS)

GGBS is a material highly durable concrete in combination with Portland cement at the beginning of the 20th century. GGBS has been used worldwide as constituent of concrete. A co-product of the iron making industry, GGBS is a blastfurnace slag, which has been dried and ground to fine powder. Iron ore, limestone and coke are fed into the blastfurnace where they reach a temperature of 1500^{o}C and the raw materials reduced to molten iron and blastfurnace slag. These are tapped off from the blastfurnace and separated for processing.

The reaction of GGBS with Portland cement and water is a complex process. It involves activation of the slag by alkalis and sulfates to form its own hydration products. Some of these combine with the Portland cement products to form further hydrates which have a 'pore-blocking' effect. The result is a hardened cement paste with more of the very small gel pores and fewer of the much larger capillary pores for the same pore volume. This type of pore size distribution gives GGBS concrete a less open hydrate structure and a lower permeability than similar grades of concrete containing Portland cement only. This low permeability greatly enhances the resistance of GGBS concrete to attack from sulfates and weak acids.

Silica Fume

It is a by-product obtained during the manufacture of metal alloys or silicon metal, such as ferrosilicon alloys. Silica fume is also known as silica flower or silica dust. One of the most beneficial uses for silica fume is in concrete. Because of its chemical and physical properties, it is a very reactive pozzolan. Concrete containing silica fume can have very high strength and can be very durable. Silica fume is available from suppliers of concrete admixtures and, when specified, is simply added during concrete production. Silica fume consists primarily of amorphous (non-crystalline) silicon dioxide (SiO_2). The individual particles are extremely small, approximately 1/100th the size of an average cement particle. Because of its fine particles, large surface area, and the high SiO_2 content, silica fume is a very reactive pozzolan when used in concrete (Khedr and Abou-Zeid 1994).

Palm Oil Fuel Ash (POFA)

It is a waste product obtained in the form of ash on burning of palm oil husk and palm kernel shells as fuel in the palm oil mill boiler. Various aspects of mortar and concrete from investigation, incorporating palm oil fuel ash suggest that, POFA is a good pozzolanic material and its durability performance is excellent (Hussin & Awal 1996).

RESULTS

Table 2 : Comparison of Chemical Composition of opc, wpfa, epfa, rha

Chemical Components		Chemical Composition (% w/w)				
Chemical constituents	Empirical Formula	OPC	WPSA	EPFA	RHA	MFA [3]
Calcium oxide (lime)	CaO	64.8	67.4	2.8	0.8	42.3
Silicon dioxide (silica)	SiO_2	20.6	20.4	65.4	94.7	5.3
Aluminium trioxide	Al_2O_3	5.8	8.85	21.3	0.7	2.8
Ferric trioxide	Fe_2O_3	3.5	na	4.2	0.3	0.9
Magnesium oxide	MgO	0.6	2.5	1.2	0.8	1.7
Sulphate	SO_3	2.4	0.41	0.2	-	5.4
Potassium oxide	K_2O	0.6	na	0.5	-	5.2

Sodium oxide	Na_2O	0.1	na	0.1	-	3.9
Insoluble residues	IR	0.8	na	na	na	-
Loss of ignition	LOI	1.3	3.51	4.1	0.7	22.6
Lime saturation factor	LSF	0.96	na	na	na	-
Free calcium oxide	F CaO	2.2	na	na	na	-

Notes:
OPC – Ordinary Portland Cement
WPSA – Waste Paper Sludge Ash
EPFA- Electrical Power Fly Ash
RHA – Rice Husk Ash
MFA – Municipal Fly ash
na : not applicable
-: Means traces or negligible amount detected

Typical Chemical Composition
Calcium Oxide 40%
Silica 35%
Alumina 13%
Magnesia 8%

Typical Physical Properties of GGBS
Colour Off white
Relative Gravity 2.9
Bulk Density 1200kg/m³

1. Portland Cement

Fress ordinary Portland cement is manufactured by Associated Pan Malaysia Cement (APMC) Sdn. Bhd., Rawang. The cement complies with the Malaysian Standard specifications for Portland cement (ordinary and rapid hardening) i.e. MS 522:1977. The chemical composition of Portland cement is given in the table above. Based on this table, the principal chemical constituents presented on these materials are lime (CaO), alumina (Al_2O_3), silica (SiO_2) and iron oxide (Fe_2O_3). The combined content of these four oxides present in the Portland cement is 91%.

2. Waste Paper Sludge Ash

Waste Paper Sludge Ash (WPSA) was obtained from Malaysia Newsprints Industries in Temerloh, Pahang and it was incinerator ash. Based on Table 1, generally the WPSA is almost within the average range of chemical in Portland Cement. The major compositions found in the samples are lime (CaO), silica (SiO_2) and alumina (Al_2O_3). Generally, the average of composition of Ca, Si and Al of the WPSA were about 67.4, 20.4 and 8.85% by weight, respectively, which were higher than those of Portland cement. The combined content of these three oxides present in the WPSA is 96.7% and it is higher than Portland cement, 91%. This high lime content may contribute to the cementitious potential of the ash.

3. Electrical Power Fly Ash

Electrical Power FA was also obtained from APMC, Rawang. The EPFA is a solid material precipitated in the burning of fuel in a local electrical power generation plant in Kapar Power Station. This FA was collected and processed by a local company and then supplied to cement mill for its own consumption. A certain percentage of EPFA is normally blended with Portland cement at the cement factory to produce a special blended pozzolanic cement namely Pulverised Fuel Ash Cement (Mascrete Cement). This special cement reported to be low heat hydration, improvement in workability, impermeability and sulphate attack, reduction of alkali silica reaction, increase in long term strength, improvement in durability and surface finish and reduction in bleeding and segregation.

4. Municipal Fly ash

Sampling and analysis of MFA from the Senoko Incineration Plant in Singapore were performed to access the variability in its physical and chemical. An electrostatic precipitator is used to filter and trap the dust and fly ash from the flue gas before the gas is allowed to escape to the atmosphere through the chimney. The ash is then stored in silo and transferred to the fly ash humidifier, to be humidified before being loaded to the ash truck for landfilling. Representative ash samples (without the humidifying treatment) were taken at this stage for analysis (Chia 2003).

5. Ground granulated blastfurnace slag (GGBS)

Ground granulated blastfurnace slag (GGBS) is a by-product from the blast-furnaces used to make iron. These operate at a temperature of about 1500 degrees centigrade and are fed with a carefully controlled mixture of iron-ore, coke and limestone. The iron ore is reduced to iron and the remaining materials form a slag that floats on top of the iron. This slag is periodically tapped off as a molten liquid and if it is to be used for the manufacture of GGBS it has to be rapidly quenched in large volumes of water. The quenching optimises the cementitious properties and produces granules similar to coarse sand. This 'granulated' slag is then dried and ground to a fine powder.

CONCLUSION

In general, past investigations showed that performance of high volume fly ash concrete either similar to or better than that for no-fly ash concrete with respect to compressive strength, flexural strength, modulus of elasticity, shrinkage, creep, etc. Therefore, additional research efforts are required to generate data on the strength and durability properties of concrete with the view to optimizing mixture proportion for such concrete. The fly ash is recycled material that, when used, has a positive effect to our environment and country. By requiring fly ash in concrete, architects and engineers express a commitment to promote sustainable growth and exercise responsible building practices. Using fly ash is an exceptional way to "Build Green", without comprising cost or quality in concrete production.

The results presented in this study suggest the potential pf WPFA as a cement replacement material. The use of WPFA as a cement replacement material may be technically and environmentally feasible. Further investigation is necessary to study the causes of varying WPFA in blended cement and the effects on the durability and quality of concrete. For further study, the resulting change in the microstructure, high accuracy chemical analysis and cement hydration in the concrete can be checked by X-ray Diffraction (XRD) spectrometer, Scanning Electron Microscopy (SEM), X-ray Fluorescence (XRF) and Energy Dispersive X-ray (EDX) spectroscopy.

There are some advantages of the other materials as cement replacement :

- reduction in water requirement
- reduction in bleeding problem
- improved workability
- increased flow properties
- obtaining reduced heat of hydration
- higher ultimate strength
- increased resistance to aggressive chemical attack
- enhanced durability
- save energy and minimize cost of construction
- environmental effect – minimum air pollution
- attaining required level of strength in concrete at ages more than 90 days.

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