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A REVIEW ON SUSTAINABLE USE OF INDUSTRIAL WASTE IN CEMENT INDUSTRY

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ABSTRACT
Environment and economic considerations demand greater utilization of the waste. Cement industry is a major contributor in the emission of CO_2 as well as in using up high levels of energy resources in the production of cement. On the other hand productions of large quantities of industrial wastes are resulting in environmental problems with its dumping. Industrial wastes contain some toxic elements and releases into the environment under natural weathering conditions. These toxic elements cause pollution of soils, surface waters and groundwater. The use of theses industrial waste as substitute of cement, control the emission of CO_2 and also control the environmental problems associated with its dumping. Industrial wastes, such as copper slag, blast furnace slag, granulated phosphorus slag and steelmaking slag are being used as supplementary cement replacement materials. These wastes exhibit not only good strength properties but also better corrosion resistance than normal Portland cement. The conversion of industrial waste in to cement required the grinding, which needs only approximately 10% of the energy required for the production of Portland cement. Thus industrial waste has great potential in cement industry. In this paper, the recent achievements in the development of high performance cementing materials using different industrial wastes are reviewed.

KEYWORDS: Cement industry, Industrial waste.

INTRODUCTION

In view of global warming, efforts are made to reduce the emission of carbon dioxide (CO_2) to the environment. Cement industry is a major contributor in the emission of CO_2 as well as in using up high levels of energy resources in the production of cement. The production of cement releases greenhouse gas emissions both directly and indirectly. The direct emissions of CO_2 are produced by a chemical process of *calcinations*, which occurs when limestone is heated, breaking down into calcium oxide and CO_2. This process accounts for 50% of all emissions of CO_2 from cement production (Rubenstein, 2012). Indirect emissions are produced by burning fossil fuels to heat the kiln. Kilns are usually heated up by coal, natural gas or oil and the combustion of these fuels produces additional CO_2 emissions, same as emitted during production of electricity. This represents around 40% of CO_2 emissions (Rubenstein, 2012). Finally, the electricity used to power additional plant machinery and the final transportation of cement represents another source of indirect emissions and account for 5-10% of the industry's emissions. Producing a ton of cement requires 4.7 million BTU of energy, equivalent to about 400 pounds of coal and generates nearly a ton of CO_2 (Rubenstein, 2012).. Cement industry accounts for around 5% of global CO_2 emissions (Worrell *et al*., 2001). Researchers from all over the world are focusing on the ways of utilizing industrial wastes, as supplementary cement replacement materials. On the other hand productions of large quantities of industrial wastes are resulting in environmental problems with its dumping. Industrial wastes contain some toxic elements and releases into the environment under natural weathering conditions. These toxic elements cause pollution of soils, surface waters and groundwater. So, the use of theses industrial waste as substitute of cement, control the emission of CO_2 and also control the environmental problems associated with its dumping. Industrial wastes, such as copper slag, blast furnace slag, granulated phosphorus slag and steelmaking slag are being used as supplementary cement replacement materials. The present paper reviews the use of different industrial waste as alternate of cement in concrete.

IRON BLAST FURNACE SLAG

Iron blast furnace slag is produced when iron ore is reduced by coke at about 1,350–1,550 °C in a blast furnace. The molten iron, main product of a blast furnace, is formed from the ore, while the other components form a liquid slag. When flowing to the bottom of the furnace, the liquid slag forms a layer above the molten iron due to the smaller density of slag. After being separated from the molten iron, the liquid slag is cooled down in the air or with water and is prepared for further use. Typically, about 220 to 370 kilograms of blast furnace slag are produced per metric ton of pig iron. In India, about 8 to 9 million tons of GGBFS is produced per year. Lower grade ore results in more slag-sometimes as much as 1.0 to 1.2 tons of slag per ton of pig iron (Kalyoncu, 1998).

The granulated slag is produced by quenching the liquid slag with large amount of water to produce sand-like granulates. Granulates normally contain more than 95 percent of glass. Normally, they are ground to fine powder, called ground granulated blast furnace slag (GGBFS).

GGBFS is used as cement replacement at levels from 20 to 80 percent, which is varied depending on the application. According to the Bureau of Indian Standards (BIS) 455, the slag content in the Portland slag cement can be up to 65 percent in mass. Table 1 present the levels of GGBFS suggested by Slag Cement Association for different applications and environmental conditions. Portland slag cement is obtained by mixing Portland cement clinker, gypsum and granulated slag, in suitable proportions and grinding the mixture to get a thorough and intimate mix between the constituents. It may also be manufactured by separately grinding Portland cement clinker, gypsum and granulated slag and then mixing them intimately. The resultant product is cement which has physical properties similar to those of ordinary Portland cement (Barnett *et al.*, 2006, Çakir and Akoz, 2008). In addition, it has low heat of hydration and is relatively better resistant to soils and water containing excessive amounts of sulphates of alkali metals, alumina and iron, as well as to acidic waters, and therefore, used for marine works (Yeau and Kim, 2005, Deja, 2003).

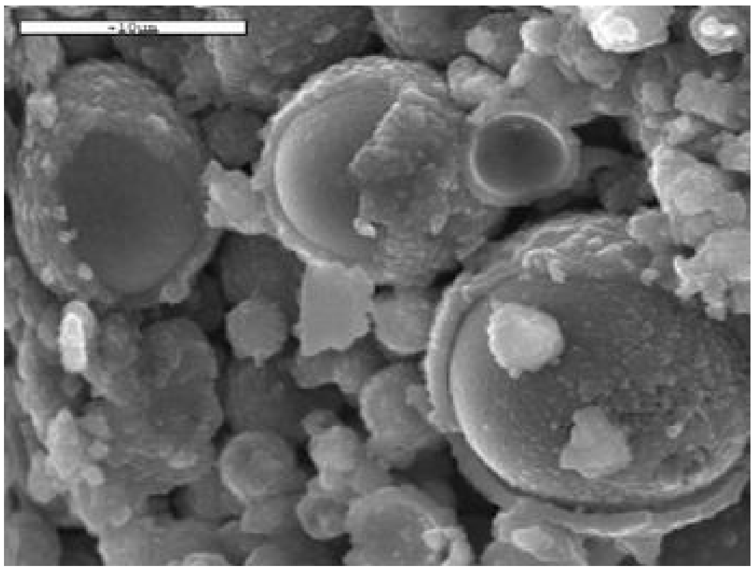
Table 1: Suggested slag cement replacement levels

Concrete application	**Percentage of** GGBFS
Concrete paving	25-50%
Exterior flatwork not	25-50%
Exposed to deicer salts	
Exterior flatwork exposed to deicer salts with w/c < 0.45	25-50%
Interior flatwork	25-50%
Basement floors	25-50%
Footings	30-65%
Walls & columns	25-50%
Tilt-up panels	25-50%
Pre-stressed concrete	20-50%
Pre-cast concrete	20-50%
Concrete blocks	20-50%
Concrete pavers	20-50%
High strength	25-50%
ASR mitigation	25-70%
Sulfate resistance	
Type II equivalence	25-50%
Type V equivalence	50-65%
Lower permeability	25-65%
Mass concrete	50-80%

FLY ASH/ALKALI-ACTIVATED FLY ASH

Fly ash (FA) is a by-product from burning ground coal in electric power generating plants. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (both amorphous and crystalline) and calcium oxide. Both of these are endemic ingredients in many coal-bearing rock strata. Fly ash particles are generally spherical in shape and range in size from 0.5 µm to 300 µm. Based on reactive calcium oxide content, fly ash is divided into two types: siliceous fly ash and calcareous fly ash. India is a resourceful country for fly ash and it is estimated that 130-145 million tons of fly ash is generated by 70 major thermal power plants of which only 6-10 % is utilized by cement, construction and road industries (Solanki *et al.,* 2013). In coming year (2016-17) it is expected that India will produce

300-400 million tons of fly ash per year which is approximately double the quantity it is produced now so the consumption should be increased subsequently (Haque, 2013). Availability of consistent quality fly ash across the country and awareness of positive effects of using fly ash in concrete are pre requisite for change of perception about fly ash from a waste material to a resource material. There are many performance reasons to use fly ash in concrete. First of all, the spherical shape of fly ash creates a *ball bearing* effect in the mix, improving workability without increasing water requirements (Jiang and Malhotra, 2000). The spherical shape of fly ash also improves the pump ability of concrete by decreasing the friction between the concrete and the pump line. Fly ash, as all pozzolanic materials do, generally increases concrete strength gain for much longer periods than mixes with Portland cement only (Siddique, 2003). The biggest reason to use fly ash in concrete is the increased life cycle expectancy and increase in durability associated with its use. During the hydration process, fly ash chemically reacts with the calcium hydroxide forming calcium silicate hydrate and calcium aluminate, which reduces the risk of leaching of calcium hydroxide and of concrete's permeability. The spherical shape of fly ash also improves the consolidation of concrete, which also reduces permeability. Fly ash in concrete provides better resistance to abrasion, chloride-ion penetration, salt scaling, freezing and thawing cycling than ordinary Portland cement (Naik *et al.*, 1998)



(a) Fly ash activated with 8-M NaOH solution

(b) Fly ash activated with NaOH + sodium silicate solution

Fig. 1. Fly ash activated with different solution

Alkaline activation is a chemical process in which fly ash is mixed with an alkaline activator to produce a paste capable of setting and hardening within a reasonably short period of time (Palomo *et al.*, 1999). The strength, shrinkage, acid and fire resistance of the resulting materials depend on the activation process variables. The alkaline activation of fly ash is consequently of great interest in the context of new and environmentally friendly binders with properties similar to or that improved on the characteristics of conventional materials (Fernandez-Jimenez and Palomo, 2003, Palomo *et al.*, 2004).

Concretes made with these materials can be designed to reach compressive strength values of over 40 MPa after short thermal curing times (Fernández-Jiménez *et al.*, 2006). Concrete made with alkali-activated fly ash (with no OPC) performs as well as traditional concrete and even better in some respects, exhibiting less shrinkage and a stronger bond between the matrix and the reinforcing steel (Sofi *et al.*, 2007). In addition to its excellent mechanical properties, the activated fly ash is particularly durable and highly resistant to aggressive acids, the aggregate-alkali reaction and fire (Fernandez-Jimenez *et al.*, 2008). This family of materials fixes toxic and hazardous substances very effectively (Phair and Van Deventer, 2001). Images of the microstructure of alkali-activated fly ash (AAFA) produced in media with different alkalinities (NaOH solution and NaOH + sodium silicate solution mix) are reproduced in Fig. 1.

COPPER SLAG

Copper slag is one of the materials that is considered as a waste material which could have a promising future in cement industry as partial substitute of cement (Shi *et al.*, 2008). It is a by-product obtained during the smelting and refining of copper. To produce every ton of copper, approximately 2.2-3 tons copper slag is generated and approximately 24.6 million tons of slag is generated from the world copper industry (Gorai *et al.*, 2003). In India three copper producers- Sterlite Copper, Birla Copper and Hindustan Copper produce approximately 6-6.5 million tons of copper slag annually at different sites (Narasimhan, 2011). Therefore, numerous contemporary researches have focused on the application of copper slag in cement production as a suitable path towards sustainable development.

Table 2: Physical and chemical properties of copper slag

Chemical component	Al-Jabri *et al.*, 2009	Khanzadi and Behnood, 2009	Brindha and Nagan, 2010
SiO_2	33.05%	27.80%	25.84%
Fe_2O_3	53.45%	52.50%	68.29%
Al_2O_3	2.79%	7.80%	.22%
CaO	6.06%	4.60%	.15%
MgO	1.56%	1.2%	.2%
Absorption	0.17%	0.4%	.5%
Specific gravity	3.4%	3.59%	3.68

Copper slag has a specific gravity varies from 3.4-3.7, which is higher than that for OPC (3.15) which may results in production of dense concrete. Copper slag usually has a good content of silicon dioxide (SiO_2), it exhibits pozzolanic properties. Due to its pozzolanic properties it reacts with the calcium hydroxide (CH), which is produced during cement hydration. Silicon dioxide combines with CH to produce additional cementing compound calcium-silicate-hydrate (C-S-H), which is responsible for holding concrete together. Table 2 present the different properties of copper slag.

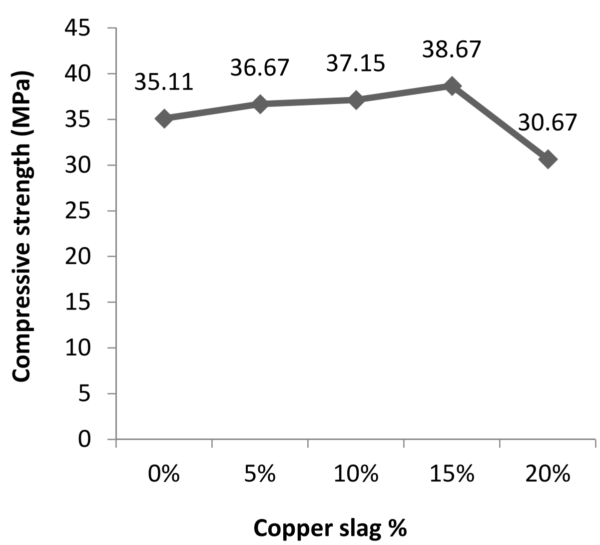


Fig. 2. 28 days compressive strength of concrete with different replacement level of copper slag

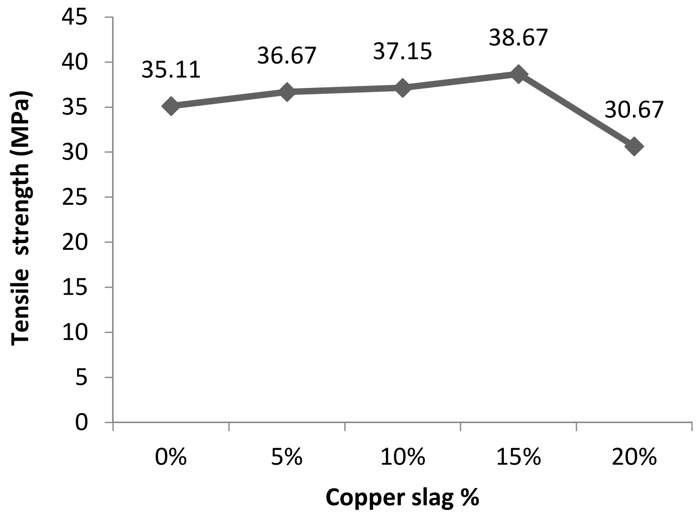


Fig. 3. 28 days tensile strength of concrete using with replacement level of copper slag

Many researchers have investigated the use of copper slag in the production of cement. Copper slag can be used as an iron adjustment material in cement clinker production (Guo, 2003). In another study, researchers used the tailings of copper slag to produce cement clinker. The performance of the cement using copper slag tailing was even better than that produced using traditional clay, limestone and mill scale (Liu, 2007). Various investigations have been conducted to determine the suitability of copper slag as a partial replacement of cement. The use of copper slag as mineral admixture in concrete seems feasible and shows better pozzolanic properties than fly ash (Yang *et al.,* 2010). Copper slag up to 15% cement replacement, increased the compressive and splitting tensile strength significantly (Tixier *et al.,* 1997, Toutanji *et al.,* 2004). The effect of different replacement of copper slag on the compressive and splitting tensile strength of concrete is shown in Fig. 2 and 3 respectively. The concrete samples with copper slag replacement exhibited better mechanical and durability properties as compare to normal concrete batches (Sanchez de Rojas *et al.,* 2008, Moura *et al.,* 2007).

GRANULATED PHOSPHORUS SLAG

Phosphorus slag is a by-product during the production of elemental phosphorus, and is composed mainly of SiO_2 and CaO. The air-cooled phosphorus slag does not exhibit cementitious properties and can be crushed for uses as ballast or aggregate. The glass content of granulated phosphorus slag may reach 98% due to the high viscosity of the molten slag. From the chemical composition (Table 3), it can be judged that granulated phosphorus slag is a latent cementitious material but less reactive than granulated blast furnace slag due to its lower Al_2O_3 content. If silica is partially replaced by aluminous materials during the production of phosphorus to increase the Al_2O_3 content in the slag, the reactivity of granulated phosphorus slag can match that of granulated blast furnace slag (Wu, 1984). Because granulated phosphorus slag contains a certain amount of P_2O_5 and is less reactive than granulated blast furnace slag, Portland granulated phosphorus slag cement usually shows longer times of setting and lower early strengths, but higher later strengths than Portland granulated blast furnace slag cement (Shi and Li, 1989). The replacement of gypsum with Na_2SO_4 can activate the potential activity of phosphorus slag and increase the early strength of Portland phosphorus slag cement very significantly (Shi *et al.,* 1991).

Table 3: A typical chemical composition of Phosphorus slag

Chemical component	% of chemical component
SiO_2	30-40%
Fe_2O_3	.5-3%
Al_2O_3	2.5-5%
CaO	35-45%
MgO	1-5%
P_2O_5	0-2.5%

CONCLUSION

This paper has reviewed the utilization of different industrial waste as cementitious materials in concrete. Blast furnace slag, copper slag, activated fly ash and Phosphorus slag shows similar mechanical properties to Portland cement and also provides better corrosion resistance. The production of Portland cement is energy-intensive process. These waste materials required just grinding and convert into Portland cement. The grinding of metallurgical slag needs only approximately 10% of the energy required for the production of Portland cement. These industrial wastes should be the prime topic for research in construction materials.

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