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Study on the Effect of Copper Slag Admixtures to Properties and Structure of Concrete

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Abstract: This study reports on an investigate the effect of using copper slag as a replacement of cement on the properties of concrete. The effects of using copper slag wastes on hydration, gelling properties, mechanical properties, pozzolanic activity and durability aspects of concrete are studied. It has been found that copper slag have micro pozzolanic effect in the study. The concrete batches with copper slag addition presented greater mechanical and durability performance. The mechanism of copper slag powder in composite cementitious materials is filling effect, activity effect and acceleration effect. The filling effect of copper slag can make matrix denser and the accelerating effect can accelerate the early hydration. The results pointed out that there is a potential for the use of copper slag as a supplementary cementing material to concrete production.

Key words: Concrete, copper slag, macroscopic properties, microscopic structure, hydration process

INTRODUCTION

The 1930s saw the beginning of using of admixtures in making of concrete largely. The admixtures are mainly fly ash. The using of fly ash not only saves the cement, but also effectively reduces the rise of the heat of hydration temperature of concrete. The mixing amount of fly ash is even to reach to 50-70% in RCC dam which emerges in 1970s. Fly ash is the most widely, the largest amount of concrete admixtures at present. It can not only ensure the performances of the strength of late period of concrete, but can offer a good solution to the problem of concrete temperature control in construction. So the fly ash plays a decisive role in concrete.

However, due to the rapid development of water conservancy, transportation, industry and civil engineering of domestic and foreign in recent decades, the shortage of fly ash is gradually come into being. Such problem has also emerged in China, especially in the southwest of it. Fly ash out of stock is also emerged frequently in other regions of China. The shortage of fly ash is evident in the water conservancy project of China in particular, because most of the hydropower project is basically in the remote areas and more large cubic metre of concrete is needed in hydropower project than other projects. The usage of concrete is usually millions of cubes and some even more than 10 million cubes. Fly ash is in great demand in this project. At the same time, the long-distance transport of fly ash will greatly enhance the unit cost of concrete. Therefore, it is imperative to find an easy access, high quality and cheap new admixture.

There are 1.5 million tons or more copper slag which is produced by China per year and more than 2500 tons have totalled at present (Liu and Zhu, 2008).The producing of one ton of copper can bring 2.2 tons of copper slag (Gorai *et al*., 2003). Yet the environmental pollution caused by by-products of the copper industry-water quenching copper slag (GCS) also affects the development of mine regions. How to use of copper slag effectively and cleanly and to promote China's green environmental protection construction is a major issue worthy of further study.

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF COPPER SLAG

The composition of a specific slag depends on the type of furnace, the metallurgical process producing it and the composition of the extracted ore. In general, the percentages of the main oxides of copper slag can be varied in the ranges as follows: Fe_2O_3: 35-60%, SiO_2: 25-40%, CaO: 2-10%, Al_2O_3: 3-15%, CuO: 0.3-2.1%, MgO: 0.7-3.5%. The chemical compositions of copper slag obtained from different regions are given in Table 1.

The physical properties of copper slag are given in Table 2. Asseen, the density of copper slag varies between 3.16 and 3.87 g cm^{-3}based on the amount of iron content. The average specific gravity of copper slag is about 3.5 g cm^{-3} that means copper slag is denser than ordinary natural aggregates. In general, water absorption of copper slag is very low. As stated previously, when liquid slag is cooled slowly, it forms a dense, hard crystalline product whereas quick solidification by pouring molten slag into water gives granulated

Table 1: Chemical composition of copper slag from different sources by mass (%)

No.	Fe_2O_3	SiO_2	CaO	MgO	Al_2O_3	SO_3	CuO	Country
1	44.78	40.97	5.24	1.16	3.78	1.06	-	Iran
2	44.80	24.7	10.9	1.7	15.6	0.28	2.1	USA
3	49.50	34.51	2.20	1.48	6.55	1.20	0.43	Canada
4	45.3	36.0	9.30	3.24	3.45	0.49	0.33	Australia
5	62	26	2.5	3.7	-	-	1.4	Brazil
6	52.0	35.5	2.11	1.06	5.90	0.14	0.88	Japan
7	60.00	30.07	0.6	0.75	3.97	0.32	0.79	Spain
8	53.72	34.3	7.91	0.94	3.83	3.02	-	Taiwan
9	36	31	4	-	6	-	0.33-0.80	Malaysia
10	41.53	37.13	-	-	-	0.11	0.79	Chile
11	39.65	31.94	3.95	2.82	2.4	-	1.01	Turkey

Table 2: Physical properties of copper slag

Appearance	Black, glassy, more esicular when granulated
Particle shape	Irregular
Density (g cm^{-3})	3.16-3.87
Water absorption (%)	0.15-0.55
Hardness (mohs)	6-7
Water soluble chloride (ppm)	<50
Soundness (%)	0.8-0.9
Aggregate crushing value (%)	10-21
Aggregate impact value (%)	8.2-16
Abrasion loss (%)	24.1
Conductivity (μs/cm)	500

amorphous slag. The granulated copper slag has a higher water absorption and less unit weight compared with air-cooled copper slag due to its more porous texture.

THE HYDRATION, GELLING PROPERTIES, POZZOLANIC ACTIVITY OF COPPER SLAG

Copper slag which consists primarily of complex copper and iron sulfides and traces of other metal sulfides, is a by-product generated during smelting to extract copper metal from the ore. The copper slag obtained may exhibit pozzolanic activity and may therefore be used in the manufacture of addition-containing cements. copper slag has the effect of micro volcanic ash; the workability of copper slag concrete is poor, but by mixing with appropriate amount of micro-aggregates its workability will be improved significantly. The largest particle size of copper-nickel blast furnace slag powder is greater than 50 μm (but its number is very less), some part of the particle size is of between 10-50 μm, the majority of particle size is less than 10 μm. If it is mixed super plasticizer with concrete, the particle size distribution can be optimized, the powder particles are fully dispersed and paste gap can be filled. Figure 1 is the ESEM photos of slurry mixed with fly ash and slurry mixed with copper slag before the initial setting. Copper-nickel blast furnace slag can react with $Ca(OH)_2$. The reaction can produce hydration product which is similar with cement hydration. The reaction of Copper-nickel blast furnace slag and $Ca(OH)_2$ is earlier and faster than the corresponding reaction of fly ash.

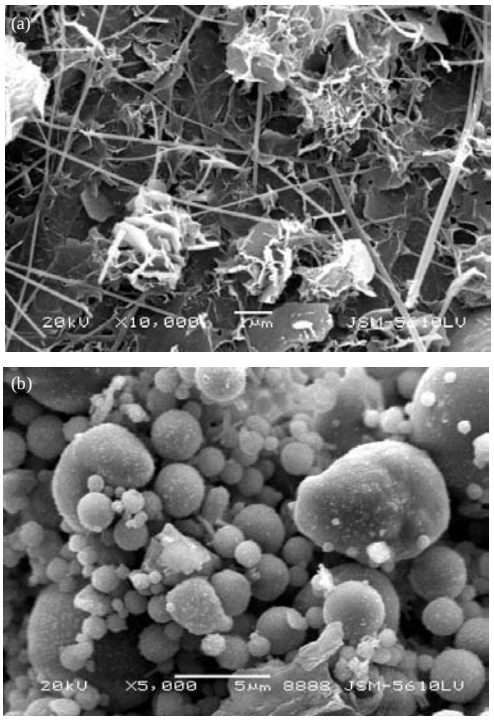

Fig. 1(a-b): ESEM photo of (a) Cement paste with copper slag and (b) Cement paste mixed with fly ash before the initial setting

Obviously, there is larger and more fly ash cement paste gap, but if the copper slag is doped, the gap and the large gap in particular, most of them can be filled and a dense network structure is formed. MIP (mercury penetration) and BSE (backscatter) test also confirmed that the copper slag has a good filling effect and can improve the pore structure of concrete.

Thus, the mechanism of copper slag powder in composite cementitious materials is filling effect, activity effect and acceleration effect. The filling effect of copper slag can make matrix denser than before; the acceleration effect can accelerate early hydration of cement (28d before).

USE OF COPPER SLAG IN CEMENT AND CONCRETE

The use of copper slag in the preparation of anti-ray heavy concrete was made by the Eighth Metallurgical Construction Research Institute of China in the late 1970s (The Eighth Metallurgical Construction Research Institute, 1977). Li Shu guang mixed copper slag with concrete instead of part of the construction sand (Li, 1988). Li Feng's research showed that: copper slag have the same physical and mechanical properties and durability with the ordinary concrete (Li, 1988). Du Hong yong and others have produced high-performance road portland cement by using of copper slag and the concrete with characteristics of a high flexural strength, the lower content of f-Cao, small drying shrinkage and good wear-resisting performance (Du *et al*., 2001). Huang Shao wen and other's experiments showed that copper slag as iron raw material to calcinations of cement clinker and to form mineral has a good adaptability and copper slag also has a certain degree of mineralization and copper slag with the raw material has a better burn ability (Huang and Yu, 2000). Tang Ming has prepared of ultra high strength, high wear resistance of cement mortar by winnowing ultrafine fly ash, copper slag aggregate and high-performance concrete admixture (Tong and Wang, 2000).

At present, the current situation of China's technology of physical treatment process to copper smelting slag is mainly performance in the following aspects:

- Used in cement manufacturing industry

It can replace iron power as mineralizer for iron correction agent in the production of Portland cement clinker to product copper slag cement. The cement is made by fine ground of mixing copper slag as main raw material with a small amount of activating agent (gypsum and cement clinker) and other materials. Compared with other varieties of cement, it has characteristics of a post-high-strength, low heat of hydration, little shrinkage, good frost resistance, resistance to corrosion and wear-resistant. It can in line with the standards of cement of GBL64-82275 about 275 and 325. The production process of it is simple and the investment can save 50%, more copper slag is used than other varieties of cement (slag accounted for the amount of cement about 60% to 70%) and energy consumption can be reduced by 50%.

Used in industrial and civil construction industry(Zong, 2003).

- Brick-making and a variety of block can use water quenching copper slag of smelting copper as aggregate. Copper slag and cement in accordance with a certain ratio can press the slag brick and insulation panels and other building materials. In such products, the added amount of copper slag as high as 90%. The product has a good advantage of light weight, insulation, impermeability
- Instead of sand used in the preparation of concrete and masonry mortar

Instead of sand, the using of steelmaking slag to the preparation of concrete and mortar, it has good mechanical properties, durability and its strength is better than ordinary concrete and mortar preparated by sand.

- Used as filling material in the mining industry

In the cementing fillings of mining, copper slag can either replace the yellow sand as aggregate or can be replaced Portland cement after fine grinding as the active material.

- Applied in the production of cast stone

The chemical composition of copper slag is similar to cast stone. If the copper slag content high iron, it can be isolated by magnetic separation of iron and then join the additional agent to the non-magnetic and cast stone can be made from it. In recent years many countries make cast stone products including sheets plate, tubes and other shapes of the products by using slag as raw material.

- Used in the construction as corrosion rust remover

Water quenching copper slag of smelting copper is made in the high temperature of 1250~1300. Its high hardness, low ash content after cooling make the performance of it better than the yellow sand which is often used as of the anti-corrosion rust. Just carrying out the drying and crushing and screening processing the corrosion rust remover is produced. It is a good anti-rust material which can be used in the ship's rail, bridges, petrochemical, water power and other sectors (Vaisdurd *et al*., 2002).

- Applied as the road sub grade and ballast

Based on the advantages of the physical and chemical properties of the copper slag, it is now widely used in roadbed construction and the copper slag must be doped with a certain amount of cementing material. This kind of sub grade has a strong mechanical strength, good

water stability, easy operation and construction, not frothing under rain erosion and plate body is strong. These make it apply to damp and rainy areas of the south in particular.

- Applied to the production of slag wool

The molten copper slag can be used to make flocculent slag wool by absorbing or centrifugal. It has advantages of thermal insulation, sound absorption, corrosion-resistant, non-combustible and low cost.

CONCLUSIONS

At present, the research on copper slag in concrete is mainly as substitutes in producing cement raw materials and fine aggregate in concrete, while few studies are on the material instead of cement as finely ground active admixture and the researches still remain on the macroscopic properties of workability and strength of hardened concrete in the fresh concrete (mortar). There are still few researches on mechanism of Copper slag as an admixture in concrete. There is not carried out the study of the mechanism of the hydration characteristics of the system of the microscopic structure and cementitious materials and the hydration process of copper slag in cementitious materials system. At the same time the in-depth study to long-term service performance of Copper slag to concrete is also not carry out and the theory and methods are not put forward to improve the structure and properties of copper slag concrete.

The studies have basically clarified the mechanism of copper slag in the composite cementitious materials in the hydration process, that is: the filling effect, activity effect and acceleration effect. But there are still many shortcomings in the studies. The shortcomings are mainly in the following:

- To build a new concrete of mix radio of design concept is needed. The existing test showed that: compare to ordinary concrete, water consumption of it to the impact of workability of copper slag concrete is extremely sensitive. The requirements of the amount of water to meet the workability are only allow small range of fluctuations. Copper slag has low water absorption, yet micro-aggregate has large water absorption. Different micro-aggregate preparation of the concrete is needed different water consumption and its strength can meet the design requirements. There is no doubt that it is necessary to establish a new concrete of mix design concept of how the mixing of micro-aggregates and proportioning of quantitative of it
- The further study is needed for the impact of copper slag on the hydration process of the composite cementitious materials. The hydration process of cement can be accelerated by copper slag, yet the quantitative analysis has not been made to the role of the effect of acceleration and the hydration kinetics model of copper complex binder is still not clear
- The influence of different degrees of fine copper slag to concrete performance is by the great difference. It is worthy of further study of what fineness of copper slag in order to achieve the optimal performance of the concrete in the end, while at the same time have a good economy contents
- The influence of copper slag to structures and long-term service performance of concrete. How the structure of the concrete is improved by copper slag? Does the improvement of this structure have any impact to long-term service performance of the concrete (such as carbonation resistance, resistance to sulfate attack, crack resistance, frost durability and the ability of resistance to long-term frozen, etc.,) What relationship is between microstructure and macroscopic properties? All of these have not yet carried out in-depth system study

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