

# **RESEARCH ARTICLE**

#### POTENTIAL USE OF COPPER SLAG IN MORTAR AND CONCRETE -A CRITICAL REVIEW

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## Manuscript Info

#### Abstract

*Manuscript History* Received: 15 August 2020 Final Accepted: 18 September 2020 Published: October 2020

*Key words:-*Sustainable Development, Copper Slag, Industrial By-Product, Mortar and Concrete The construction activities are increasing day by day. Due to this the natural sand is increasing its scarcity and its price in all parts of the country. Therefore reducing the consumption of natural sand in construction is a major issue while considering the both environment and economic view. The sustainable development for construction involves the use of nonconventional, innovative materials and recycling of industrial by products in order to compensate the lack of natural resources. Copper slag is one of the industrial by-product obtained during manufacture of copper. This paper reviews the characteristics of copper slag and its effects on the engineering properties of cement, mortar and concrete.

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#### **Introduction:-**

In India, there is great demand for aggregates mainly from civil engineering industry for road and concrete constructions [17].Concrete is one of the major construction material being used worldwide. Aggregate besides cement and water forms one of the main constituent materials of concrete since it occupies nearly 55%–80% of concrete volume [10]. Use of some waste materials has been well documented in design specifications. Large quantities of slag are produced as a byproduct of metallurgical operations, resulting in environmental concerns with regard to disposal [2].New by-products and waste materials are being generated by various industries. Therefore, uses of these waste materials have a great potential in improving the properties of fresh and hardened concrete. Industrial By-products such as pulverized fuel ash, silica fume and ground granulated blast furnace slag (GGBFS) are added in different proportions to concrete mixes as either a partial substitute to Portland cement or as admixtures. Concrete prepared with such materials showed improvement in workability and durability compared to normal concrete and has been used in the construction of power, chemical plants and under-water structures [9]. The utilization of slag from copper mining operations for applications such as Portland cement replacement in concrete and / or as a cement raw material has the dual benefit of eliminating cost of disposal, while lowering the cost of concrete [13]. Slag can also be used partially or fully as a replacement to fine and coarse aggregate [8].

### **Production of Copper Slag**

Copper slag is a by-product obtained during the matte smelting and refining of copper. Major constituents of a smelting charge are sulphides and oxides of iron and copper. The charge also contains oxides such as  $SiO_2$ ,  $Al_2O_3$ , CaO and MgO, which are either present in the original concentrate or added as flux. It is iron, copper, sulphur, oxygen and their oxides which largely control the chemistry and the physical constitution of the smelting system. A further important factor according to Gorai et al., is the oxidation/reduction potential of the gases which are used to heat and melt the charge [8]. As a result of this process, copper-rich matte (sulphides) and copper slag (oxides) are

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formed as two separate liquid phases. The addition of silica during smelting process forms strongly bonded silicate anions by combining with the oxides. This reaction produces copper slag phase, whereas sulphides form matte phase due to low tendency to form the anion complexes. Silica is added directly for the most complete isolation of copper in the matte which occurs at near saturation concentration with SiO<sub>2</sub>[6]. The slag structure is stabilized with the addition of lime and alumina. The molten slag is discharged from the furnace at 1000–1300°C. When liquid slag is cooled slowly, it forms a dense, hard crystalline product, while as quick solidification by pouring molten slag into water gives granulated amorphous slag [6].Fig.1 shows the General process diagram for copper slag production.



Fig. 1: General process diagram for copper slag production.

### **Chemical Composition of Copper Slag**

Chemical analyses of various origins of copperslags are shown in Table.1. Copper content is limited to 0.5 - 2%. Major constituents are iron, silica, alumina and calcium oxide. [8]

• •	<b>1</b>			
Origin	1	2	3	4
Fe,%	47.8	44.7-47.7	47.13	44
SiO <sub>2</sub> ,%	29.9	28.5-32	-	28
CaO,%	-	1.6-3.9	-	-
MgO,%	-	-	-	-
Al <sub>2</sub> O <sub>3</sub> ,%	-	-	-	-
S,%	-	0.3-0.9	1.47	-
Cu,%	0.7	0.5-0.95	0.68	0.6
Co,mg/kg	-	Tr-8	2200	1300
Mn,mg/kg	-	-	300	-
Ni,mg/kg	-	14-20	500	600
Zn,mg/kg	-	1700-2850	500	-
$(\mathbf{D}_{1}, \mathbf{f}_{1}, \dots, \mathbf{f}_{n})$				

**Table 1:-** Typical chemical compositions of the copper slag.

(Data from [8]).

### **Phisical Properties of Copper Slag**

Some physical and mechanical properties of copper slag are shown in Table 2. Aircooled copper slag has a black colour and glassy appearance. The specific gravity varies with iron content, from a low of 2.8 to as high as 3.8. The unit weight of copper slag is somewhat higher than that of conventional aggregate. The absorption capacity of the material is typically very low (0.13%). Granulated copper slag is more porous and therefore, has higher specific gravity and lowerabsorption capacity than air-cooled copper slag. The granulated copper slag is made up of regularly shaped, angular particles, mostly between 4.75 and 0.075 mm in size. The air-cooled and granulated copper slag has a number of favourable mechanical properties for aggregate use, including excellent soundness characteristics, good abrasion resistance, and good stability. It has high friction angle due to sharp angular shape. However, the slag tend to be vitreous or glassy, which adversely affects their frictional properties (skid resistance), a potential problem if used in pavement surfaces [8]. Fig. 2 shows some surface features of copper slag and natural sand.

Appearance	Black, glassy
Unit weight	2800-3800(kg/m <sup>3</sup> )
Water absorption %	0.13
Bulk density	2352 (kg/m <sup>3</sup> )
Conductivity	500µs/cm
Specific Gravity	2.8-3.8
Hardness	6-7 Moh
Moisture content	< 5%
Water soluble chloride	<50 ppm
Abrasion loss, %	24.1
Sodium sulphate soundness loss ,%	0.90
Angle of internal friction	40°-53°

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Fig. 2:- Copper slag and Natural sand passing through 4.75mm and retained on 2.36mm.

## Use of Copper Slag in Cement Clinker Production

As shown in Table.1, copper slag has a high Fe content and has been used as an iron adjustment material during the cement clinker production. Since the main composition of copper slag is vitreous FeSiO<sub>3</sub>, it has low melting point and could reduce the calcination temperature for cement clinker [6]. Copper slag wastes, even if treated via processes such as flotation for metal recovery, still contain heavy metals with hazardous properties posing environmental risks for disposal. This study reports the potential use of Flotation Waste of a Copper Slag (FWCS) as iron source in the production of Portland cement clinker. The FWCS appears a suitable raw material as iron source containing greater than 59% of Fe<sub>2</sub>O<sub>3</sub> mainly in the form of fayalite Fe<sub>2</sub>SiO<sub>4</sub> and magnetite Fe<sub>3</sub>O<sub>4</sub>. The clinker products obtained using the FWCS from the industrial scale trial operations over a 4-month period were characterised for the conformity of its chemical composition and the physico-mechanical performance of the resultant cement products was evaluated. The data collected for the clinker products produced using an iron ore, which is currently used as the cement raw material were also included for comparison. The results have shown that the chemical compositions of all the clinker products including those of FWCS are typical of a Portland cement clinker. These findings suggest that FWCS can be readily utilised as cement raw material due to its availability in

large quantities at low cost with the further significant benefits for waste management/environmental practices of the FWCS and the reduced production and processing costs for cement raw materials. Guo et al., reported that copper slag was successfully used as an iron adjustment material in cement clinker production. Liu et al., used the tailings from Mo ores and copper slag to produce cement clinker. Theperformance of the cement was even better than that produced using traditional clay, limestone and mill scale.

### Use of Copper Slag in Blended Cement

The most common type of slag produced in metallurgical operations is blast furnace slag. Long-term performance records in manufacturing blended cement, lightweight aggregates, and pozzolans for portland cement have demonstrated blast furnace iron and steel slag to be economical and durable [13]. The use of copper slag in blended cement production is conditioned by the selecting of the right proportions of Portland cement and slag in order to attain synergistic effects which give long-term improved durability properties to mortar and concrete produced with such blended cement [18]. The optimum ratio value of copper slag determined according to the theoretical method can be used as guidance in the production practice [12]. The use of copper slag as a pozzolanic material for ordinary Portland cement and its effects on the hydration reactions and properties of mortar and concrete have been reported in several applications (Al-Jabri et al., Tata et al., Malhotra, and Tixier et al.). Arino and Mobasher suggested that up to 15% of copper slag can be used as a cement replacement with constant w/c ratio of 0.4. This gives higher compressive strength than ordinary cement. The compression test results indicated that copper slag concrete was significantly stronger but more brittle than ordinary Portland cement concrete. Fracture test results confirmed that the increased brittleness of concrete was due to the use of copper slag in the mentioned study. Roper et al., reported that copper slag does not need to be completely glassy for significant hydration to occur. One potential concern for such materials is their heavy metal content and the leaching characteristics. Moura et al., investigated the compressive and flexural strength of concrete containing copper slag as 10% of the cement by mass. The results indicated that concrete with copper slag had lower compressive strength than concrete without copper slag admixture up to 91 days. The flexural strengths of concrete with and without copper slag were similar for water to cement ratio of 0.4–0.5.Zain et al., reported an optimum strength performance of the copper slag mortars containing 5-7.5% copper slag by cement weight [21]. Dai et al. was found that the replacement of 10-15% cement clinker does not have a significant effect on compressive strength, but significantly increases the abrasion resistance of the cement mortar [5].

## Use of Copper Slag in Cement Mortar and Concrete

Hwang et al., reported that the workability and strength of the concrete were enhanced by the addition of copper slag. However, as the content of copper slag exceeded.



Fig. 3:- Compressive strength of copper mortars as a function of replacement level. (Data from [6]).

80%, lower strength was obtained possibly due to the formation of ettringite[19].Shoya et al., reported that the amount and rate of bleeding are increased by using copper slag fine aggregate depending on the water to cement ratio, the volume fraction of slag and air content. They recommended using less than 40% of copper slag to control the amount of bleeding to less than 5  $1/m^2$  [3]. Shoya et al., also observed that because of the heavy specific weight and glass-like surface properties with irregular grain shape, the more the volume fraction of copper slag as a fine aggregate, the greater the bleeding[19].

Antonioet al., observed that the compression-test results using Ground Copper Slag (GCS) concrete was stronger but more brittle than ordinary portland cement concrete. As long as rapid strength gain is not a major design constraint, it was shown that use of GCS increased the strength significantly. Fracture test results confirmed the increased brittleness of concrete due to the use of GCS. An R-curve model was developed to characterize the effect of stable crack growth on the increased toughness demand of GCS concrete specimens. Long-term results showed equal or higher strengths for the GCS specimens without concern for degradation of other properties [2]. Khalifa S. Al-Jabri et al., observed that the surface water absorption of concrete was reduced with up to 40% copper slag replacement for sand. The volume of permeable voids decreased with the replacement of up to 50% copper slag. Copper slag, in the range of 40–50%, could potentially replace sand in concrete mixtures [9].

Hwang et al., also reported that the amount of bleeding of mortar made with copper slag comparatively is less than that using natural sand. However, the heavy specific weight and the glass-like smooth surface properties of irregular grain shape of copper slag aggregates are effective on characteristics of bleeding. The shrinkage of specimens containing copper slag fine aggregate is similar or even less than that of specimens without copper slag [3]. Tixier et al., reported that the use of copper slag up to 15% by weight of cement can be allowed replace the Portland cement together with up to 1.5% of hydrated lime as an activator for pozzolanic reactions. Results indicated a significant increase in the compressive strength for up to 90 days of hydration. Also, a decrease in capillary porosity and an increase in gel porosity were observed [9].

Shi et al., observed that when bleeding was excessive, harmful effects arose in the concrete by producing defects, such as the formation of water channel, water pocket beneath aggregates, the increase of water-cement ratio near the top of surface and finally the formation of a weak top layer[19]. Li et al., presented that the concrete containing copper slag exhibited similar mechanical properties and durability as that of concrete containing the conventional sand[19]. Ueno et al., suggested a grading distribution of fine aggregate based on particle density. The study investigated the maximum size of copper slag fine aggregate that does not significantly influence the amount of bleeding and the required plastic viscosity of paste to control the amount of bleeding by the variation of water-to-cement ratios [9].

Al-Jabri et al., observed that the workability of High Performance Concrete (HPC) using copper slag as a sand replacement with superplasticizer at a water-cement ratio of 0.35 improved rapidly with the increase of copper slag percentage and the 28 days quasi-static compressive strength was the largest at 50% copper slag substitution, after which the strength profile declined [11]. Khalifa S. Al-Jabri et al., also investigated that the use of copper slag as sand substitution improves High Strength Concrete (HSC) strength and durability characteristics at same workability while superplasticizer is very important ingredient in HSC in order to provide good workability and consistency for the concrete matrix and produce HSC that meets strength and durability design requirements [10].



Fig.4: Compressive strength of NaOH activated copper slag and Portland cement mortars. (Data from [6]) .

Wu et al., also investigated the mechanical properties of HSC incorporating copper slag as a fine aggregate.Results indicated that the strength of concrete, with less than 40% copper slag replacement, was higher than or equal to that of the control specimen.



Fig.5:- Strength of alkali – activated copper slag and Portland cement mortars(Data from [3]).

The microscopic view demonstrated that there were limited differences between the control concrete and the concrete with less than 40% copper slag content [9]. Mostafa Khanzadi et al., observed that, the incorporation of copper slag as coarse aggregate increases the mechanical properties of HSC may be due to the strength characteristics of copper slag and the stronger bonding between copper slag aggregate and the cement paste matrix [14].

Ishimaru et al., was concluded that up to 20% (in volume) of copper slag as fine aggregates substitution can be used in the production of concrete suitable for structures in order to control the bleeding in concrete mixtures when incorporating copper slag as fine aggregates [9].Wu et al., investigated the mechanical properties of copper slag reinforced concrete under dynamic compression. Results showed that the dynamic compressive strength of copper slag reinforced concrete generally improved with the increase in amounts of copper slag used as a sand replacement up to 20%, compared with the control concrete, beyond which the strength was reduced [20]. Alnuaimi observed that the reduction in strength resulting from increasing copper slag is due to increased voids due to the fact that copper slag possesses fewer fine particles than natural sand. It could also be due to the increase of the free water because the copper slag absorbs less water than the natural sand. It is recommended that the effect of copper slag change on total void volume and amount of free water content be studied separately [1].

Ayano et al., concluded that the presence of copper slag causes the delay in setting time although this did not have any influence on its durability [19]. Brindha et al. observed that copper slag concrete exhibits good durability characteristics, it can be used as an alternate to fine aggregate and also be utilized in cement as a raw material for making blended cements. From acid resistance test, it was observed that the concrete containing copper slag was found to be slightly low resistant to the  $H_2SO_4$  solution than the control concrete. Accelerated corrosion test reveals that the corrosion rate of copper slag admixed uncoated rebar is somewhat higher when compared to controlled specimens. But when the rebar is coated with zinc phosphate paint the corrosion rate had became zero [5].Goni et al., investigated that the unaggressivity of sulfate in the presence of chloride ion is due to the preferential diffusion process of Cl<sup>-</sup> and Na<sup>+</sup> ions versus sulfate ions. It seems that the high NaCl content in the pore solution activates the slag pozzolanic reactivity, leading to the formation of hydrated aluminates of layered structure which are subsequently transformed into Friedel's salt via OH-Cl ionic exchange inside the basal space. These processes decrease the porosity of the materials, thus increasing their flexural strengths [7]. Najimi et al., observed that the application of copper slag waste effectively reduced the deteriorative sulfate expansions as much as replacing of cement by 5%, 10% and 15% of copper slag led to 57.4%, 63.4% and 64.7% lower expansion than that of concrete without copper slag. The copper slag contained concretes showed better compressive strength performance in sulfate comparing with the control concrete specimens. Although the strength of copper slag contained concretes observed to be lower than control concerts in normal condition, they could develop their strength up to or even more than the control concrete mixture in sulfate attack condition. Microstructural studies detected the formation of deteriorative Ettringite in concrete without copper slag while those destructive crystals were not seen in copper slag contained concretes [16].

### **Conclusion:-**

This paper reviews the engineering characteristics of copper slag and its effects on the properties of cement and concrete. Favourable physico-mechanical and chemical characteristics of copper slag lead to its utilisation to prepare various value added products such as cement, as aggregate in mortar and concrete etc... These materials have been found to be possessing superior mechanical properties and they may be of cheaper varieties than the similar conventional materials. When copper slag is used as a raw material for clinker production, it can act as both iron adjusting and mineralizing component. Further, it also improves the grindability of the clinker. When it is used as a cement replacement or an aggregate replacement, the cement, mortar and concrete containing different forms of copper slag have good performance in comparison with ordinary Portland cement having normal and even higher strength. Alkali-activated copper slag exhibit not only higher early and later strength, but also better corrosion resistance than normal Portland cement. The production of Portland cement is an energy-intensive process, while the grinding of metallurgical slag needs only approximately 10% of the energy required for the production of Portland cement. Above studies will be more important due to the fact that the production of Portland cement is an energyintensive process which releases significant amount of pollutants such as CO<sub>2</sub>. Also, the production of cement has many environmental problems as well as some economic considerations. Furthermore, it can be concluded that the utilization of copper slag in cement and concrete provides additional environmental as well as technical benefits for all related industries, particularly in areas where a considerable amount of copper slag is produced. However, the economic considerations need further evaluations in different areas. The review of the results of other works which were presented in this paper encourages increasing the rate of reuse and recycling of properly prepared copper slag.

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