# Study on Influence of Copper Slag, Furnace Slag and Metakaolin In The Properties Of Concrete

Estudio sobre la influencia de la escoria de cobre, la escoria de horno y el metacaolín en las propiedades del hormigón

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Fecha de Recepción: 11/03/2022 Fecha de Aceptación: 25/01/2023 Fecha de Publicación: 30/12/2023 PAG: 461-472

#### Abstract:

The wastes from the industries can be reused, recycled and reduced by the effective consumption. Moreover, these materials are effectively used as construction materials; the production of sustainable environment is possible. The secondary materials are throwing away from every metal making industries and the wastes are discharged to land, water and air bodies. The waste disposal to land makes the soil unhealthy. The living and non-living things in water bodies are also spoiled. The effective exploitation of industrial wastes is done by using the waste materials in making of concrete. Budding graduates have to overcome very far these issues with alternate construction materials. As a trigger to them here, it is extended from the earlier study to investigate the properties of concrete subjected to acid attack, the behaviour on concrete in reinforced structural members and also the microstructure study usin X-Ray Diffractometer and Fourier Transform Infrared Spectroscopy.

Keywords: GGBS; Copper Slag; Metakaolin.

#### **Resumen:**

Los residuos de las industrias pueden ser reutilizados, reciclados y reducidos mediante un consumo eficiente. Más aún, si estos materiales se utilizan de manera efectiva en la construcción, es posible crear un entorno sostenible. Los materiales secundarios son desechados por todas las industrias metalúrgicas, y los residuos se descargan en tierra, agua y aire. La disposición de residuos en el suelo afecta la salud del suelo. Los seres vivos y no vivos en los cuerpos de agua también se ven afectados. La explotación efectiva de los residuos industriales se logra utilizando estos materiales en la fabricación del concreto. Este artículo extiende un estudio anterior para investigar las propiedades del concreto sometido a ataques ácidos, el comportamiento del concreto en elementos estructurales reforzados y también el estudio de la microestructura utilizando difractómetros de rayos X y espectroscopía infrarroja por transformada de Fourier.

Palabras clave: GGBS; Escoria de Cobre; metacaolín

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## 1. Introduction

The concrete is the main construction matrix to buildings. Cement manufacturing industry plays an important role for modern society and modern infrastructure. However the energy consuming by cement factory gives major drawback to environment. This leads to environmental pollution, global warming and climate change. On the other hand, the generation of heat during the production of GGBS and metakaolin is remarkably less than cement clinker production. This will lead to diminish the greenhouse gas emission and provide environmental sustainability. The industrial development consumes nature energy and natural resources. Partial replacement of industrial wastes for natural sand decreases the natural resource consumption as well as environmental protection. The depletion of natural river sand can be minimized by replacing sand with industrial wastes in order to protect the natural resource. (Khalifa at al., 2011); (Mithun and Narasimhan, 2015) reported that the higher density concrete is produced by the higher content of copper slag than control concrete. The low water absorption property of copper slag increases the water demand in concrete which enhances the workable property of concrete. (Khalifa et al. 2009) examined and result revealed that the workability of concrete is increased due to its low water absorption and glassy surface properties while increasing copper slag content and increases the excess water content due to its low water absorption property and increases workability which is suitable for low water cement ratio concrete. (Wei Wu et al. 2010) revealed that the slump value is increased while raising copper slag content. The first reason is low moisture absorption property of copper slag which enhances the workability of concrete. Another reason is shear resistance is lowered by copper slag due to its smooth glass surface texture which improves workability of concrete. (Ayano et al., 2000) gained information that the bets workability is achieved for the concrete containing copper owing to smooth glassy surface texture and low water absorption of copper slag. This is caused the lubricant between solid particles and reduce the inter particle frictional force. (Zain et al. 2004) leant that the requirement of water content with 10% copper slag replacement is lower than control mix due to its low moisture absorption property. The reason for increase in setting time is that the compounds of Cu, Pb, Zn in the copper slag are set inhibiting. (Rafat and Juvas, 2009) examined that the CH content is lowered up to 15% metakaolin replacement by the pozzolanic action. Beyond 15% metakaolin replacement, Ca(OH)2 content is increased owing to the hydration of OPC. The metakaolin insertion reduces slump values and increases setting time. For 10% metakaolin replacement, the setting time is same as OPC concrete and diminished for 20%. (Poon et al., 2001) noticed that the highest compressive strength is obtained for 10% metakaolin replacement. The porosity and pore diameter is lessened by the addition of metakaolin as a result of its filling action and pozzolanic action. (Jin and Li 2003) reported that the mechanical strength and modulus of elasticity of concrete is improved by the inclusion of metakaolin. (Bohac et al., 2014) found that the portland cement concrete has elevated heat flow than blast furnace slag and metakaolin blends. Form the isothermal calorimetry results; it is observed that the heat of hydration blast furnace slag and metakaolin blends is dropped owing to their dilution effect and pozzolanic activity. The combined effect of metakaolin and GGBS diminishes the total heat of hydration. (Dinakar et al. 2013) examined that the replacement of metakaolin increase when increasing superplasticizer. The high specific area of metakaolin makes the concrete more agglomerate increases the electrostatic force between the cement and particles. The addition of superplasticizer disperses the agglomerated particles and improves the workability of concrete. (Chiocchio and Paolini, 1985) found that the workability of concrete is increased by the addition of superplasticizer than concrete without Superplasticizer. (Crossin, 2015) found that the drying shrinkage is reduced in concrete containing GGBS from 15 to 25% owing to its more fineness. (Susanto et al., 2013) gained information about that the porosity of GGBS concrete is lowered 18% and 22% than control mix with 0.35 and 0.28 water cement ratio respectively. (Gulden and Recep, 2015) noticed that the following properties are enhanced in concrete incorporation with GGBS; durability, strength, performance, mechanical properties, workability, chemical resistance. (Hong et al., 2015) found that the packing density in lessened with increase in GGBS due to the small flocculation of GGBS particles than cement. Similarly the good permeable property is attained with incorporation of GGBS. (Ping et al., 2013) Likewise the carbonation depth and chloride ion penetration is diminished and durability properties are upgraded due to the addition of GGBS and metakaolin. (Erdogan et al., 2016) investigated that the workability of GGBS concrete is improved owing to its smoothness, cementitious property, dense, and low water absorption. Up to 30% replacement of GGBS, the better flow ability is improved due to its high specific surface area, roughly spherical particles. The highest level heat of hydration is attained for 60% GGBS replacement due to the acceleration of GGBS. The initial and final setting time is increased up to 60% GGBS replacement. GGBS has favourable properties when added in concrete in particular better workability and higher pumpability, less heat of hydration, strength improvement, permeability, high prevention to sulfate attack, chloride penetration sulfate attack and Alkali Silica Reaction. GGBS has low specific gravity and finer than cement. (San Nicolas et al., 2014) examined that the metakaolin concrete gives lower permeability, high strength concrete. Metakaolin decreases the chloride ion penetration. The overall water demand is reduced and workability is improved by metakaolin concrete. Metakaolin has larger surface area and its irregular or plate like shape than cement which raises the water demand in concrete. To solve this problem, Super plasticizers are

added and the merger activity of MK and SP produces better workable concrete than Normal concrete. Hence in this study, the above three materials copper slag, GGBS and metakaolin are simultaneously replaced in concrete mixture for sand and cement respectively.

# 2. Materials

The Ordinary Portland Cement 43 grade confirming to IS 8112-1989 was used in this study. The compressive strength of cement was 53.5 Mpa at 28 days. Metakaolin is the natural pozzolanic material which is produced as a result of activating ordinary clay and kaolinitic clay which having the temperature between 500°C and 800°C. The specific gravity of metakaolin was 2.6. The locally available natural river sand confirming to IS383-1978 is used. The confirmation grading zone was Zone II and the specific gravity was 2.58. The specific gravity of GGBS used was 2.87. The specific gravity of copper slag used was 3.33. The locally available 20 mm size coarse aggregate was used and it was confirming to IS383-1978 was used. The specific gravity of coarse aggregate was 2.71. The water is one of the ingredients of concrete and important one. Potable drinking water is used for mixing concrete and for curing the specimens. In the present study, Enfiiq Super Plast 400 is used as the high-range water-reducing admixture. The dosage of super plasticizer is constant at 0.75% of weight of cement.

# 3. Methodology

In this experimental work, seven concrete mixes of M30 grade concrete were prepared including control mix as per the guidelines given in IS 456-2000 and IS 10262-2009. (Table 1) shows the mix ratio of concrete mix.

Material	Mix Ratio
Cement	1
Sand	1.63
Coarse Aggregate	3.18
Water	0.38
Super Plasticizer	0.0075

Table 1. Coarse aggregate properties.

The concrete contains coarse aggregate, binder (OPC, GGBS and Metakaolin), Fine aggregate (river sand and copper slag), Super plasticizer (SP) and water. The metakaolin replacement at 5 and 10 % by the weight of cement and GGBS replacement at 5 and 10 % by the weight of cement were used. Copper slag partial replacement for sand at 20, 40, and 60% was used.

The acid resistance was determined as per ASTM C267 – 01: 1997. The specimen of 100 mm cubes were cast for acid attack test. After 28 days curing, the specimen was taken and cleaned and the weight (W2) was measured. The specimens taken from curing was kept in acid medium for 28 days. The acid medium was prepared by diluting 1% acid with water. The specimens were surface cleaned after taking from acid medium and the weight of the specimens (W1) was taken. The loss was calculated by ratio of change in weight or strength to the weight or strength before immersion. The beams of 150mm x 150mm x 1000mm casted and taken from 28 days curing were tested under 500 kN capacity loading frame. The flexural toughness test was performed under four-point loading on 900 mm span of a beam with simply supported at one end and roller support at the other end. The deflections were estimated by placing dial gauges at a mid-span and at the loading points. A hydraulic jack was used to apply the load and it was raised until the failure of beams. The First crack load and the

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failure load were observed. The specimens cured at 28 days are broken. Approximately 20 grams of hardened cement paste passing through 90 micron sieve is collected for studying microstructure. X-Ray Diffractometer (XRD) patterns were gotten with copper K-Alpha radiation at 30 mA, 40 kV for examining generation of CSH and CH, material composite recognition, degree of cement hydration and a step size of 0.02° was chose over a 2 theta range from 10° to 90°. Fourier Transform Infrared Spectroscopy (FTIR) spectra were obtained by FTIR spectrometer with a range of 4000cm-1 - 400cm-1 for analyzing the products of hydrated cement and the hydration mechanism.

### 4. Results and discussion

1. An approach on these ternary blended cement concrete was made and presented with workability, mechanical and durability aspects band SEM micrographs. As the investigation (Sakthieswaran and Shiny, 2019) published earlier showed that the addition of GGBS and copper slag also considerably improved the workability of the concrete. On contrary, the inclusion of MK diminished the workability and this effect was overcome by the addition of SP. The optimum percentage of replacement of the fine aggregate by copper slag is 40% and 10% by GGBS and MK each to meet the compressive strength requirement of concrete. Hence it can be conducted that the merger action with optimum replacement of copper slag, GGBS and MK significantly enhances the compressive strength of concrete. The flexural strength of the concrete containing copper slag, metakaolin and GGBS was also improved than the normal concrete. The split tensile strength was also improved due to the substitution of fine aggregate by 20% copper slag and cement by 10% metakaolin and 10% GGBS. The presence of excess amount of free water and the glassy structure of the copper slag can be considered as the main reason for the strength decrease beyond the addition of 20%. Enhancement of impact strength was owing to the high compressibility of the copper slag which consumes the impact energy acting on the concrete. Furthermore increment of impact strength due to pozzolanic effect of the pozzolanic materials (GGBS and metakaolin). The inclusion of metakaolin and GGBS enhanced the shear strength of the concrete which eventually raises the bond strength of concrete owing to their filling effect. Though copper slag does not absorb water the improved water absorption was due to the creation of free channels for easier movement of water due to the substitution of fine aggregate by copper slag beyond 40%. Regarding GGBS and MK, the pozzolanic action of GGBS and MK generates less permeable concrete. The porosity of the concrete was also increased due to the addition of copper slag beyond 40%. The metakaolin and GGBS proved to be efficient in filling the pores of the concrete. The surface water absorption of the concrete was reduced mainly due to the filling behaviour exhibited by metakaolin and GGBS. The SEM studies conducted on the concrete mixes containing copper slag and GGBS and metakaolin showed improved pore structure of the concrete. The addition of metakaolin and GGBS reduced the pore size of the concrete which subsequently led to increase in the durability and strength performance of the concrete on account of its pore blocking effect. In addition to the previous approach, it is presented here the effect of ternary blended cement concrete under acidic environment, the structural member behaviour and the microstructure study extended with XRD and FTIR analysis.

#### 4.1 Acid attack

#### 4.1.1 Hydrochloric acid

The change of mass of the concrete specimens after exposure to acid is the mainly used method for the assessment of the deterioration of the concrete subjected to acid attack. The measurement of the strength of the specimens after exposure to the acids is the measure of the resistance of the concrete to the acid attack. The loss in mass of the sample of the concrete specimen with and without metakaolin and GGBS replacements for cement and copper slag replacement for fine aggregate after exposure to hydrochloric acid and the corresponding loss in strength of the concrete specimens are shown in (Figure 1). It can be seen that the concrete containing 10% metakaolin, 10% GGBS and 60% copper slag replacement showed a progressive loss in weight of the specimen after exposure to hydrochloric acid. This loss in the compressive strength was about 27% higher than the normal concrete. Generally the mass change is a result of the dissolution caused by the hydrogen ions present in the acid. This dissolution causes mass loss and may finally result in excessive expansion and cracking of the concrete specimen. The weight loss of the specimen after exposure to hydrochloric acid increased with increasing percentage of copper slag. The higher loss in weight of the concrete specimen due to copper slag addition may be attributed to the higher porosity of the specimens caused due to the addition of copper slag. This is attributed to dissolute the hydrogen ions freely through concrete which leads to more weight loss. It can be seen that the loss in compressive strength increased linearly throughout all the mixes.

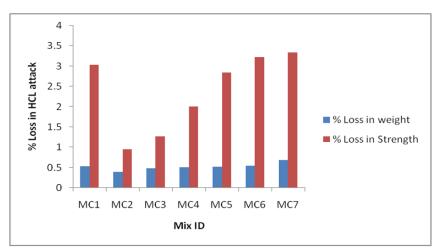


Figure 1. Percentage Loss In Weight And Strength Of Concrete Mixes Due To Hcl Attack

The lowest loss in the strength was observed for the mix MC2 which is about 69% lower than the strength loss of the normal concrete MC1. Thus the effect of metakaolin and GGBS with copper slag on the improved resistance to acid attack can be inferred owing to their filling and pozzolanic effect. The loss in the strength of the specimen became pronounced with increasing percentage of copper slag addition. However the addition of copper slag up to 40% proved to be efficient in improving the strength of the concrete against acid attack. Thus it can be clearly shown that the optimum replacement of fine aggregate by copper slag is 40% when the concrete specimens are exposed to aggressive acids is taken into account. The mass loss of concrete specimens which contained equal percentage of copper slag replacement were almost equal indicated that the loss in the weight in the concrete specimen after exposed to acids was mainly dependent in the copper slag addition. The increase in the strength of the concrete mixes due to the acid attack was observed for the mixes MC2, MC, MC4 and MC5 than the normal concrete mix MC1. This shows that the replacement of the fine aggregate by copper slag up to 40% and Portland cement by GGBS and metakaolin proves to be efficient in improving the compressive strength of the concrete against hydrochloric acid attack.

#### 4.1.2. Sulphuric Acid Attack

Generally sulphuric acid is more aggressive than hydrochloric acid and hence the loss in weight of the concrete specimens is much higher than the concrete specimens after exposure to the hydrochloric acid. However the concrete specimens containing higher percentage levels of copper slag suffered lesser loss in weight of the specimens after exposure to acids. The loss in weight of the specimens containing the GGBS and metakaolin were found to reduce the mass loss of the concrete after exposure to acids owing to their pozzolanic and filling capacity. The loss in the weight and strength of the concrete specimens followed the same trend as of the HCl attack but the loss in strength of the concrete mixes after exposure to sulphuric acid was higher than the HCl attack due to the ingress of the sulphate ions from the sulphuric acid. However the loss in weight of the specimen due to sulphuric acid attack was almost lower than the hydrochloric acid at higher percentage levels of replacement of fine aggregate by copper slag. The strength loss of the concrete specimens after exposure to sulphuric acid was found to increase at a greater rate than the strength loss due to hydrochloric acid. The mix containing MC7 10% metakaolin, 10% GGBS combined with 60% copper slag replacement was found to exhibit higher loss in the strength which is about 15% higher than the normal concrete mix MC1. This further confirms the negative influence of the higher percentage of copper slag replacement in reducing the strength of the concrete after exposure to sulphuric acid. The increased porosity of the concrete allowed the easier ingress of the hydroxyl ions at a greater penetration depth throughout the concrete specimens. Hence the diffusion of the acids through these pores caused serious degradation of the concrete due to acid which led to the corresponding loss in weight and strength of the concrete mixes. (Figure 2) shows the percentage loss in weight and strength of concrete mixes subjected to sulphuric attack.

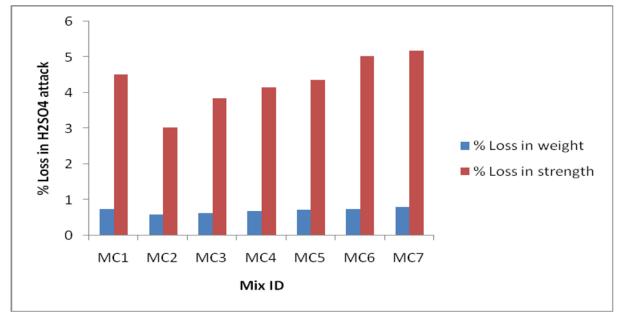


Figure 2. Percentage Loss In Weight And Strength Of Concrete Mixes Due To H2SO4 Attack

#### 4.2 Flexural Behaviour of RCC beam

The flexural performance of concrete is determined from the flexural toughness of concrete. Generally, the flexural toughness in the concrete is attained by measuring the area under the load deflection graph up to a certain deflection. The flexural toughness of the concrete as measured from the load deflection graphs obtained from the bending tests is shown in (Figure 4). The flexural toughness of the concrete was higher for the concrete mix MC4 containing 5% metakaolin, 5% GGBS and 40% copper slag replacement. This enhanced flexural toughness of concrete is the reason for the ductility of concrete. The toughness increase in the concrete mix MC2 which contained 5% metakaolin and GGBS each and 20% copper slag replacement was about 32 % than the normal concrete. The difference in the flexural toughness of the concrete mixes MC2 and MC3 and between MC 4 and MC5 the mix was measured to be 15%. This shows that at equal copper slag content but at increasing metakaolin and GGBS replacements the toughness of the concrete is decreased. The flexural toughness of concrete consisting minimum percentage (5%) of GGBS and MK is raised on account of their pozzolanic action. Beyond 5% of MK (that is 10%) the flexural toughness diminishes owing to the agglomeration of metakaolin that made discontinuity in the concrete paste. Furthermore the angular surface texture of the GGBS and copper slag that raises the cohesion of the concrete only up to a certain extent beyond which it adversely affects the flexural toughness of the concrete by transforming the concrete to a brittle material. The toughness increase of the concrete mix MC4 was about 48% compared to control concrete MC1. The flexural toughness of the concrete mixes rose linearly for all mixes consisting copper slag up to 40%. The concrete mix MC5 and MC6 suffered a loss in the flexural toughness of the concrete due to the higher percentage replacements of copper slag as fine aggregate. Though copper slag is highly compressible and shows improved strength performance the addition of copper slag above 40% is detrimental to the toughness of the concrete. The reduced toughness of the concrete mixes MC6 and MC7 may be attributed to the poor bonding between the copper slag particles and the cement matrix. The load deflection graph of the concrete beams when subjected to bending tests is shown in (Figure 3).

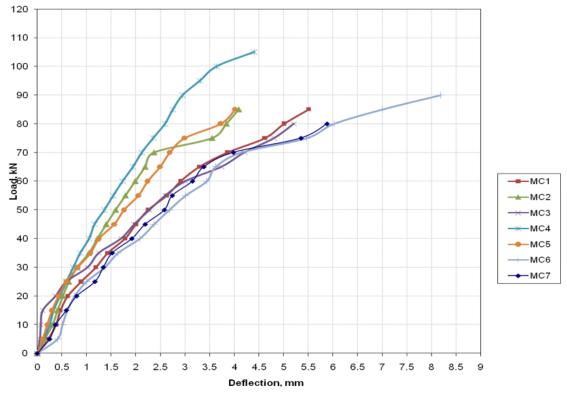


Figure 3. Load Deflection Graph of Concrete Mixes

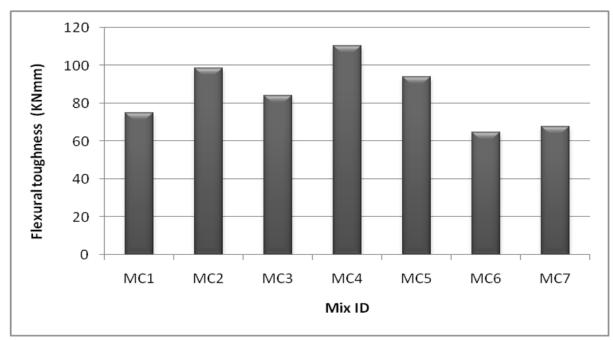


Figure 4. Flexural Toughness of Concrete Mixes

#### 4.3 XRD Analysis

The X-ray diffraction patterns of the concrete mixes are shown from (Figure 5). The main hydration products of

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concrete is Calcium hydroxide (Ca (OH)2) and CSH gel. The intensity of the peaks formed due to these reaction products is a measure of the performance of concrete. The peaks corresponding to the reaction products are indicated in the figures. The formation of the CSH gel was observed to increase with increase in the percentage replacement of the cement by using metakaolin and GGBS. The intensity of the CSH gel formed was also strong in the concrete mixes containing metakaolin and GGBS. Thus it further supports the results stated above that the formation of the higher intensity CSH gels improves the pore structure of the concrete owing to their filling and pozzolanic activity.

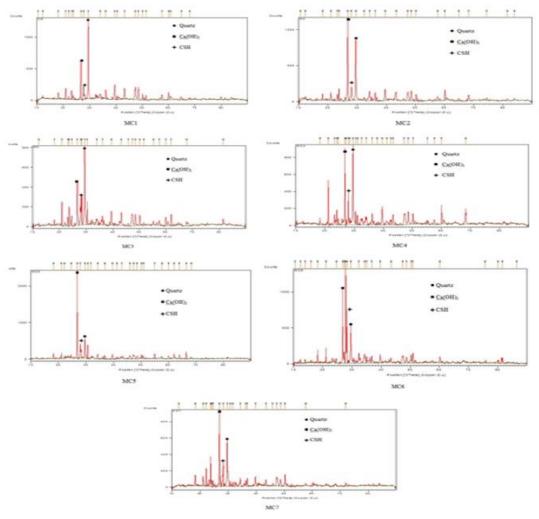


Figure 5. XRD patterns of Concrete Mixes

#### 4.4. FTIR Analysis

The FTIR spectra of concrete mixes having copper slag, GGBS, metakaolin and control mix are shown from (Figure 6). The broad highest point gotten around 3400 cm-1 refers to the –OH bond exist in the water molecule. Thus this peak appears due to the presence of physically absorbed water molecule by the constituents of the concrete. This –OH stretching bond of the hydroxyl group was present throughout the concrete mixes which indicates that the hydration has taken place in the concrete. The double degenerate planar bending band was observed at the wavelength around 1423 cm-1 which corresponds to the presence of calcium hydroxide in the concrete. The presence of quartz was confirmed by the absorption peaks occurring around 780cm-1 and 800cm-1.

The sharpening of the band appears around 1423 cm-1 which corresponds to the carbonate groups is due to the hybridized product formation of the concrete mixes after replaced with metakaolin and GGBS. The asymmetrical stretching vibration occurs at the absorption peaks around 1090 cm-1 which corresponds to the Si-O-Al stretching vibration. The presence of band around 1000 cm-1 and 780 cm-1 corresponds the crystalline phases of quartz present in the concrete. The

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prominent binder in the concrete is CSH gel which is identified from the corresponding peaks obtained around 1015 cm-1. It can be clearly observed that the variation occurs around 1015 cm-1 in all the FTIR spectra of concrete. This confirms the interaction of the GGBS and metakaolin in modifying the structure of the CSH gel formed. The absorption band around 1645 cm-1 also corresponds to the chemically bound water molecules to the concrete. It can be clearly seen that this band was varied for each concrete mixes depending on their composition.

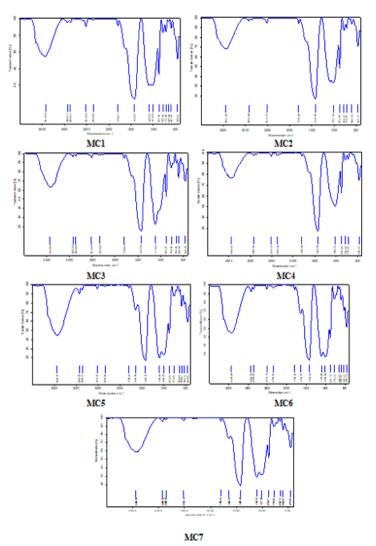


Figure 6. FTIR spectrum of concrete mixes

#### 4.5. Regression Analysis

There is necessary to get knowledge about the connection between the various strength parameters of the concrete in order to produce the concretes with high conformity and quality. The regression analysis is the most commonly used statistical tool to establish the relationship between the different variables and also to propose a model that well fits the relationship between the variables. The regression analysis can also be used for easier and accurate prediction of strength of the concrete by determining the various factors on which the strength depends upon. The compliance of the concrete produced with any admixtures or replacement with the specifications and standards is very essential for the conformity of good concrete. Since the strengthening of the concrete is a complex phenomenon which depends on a number of variables the regression analysis thus holds whether the obtained results match the specification by establishing the regression coefficient R2. When the obtained R2 value is higher, it means that the obtained variables in the concrete yielded reasonable results. From the results, it is noted that the data of experimental results gotten from the regression analysis carried out and the excellent model perfectly matches the various parameters of concrete. And the relationship between the different parameters is shown from (Figure 7), (Figure 8) and (Figure 9). The Regression coefficient value (R2) gotten were nearly greater and it ENGLIGH VERSION ...

is shown that the strength variables of concrete are inter-connected to each other and proceeds a linear behaviour.

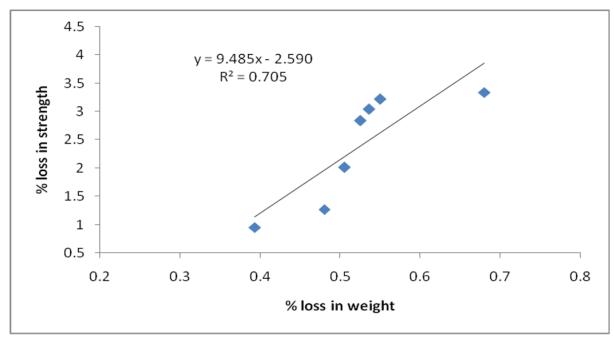


Figure 7. Relationship between % Loss in Strength And % Loss in Weight of Concrete Due To HCl Attack

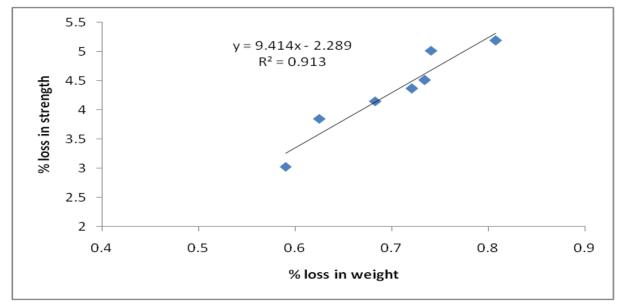


Figure 8. Relationship between % Loss in Strength And % Loss in Weight of Concrete Due To H2SO4 Attack



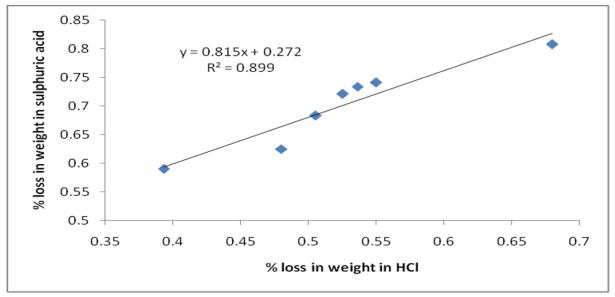


Figure 9. Relationship Between % Loss In Weight Of Concrete Due To HCl And H2SO4 Attack

# 5. Conclusions

This work also encourages the undergraduate and postgraduate professional students to study and find scoping ideas of utilising alternate materials in the construction industry. It is concluded here from the experimental research investigated on concrete by replacing sand with copper slag and by replacing cement with metakaolin and GGBS at various percentages. Hereby, it is concluded that the flexural toughness of concrete was raised when including the copper slag up to 40% and the cement was replaced by each 5% of metakaolin and GGBS. The higher addition of metakaolin creates the compounding effect on the cement matrix which makes the concrete brittle. The flexural toughness was raised by GGBS and MK which possesses the pozzolanic activity. The resistance of the concrete after subjected to aggressive acids such as HCL and H2SO4 was much improved when the copper slag was maintained at 20%. The increasing percentage addition of copper slag makes the concrete easily prone to the attack of acids. And the pozzolanic effect of GGBS and MK prevents the acid remarkably at 5% each. The FTIR and XRD analysis done on the concrete mixes showed the improved formation of hydration products than the normal concrete. The CSH gel formation of the concrete was improvised in the concrete containing GGBS and metakaolin and the amount of the formation of hydration products was also higher due to their pozzolanic effect. The regression analysis performed on the strength parameters of the concrete yielded models that exactly fit the experimental data. The proposed model also showed the inter dependency of the various strength parameters of the concrete with a clear understanding of the content of the effect of substitution of copper slag as fine aggregate and metakaolin and GGBS as cement substitutes. The final conclusion can be withdrawn that copper slag is the best substitute for fine aggregate and the metakaolin and GGBS substitution for cement proves to be better solution to manufacture concrete with remarkable enhancement in strength, durabile and micro structure properties. It is also suggested that the perfect replacement level of copper slag for sand and GGBS and Metakaolin for cement should be optimized by proper consideration from the experimental results which shows higher performance in concrete characteristics.

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