Resistance to Sulphate and Acid Attack of Rice Husk Ash and Fly Ash Based Composite Cement

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Abstract

The current exploration work contains the preparation and examination of the properties of cement-based composite materials. Two kinds of composite materials specifically, Rice Husk Ash Composite Cement and Fly Ash Composite Cement were examined. Rice Husk Ash Composite Cement and Fly Ash Composite Cement was treated with Na_2SO_4 and HCl solution to check the resistance towards sulphate and acid attack respectively. Sulfate attack has been resolved in this work by estimating weight loss/gain of Ordinary Portland Cement (OPC) and the Composite Cements created from FA and RHA when plunged into 0.5 M and 0.75 M Na_2SO_4 solution. A loss in weight has been seen at the underlying stage i.e. Following 7 and 14 days when OPC is immersed in sulfate media, however, in the long run there was gain in weight of the composite made with OPC. The loss of weight occurred when the entire test sample is treated with 1.0 M HCl. Results on acid resistance and sulphate attack revealed that Composite cements are better acid resistant but more susceptible to sulphate attack. It was also observed that FAC composite is more susceptible to sulphate attack than RHAC composite. The $Ca(OH)_2$ leaching tests indicate that Composite Cements are effective in reducing the amount of $Ca(OH)_2$ leaching compared to pristine OPC.

I. Introduction

Composite cement is a sort of cement grew as of late. Composite cements are made by the fractional substitution of Ordinary Portland Cement (OPC) by industrial by-products, squander or rural waste which is getting well known on the grounds that they are financially savvy and they offer an environmentally friendly method uses of waste. Then again, the gathering of different sorts of agricultural by-products, industrial wastage and so on presented environmental contamination. In this manner, the abuse of local assets, the developments of creative methods are of extraordinary enthusiasm to the researchers and technologists. Composite Cement has become a wide spread acceptable structure material in numerous nations of the world for economical turn of events.

Different materials are included, for example, fly ash, rice husk, and admixture to get composite cement of desired property. The nature of the composite cement is evaluated by quality of the paste[1]. The success of acquiring a net less strong composite cement relies on the cautious mixing of the ingredients. Fly ash can be produced as a byproduct from burnt coal and rice husk ash, which is found to be as the by-product of burned rice husk at higher temperature from paper plant[2].

Rice plant is one of the plants that retains silica from the dirt and absorbs it into its structure during the development[3]. Rice husk is the external covering of the grain of rice plant with a high grouping of silica, for the most part more than 80-85%[4]. It is liable for around 30% of the gross load of a rice piece and regularly contains 80% of organic and 20% of inorganic substances. Rice husk is created in a large number of tons every year as a waste material in farming and modern procedures. It can contribute about 20% of its weight to Rice Husk Ash (RHA) after cremation[5]. RHA is profoundly a pozzolanic material.[6] The non-crystalline silica and high explicit surface zone of the RHA are liable for its high pozzolanic reactivity.

Fly ash has pozzolanic properties like normally occurring pozzolanic material[7]. Over the previous years, there has been an expanding number of papers on the utilization and usage of industrial, farming plants by-products in the production of composite cement. Various materials with pozzolanic properties, for example, Fly Ash, consolidated silica fume and rice husk debris have had a significant influence in the production of superior composite cement[7]

Both the specialized points of interest offered by basic cement containing rice husk ash and the social advantages identified with the decline in number of issues of ash removal in the earth have reproduced the improvement of investigation into

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the possibilities of this material[8]. Rice husk ash is perilous to environment if not dispose appropriately[9]. This paper deals with the study of observations of composite cement which consists of Rice husk ash and fly ash with Ordinary Portland Cement are treated with sulphate and acid attack and findings are reported as one of the important physico chemical properties of the Cement composite.

II. Experimental

Preparation of Rice Husk Ash (RHA) and Fly Ash (FA) composite cements

CEMEX brand cement sample was collected from the factory and used for the preparation of RHA and FA composite cements. Composite cements were prepared by mixing 75% OPC and 25% RHA and 75% OPC and 25% FA to prepare RHA and FA composite cements respectively. The mixtures were then ball milled in a porcelain pot with a number of porcelain balls of different sizes. Three fourth of the pot was filled with the composite mixture and the ball milling was continued for three hours. The mixtures were then kept in sealed plastic container to preserve it from moisture when physical, chemical and microstructural analyses were being carried out.

CEMEX brand concrete sample was gathered from the manufacturing plant and utilized for the readiness of RHA and FA composite concretes. Composite concretes were set up by blending 75% OPC and 25% RHA and 75% OPC and 25% FA to get ready RHA and FA composite concretes separately. The blends were then ball processed in a porcelain pot with various porcelain wads of various sizes. Three fourth of the pot was loaded up with the composite blend and the ball processing was proceeded for three hours. The blends were then kept in fixed plastic holder to protect it from dampness when physical, substance and microstructural examination was being completed.

XRD analysis

The phase composition of the OPC, RHA and FA composite cement was determined by the XRD analysis of the sample with Philips X-ray Diffractometer model operating with a CuKα radiation source (Kα=1.5406 Å). The samples were ground to a fine powder and loaded on a silicon low background sample holder over baseline adhesive. The XRD scans were recorded from 10 - 80° 2θ with 0.20° step-width and 5.1 s counting time for every step. Phase analysis was performed by comparing the d values and intensity ratios of the main fundamental peaks with data available in the data book published by the Joint Committee of Powder Diffraction Standards.

DTA/TGA analysis

DTA/TGALabsys ™ from SETARAM was used to evaluate the thermal behaviors of the sample. The heating rate for DTA/TGA analysis was 10°C/min. The temperature difference between an inert (Alumina) and the sample was recorded and mass loss was calculated from the TG curve.

Sulphate attack and acid corrosion

Chemical resistance was determined by weight loss procedure. Samples were first over dried at 110 ± 5 °C and then test specimens were immersed in 0.5 and 1.5 M acid solution. For the sulphate resistance test, the test specimens were taken out of the container and washed thoroughly with laboratory tap to clean the surface of the test specimens.

Samples were then oven dried at 110 ± 5 °C and then test specimens were recorded. The acid resistance and sulphate attack was determined from the loss/gain in weight of the test specimens. The same test specimens were used to carry out the test for different period of time. The last specimens were then immersed in fresh acid solution and sulphate solution till the day of testing.

Method of determination of Ca(OH)$_2$ leaching from the OPC and Composite Cements

Sample preparation for determining Ca(OH)$_2$ leaching from the cement and the Composite Cements. For making cement paste and Composite Cements paste, the materials were taken in a suitable porcelain pan.

Specimen mold was a cylinder of 1 inch in diameter by 1 inch in height of plastic tube having sufficient wall thickness to be rigid and retain dimensional stability during the molding operation. A flat plastic sheet was used on which one open end of each section can be rested. The other end was sealed with a cement paste and composite cement paste was prepared by mixing the material with required amount of water in the porcelain container. The molds are filled with this paste. The test specimens were cured for one day in moist cabinet and the specimens were then demolded. Then the test specimens were dipped in wide mouth containers distilled water, 3 test specimens being in each container. Test was carried out for 1, 7, 28, 64 and 90 days.

Method for determination of Ca(OH)$_2$ leached out from the paste samples

The test specimens were removed from the container and washed with distilled water to remove the adhering CH from the surface of the test specimen. The washing liquid was added to the original container. Small amount of dilute hydrochloric acid was added to dissolve the CH crystals. The solution was heated till it boils, then 5% ammonium chloride solution was added. Calcium was precipitated as calcium oxalate. The solution was kept undisturbed for 2-3 hours before filtration. It was then filtered and washed with 0.1% ammonium oxalate solution. The filter paper was ignited at 1000 °C in a previously weighed platinum crucible. The difference in the weight of the crucible indicated the amount of CH leached out from the paste samples.

III. Results and Discussion

### Durability of OPC and Composite in Relation to Acid Attack and Sulphate Expansion

Some chemical reactions that can influence the stability of concrete structure are associated with the corrosion of concrete structure or formation of expanded products that can occupy greater volume within the cement matrix. Internal stresses can be generated within the concrete structure when this expansive compound is forced to occupy space that is not readily available.

Two types of reactions likely to affect the stability of cement concrete structure throw expanded product formation, which are

(a) Alkali-aggregate reaction (AAR)

(b) Sulphate attack

Sulphate attack in OPC and Composite Cements

In the presence of sufficient amount of moisture, sulphates present in concrete can readily be dissolved in water and it reacts with various cement hydrates, which can be identified as follows: A reaction between the crystalline CH in the hydrated cement and the environmental sulphate occurs, yielding soluble hydroxide together with crystalline $CaSO_4\ 2H_2O$.

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O = 2NaOH + CaSO_4.2H_2O$$
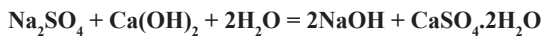
The gradual removal of calcium hydroxide results in the loss of strength but expansion does not usually occur. However, substantial deposits of $CaSO_4.2H_2O$ within the silicate hydrate structure may cause expansion by gypsum crystal growth in weakened pastes.

(a) Environmental Sulphates react with the calcium aluminate/calcium mono-sulpho-aluminate hydrates in the hydrated cement for ettringite.

(b) $3\,CaO.Al_2O_3.3CaSO_4.12H_2O + 4Na_2SO_4 + 2Ca(OH)_2 + 20H_2O$ $= 3CaO.Al_2O_3.3CaSO_4.32\ H_2O + 8NaOH$
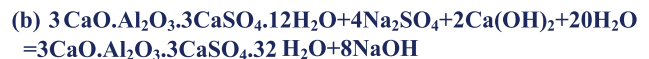
The formation of ettringite usually results in expansion & eventually in disruption. The incorporation of SM makes it more complex. Attempt has been taken to explain sulphate attack in OPC & composite cements. Though there are disagreements among the investigators[10] regarding sulphate attack, the mechanism of sulphate attack has been studied by many workers[10-11] C_3A and C_4AF contents in PC is thought to be particularly important in determining sulphate (SO_4^{2-}) resistance[13-14]. A possible process is ettringite crystal nucleation and growth. Expansion is thus avoidable increasing the solubility of the ettringite by reducing $Ca(OH)_2$ level or increasing the temperature[12], Sulphate attack has been determined in this work by measuring weight loss/gain of OPC and the Composite Cements produced from FA and RHA when dipped in Na_2SO_4 solution (0.5M and 0.75M Na_2SO_4 solution). A loss in weight has been observed at the initial stage i.e. after 7 and 14 days when OPC is dipped in sulphate media but eventually, there was gain in weight of the specimen made with OPC (Figures **1a** and **1b**). The loss in weight during the initial period of investigation may be due to surface erosion of the test specimen. The gain in weight of the test specimen may be due to salt deposition or expansive compound formation.
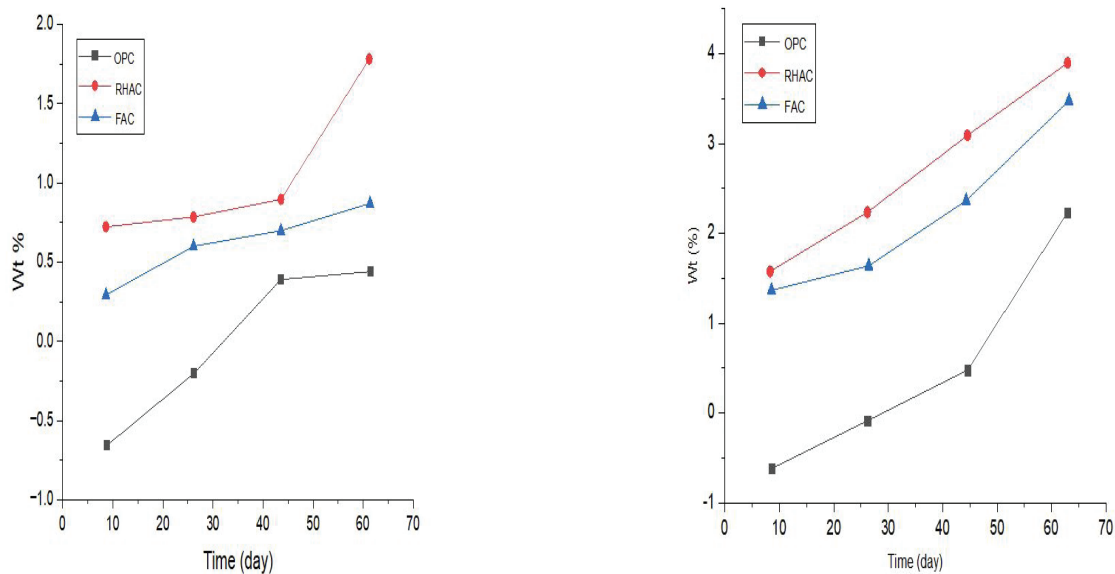
Fig.1. Weight loss/gain of OPC and Composite Cement in 0.5 M (1a, left) and 0.75 M (1b, right) Na_2SO_4 solution

It is interesting to note that an increase in weight was observed in mortar specimens of RHAC and FAC Composites after 7 days and it continues till the observation carried out up to 60 days and this increase is more in case of RHAC.

The mortar specimens when dipped in strong aggressive sulphate media, the main corrosion process consists of the C-S-H due to leaching of Na_2SO_4, which forms crystalline salt.

In the wetting and dry cycles, the specimens were exposed to changes in the temperature and/or relative humidity that causes the transformation of thenardite or metabolite. This reaction causes a large expansion and salt distress is largely extended when specimens present a fine poor structure. This salt crystallization effect was detected[13] in concrete specimens made with

(i) OPC containing $C_3A = 8.5$ and W/C = 0.52

(ii) Composite Cement containing 20% natural pozzolana

(iii) 40% natural which were half buried to high permeable

soil for 10 years

The initial weight loss in OPC-SO_4^{2-} mortar specimens may be due to break down of C-S-H phase [13].

The gain in weight may be associated with the corrosion products depositing in the pores results in weight gain. This has been confirmed by the XRD investigation, which exhibits reflections of thenardite formed from the dehydration of sodium sulphate decahydrate, the intensity of which is more in OPC (**Fig. 2**) and RHAC composite (**Fig. 2**) compared to FAC composite (**Fig. 3**)
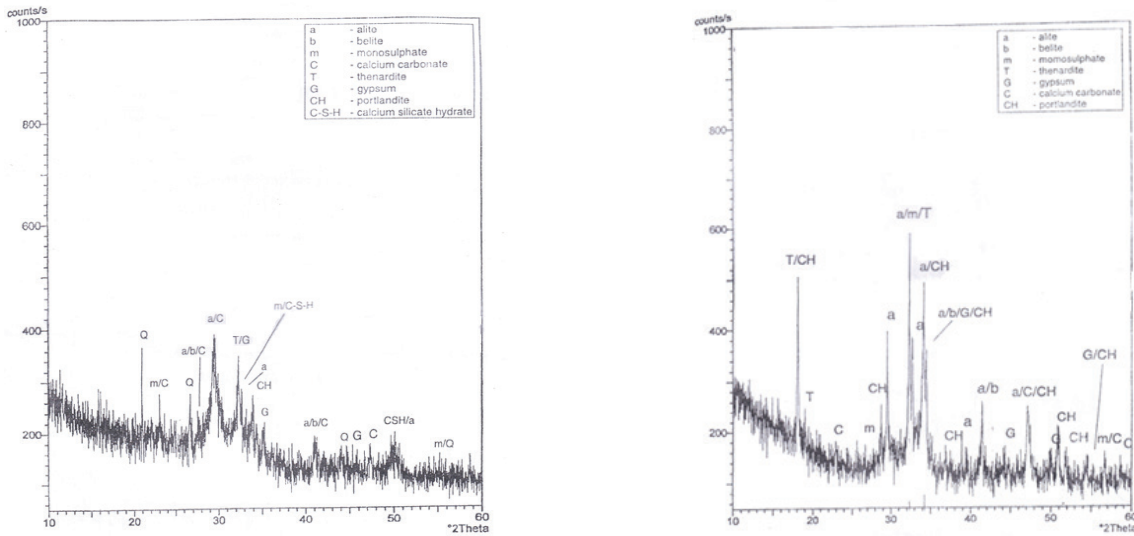
Fig. 2: X-ray diffractogram of 2 months old hydrated OPC paste (left), OPC-RHA paste (1:1) (right) impregnated with 0.75 M Na_2SO_4 solution.
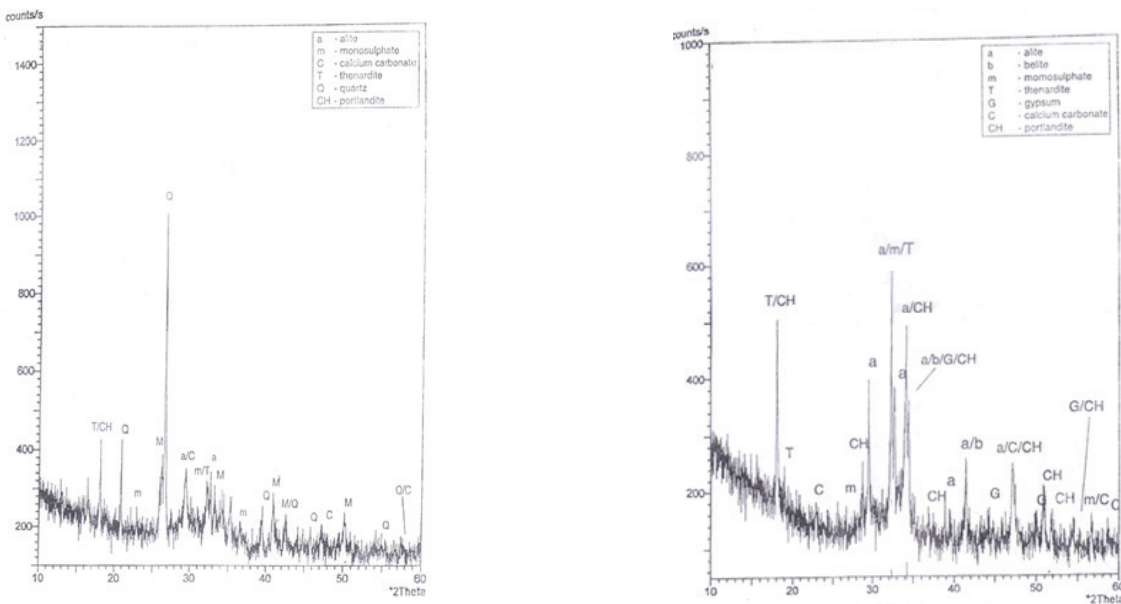
Fig. 3. X-ray diffractogram of 2 months old hydrated OPC paste (left), OPC-FA paste (1:1) (right) impregnated with 0.75 M Na_2SO_4 solution

DTA studies were carried out to estimate the sulphate attack in OPC as well as in composite cements. It is interesting to note that when 1 day hydrated OPC paste clearly indicated the characteristic gypsum doublet at 145 and 170⁰C, this gypsum peak is absent in 2 days hydrated OPC-SO$_4^{2-}$ paste which was expected. But after 7 and 28 days the gypsum peak was evident in OPC-SO4^{2-} hydrated paste (Fig. 4a), but gypsum was absent in 28 days OPC-SO4^{2-} paste (Fig. 4b).
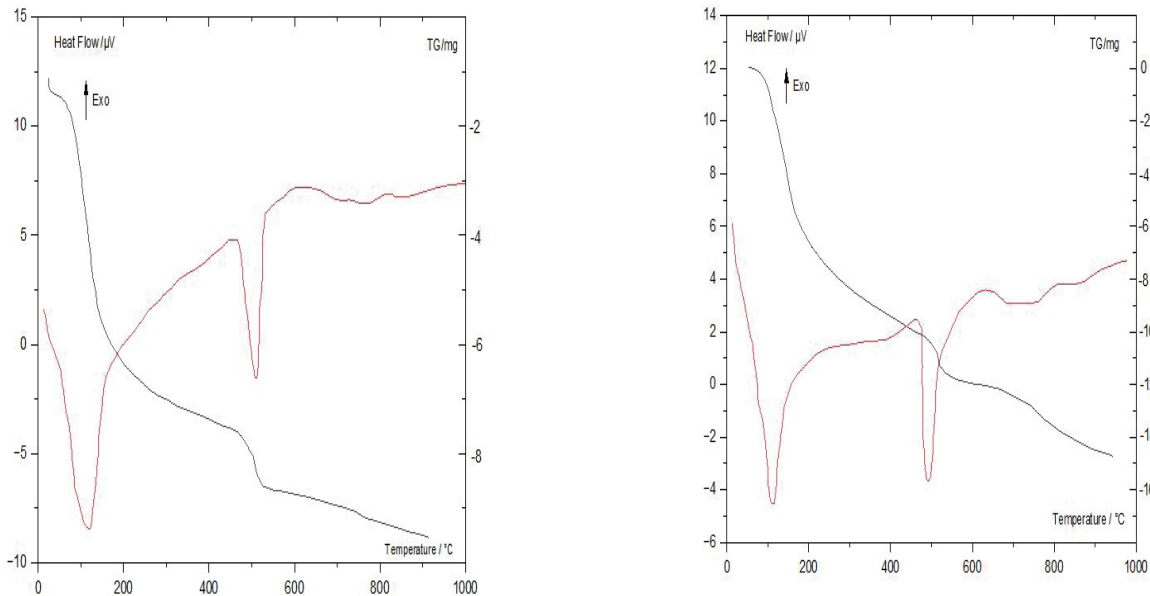

Fig. 4. DTA/TGA curves of 7 days old (4a,left) and 28 days old (4b, right) hydrated OPC paste impregnated with 0.75 M Na$_2$SO$_4$ solution.

The first endotherm in the 2 days hydrated OPC-SO$_4$ is the transformation product of sulphoaluminate or C-S-H. The presence of monosulphate was detected by XRD in the Composite Cements of RHA. The worst performance of blended cement may be attributed to the salt crystallization phenomenon[14,15] and also may be due to decomposition of C-S-H phase and its decalcification[16], when 7, 24, 28 and 60 days hydrated RHAC was compared to 2,7 21 and 28 days hydrated RHAC-SO$_4^{2-}$ paste which shows that the intensity of the endotherm in the region 50-170⁰C is more in RHAC-SO$_4^{2-}$ paste, which is not only from evaporation of surface moisture and C-H-S hydrated phase but also form dehydrated paste. The endothermal effect at 450-550⁰C due to dehydration of CH of CH is only present after two days in the hydrated RHAC-SO$_4$ paste, but it was absent in 7, 21 and 28 days RHAC-SO$_4^{2-}$,which may be due to decalcification[16] and this endotherm was not detected throughout this investigation in RHAC-SO$_4^{2-}$ paste. But the strong exotherm is still present at 760⁰C when only peak shifting has occurred which is due to C$_2$SH$_2$ phases[20].

Although FAC- SO$_4^{2-}$ paste did not show the endothermal effect due to dehydration of CH after 2 days (Fig.5), in 7, 21 and 28 days hydrated pastes it was present. Therefore, this investigation indicates that decalcification is not pronounced in FAC- SO$_4^{2-}$ paste as it occurred in RHAC-SO$_4$ paste. The well-defined CaCO$_3$ peak was also presented similar to hydrated FAC paste but DTA failed to detect in RHAC. In fact, due to the presence of crystalline quartz, mullite phases and sulphate attack is not very severe in FAC, although weight gain in SO$_4^{2-}$ paste was observed throughout these investigations that are because of salt deposition in the pores.
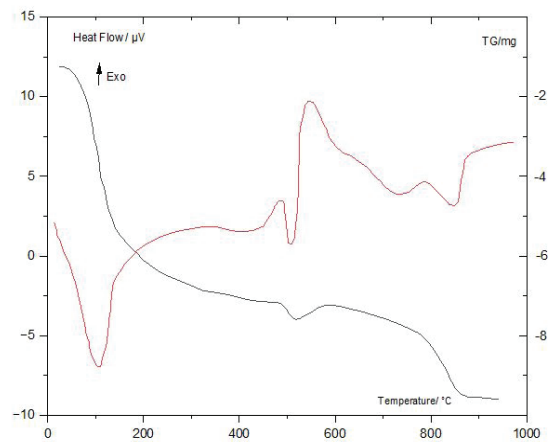

Fig. 5. DTA/TGA curves of 2 days old hydrated OPC-FA (1:1)] cement paste impregnated with Na$_2$SO$_4$ solution

The FAC composite, which contain more Al$_2$O$_3$ than RHAC, is associated with the formation of calcium aluminate hydrate in course of pozzolanic reaction[17, 18] than it can have a negative effect on the resistance to sulphate aggression. In more concentrated sulphate solution, ettringite is transformed to gypsum[19, 20]. If the cementing material does not contain sufficient amounts of Al$_2$O$_3$, which is true for RHAC necessary

to form complex salts considerable amount of gypsum can be observed in the corrosion products. If the concentration of sulphate has a high deficiency of CH might take place which is required to maintain equilibrium with the C-S-H and its decalcification[21]. In the opinion of some authors[22] the lower resistance of pozzolanic cement material to the aggressive sulphate medium is due to reduce content on CH as some of the CH supplies Ca^{2+} ions necessary for formation of gypsum to prevent the decomposition of the C-S-H phase.

The performance of OPC-PFA Composite Cement is dependent on the C_3A content of PC. In fact, the net sulphate resistance of OPC-PFA Composite Cement depends to some extend on the C_3A content of the OPC. Different behavior has been observed[23] with Composite Cements made with PFA from different sources.

Acid Corrosion in OPC and Composite Cements

It is known that OPC is not acid resistant. Direct decomposition of cement mortar/concrete occurs due to attack from acidic condition. This direct decomposition of OPC can lead to the progressive breakup of the bonds that the holds cement, fine aggregate, coarse aggregate together in the concrete fabric.

In this section the effect of acid on the mortar sample of OPC, RHA based Composite Cements has been investigated (**Fig. 6a** and **6b**) show the change in weight of the mortar sample of OPC, RHA and FAC as the length of the immersion time in acid solution increases. Loss in weight for the entire test specimens with increase in concentration of acid (1M-1.5M) is obvious. In due course the highly corrosive HCI enters the cement matrix and attack the cement aggregate bond thereby weakening the mortar specimen. This leads to gradual decrease in the weight. It is important to note that reduction in weight of composite cements made from RHA and FA is less than the control (OPC). The OPC mortar undergoes a remarkable decrease in weight after 30 days immersion period than the composite cements mortar specimens. This indicates that composite cements is more acid resistant than OPC. This is agreement with Linghua Jiang et al.[24]. This may be due to denser structure of composite cements than OPC as fine siliceous material contributing to the particle packing of the cement mortar matrix and filling of the capillary pores. It is also evident from these investigations that weight loss in case of fly ash composite cements specimens was to a greater extent than RHA composite with all specimens.
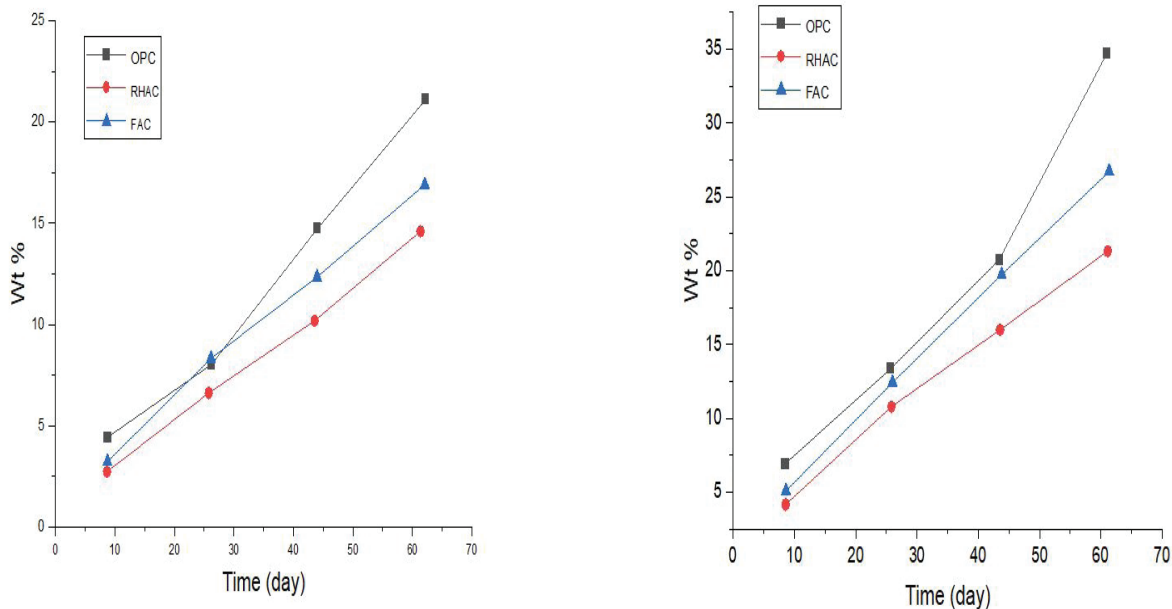

Fig. 6. Weight loss of OPC and Composite Cement in 1.0 M HCl (**6a**, **left**) and 1.5 M HCl acid (**6b**, **right**) with time

The Composite Cements based mortar specimen were attacked by acid to smaller degree than the control, the OPC mortar specimen. The outer layer of about ¼ - ½ inches had deteriorated by leaching in all the test specimen. The specimen became round shaped and gritty particle remain on the bottom of the container. Exposer to the solution, however, change the original color of mortar specimens from dark grey color to little yellowish.

IV. Conclusions

Sulphate attack in OPC and Composite Cements reveals that Composite Cements from RHA and FA are more susceptible to sulphate attack while acid attack is more pronounced in OPC rather than composite cement. Between the two Composite Cements, Sulphate expansion is greater in FAC than RHAC and RHAC is more acid resistant than FAC. The worst performance of composite cements in sulphate media may be due to salt crystallization. The acid corrosion is more

severe in OPC in comparison to composite cements from RHA and FA. The main reason could be the non-availability of CH, which has been used by the pozzolanic reaction. Other reason may be due to the denser microstructure of the composite cements. It is expected that pozzolanic additives in cementitious system increases their corrosion resistance owing to the decrease in CH content, pore refinement and increase of water tightness, thus impeding the penetration of aggressive media which is an agreement with the present investigation in relation to acid attack. On the contrary, in sulphate media the OPC showed less expansion than the composite cements, which has been discussed.

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