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Sulfate attack and embedded steel corrosion resistances of volcanic-aggregate concrete with fly ash and silica fume

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Abstract

Construction materials are increasingly on high demand in the developing world. The construction industry has a challenge of discovering, new alternative construction materials to conventional materials which are locally available materials in environmentally friendly manner. The experimental tests are conducted on volcanic concrete system to analyze its properties especially corrosion resistance potential for its applicability in construction. The major aim is to investigate its suitability and corrosion resistance potential especially when used in construction of structures with embedded steel. The test results of the material show that volcanic concrete system with 30% fly ash and 10% silica fume cementing materials is an alternative green construction material. Permeability properties are reduced by 8% and 24% with 30% fly ash and 10% silica fume respectively. Tests also indicate that Compressive strength, Corrosion potential and polarization resistance in volcanic concrete system with supplementing cement materials has more potential to resist sulfate attack when compared with conventional volcanic concrete systems. The supplementary cementing materials (SCM) reduce the pore system and hence decrease the ingress of corrosive ions and water in concrete. Corrosive ions, moisture and air would initiate corrosion to the embedded steel in concrete leading to reduced service life such structures.

Key word: Supplementary Cementing Materials, Sulfate attack, volcanic concrete system, Granite powder, river sand, Corrosion of embedded steel

I. Introduction

The main function of concrete cover is to protect reinforcement in order to minimize its corrosion from environmental effects. However, corrosion of embedded steel has significantly affected the performance of concrete structures, especially those with long designed service life. Corrosion of embedded steel in concrete is usually due to porous nature of concrete, which paves the way for ingress of corrosive elements. When moisture, air and corrosive ions penetrate concrete up to the embedded steel surface, there is a high risk of corrosion initiation. The ingress of different species depends on the porous nature of concrete or else on other defects like cracks and the quality of the materials that compose the concrete. This shortens the service life of -concrete structures but also negatively affect the environment and in general, retards the sustainable development (Jungle et al.2011; Schneider et al. 2011; Shi et al. 2011). Among other factors, concrete deteriorates due to sulfate attack by expansion effect. Researchers have suggested alternative concrete material ingredients from various sources for different applications. Waste industrial materials and granite powder can be used as alternative fine aggregates to natural sand in concrete mixes Halifax et al. (2009). Quarry waste and Lime stone dust, siliceous stone rock powder, are examples of materials used as an alternative to natural fine aggregates (Halifax et al. 2009). The utilization of locally available materials like volcanic rock aggregates was recommended by various researchers (Abaho and Pranesh (2016); Schittich (2012); Red DURAR (1998). Porosity in concrete sooner or later can lead to both steel cover deterioration and embedded steel corrosion Rasheed uzzafar et al. (1990). The sulfate permeation can be minimized by: increasing concrete compactness, use of low water-to-cement ratio, proper curing, surface treatment, and use of precast concrete than cast-in-situ concrete as proposed by ACI Committee (1991); Hossain (2004); Kalousek et al. (1972); Al-Amoudi et al. (1994); Young et al. (1998). Irassar et al. (2000) found that cements with low C_3S/C_2S ratio have low resistance to sulfate attack. Researchers like Rasheed uzzafar (1990); Kalousek et al. (1972); Lawrence (1990); found that tri calcium aluminate (C_3A) content is not the major reason for sulfate attack in concrete. Mehta (1993) concluded that Type V cement cannot resist the initiation of sulfate expansion in concrete. It is more useful when calcium sulfate is the slate to concrete medium; it is again effective in prevention of gypsum owing sodium sulfate attack. Neville (2004) observed that significant progress has been made with regards to the mechanism of sulfate attack in concrete, however, he stated that its knowledge and full understanding remains inadequate. It is still not clear whether tri calcium aluminate, water content and pozzolanic material has a significant role in sulfate attack. Performance evaluation of the SCMs in volcanic concrete system mix with granite powder to sulfate attack resistance and corrosion of embedded steel in concrete is a potential area of research. In this study, a volcanic concrete system has been developed with locally available materials of volcanic rock aggregates (VRA), granite powder, partly replacing river sand (RS) and Fly ash and silica fume as Supplementary Cementing

Materials (SCM). This paper intends to investigate the resistance potential to both sulfate attack and corrosion initiation of a concrete system produced with concrete mix ingredients mentioned above.

2. Materials and Methods

Table 1 Mix Design with Mix Proportions

No	Designation of Mix	Volcanic Rock coarse aggregate (%)	River Sand fine aggregate (RS) (%)	Replacement for river sand by granite powder (%)	Cement (%)	Replacement for Cement (%)
The original mixing ratio of volcanic coarse, fine and cement concrete was 1:2:4 before replacement. The 30% granite powder in replacement of river sand fine aggregate is appropriate, Abaho and Pranesh (2016)						
1	Compound Portland Cement (CPC)	100	70	30	100	0
2	Fly Ash (FA)	100	70	30	70	30
3	Silica Fume (SF)	100	70	30	90	10

The study conducted tests and experimental setups in three sets. The aggregates were 100% volcanic coarse aggregates along with 30% granite powder in replacement of river sand fine aggregates: One set was produced with 100% CPC; another set was made with 30% FA in partial replacement of CPC, and finally, another set was made with 10% SF in partial replacement of PCC. These specimens were cured for 28 days in a chamber with temperature of 28 $\pm 2^0$C and 98±1% of relative humidity.

2.1 Concrete materials

The materials used were basically from Rwanda except Silica fume and Fly-Ash which were sourced from India. Compound Portland cement is manufactured from chalk, clay and gypsum is added to the clinker, when hardened resembles Portland stone hence the name. Grade 43 Compound Portland Cement (cement manufactured Rwanda), purified drinking water, volcanic rock aggregates from Ruhengeri-Northern province, Kagugu river sand and granite rock powder from East Africa granite plant at Nyagatare in the eastern province used as fine aggregates and silica fume as supplementary cementing material were the materials used. The result of sieve analysis for the coarse and fine aggregates in Tables 2 and Figure 1, the results of the tests for the chemical properties of the cementing materials, and aggregates in Table 4 to 7 presented in this paper are part of generated data in the previous published research paper Abaho and Pranesh (2016). With sieve analysis, crushed volcanic rock aggregates size were in the range between 20mm to 6.3mm while the size of fine aggregates used ranged between 4.75mm to 150micro. The bigger size of volcanic rock coarse aggregate used was 19 mm. Table 2 shows sieves analysis results for coarse aggregates.

Table 2 Sieve Analysis results of coarse aggregates.

No	Sieve Size (mm)	Percentage Passing
1	25	100
2	20	98
3	16	87
4	12.5	64
5	10	26
6	6.3	03
7	4.75	00

The results obtained after conducting sieve analysis for both granite fine aggregate as compared with natural sand (river sand) are shown Fig 1.

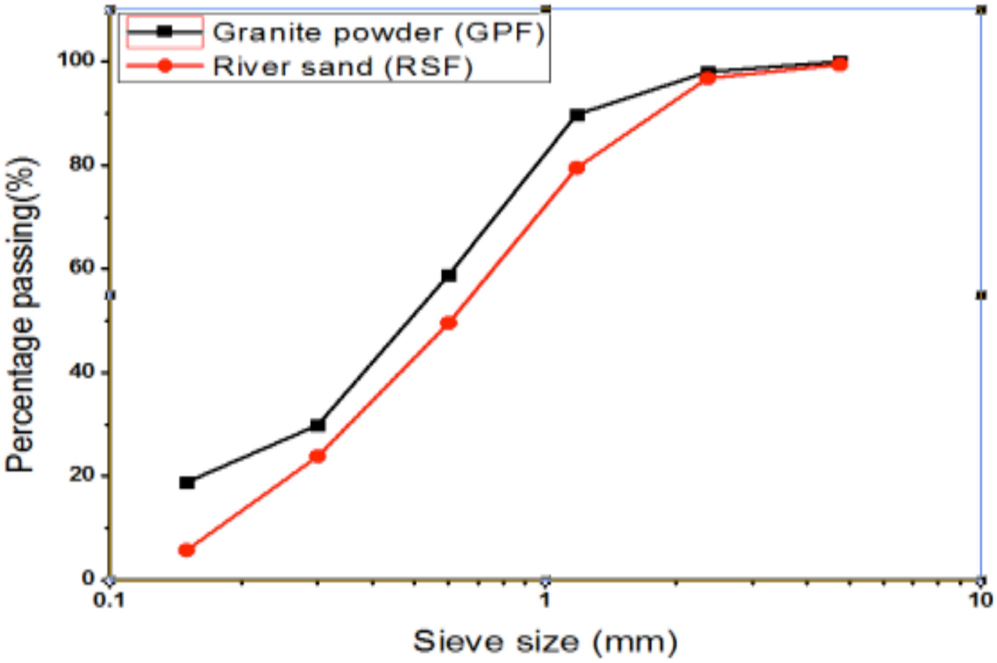

Figure 1 Sieve analysis of fine aggregates

It was considered important to properly proportion the materials used in the concrete mix which was done as shown in Table 3.

Table 3 -Mix design (by 1m^3 of concrete)

Materials (Kg)	Mix identification		
	VRA- 30%GPF 100 %CPC	VRA 30%GPF 30% FA	VRA 30%GPF 10% SF
Water	213.31	213.31	213.31
Cement	444.44	444.44	400.00
RSF	915.35	640.745	640.745
GPF	0.000	274.605	274.605
VCA	870.58	870.58	870.58
SCM	0.000	0.000	44.44
Super Plasticizer 1% of cement mass was used in the mix			

For better proportioning of fine aggregates to coarse aggregates ratio, particle size for both coarse and fine aggregates was graded. For conformity with grading limit (IS: 383-197), the granite aggregate fall in zone II of crushed aggregate and river sand aggregates fall in zone II grading limit of fine aggregates. The surface index method helps in the proportioning of fine to coarse aggregates (Murdock and L. J (1960). Table 4, 5, 6 and 7 presents both the physical and chemical properties of the materials used.

Table 4 Chemical properties of the aggregates used in concrete mixtures

No	Materials	Description
Physical properties of aggregates and super plasticisers		
1	Volcanic rock aggregate	Specific gravity-2.42-2.7, Fine modulus- 2.43,Mamum size-19 mm, Bulk Density(Kg/lit)- Loose - 1.216, rounded - 1.360
2	River sand	Specific gravity-2.58, Fine modulus- 2.43, Humidity Module (%) – 6.66, Fineness Module (%) - 2.73, Relative density (g/cm3) – 2.43, Absorption (%) – 0.44, Particle size range from less than 0.25mm - 6.3mm Maximum size module (%) – 6.3, Humidity (%)-0.28
3	Granite powder	Specific gravity-1.220-2.6, Soundness (% by mass after 5 cycles) Sodium sulphate - 4.86, Magnesium sulphate-5.48, Fine modulus- 2.43,water Absorptio (%)-13,
4	superplasticisers	Specific gravity- , Chloride content-Nil , Recommended dosage- 2-4% of cement, Air attrainment-1% at normal dosage, solid content-40%, operating temperature-(10-40)^{O}C, Compatibility- All types of cement except high allumina cement

Table 5 Chemical properties of Aggregates: (Chemical composition in % by mass)

Material	**SiO_2**	**AlO_3**	**Fe_2O_3**	**CaO**	**SO_3**	**K_2O**	**Na_2O**	**Mg O**
VCA	59.42	12.36	5.99	4.63	0.007	-	-	1.81
GPF	19.94	4.40	0.82	3.18	0.05	0.42		-

Table 6 Chemical properties of cementing materials

Chemical composition (% of weight)								
Material	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**SO_3**	**K_2O**	**Na_2O**	**MgO**
CPC	19.94	4.40	2.97	63.50	3.08	0.42	0.12	-
FA	58.84	16.72	3.52	7.35	0.13	0.79	0.94	1.76
SF	95.22	0.08	2.37	0.26	0.11	0.56	0.30	0.24

Table 7 Physical properties of cementing materials

Material	**Density (g/cm^3)**	**Specific surface, BET (m^2/kg)**	**Average size(µm)**
CPC	3.15	1400	15-25
FA	2.15	1200	5-15
SF	2.20	19600	0.1- 0.2

2.2 Methods

Total experimentation consisted of workability slump test, compressive strength, corrosion potential and linear polarization resistance tests. For workability, the study adopted the use of surface index which is an empirical number which gives more weight to the finer fractions as suggested by Murdock (1960). Thereafter the slump test was conducted with samples from each set. Compressive strength test was conducted on cube with the dimensions of 150mm x 150mm x150mm specimens using compression strength testing machine (CTM) of 3000 kN capacity. The compressive strength was determined at different curing ages of 1, 3, 7 and 28 days with the addition of 1% superplasticizers of cement and the average test results were considered for analysis and comparison. The effect of sulfate attack and corrosion of embedded reinforcing steel was studied on three set-up concrete assemblies, cylinders with 15 cm in diameter and 30 cm in height, with the two centrally embedded steel bars were casted. Specimens were immersed in a 3.5% of $NaSO_4$ aqueous solution environment after drying in air for a day in a laboratory atmosphere at temperature of (21 ± 2°C) and then weighed. The results of weight loss (WL) were calculated using the equation 1

$$\mathrm{WL}(\%) = \frac{\mathrm{Wi}-\mathrm{Wt}}{\mathrm{Wi}} \mathrm{x} 100\ \% \qquad (1)$$

Wi is the average weight of triplicate specimens before exposure in grams (g);

Wt is the average weight of triplicate specimens after exposure period (g).

For measuring corrosion state or corrosion potentials (Ecorr), high impedance voltmeter was used and recordings were done with respect to a copper/copper sulfate electrode as reference electrode. The linear polarization resistance (LPR) technique was employed to measure the polarization resistance of the specimen. Song and Saraswathy (2007) in their research work successfully measured the polarization resistance of embedded steel in concrete using the same technique as used in work. The test scan used was ± 20 mV to indicate polarization resistance of embedded steel in concrete at a scan speed of mV/min. Basically the set up and the experimentation process and steps are commonly known from principle of electrochemical corrosion of reinforced concrete. This is shown in Figure 2 below:

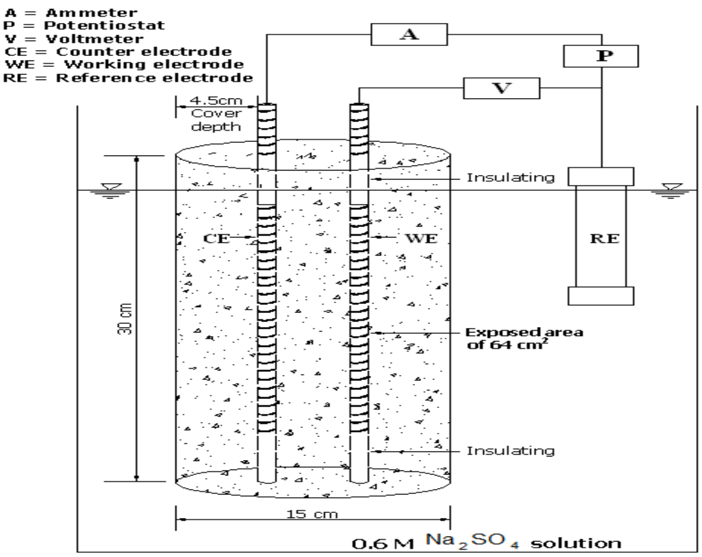

Figure 2 Electrochemical corrosion of reinforced concrete schematic setup for testing LPR [(Dao et al.2010) and (Bentur et al.1998).]

With the use of curves for the potentials plotted against current density, the Rp of the concrete systems in study was obtained.

$$i\ corr = \frac{B}{Rp} \qquad (2)$$

Equation 2 of Stern and Geary where B is Tafel constant, it value was adopted and used to calculate the corrosion current density as recommended by various researchers including Dhir et al. (1993); González et al. (1996); Gowers and Millard (1993); Mangat and Mollay (1992).

3. Results and Discussion

3.1. Workability

Slump test results were 82, 100 and 110 for concrete mixes without SCM replacement, with 30% FA and 10% SF respectively. It shows that mixes with 10% SF produce higher slump than other mixes, 30% FA mixes was more workable than the mixes with no SCM. A positive effect for silica fume to cause good grading of particles in concrete along with admixtures is significant. Fine particles ranging between150-300 microns reduced internal friction between bigger particles and hence improved workability.

3.2. Compressive strength test

Table 8 Compressive strength of concrete with Supplementary Cementing Materials (SCM)

Mix identification	No of specimen	w/c Ratio	Compressive Strength (MPa) -Age of concrete test			
			1-Day	3-Days	7-Days	28-Days
100% CPC	12	0.45	11.00	22.20	29.60	35.0
30% FA	12		13.2	23.5	30.0	37.5
10% SF	12		15.4	27	36.2	41.0
100% CPC	12	0.40	13.45	25.50	36.40	45.4
30% FA	12		15.9	27.5	38.2	46.0
10% SF	12		16.2	29.2	39.5	47.9
100% CPC	12	0.35	24.96	32.9	38.9	54.25
30% FA	12		26.55	36.20	45.10	54.50
10% SF	12		28.20	39.6	45.50	55.50

The compressive strength test results indicate that concrete mix with 10%SF has the highest strength in all age of curing in days-. Also, it is observed that the hydration and curing process affects the compressive strength as it increases with increasing curing age as observed in Fig 3 below.

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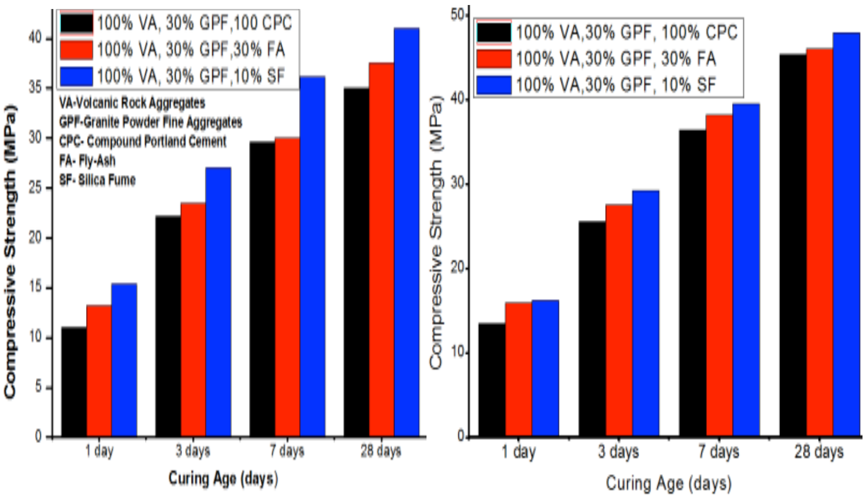
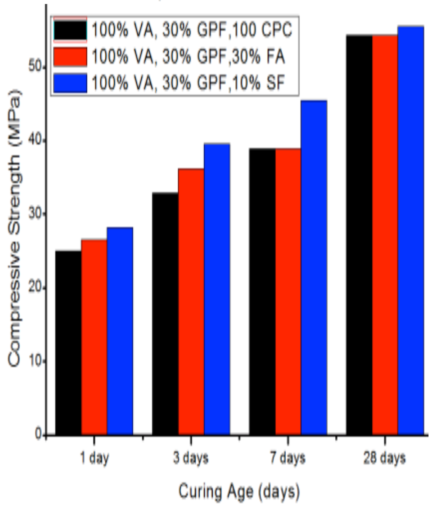


a) w/c = 0.45

b) w/c = 0.4



c) w/c = 0.35

Figure 3 a, b and c: Compressive strength with 0.45, 0.4 and 0.35 w/c ratio respectively.

The figures **3** a, b and c show that the lower the w/c used the more the compressive strength the concrete gained in early curing ages. This may be due to reduced aggregate cement transition zone that increases with increase in water-cement ratio. This is because the cement particles are held at a small interval in case of lower w/c ratio than higher w/c ratio.

3.3. **Concrete weight loss**

The test results of specimen in general show that the concrete specimens lose weight. This was when the weight of specimens after immersed was compared with their weights before immersion in the test solution. It shows that the specimen gained weight on their immersion to solution. Weight loss significantly increased after three months in mixes with no SCM and insignificant increase was observed after four months in the mix with SCM. This was because the expansion products formed after the reaction of the mixed materials filled the pore spaces which makes the concrete system denser and hence increases the weight. Then, the expansion of these products stresses the concrete to the extent of causing fractures in the concrete matrix system, leading to the loosening and loss of the loosened materials, resulting in the reduction in the weight of the specimens

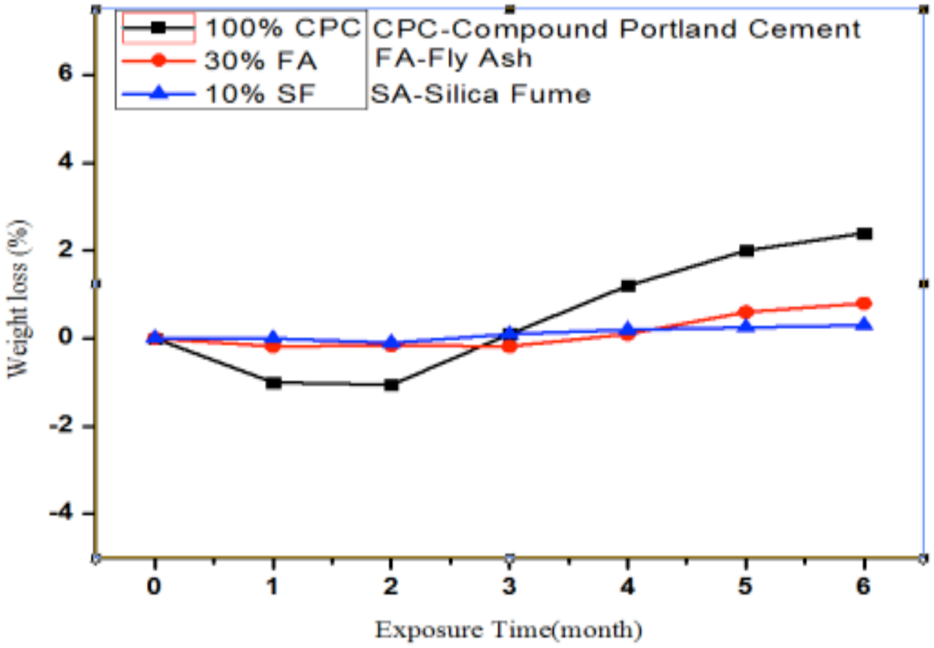
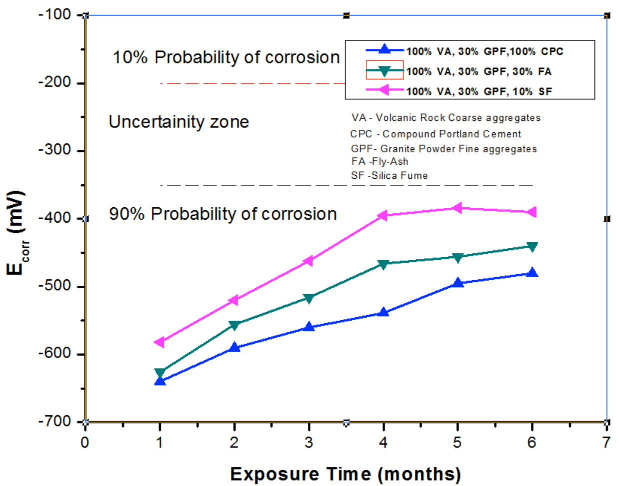


Figure 4 Weight loss of concrete specimen in sulfate environment

The maximum weight loss was 24% duration the six months of exposure of the volcanic concrete mix with 100% CPC, followed by 0.8% in the mixes with 30% FA, The maximum weight loss observed for concrete system mixes with 10%SF was 0.3 %. From these results, it is clear that the contribution of SCM, especially, the concrete with 10% SF in filling pores of the concrete matrix is significant. The filling of the void in the concrete by the reaction products of the SCMs controls the easy with which sulfate ions penetrate into the concrete.

3.4. Corrosion potentials

Figure 5 shows the results of corrosion potentials of the test specimens. The horizontal broken lines corresponds to the corrosion probability as expressed by ASTM C876 (2009) standards.



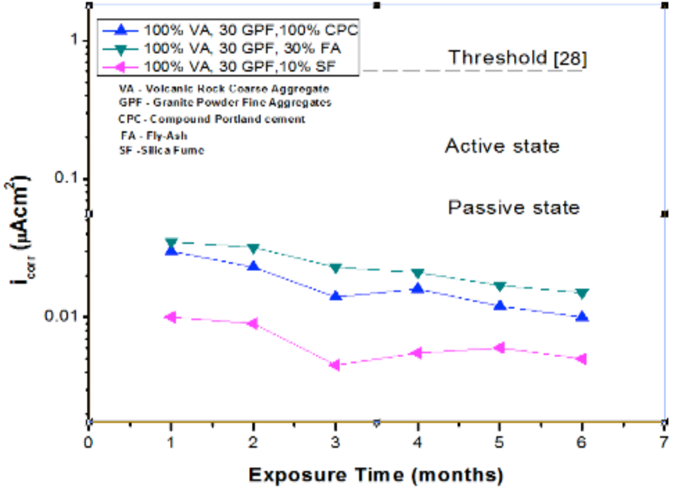


Fig. 5 **Fig.6**

Figure 5: Corrosion potential of the embedded steel in concrete as a function of the exposure time.
Figure 6: Corrosion current of the embedded steel in concrete as a function of the exposure time.

In the six months of specimen exposure, the corrosion potentials, of all the reinforced concrete systems, show fluctuation ranging from -696 to -380 mV/ Cu-$CuSO_4$ with a small decrease during the six month, towards more -stable values. According to ASTM C 876, these Ecorr values show that there exists a 90% chance of active corrosion during all the exposure time; but, the criterion is for partly saturated not totally saturated specimens. ASTM C 876 criterion is applied in fully merged structures or specimen environment reinforcement corrosion tests. Therefore, probably all embedded steel were in a passive state during the six months of specimen immersion in the sulfate solution. Otherwise, concrete system with 10%SF could have performed better in as far as resisting corrosion of steel reinforcement as shown in fig.6. Since the concrete system with 10% SF presented the better corrosion potentials during the exposure time. The 10% SF concrete samples presented corrosion potentials between -520 to -380 mV /Cu-CuSO4 compared -696 to -518.7mV/ Cu-$CuSO_4$ for 30% FA concrete systems. This shows that 10% SF contribution to the inhibition of corrosion of the reinforcement was significant. This testing technique provides qualitative information on reinforcement corrosion. Therefore, quantitative information on reinforcement corrosion could be developed by employing the linear polarization resistance technique presented in Fig.6

3.5. Polarization resistance

From the curves of corrosion potential against current density, polarization resistance (Rp) was obtained for all the systems in study and corrosion current density (icorr) was calculated representing the results in Figure 6; the horizontal broken line point out the threshold of active to passive corrosion as was drawn by Andrade and Alonso (1996).

In Figure 6; it can be observed that the system steel-concrete that presents the highest corrosion resistance induced by sulfates is the one with 10%SF, because its corrosive activity was the lowest for all the exposure time as shown in fig.6 and decreased significantly until it reached a lowest level of corrosion (0.0003 μA/cm^2). The 10% SF system showed levels of corrosion between (0.0001 - 0.0003) μA/cm^2, 30% FA ranges of (0.0001 - 0.0008) μA/cm^2 and 100% CPC showed levels of corrosion range of (0.06 - 0.0024) μA/cm^2. This shows that concrete system with 10%SF has more potential to reduce the ingress of corrosive agents into concrete when compared to systems with 30%FA and100%CPC mixtures. The significant effect this material to inhabit corrosion current density is due to reduction of pores size and pore distribution in concrete system that makes the possible dense structure of pores formed. Because of that, it is deduced that the microstructure of concrete with 10%SF becomes denser than the rest of the concrete system mixes. Therefore, it reports a decrease in both sulfate ion penetrability and corrosion current density. According to Powers (1958), several mineral additions have also been shown to improve the resistance of concrete materials to the penetration of aggressive ions. This research intends to contribute to the construction industry material requirement in as regards concrete system with potential to resist sulfate attack and corrosion of steel in concrete.

4. Conclusions

The analysis of the primary data collected by experiments and tests on workability, compressive strength, weight loss, corrosion of embedded steel potentials and its linear polarization resistance of concrete systems lead to the hereafter enclosed conclusion. Granite aggregates is an alternative construction material in volcanic concrete system with more chances of improved permeability properties especially when SCMs are used. The use of volcanic rock concrete systems are less costly and environmentally friendly in countries like Rwanda when compared to convention concrete. The use of 30% FA can increase the compressive strength of the concrete system by 2% while it increases by 3.23% when 10%SF is used in the volcanic concrete system compared to the use of 100% CPC in the same concrete system. Replacement of cement with 10% SF and 30% FA in concrete reduces around 24 times and 8 times of the concrete weight loss respectively by sulfate attack; compared to conventional concrete with no cement replacement. Polarization resistance test has proved 10% SF volcanic concrete system to be more resistant to corrosion of steel reinforcement compared to concrete made of 100% CPC. SCM increased the density of the concrete system and reduced the pore size and distribution in volcanic concrete systems. Therefore, corrosion of embedded steel reinforcement due to sulfate attack in volcanic concrete system can be reduced with the use of SCM than using 100% CPC. However, superplasticizer 1% of cement mass could be used to improve workability of the concrete mixture.

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