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Corrossion of Steel in Fly Ash Basedgeopolymer Concrete

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Abstract: Corrosion of steel in concrete is a major problem in structures exposed to severe corrosive environments like marine environment. The present study is an effort to assess the corrosion characteristic of fly ash based Geopolymer concrete where sodium silicate and sodium Hydroxide were used as an activator.The corrosion behavior of steel in Geopolymer concretes was studied using resistivity, potential, pH and chloride permeability technique. The results were compared with corresponding normal concrete at equal strength grades. The half-cell potential measurements indicated the passivity of steel bar in Geopolymer concretes. From the corrosion studies it was also observed that Geopolymer concrete performed similar to that of normal concrete.
Keywords: Geopolymer, Resistivity, Potentials, Corrosion, pH, Sodium silicate, Sodium Hydroxide.

1.Introduction

The use of pozzolanic admixtures in concrete has been motivated by several issues[1]. Firstly, there is always a need to improve the durability of concrete, especially when it is subjected to aggressive environments, particularly the marine environment. The environmental forces and their variations lead to the deterioration of the concrete and to the corrosion of reinforcement, which is a major cause for degradation of concrete structures. Secondly, there is a need to minimize the consumption of cement by partially substituting it with naturally occurring materials that are less energy intensive and more environment-friendly. Thirdly, certain conditions to which the concrete may be subjected, such as sulphate attack, phenomena that may occur due to use of some reactive components, such as alkali-aggregate reactivity, or special applications of concrete, such as in radioactive waste immobilization, necessitate the use of unconventional admixtures to provide appropriate performance in concrete[2].

Geopolymer concrete is a relatively new product in the concrete industry[3], considering conventional Portland cement has been in use since 1824. Fly ash as a mineral admixture in concrete is of great utility to the present day construction industry. It is available in abundance due the combustion of coal in thermal power stations and its characteristics primilarly depend on the geological factors related to the coal deposit. Use of fly ash in concrete has been widespread, particularly because the resulting concretes are not only economical but also durable. This study is to assess the corrosion characteristics of fly ash based Geopolymer concrete.

2.Experimental Investigations

A detailed experimental program was planned to evaluate the corrosion characteristics of Geopolymer concretes (GC). The properties of materials, along with description of mixture design and test methods conducted in this investigation are presented.

2.1 Material

2.1.1 Cement

Ordinary Portland cement (OPC) of 53 grade conforming to the requirements of IS: 12269[4] was used in all investigations. The chemical and physical characteristics of the cement used in the present investigation are presented in Table 1.

2.1.2 Fly Ash

According to ASTM C 618[5] , there are two types of fly ashes (Class C or F) based on the CaO content. Fly ashes thus produced fall in the category of class F. The chemical composition of fly ash, as determined by X- Ray Fluorescence (XRF) analysis is shown in Table 1.

2.1.3 Silica fume

The silica fume used in the present investigation was obtained from Elkem materials. The chemical characteristics of silica fume are presented in Table 1.

Table 1 Chemical composition of Cement, Fly ash and Silica fume

S.	Composition	Cement	Fly Ash	Silica
1.	(SiO_2)	21.78	58.29	82.16
2.	(Fe_2O_3)	4.13	5.86	4.09
3.	(Al_2O_3)	6.56	31.74	2.06
4.	(CaO)	60.12	1.97	2.34
5.	(MgO)	2.08	0.14	0.91
6.	(Na_2O)	0.36	0.76	2.58
7.	(K_2O)	0.42	0.76	4.20
8.	(SO_3)	2.16	0.15	0.75
9.	(LOI)	2.39	0.31	1.19

2.1.4 Activators

Two activators were used in this study - sodium silicate and sodium hydroxide. The chemical composition of the sodium silicate solution is presented in Table 2. Sodium hydroxide (NaOH) in pellet form was made into a solution of required concentration by mixing with distilled water**.** The masses of NaOH solids for various concentrations are shown in Table 3.

Table 2 Chemical composition of Sodium Silicate solution

Solids (%)		Liquids	Specific
SiO_2	Na_2O	(%)	Gravity
28	8	64	1.48

Table 3 Chemical composition of Sodium Hydroxide solutions

Molarity	Solid	Distilled water %
8	26.2	73.8
12	36.1	63.9
14	40.4	59.6
16	44.4	55.6

2.1.5 Sand

In the present investigation, well graded river sand was used. The sand was sieved through 2.36 mm sieve to remove the larger grains of pebbles or organic matter (if any).

2.1.6 Coarse aggregates

Good quality well graded crushed granite was used as coarse aggregate. For the development of normal concrete and Geopolymer concretes, the coarse aggregates passing through 12.5 mm and 6.3 mm were considered.

2.1.7 Superplasticiser

The superplasticizer (SP) used in this study was a commercially available sulphonated naphthalene formaldehyde (SNF) condensate. It is a dark brown free flowing liquid with a relative density of 1.27 ± 0.02 at 25 $^{\circ}$C. Its pH value is greater than 6, and chloride ion content is < 0.2%.

2.2 Mix proportioning for concrete

No standard mix design methodology similar to that for normal concrete is available in the literature for designing Geopolymer concrete. Rather there are guidelines for mixture proportioning published in various studies[6]. Due to the fact that Geopolymer can be achieved through various methods, no single mixture design encapsulates all mixture variables. In this study, the sol/b ratio and SS/NaOH ratio that resulted in the highest strength for the Geopolymer mortars, was used for the design of the concrete mixtures. Mix details of normal concretes (NC) and Geopolymer concretes are shown in Tables 4 and 5.

Table 4 Details of normal concrete

Mix No	Cement	Silica Fume	Aggregate	Water	slump	w/c
	kg/m^3	kg/m^3	kg/m^3	kg/m^3	mm	ratio
2NC	315	-	1874	185	210	0.59
4NC	356	-	1780	185	135	0.52
6NC	428	22	1720	185	95	0.41

Explanation of nomenclature: 2NC–20MPa Normal Concrete, 4NC– 40 MPa Normal Concrete and 6NC 40 MPa Normal Concrete

Table 5 Details of Geopolymer concretes

S. No	Mix No	FA	Aggregate	SS	NaOH	Extra Water added	slump	H_2O to Na_2O
		kg/m^3	kg/m^3	kg/m^3	kg/m^3	kg/m^3	mm	ratio
1	2GC	450	1725	135	90	26.5	175	13.36
2	4GC	450	1725	135	90	19.2	125	12.61
3	6GC	450	1725	135	90	10	75	11.91

Explanation of nomenclature: 2GC – 20MPa Geopolymer Concrete, 4GC– 40 MPa Geopolymer oncrete, 6GC- 60 MPa Geopolymer Concrete.

2.3 Methods of testing

The performance of Geopolymer concretes in terms of the corrosion of embedded steel was investigated to assess their suitability to aggressive environments. The corrosion behaviour of steel in Geopolymer concretes was studied in two parts, in terms of the parameters related to the concrete (resistivity, alkalinity and chlioride permeability) and those related to the steel in concrete (potentials) and these were compared with the corresponding normal concretes at equivalent strengths.

2.3.1 Specimen preparation

The different parameters chosen for investigation through the different test methods needed different types of specimens. The corrosion study namely, potential was performed on 100x200 mm cylinders with an embedded 8 mm diameter cold twisted high yield strength deformed bar of 100 mm length. The rust products on the bars were cleaned. At the end of the bar, a 24 strand well insulated tin coated copper wire of low resistance was soldered to facilitate the measurement of different parameters in corrosion studies. The bar was placed centrally in the cylinder (100 x 200 mm) by ensuring at least 45 mm cover on all the sides. The details are shown in Fig.1. A minimum of three specimens were used for any test at a specific age. A comprehensive list of number of specimens prepared for each of the tests is presented in Table 6.

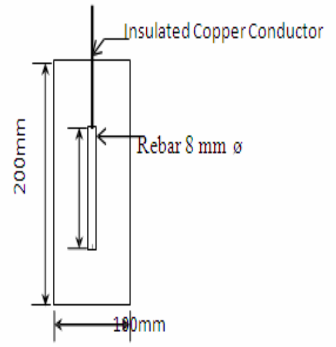

Fig. 1 Typical details of test specimen for corrosion studies

Table 6 Details of tests and specimens used in this investigation

Sl. No.	Type of test	Specimen size	Number and age at testing
1	Rapid chloride penetration test	100 x 50 mm cylinders	3 Nos. for each concrete tested @ 90 days.
2	pH value	100 mm cubes	3 Nos. for each concrete tested @ 28 & 90 days.
3	Resistivity	100 mm cubes	3 Nos. for each concrete tested @ 1, 3, 7, 28 & 90 days.
4	Potentials	100 x 200 mm cylinders with 8 mm dia. Steel rods embedded centrally.	3 cylinders for each concrete and each tested @ 1, 3, 7, 28, 60, 90 days.

2.3.2 Resistivity studies

The resistivity of concrete is an important parameter in the study of the corrosion behaviour of embedded steel. The corrosion of steel is an electrochemical process, which occurs within the electrolyte formed by pore water in the concrete. The rate at which the steel is able to corrode is dependent on the conductivity of the concrete, which is related to its moisture content. A higher resistivity of concrete means a lower rate of corrosion. Therefore, from the resistivity measurements it is possible to predict qualitatively the likely corrosion rate of the embedded steel in concrete. The present study is motivated by the fact that there is no information available in the literature on the resistivity of Geopolymer concrete, though normal concretes have been studied[7] at different ages. Concrete resistivity can be used to assess the corrosion probabilities as suggested by CEB (1989)[8], which are presented in Table 7

Table 7 CEB (1989) assessment criteria for resistivity

Concrete Resistivity (ohm-m)	Likely Corrosion Rate
> 20	Negligible
10 - 20	Low
5 – 10	High
< 5	Very High

2.3.3 Alkalinity studies

The highly alkaline environment, i.e., pH >12.5[9], in the concrete favors the passivation of steel, thereby limiting the corrosion of steel in concrete. In case of Portland cement concrete the alkaline environment is largely provided by the alkalis from the cement and the $Ca(OH)_2$ produced during the hydration of cement. This $Ca(OH)_2$ content may drop below the level required for passivation of steel, due to leaching of $Ca(OH)_2$ out of concrete and/or its conversion to calcium carbonate by atmospheric carbonation. In the present investigation, alkalinity of the different concretes was evaluated at the age of 28 and 90 days.

2.3.4 Corrosion potential of steel in concrete

ASTM C876-80[10] is a method to measure the reinforcement potential with reference to copper/copper sulfate electrode. Earlier investigators[11-12] used saturated calomel electrode (SCE) and conditioned freely corroding zinc as a reference electrode particularly for marine environment and proved that with this electrode stable and reproducible results can be obtained.In this study, the open circuit potential of steel in different concretes was measured using a saturated calomel electrode (SCE i.e. Ag/AgCl). Also, the limits suggested by ASTM C876-80 for $Cu/Cu(SO)_4$ reference electrode were appropriately modified by adopting standard conversion factors given by Shrier (1980)[13] for different electrodes and the corrected probabilities are presented in Table 8. The details of specimen used is shown in Fig.1

Table 8 Corrosion probability from half-cell potentials of steels in concrete (based on ASTM C 876 (2008)[2] and Shrier (1980)[13])

Probability of Corrosion (%)	E_{corr}(mV)		
	$Cu/CuSO_4$	Ag/AgCl (SCE)	Zn in sea water
5 % (no corrosion will occur)	> -200	> -120	>-920
50 % (uncertain)	-200 to -350	-120 to -270	-920 to -770
95 % (corrosion will occur)	< -350	< -270	< -770

2.3.5 Chloride permeability studies

In this study, the rapid chloride permeability test as per ASTM C1202[14] was used to rapidly assess the chloride permeability of different types of concrete. The test setup is shown in Fig.2. For this test 100 mm diameter x 50 mm thick specimens were used. Further, the resistance was also calculated based on initial current at 60 V, and an initial resistivity value was calculated for all concretes. The concrete quality was assessed based on the limits given by ASTM C1202 (Table 9).

Fig.2 Chloride permeability test setup

Table 9 ASTM 1202 assessment Criteria for chloride permeability

Chloride Permeability	Charge passed (Coulombs)
High	> 4000
Moderate	2000 to 4000
Low	1000 to 2000
Very low	100 to 1000
Negligible	< 100

3. Results And Discussion

3.1 Resistivity

The evolution of resistivities with age of all concretes is presented in Table 10. Figs. 3 to 5 show the variation of resistivities of the different concretes with age. Geopolymer concretes showed higher resistivity values compared to normal concretes. It can be seen that the resistivity of all Geopolymer concretes does not increase with age. The resistivity of the concrete can be related to the permeability characteristics of the concrete. Higher the permeability, higher the water absorption, and lower is the resistivity. The higher resistivity in the Geopolymer concretes can be attributed to reduced pore connectivity, as well as to the absence of free water. It was also observed that both normal and Geopolymer concretes at 90 days showed negligible rate of corrosion as per the limits suggested by CEB (1989) presented in Table 7.

Table 10 Resistivity of concretes investigated

S. No	Concrete	Resistivity (Ω m)				
		at 1	at 3	at 7	at 28 days	at 90
1	2NC	-	8	15	24	57
2	2GC	-	90	92	94	94
3	4NC	13	18	24	40	66
4	4GC	-	12	12	128	13
5	6NC	23	28	35	52	78
6	6GC	-	13	13	139	14

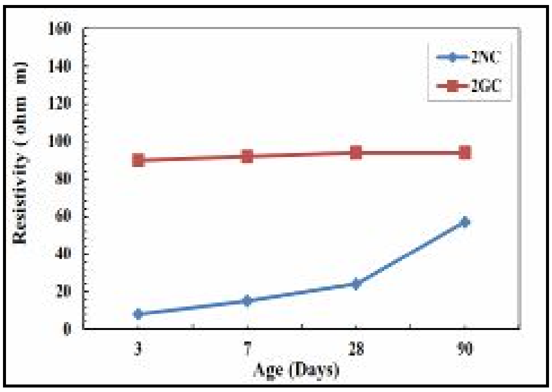

Fig. 3 Resistivity variation with age for 20 MPa concrete

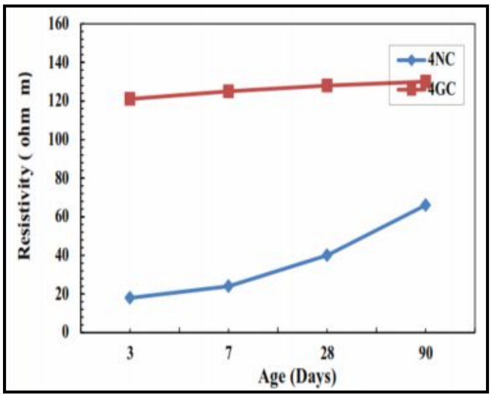

Fig. 4 Resistivity variation with age for 40 MPa concrete

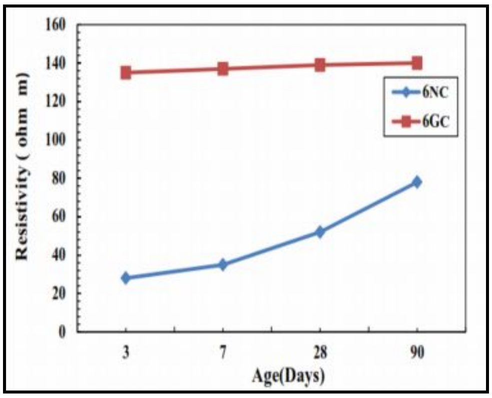

Fig. 5 Resistivity variation with age for 60 MPa concrete

3.2 Alkalinity studies

The results of pH measurements are given in Table 11. These indicate that the pH values did not vary significantly for different fly ash contents. All the Geopolymer concretes and normal concretes show pH of around 12.0. All these values were observed to be above the threshold value of 9.5 mentioned earlier by Hobbs (1988)[15] as necessary for depassivation, and also the threshold value for the initiation of corrosion (CEB, 1989). Further, the grade of concrete had no specific effect on the alkalinity,which agrees well with literature[16].

Table 11 Alkalinity of concretes

S.No	Concrete	Alkalinity (pH)	
		at 28 days	at 90 days
1	2NC	11.35	11.53
2	2GC	12.19	12.20
3	4NC	12.04	12.45
4	4GC	12.14	12.22
5	6NC	12.32	12.54
6	6GC	12.22	12.30

3.3 Potentials

The potentials obtained are presented in Table 12, and in Figs.6, 7 and 8. It can be seen that the potential values generally tend to decrease with age. Since the values obtained at later ages are more reliable[17], only the potentials obtained at 90 days are considered for further discussion. From the results, it can be seen that Geopolymer concretes showed higher potential values (50% Probability of corrosion) compared to normal concrete at a period of 90 days. It should be noted that the saturated state of the specimen is expected to give potentials that are more negative than in realistic conditions. Therefore, the corrosion potentials can be misleading[18]. Also, the half-cell potentials "may or may not be indicators of corrosion current" (ASTM C 876) and, therefore, cannot be taken as absolute indicators of corrosion reactions. Similar to normal concrete potential values increased with increase in strength for Geopolymer concrete. From the limits given in Table 8, we can observe that most of the potentials are in the range of "uncertain" corrosion probability i.e. 50% probability of corrosion. However, the potential for 40 and 60 MPa strength concretes is close to the limits indicating high probability that corrosion will not occur. It is noted in all the concretes that the potential is decreasing with age in case of normal concrete, but there is not much variation in case of Geopolymer concrete; however the probability of decrease in potentials will not be there in Geopolymer concrete as 90 % of reaction is completed within 3 days, and there will be only slight variation in potentials as shown by the trend in Figs. 6 -8.

The reason could be the shorter duration of test period, which is inadequate to form the stable passive film on the steel surface. It is known that to form the passive film (γ – FeOOH)[19] on the steel surface, a longer period of at least 1 year is required. The potentials which are obtained in these tests are nothing but the corroding potentials of this passivating film. Therefore, it is difficult to assess the corrosion characteristics through potential measurement within a short duration, as attempted in this study.

Table 12 Half-cell potentials of steel in concretes

		Potentials (- mV)				
		at 1	**at 3**	**at 7**	**at 28**	**at 90**
1	2NC	325	348	321	310	297
2	2GC	-	195	200	177	165
3	4NC	256	210	197	189	170
4	4GC	-	152	165	145	120
5	6NC	280	210	165	167	90
6	6GC	-	119	121	120	110

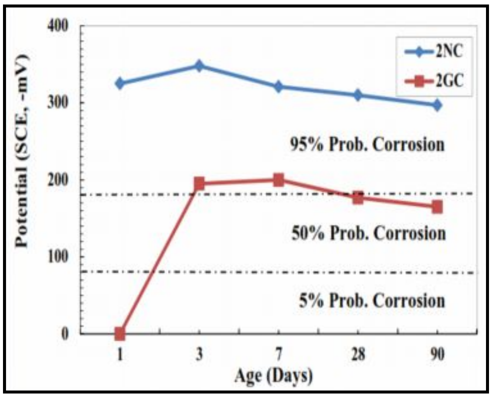

Fig. 6 Variation of potentials with time for 20 MPa concrete

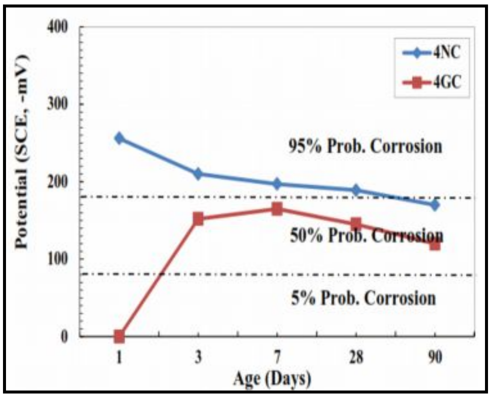

Fig. 7 Variation of potentials with time for 40 MPa concrete

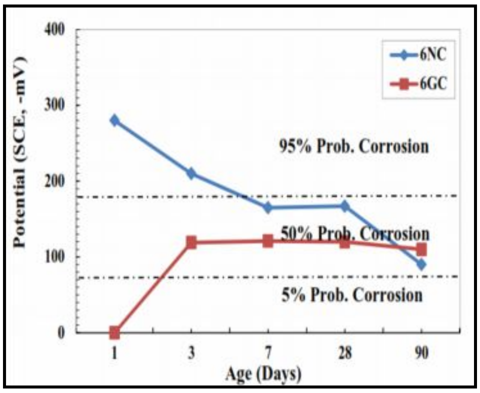

Fig. 8 Variation of potentials with time for 60 MPa concrete

3.4 Chloride permeability

The results clearly show that all the normal concrete specimens were still in an active state.

In all three categories (strength grades) of concrete, the normal concretes were placed in one category lower than the corresponding Geopolymer concretes as per the ASTM C1202 assessment criteria. It can be concluded from this investigation that although the amount of total charge passed in Geopolymer concrete is higher than normal concrete (Fig. 9). The higher chloride permeability values for the geopolymer concretes can be attributed to the presence of the unreacted alkali cations.

Table 13 Rapid chloride permeability test results

Time min.	2NC	2GC	4NC	4NC	6NC	6GC
0	0.143	0.22	0.042	0.122	0.034	0.071
30	0.141	0.214	0.044	0.124	0.035	0.072
60	0.145	0.214	0.044	0.124	0.037	0.071
90	0.143	0.216	0.046	0.126	0.037	0.071
120	0.141	0.216	0.046	0.126	0.037	0.071
150	0.141	0.216	0.046	0.126	0.037	0.071
180	0.143	0.217	0.047	0.127	0.038	0.071
210	0.143	0.218	0.048	0.128	0.038	0.071
240	0.141	0.219	0.049	0.129	0.038	0.071
270	0.141	0.219	0.049	0.129	0.039	0.071
300	0.141	0.220	0.050	0.130	0.039	0.071
330	0.141	0.220	0.050	0.130	0.039	0.071
360	0.141	0.220	0.050	0.130	0.039	0.071
Total charge passed (coulomb))	3065	4698	1030	2754	815	1536

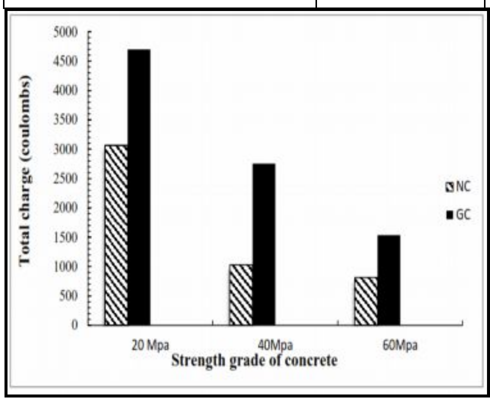

Fig. 9 Chloride permeability Characteristics of concrete

4. Correlations Between Different Parameters Investigated

The results of the corrosion studies were re-examined to study the relationships between the different parameters investigated. The different relationships between 90 day compressive strength, potentials and resistivity are presented in Figs.10 and 11. In general, the resistivity increased with increasing strength for normal and Geopolymer concretes. The relation between 90 day strength and potentials showed that as the strength increased the potentials decreased to levels below the 5% probability of corrosion. Geopolymer concretes generally showed lower potentials than normal concretes at all the strength grades. These results show that for normal concretes, as the strength increases, the initial current and 6 hours charge also decreases. On the other hand, for Geopolymer concretes, in spite of higher initial currents, the 6 hours charge passed is low, which indicates the lower penetration characteristics of Geopolymer concretes.

In general, for equivalent strength:

1. Potentials are lower for Geopolymer concrete

2. Resistivites are higher for Geopolymer concrete

3. Intial currents are higher for Geopolymer concrete

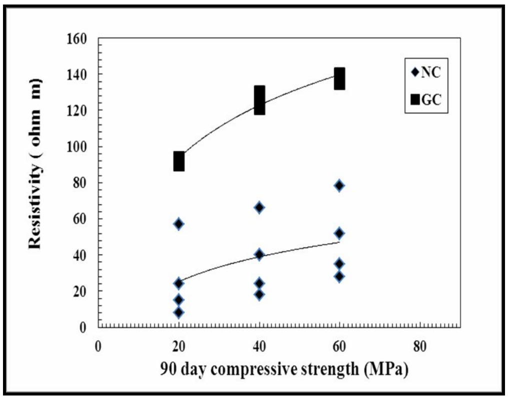

Fig. 10 Variation of resistivity with Strength

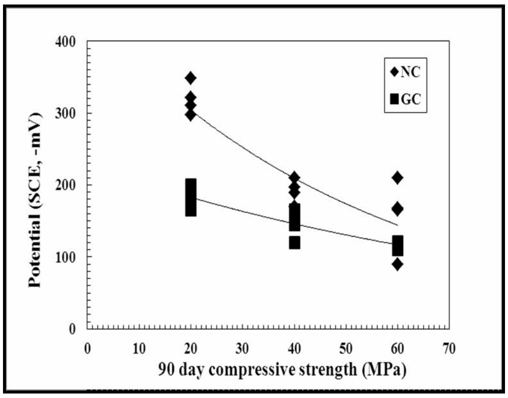

Fig. 11 Variation of potential with Strength

5. Conclusion

1. Resistivities of Geopolymer concrete were higher than normal concrete for all strength grades. The higher resistivity of Geopolymer concrete is due to reduced pore connectivity and absence of free water. All the concretes were seen to be "very good" in terms of the resistivity values, as per the guidelines given by CEB (1989).
2. The variation of fly ash content or variation in the activator solution did not have any influence on the alkalinity of Geopolymer concrete. The pH values measured from the inner core samples show that Geopolymer concretes possessed pH close to 12, well above the threshold limit of 9.5 as necessary for depassivation of steel[13].

3. Half-cell potentials of most Geopolymer concretes were in the range of 'uncertain' corrosion probabilities. However, the potentials for 40 and 60 MPa strength concretes were close to the limits indicating high probability that corrosion will not occur. All the Geopolymer concretes can be classified as having "low to moderate corrosion" potential, according to the assessment criteria[15].
4. Geopolymer concretes showed significantly higher chloride permeability values compared to the corresponding normal concretes, due to the presence of unreacted alkali cations in the system.

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