Further, the water in blast furnace slag cement is present in a much finer pore distribution than that of plain cement. The presence of moisture in a much finer pore structure impedes the access of oxygen. Due to the limited access of oxygen, the passive film cannot be maintained, as such embedded steel may become active. The corrosion rate, however, remains very low - as low or lower than in the passive state [14]. However, if the specimens are allowed to dry, thus making more oxygen available, the steel will repassivate easily. In summary, the high potentials measured in the blast furnace slag cements, do not indicate initiation of corrosion. ASTM C 876 criterion of -270 mV SCE for initiation of corrosion are not useful for detecting the onset of corrosion in blast furnace slag cements [15]. Another criterion normally used to detect corrosion initiation is a substantial increase in the corrosion activity marked by a sudden jump in the half-cell potential-time curve. Such a transition has not been observed in the potential-time curve for bars in blast furnace slag cement concrete. This indicates that reinforcement steel in the blast furnace slag cement concrete is in a passive condition, i.e., corrosion has not yet initiated.

The half-cell potentials of steel in plain, fly ash, silica fume and blast furnace slag cements exposed to the test solution for 540 days are shown in Figure 5. These data indicate a better performance by blended cements, viza-viz corrosion of reinforcement. The best performance was indicated by silica fume cement concrete, followed by blast furnace slag, fly ash and Type I cement concretes in decreasing order. The half-cell potentials of steel in Type I, fly ash, blast furnace slag and silica fume cement concretes being - 773, -751, -585, and -240 mV SCE respectively.

The corrosion rate of bars in specimens placed in the test solution for 540 days and measured using linear polarization resistance technique are shown in Figure 6. The corrosion rate of steel in plain cement concrete was 42  $\mu$  m/year, compared to a value of 17  $\mu$  m/year detected in fly ash blended cement concrete. The average corrosion rate of bars in blast furnace slag cements was 4  $\mu$  m/year, while steel was corroding at a negligible rate of 1.5  $\mu$  m/year in silica fume cement concrete.

### DISCUSSION

The effect of chloride-sulfate solution on the durability performance of plain (Type I) and blended cements was evaluated by studying its effect on surface deterioration, loss in cohesion resulting in reduction of strength, and reinforcement corrosion.

Blast furnace slag and silica fume cement mortar specimens exhibited a greater degree of surface deterioration compared to plain and fly ash blended cement mortar specimens. The degree of deterioration being greater in blast furnace slag cement compared to silica fume cement. Moderate deterioration was observed in plain and fly ash cement mortar specimens. Data on

reduction in compressive strength due to immersion in the chloride-sulfate solution show a similar trend.

The deterioration of silica fume cement specimens is attributed to the presence of  $Mg^{++}$  cations in the sulfate solution.  $Mg^{++}$  cation is known to be destructive to the hydrated calcium silicate hydrate (C-S-H) gel by partially converting it to a cohesionless, porous, reticulated magnesium silicate hydrate (M-S-H) gel. The enhanced deterioration of silica fume blended cement paste in the magnesium sulfate environment has also been observed by Cohen and Bentur [16]. They reported that brucite (MH) was not traceable in silica fume blended hardened cement pastes which had undergone deterioration due to magnesium sulfate attack. MH is relatively insoluble in water and is known to block the pores of the hardened cement paste matrix, thereby providing a protective shield to the ingress of sulfate ions. In view of this position it may be hypothesized that the absence of MH in the deteriorated silica fume blended cements, in contrast to its presence in plain cements, presents a more open structure thereby making silica fume blended cement concrete more vulnerable to magnesium-based sulfate attack.

Deterioration of the surface skin, leaving the aggregates exposed to environment (scaling), was also observed to be noticeably higher in blast furnace slag cement concretes compared to plain cements in exposure studies carried out by one of the authors [17]. Schroder and Smolzyck [18] commented that the vast majority of laboratory reports on blast furnace slag cement in sulfate and sea-water environments show high stability, but that a significant minority show poorer resistance. A minimum glass content of the slag (> 61%) was found to be necessary for improving the sulfate resistance of the blend [19]. The performance of fly ash blended cement in resisting sulfate attack is normally related to the C3A content of the cement. Building Research Establishment (BRE) [20] state that the net sulfate resistance of fly ash blended cements depend to some extent on the C3A content of the plain cement and BRE Digest 250 in its current form makes allowance for this by not equating the performance of these composite cements with that of sulfate resisting cement. Data developed in this investigation, though very limited in nature, support this hypothesis.

The corrosion data indicate that silica fume and blast furnace slag cement concretes have a definite superiority over both fly ash and plain cement concretes in resisting reinforcement corrosion in concretes exposed to high chloride-sulfate environments. Even though surface scaling and considerable reduction in strength was observed in the blast furnace and silica fume cement mortar specimens, the rate of reinforcement corrosion in concrete specimens made with these cements was much lower than in plain and fly ash cement concretes. The corrosion rate of steel in fly ash, blast furnace slag and silica fume concretes was 2.5, 10.5 and 28 times lower than in plain cement concrete. This indicates that surface deterioration of blended concretes when exposed to high chloride-sulfate environments does not accelerate the reinforcement corrosion process. Further, it should be realized that the magnitude of deterioration observed in the mortar specimens is probably due to the sample size. It is possible that surface deterioration and

reduction in strength due to sulfate ions in the actual structures may not be as high as that observed in the small laboratory specimens. In an investigation carried out by Al-Rabiah et al. [17], concrete specimens were placed in the splash zone at an exposure site on the Arabian Gulf, and the chloride concentration profiles after about 2 years of exposure were studied. The chloride concentrations although high on the surface in the blast furnace slag cement specimens, decreased very sharply at a depth of 10 mm. The chloride concentrations in plain cement were 3 to 5 folds higher compared to chloride concentrations in blended blast furnace slag cements.

In general, data developed in this investigation indicate that for high durability performance in environments characterized by the conjoint prevalence of high concentrations of chloride and sulfate salts, blending cements with either silica fume or blast furnace slag may prove useful in protecting the structures from reinforcement corrosion. Use of these cements, however, in such environments may be subject to deterioration due to sulfate attack, particularly if magnesium cation is associated with sulfate salts. A convenient approach can be the use of silica fume cements to alleviate the corrosion problem along with coating the concrete surface with a water-resistant epoxy-based coating to prevent surface deterioration of concrete elements due to sulfate attack.

## CONCLUSIONS

Mortar and concrete specimens prepared using Type I cement and Type I cement blended with fly ash, blast furnace slag and silica fume were immersed in a 2.1% SO<sub>4</sub><sup>--</sup> and 15.7% Cl<sup>-</sup> solution for a period of 540 days. The performance of these cements was evaluated by conducting visual inspection, and measuring reduction in compressive strength, and monitoring reinforcement corrosion using electrochemical techniques. The conclusions from the data developed in this study are:

- 1. Surface deterioration to a greater extent was observed in blast furnace slag and silica fume cement mortar specimens compared to that noted in mortar specimens made with Type I and fly ash cements.
- 2. The reduction in compressive strength due to immersion in the chloride-sulfate solution, was of the order of 70% in blast furnace slag cement compared to 50 and 25% respectively exhibited by silica fume and fly ash/Type I cements. The reduction in compressive strength in Type I and fly ash blended cement mortar was of a similar magnitude.
- 3. The corrosion rates of steel reinforcement embedded in silica fume and blast furnace slag cement concrete specimens partially immersed in chloride-sulfate solution was lower than in fly ash and Type I

cement concrete specimens. The corrosion rate of steel in silica fume, blast furnace slag and fly ash cement concretes was 28, 10.5, and 2.5 times lower than in plain cement concrete.

4. Data developed in this investigation indicate that for high durability performance, in environments characterized by the conjoint prevalence of high concentrations of chloride and sulfate salts, blending cements with either silica fume or blast furnace slag should prove useful in retarding reinforcement corrosion. Additional, precautionary measures like coating the exterior surface with a water-resistant epoxy-based coating will be necessary to protect concrete from exterior deterioration.

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Constituent (Wt. %)	Fly Ash	BFSC	Silica Fume	Type I Cement
Silicon Dioxide	52.3	27.7	92.5	20.5
Aluminum Oxide	25.2	12.8	0.4	5.6
Ferric Oxide	4.6	1.2	0.4	3.8
Calcium Oxide	10.0	44.0	0.5	64.4
Magnesium Oxide	2.2	8.8	0.9	2.1
Sulfur Trioxide	0.6	3.1	0.5	2.1
Loss on Ignition	0.4	0.9	2.6	0.7
Potassium Oxide		••	0.4	0.3
Sodium Oxide			1.1	0.2
C <sub>3</sub> S				56.7
C <sub>2</sub> S				16.1
C <sub>3</sub> A				8.5
C <sub>4</sub> AF			••	11.6

# TABLE 1--CHEMICAL COMPOSITION OF CEMENTS AND THE BLENDING MATERIALS

### **TABLE 2--AGGREGATE GRADING**

Coarse Aggregate (Crushed Limestone)		Fine Aggregate (Dune Sand)	
- Sieve opening (mm)	Cumulative % Retained	Sieve openin (mm)	ng Cumulative % Retained
19.0	10	4.75	0
13.0	45	2.4	0
9.5	80	1.2	0
4.75	100	0.6	3.8
		0.3	38.6
		0.15	78.1
		0.075	99.0

TABLE 3RESULTS	OF VISUAL	INSPECTION	OF SPECIMENS	IMMERSED
IN CHLORIDE-SULI	FATE SOLUT	TION FOR 540	DAYS	

Cement Type	Deterioration Rating	Observations
Type I Cement	2	Deterioration at edges
Type I + 20 % Fly Ash	2	Deterioration at edges
Type I + 10% Silica Fume	4	Deterioration of the surface skin,internal structure appears to be stable
Blast furnace Slag Cement	5	Deterioration of the surface skin, internal structure is not stable

\*A rating of 0 denotes no deterioration, while a rating of 5 denotes failure of the specimen.



Fig. 1--Test setup for corrosion monitoring



Fig. 2--Strength development in plain and blended cement mortar specimens



Fig. 3--Reduction in strength due to immersion in chloride-sulfate solution



Fig. 4--Potential-time record for steel in concrete partially immersed in chloride-sulfate solution