Influence of Coal Tar Epoxy Paint on Concrete Exposed to Sulfate Exposure

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Abstract – *The sulfate attack in concrete is a very common durability problem in concrete exposed to Sulfate environment. In real construction field concrete has to face such types of Sulfate exposure from different source like concrete in sewerage treatment plant, Effluent treatment plant, concrete in marshy organic soil, sea water where Sulfate concentration in soil or water is sufficient enough to initiate Sulfate attack in concrete .So different types of preventive measures are generally adopting in concrete either internally or externally to prevent Sulfate attack in concrete exposed to Sulfate environment. Here in this paper a detail research was carried out on different types of concrete specimen with or without protective surface coating of Coal tar epoxy paint exposed to 4% Na_2SO4 for a period of 12 month. From the experimental investigation it has revealed that concrete with coal tar epoxy painted surface shows excellent resistance against Sulfate attack in concrete than concrete samples without having coal tar epoxy paint on its surface. The research work also shows that even the concrete is being treated internally like using of pozzolonic materials like Fly ash and GGBS partially along with Portland cement used in the concrete, but still it has been observed that the concrete with surface coating by using coal tar epoxy paint shows more resistive and durable than concrete without having surface protection by using coal tar epoxy paint.*

Key Words: Portland cement CEM-I, Fly ash, GGBS, Coal tar Epoxy, Ettringite, SEM, EDS.

1. INTRODUCTION

The Sulphate attack in concrete is one of the important durability problem in concrete used in industrial application and also concrete exposed to sea water and marshy organic soil where sulphate concentration ($SO4^-$) in water or soil is sufficient enough to initiate sulphate attack in hardened concrete, which in turn formation of Expansive Ettringite compound within the hardened cement paste & resulting disruption of concrete start from concrete core to surface due to its continuous increase in volume within the same specified volume [3]. Considering the durability problem of concrete exposed to sulphate exposure there are many ways of preventive measures are usually adopting in practice either internally or externally. The present study was conducted on concrete sample which were treated both internally by using different form of cement, partial substitution of Portland cement with Fly ash and GGBS and the same sample with application of coal tar epoxy paint on its surface & were allowed to expose to 4% Na_2SO_4 for a period of 12 month. The samples after 12 month of exposure in 4% Na_2SO_4 are investigated for both physical damage with mass losses and microstructural studies of concrete through SEM and EDS on the specimen collected from the samples after the exposure period. The investigation results shows that concrete with external protective coating of coal tar epoxy paint shows no physical damage & negligible mass losses than concrete samples with different form internal preventive measure like using of composite cement and substitution of Portland cement with Fly ash & GGBS in concrete but without any protective coating of coal tar epoxy paint on its surface.

2. MECHANISM OF Na_2SO_4 ATTACK IN CONCRETE

The Sodium Sulfate attack in concrete is more severe and detrimental than Calcium sulfate attack in concrete due to high solubility of Sodium sulfate than Calcium sulfate. The sodium sulfate is reacting with hydration product of cement Calcium hydroxide present in concrete to form Calcium sulfate (gypsum), which is then react with Tri calcium aluminate (C_3A) to form Calcium Sulphoaluminates (Ettringite) which is hydrophilic in nature & absorb water resulting increase in volume within the hardened concrete & disruption of concrete will start [6] .The step wise reaction mechanism of Sodium sulfate in concrete are hereby stated below in equation (1) and (2).

Step-I: $Na_2SO_4 + Ca(OH)_2 = CaSO_4 .2H_2O + NaOH$ (1)

Step-II: $3CaSO_4.2H_20 + 3C_3A + 26\ H_2O = C_3A\ 3CaSO_432H_2O$ (Ettringite) (2)

3. MATERIAL AND METHOD

The materials used for the research work are different form of cement like Portland cement CEM-I, Composite cement CEM-II/A-M and CEM-II/B-M as per BSEN-197, Part-1 and pozzolonic materials Fly ash (F-type) and GGBS as a partial substitute of Portland cement in concrete. The coarse aggregate used for the experiment is of crushed Basalt rock & Fine aggregate of coarse river sand. The high range water reducing admixture is used in the concrete is of PC based water reducing admixture. The control mix concrete grade used for the research work was C-30/37 grade concrete with Portland cement CEM-I , 438 kg/m3 , Coarse aggregate 1142 kg/m3 , Fine aggregate content 685kg/m3 , water content

175kg/m3 and Superplasticizer 3.5kg/m3. The test properties of different materials used in the research work are tabulated below.

Table-1
Physical properties of different form of cement and Pozzolonic materials Fly ash & GGBS.

Test Parameter	Sp Gravity	Fineness in m2/kg
CEM-I	3.15	365
CEM-II/A-M	3.01	328
CEM-II/B-M	3.11	369
Fly Ash	2.31	234
GGBS	2.92	323

Table-2
Chemical composition of different form of cement and pozzolonic materials Fly ash and GGBS.

Compound %	CEM-I	CEM-II/A-M	CEM-II/B-M	Fly Ash	GGBS
CaO	63.7	62.5	57.58	2.15	39.3
SiO_2	21.68	20.32	23.71	57.4	34.7
Al_2O_3	5.12	4.28	6.34	22.8	18.93
Fe_2O_3	3.87	3.21	3.58	4.92	1.18
MgO	1.81	2.54	1.44	0.431	5.43
SO_3	1.22	3.11	2.38	1.27	0.765
Na_2O	0.176	0.342	0.096	0.35	0.276
K_2O	0.489	1.21	1.07	1.93	0.08

Table-3
Physical test parameter of Coarse Aggregate.

Parameter	Test Results
Sp Gravity	2.83
Dry rodded Bulk Density in Kg/cum	1627
Magnesium Sulphate Soundness in %	12
Combined Gradation (19 mm-12.5 mm) as per ASTM C-33	Satisfactory

Table–4
Physical test parameter of Fine Aggregate

Parameter	Test Results
Sp Gravity	2.57
75 micron passing in % by weight	1.56
Fineness Modulus	2.73
Water absorption in % by weight	1.51

Table-5
Test parameters of mixing water.

Test Parameter	Test Results
pH	7.6
Chloride in mg/l	234
Sulphate (SO_4^{-2}) in mg/l	2.6
TDS in mg/l	852

Table-6
Test parameters of Coal tar epoxy paint.

Test Parameter	Test Results
Colour	Black
Sp gravity	1.5
Pull off adhesion on concrete(Mpa)	2.6
Touch dry@ 30^0 C , Hours	2.5
Wet film thickness , micron	376

The details of different concrete mix proportions used in the experimental work with constant w/c ratio 0.4 , water reducing dosage of 3.5 kg/m3, Coarse aggregate 1142 kg/m3 , Fine aggregate 685 kg/m3 . The only changes in cementing materials for different sample ID as per the Table-7 as explained below.

Table-7
Test Cementing materials type and proportion in different Sample mix used for the experimental work.

Sample ID	Cement type and Qty in kg/m3	Fly Ash in kg/m3	GGBS in kg/m3
S-1 / S-1'	CEM-I ,438	0	0
S-2 / S-2'	CEM-II/A-M ,438	0	0
S-3 / S-3'	CEM-II/B-M,438	0	0
S-4 / S-4'	CEM-I, 372.3	65.7	0
S-5 / S-5'	CEM-I, 350.4	87.6	0
S-6 /S-6'	CEM-I, 328.5	109.5	0
S-7 / S-7'	CEM-I, 219	0	219
S-8 / S-8'	CEM-I, 175.2	0	262.8
S-9 / S-9'	CEM-I, 131.4	0	306.6

The casted samples were moist cured for 28-days and then after the samples were oven dried till it reaches stable weight. The oven dried samples (S-1 to S-9) which on which protective coating will not be applied shall be put in to 4% Na_2SO_4 solution for 24 hrs & then record the mass of cube specimens. However the sample (S-1' to S-9') immediately after oven dry apply two coat of coal tar epoxy paint were applied & were allowed for complete drying. Once the paint were dried then put the samples in 4% Na_2SO_4 solution for 24 hrs & then after record the mass of cube samples. The samples were then put in to 4% Na_2SO_4 solution for a period of 12- month. The samples after the test period of 12-month are then evaluated physically through mass changing record after the test period. The samples microstructure were also studied after the test period by using SEM and EDS on specimen collected from the exposed samples

Figure 1: Durability test of concrete with or without protective surface coating of coal tar epoxy paint on concrete surface exposed to 4% Na_2SO_4 solution

3. Results & Discussions

3.1 Physical Damage studies of Concrete.

The physical investigation of different concrete samples with or without protective surface coating of coal tar epoxy paint on concrete surface & 12- month exposure to 4% Na_2SO_4 solution effect on physical damage & changing of mass are hereby explained in Table-8 as follows.

Table-8
The physical & mass changing on different samples after 12- month exposure to 4% Na2SO4 solution.

Sample ID	Physical appearance of both coated & uncoated samples	Mass losses % of uncoated sample (S)	Mass losses % o coated sample (S'
S-1 and S-1’		4.75	0
S-2 and S-2’		5.23	0
S-3 and S-3’		5.82	2.1
S-4 and S-4’		3.25	1.01
S-5 and S-5’		1.73	0
S-6 and S-6’		1.12	0
S-7 and S-7’		6.31	1.07
S-8 and S-8’		2.75	0
S-9 and S-9’		1.31	0

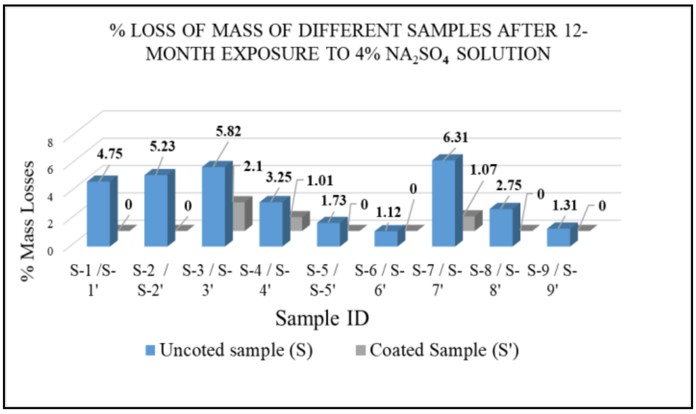

Figure-2: Mass losses of different samples with or without coal tar epoxy paint after 12-month exposure to 4% Na_2SO_4

From the physical investigation of all the coated and uncoated samples exposed to 4% Na_2SO_4 solution, it has been observed that samples with external protective coating of coal tar epoxy paint of 300-400 micron thickness shows minimum & significantly negligible physical damage and mass losses phenomenon of different concrete samples than samples without protective coating of coal tar epoxy paint, thus coal tar epoxy paint has excellent capability to make concrete impermeable and helps to resist penetration of Sulfate ions (SO_4^-) in concrete and resulting to make the concrete excellent resistance against sulphate attack. The coal tar epoxy paints helps to fill the both macro and micro pores in concrete surface & resulting formation of impermeable concrete. The research work also shows that even the concrete with Portland cement of limiting C_3A content up to 8% still it shows significant amount of physical damage & mass losses phenomenon in concrete due to Sulfate attack in concrete, but on application of coal tar epoxy paint on concrete surface even the cement is having high C_3A content in its composition, still the sample with protective surface coating of coal tar epoxy paint shows excellent resistance against sulfate attack. The research work also shows that physical damage is maximum in concrete with 50% GGBS and also concrete with Composite cement CEM-II.B-M[10] due to high Alumina content in GGBS as well as CEM-II/B-M[10] cement, however it is also observed that concrete with GGBS content more than 50% shows reduction in physical damages in concrete, thus the investigation revealed that high Alumina GGBS in concrete up to 50% shows adverse effect in concrete against sulfate attack while concrete with 70% GGBS shows improved resistance against sulfate attack in concrete. The physical damage in concrete with composite cement CEM-II/B-M [10] is higher than CEM-II/A-M[10] against sulfate attack, The research work also shows that concrete with Fly ash content as a partial substitute of Portland cement shows potential resistance against sulfate attack on increasing the Fly ash content in concrete, the experiment shows 25% Fly ash shows more resistance against Sulfate attack than 15% Fly ash.

3.2 Microstructural studies of both coated & uncoated concrete sample exposed to 4% Na_2SO_4 solution by using SEM & EDS

The SEM photographs of different samples and Elemental distribution of different concrete samples by using EDS after 12-month exposure to 4% Na2SO4 solution is here by stated below.

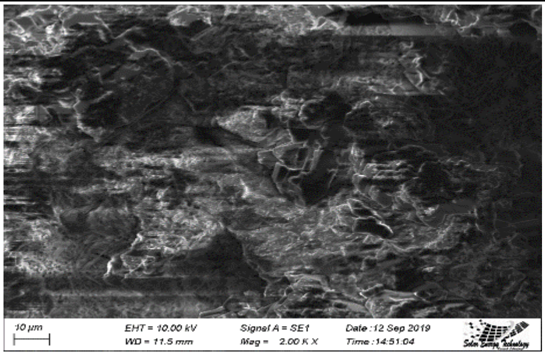

Figure 3: SEM Photographs of sample ID-S1

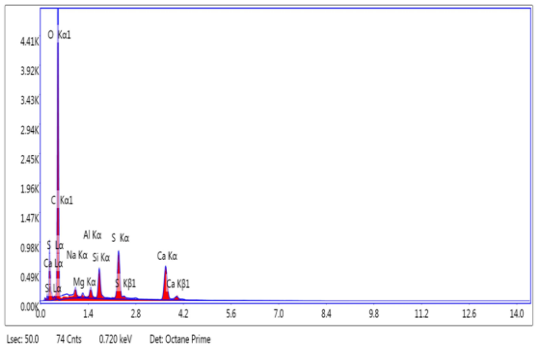

Figure 4: EDS of sample ID-S1

C	O	Na	Mg	Al	Si	S	Ca
9.94	50.95	0.77	0.39	1.31	4.11	10.9	21.56

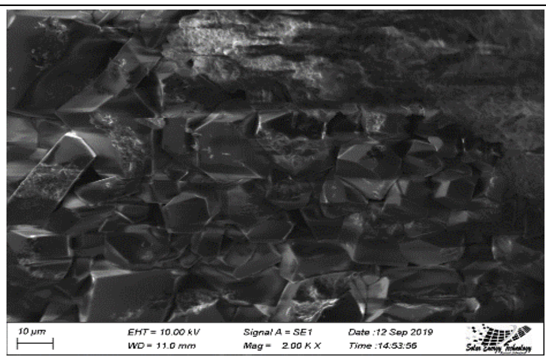

Figure 5: SEM Photographs of sample ID-S2

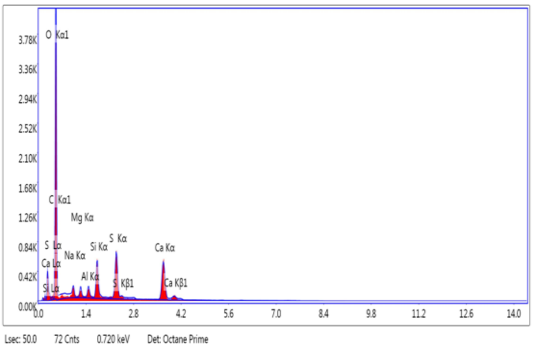

Figure 6: EDS of sample ID-S-2

C	O	Na	Mg	AI	Si	S	Ca
5.23	51.24	0.76	1.07	1.30	5.19	10.56	24.66

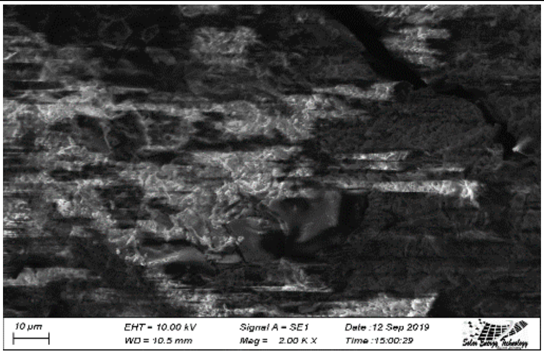

Figure 7: SEM Photographs of sample ID-S3

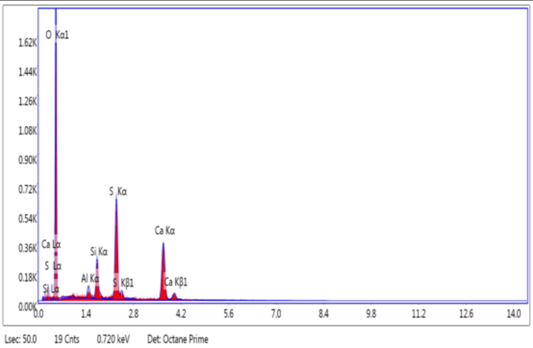

Figure 8: EDS of sample ID-S-3

C	O	Na	Mg	AI	Si	S	Ca
-	46.36	-	-	1.22	4.58	18.53	29.31

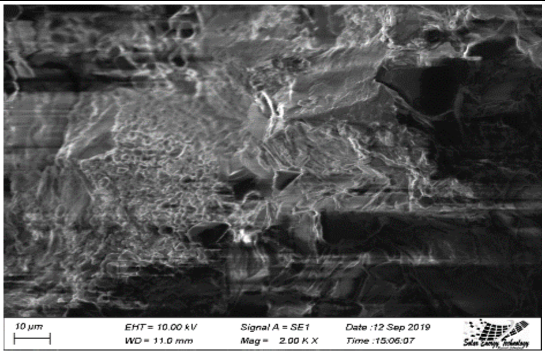

Figure 9: SEM Photographs of sample ID-S-4

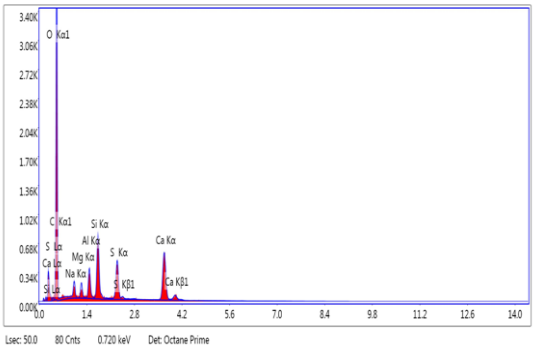

Figure 10: EDS of sample ID-S-4

C	O	Na	Mg	AI	Si	S	Ca
4.76	47.14	1.66	1.43	3.19	7.8	7.58	26.44

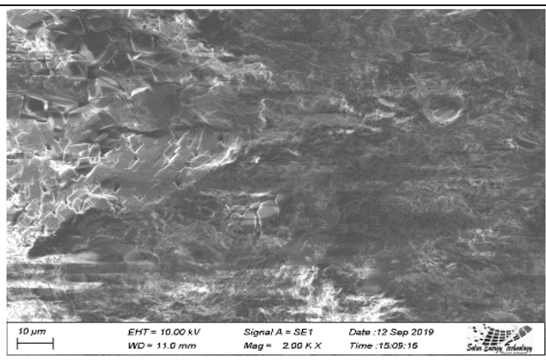

Figure 11: SEM Photographs of sample ID-S-5

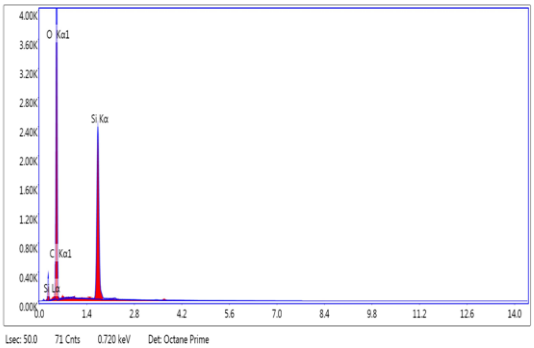

Figure 12: EDS of sample ID-S-5

C	O	Na	Mg	AI	Si	S	Ca
10.74	54.2	1.66	-	-	35.06	-	-

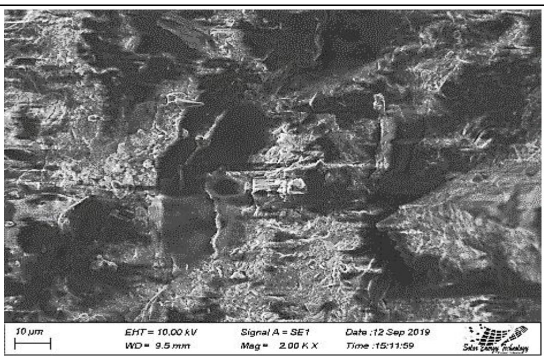

Figure 13: SEM Photographs of sample ID-S-6

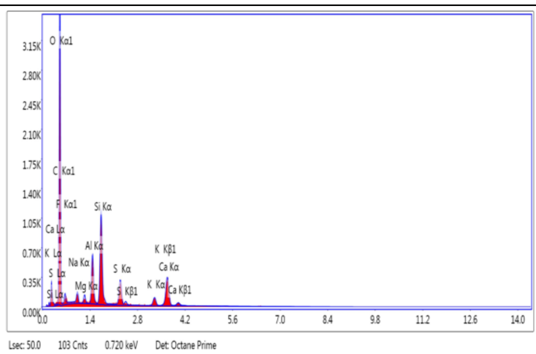

Figure 14: EDS of sample ID-S-6

C	O	Na	Mg	AI	Si	S	Ca
4.17	47.2	1.16	0.85	5.95	12.3	5.47	17.75

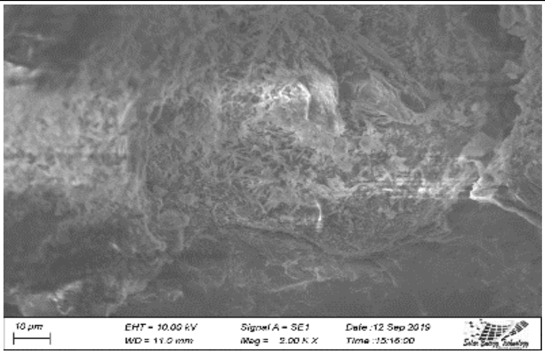

Figure 15: SEM Photographs of sample ID-S-7

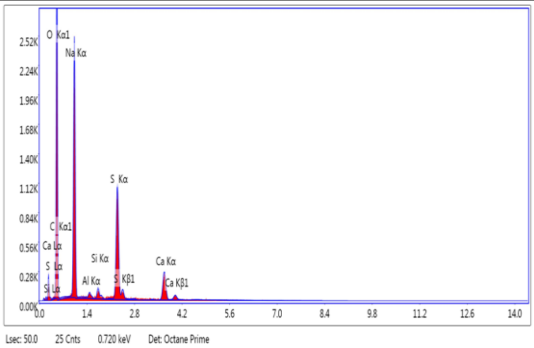

Figure 16: EDS of sample ID-S-7

C	O	Na	Mg	AI	Si	S	Ca
4.51	35.24	25.53	-	0.44	1.20	19.4	13.6

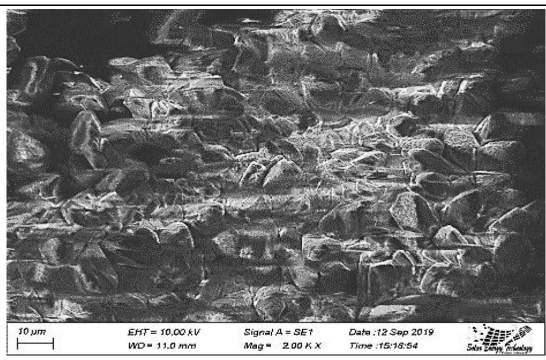

Figure 17: SEM Photographs of sample ID-S-8

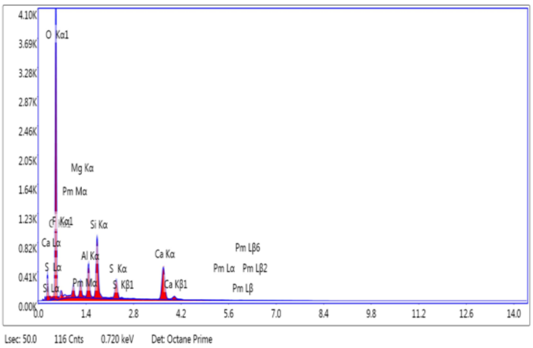

Figure 18: EDS of sample ID-S-8

C	O	Na	Mg	AI	Si	S	Ca
4.89	49.23	-	2.01	4.55	8.94	4.65	21.64

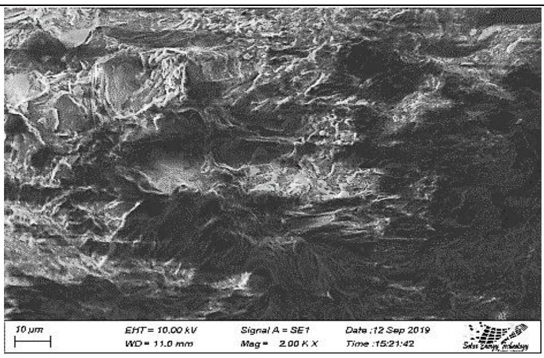

Figure 19: SEM Photographs of sample ID-S-9

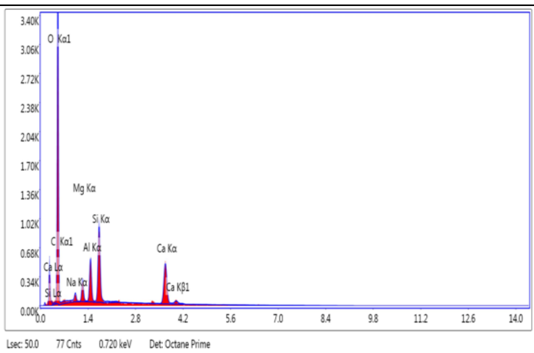

Figure 20: EDS of sample ID-S-9

C	O	Na	Mg	AI	Si	S	Ca
6.26	49.48	0.8	2.49	5.22	10.51	-	25.23

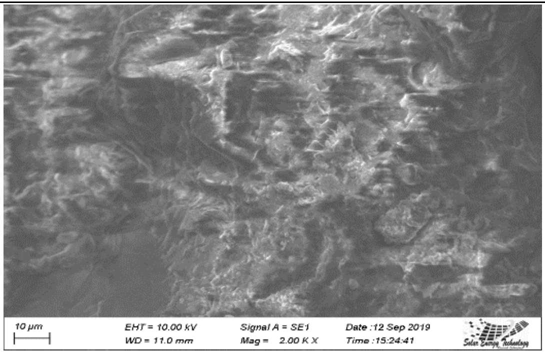

Figure 21: SEM Photographs of sample ID-S-1'

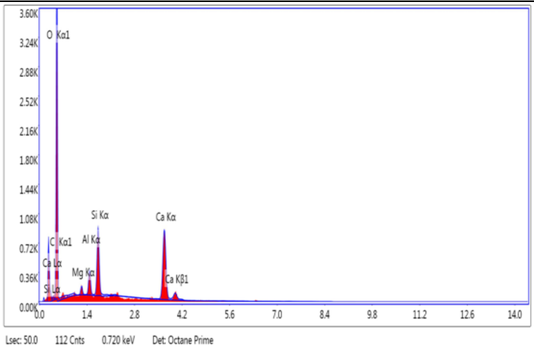

Figure 22: EDS of sample ID-S-1'

C	O	Na	Mg	AI	Si	S	Ca
6.31	47.6	-	0.81	2.46	7.44	-	35.39

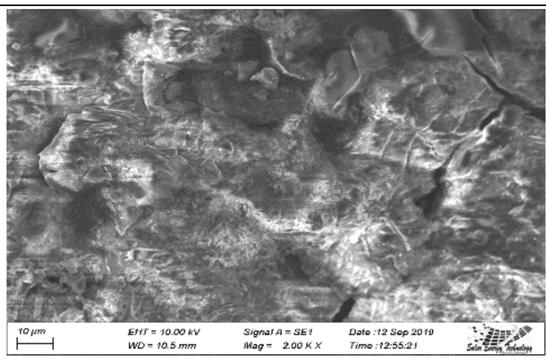

Figure 23: SEM Photographs of sample ID-S-2'

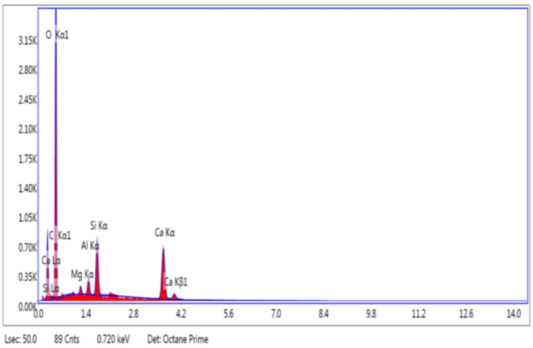

Figure 24: EDS of sample ID-S-2'

C	O	Na	Mg	AI	Si	S	Ca
-	49.5	-	1.23	13.75	23.2	-	7.19

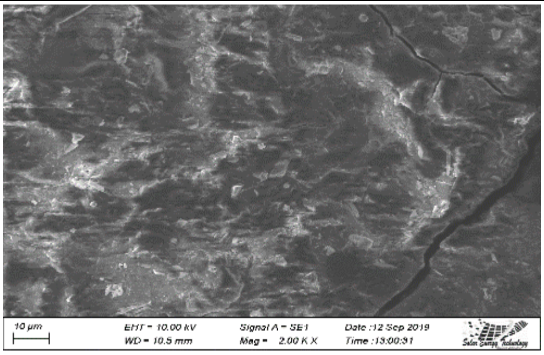

Figure 25: SEM Photographs of sample ID-S-3'

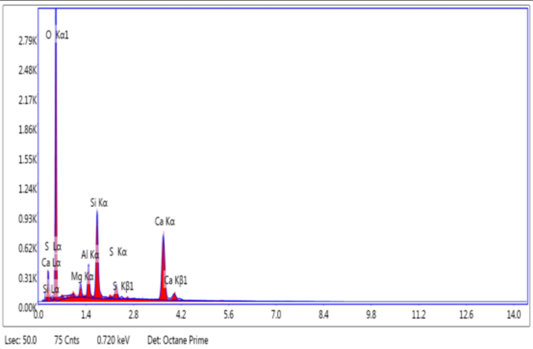

Figure 26: EDS of sample ID-S-3'

C	O	Na	Mg	AI	Si	S	Ca
-	48.1	-	1.33	3.4	10.0	2.65	34.51

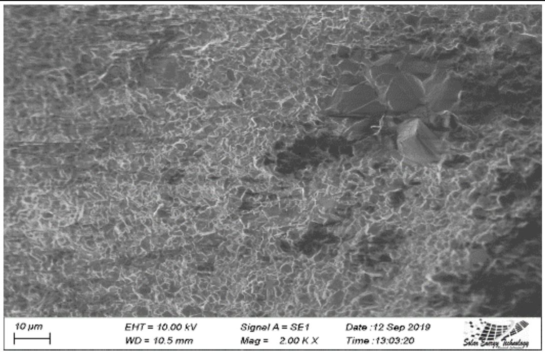

Figure 27: SEM Photographs of sample ID-S-4'

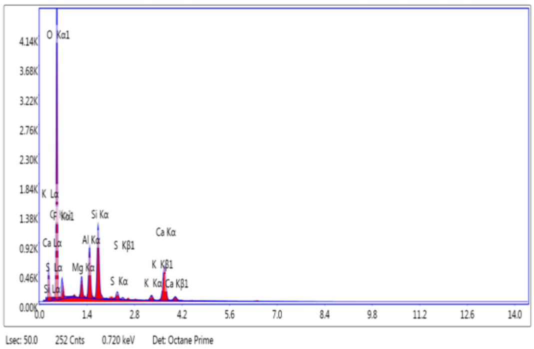

Figure 28: EDS of sample ID-S-4'

C	O	Na	Mg	AI	Si	S	Ca
5.76	47.6	-	2.26	6.25	9.83	1.52	21.48

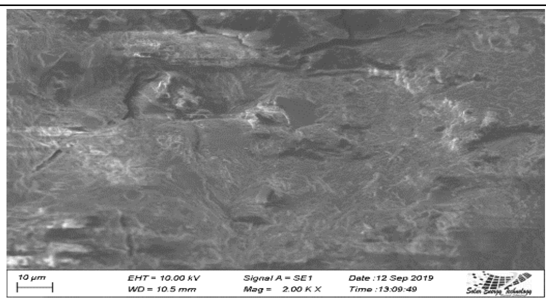

Figure 29: SEM Photographs of sample ID-S-5'

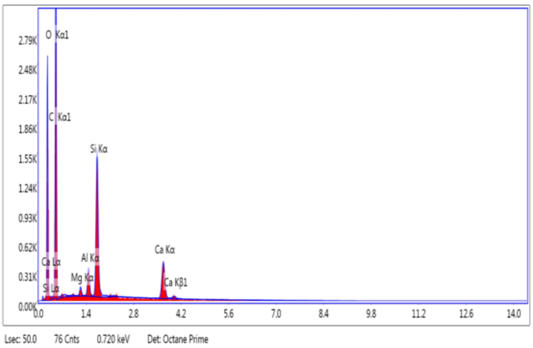

Figure 30: EDS of sample ID-S-5'

C	O	Na	Mg	AI	Si	S	Ca
26.3	39.4	-	0.67	2.45	14.2	-	16.9

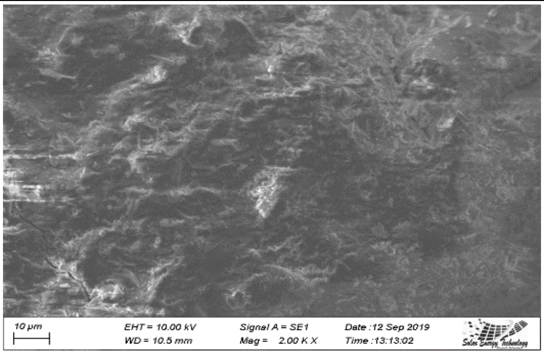

Figure 31: SEM Photographs of sample ID-S-6'

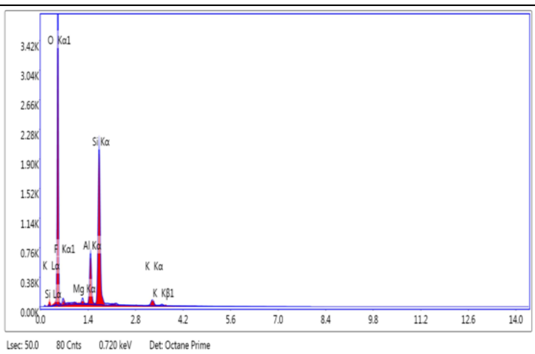

Figure 32: EDS of sample ID-S-6'

C	O	Na	Mg	AI	Si	S	Ca
51.18	1.17	-	0.88	9.35	33.0	0	-

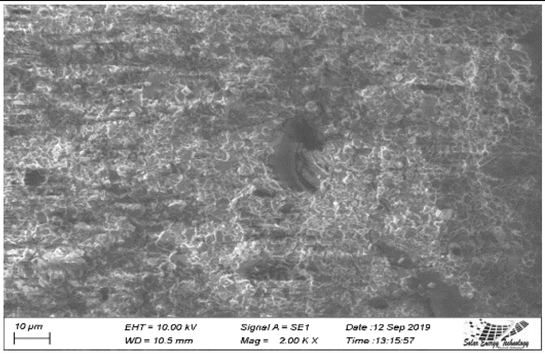

Figure 33: SEM Photographs of sample ID-S-7'

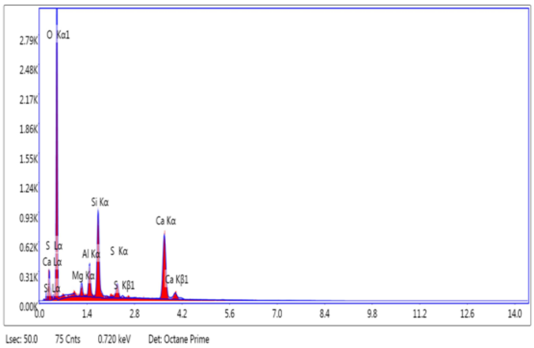

Figure 34: EDS of sample ID-S-7'

C	O	Na	Mg	AI	Si	S	Ca
44.65	30.89	1.10	0.93	2.13	8.88	3.72	11.52

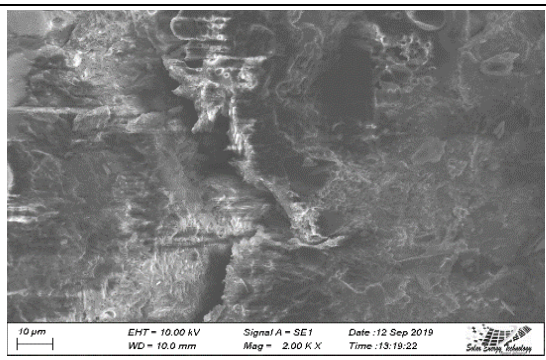

Figure 35: SEM Photographs of sample ID-S-8'

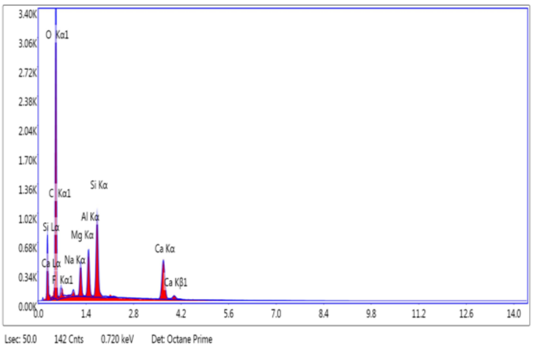

Figure 36: EDS of sample ID-S-8'

C	O	Na	Mg	AI	Si	S	Ca
9.52	46.25	0.52	3.54	5.31	10.5	0	22.63

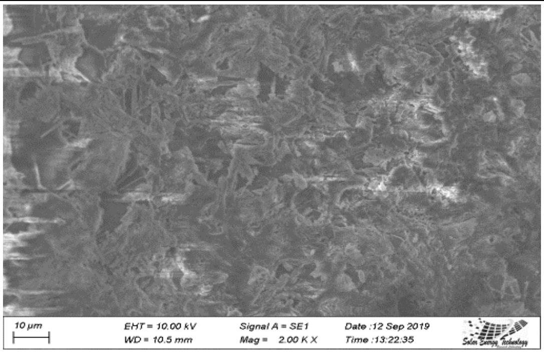

Figure 37: SEM Photographs of sample ID-S-9'

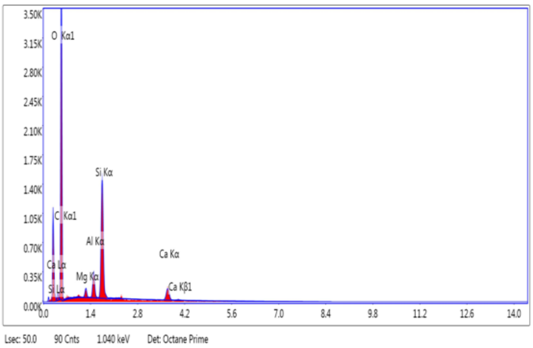

Figure 38: EDS of sample ID-S-9'

C	O	Na	Mg	AI	Si	S	Ca
2.15	48.13	-	1.07	3.49	18.0	-	8.10

Table -9
Sulphur & Calcium concentration of different samples after 12-month exposure to 4% Na_2SO_4 Solution.

Sample-ID	Sulphur & Calcium Concentration % wt in both coated & uncoated sample			
	Uncoated Samples		Coated Samples	
	S	Ca	S	Ca
S-1/S-1'	10.97	21.56	0	35.39
S-2/S-2'	10.56	24.66	0	7.19
S-3/S-3'	18.53	29.31	2.65	34.51
S-4/S-4'	7.58	26.44	1.52	21.48
S-5/S-5'	0	0	0	16.9
S-6/S-6'	5.47	17.75	0	0
S-7/S-7'	19.40	13.69	3.72	11.52
S-8/S-8'	4.65	21.64	0	22.63
S-9/S-9'	0	25.23	0	8.10

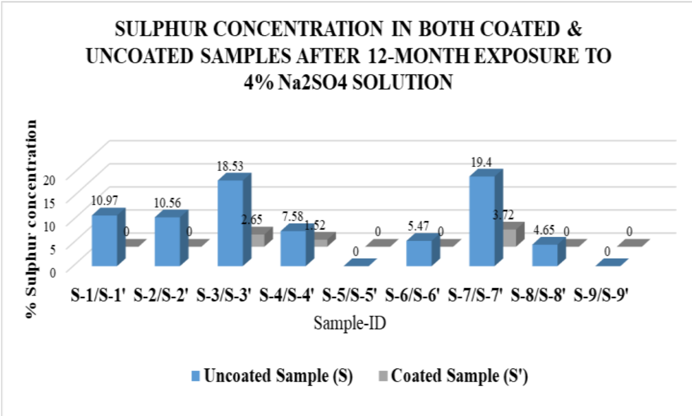

Figure-39: Sulphur concentration in both coated and uncoated samples after 12-month exposure to 4% Na_2SO_4 solution.

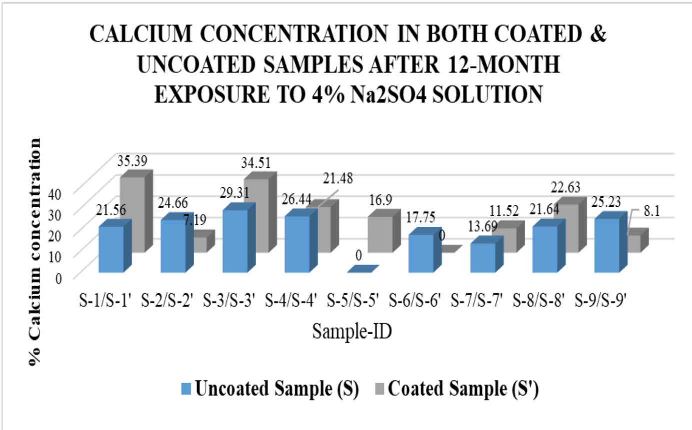

Figure-40: Calcium concentration in both coated and uncoated samples after 12-month exposure to 4% Na_2SO_4 solution.

From the microstructural studies of concrete samples after 12-month exposure to 4% Na_2SO_4 solution through SEM and

EDS it has been observed that the Sulphur concentration in the uncoated samples are very high whereas the Sulphur concentration in coated samples are nil or negligible in all different samples in a broad way , thus it is simply indicate that the Sulfate attack in concrete with coated samples are nil or negligible i.e. the influence of Sulfate ions in coated samples are nil or negligible, however concrete without any coating shows significantly higher amount of Sulphur concentration which is again indicate the influence sulfate ion (SO_4^-) in the concrete. In detail studies the result shows that uncoated concrete sample with Portland cement having C3A content less than 8% but still it has significant effect of Sulfate attack in the concrete. The Uncoated concrete samples with composite cement CEM-II/B-M [10] shows more concentration of Sulphur than CEM-II/A-M [10] which indicate that composite cement CEM-II/B-M[10] with higher alumina content shows more susceptible against sulfate attack in concrete. The results of the research work also shows that addition of 25% fly ash in concrete has more resistant against sulfate attack than concrete with 15% fly ash, thus addition of Fly ash in concrete as a substitute of Portland cement shows significant potential to resist sulfate attack in concrete. On the other hand uncoated concrete sample with GGBS up to 50% shows higher concentration of Sulphur, but on further increase in the dosage up to 70% it shows significant reduction in Sulphur concentration, thus it has been concluded that high Alumina GGBS with minimum dosage less than 50% is not effective against sulfate attack, but on further increase of dosage up to 70% shows significant reduction in Sulfate attack in concrete. After comparing both the ways of preventive measures for sulfate attack in concrete either internally or externally it has been observed that external treatment like coal tar epoxy paint application on hardened concrete surface shows excellent resistance against sulfate attack in concrete. However application of pozzolonic materials like Fly ash and GGBS as a partial substitute of Portland cement can reduce the sulfate attack in concrete up to some extent. From the EDS analysis it is also observed that % of Calcium is getting reduced on addition of pozzolonic materials in concrete due to pozzolonic reaction [3], thus reduction of Calcium % simply helps to mitigate sulfate attack in concrete.

4. CONCLUSIONS

The following are highlighted outcome of the research investigation:

- Concrete samples with coal tar epoxy paint shows no physical damage, no mass losses phenomenon after 12-month exposure to 4% Na_2SO_4 solution.
- The concrete samples without having coal tar epoxy paint shows significant physical damage & mass losses phenomenon after 12-month exposure to 4% Na_2SO_4 solution.
- The concrete with Portland cement CEM-I having C_3A content less than 8% still it shows significant influence of sulfate attack like physical damage & mass loss.
- The concrete with composite cement CEM-II/B-M [10] is more susceptible to sulfate attack than concrete with composite cement CEM-II/A-M [10].
- The concrete with Fly ash as a partial substitute of 25% shows more resistance against sulfate attack than concrete with 15% Fly ash.
- The concrete with 50%GGBFS adverse effect against sulfate attack in concrete due to its high composition of Alumina 18.93%. However high Alumina GGBS of 70% shows significantly higher resistance against sulfate attack.
- The application of high Alumina GGBS of minimum dosage (< 50%) in concrete is harmful against sulfate attack in concrete.

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