Sulphuric Acid Durability Studies of Concrete with Portland Cement (CEM-I), Portland Composite Cement of different Types (CEM-II/A-M &CEM-II/B-M) & Partial Replacement of Portland Cement with Different Types of Pozzolonic Materials

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Abstract - *The Sulphuric acid durability studies of concrete with different types of cement in a standard design mix of C-30/37 with Portland cement & complete replacement of Portland Cement (CEM-I) with Portland Composite cement of type CEM-II/A-M & CEM-II/B-M & also partial replacement of Portland cement (CEM-I) with 15%, 20% & 25% amount of Fly Ash & 50%, 60% & 70% amount of GGBFS in reference mix with normal Portland cement. In addition to the replacement of Portland Cement by other types of cement & partial replacement of Portland cement by using Fly ash & GGBFS , a mix with higher cement content than reference mix were used keeping all other ingredients remain same as per design mix of C-30/37 grade used for research work..*
To evaluate the durability performance of all different types concrete against Sulphuric acid attack, concrete cube specimens of 50mmx50mmx50mm sizes were kept submerged in 5% H_2SO_4 solution having pH value of 1 for 90-days continuously after 28-days of moist curing of cube specimen in normal water. From the experimental results it has been observed that concrete with higher amount of Portland cement has severely affected as compared to other mixes & at the same time mix with Portland composite cement of type CEM-II/B-M shows more durable against Sulphuric acid attack. It is also observed that on partial replacement of normal Portland cement(CEM-I) with pozzolonic material Fly ash of 25% & GGBFS of 70% shows more durable with regards physical damage against Sulphuric acid attack.

Key Words: Portland cement (CEM-I), Portland Composite cement (CEM-II/A-M & CEM-II/B-M), Fly Ash, GGBFS, Admixture, Sp Gravity, Fineness, Compressive Strength, SEM, EDS, Sulphur, Ettringite, Gypsum.

1. INTRODUCTION

Concrete is vulnerable to attack by Sulphuric acid produced from sewerage, Sulphuric acid dosing in power plant raw water system & sulphur dioxide present in the atmosphere. The acid attack on concrete is prominent due to its high alkalinity. Sulphuric acid attack is more corrosive in concrete is due to Sulphate ion involvement during sulphate attack & at the same time dissolution caused by Hydrogen ion [7]. Sulphate attack in concretes involves the formation of expansive sulphate phases like Ettringite ($3CaO\bullet Al_2O_3\bullet 3CaSO_4\bullet 32H_2O$), and gypsum ($CaSO_4$ $2H_2O$). Delayed Ettringite formation (DEF) in concrete is deleterious because it is highly expansive in nature & also it affect the main hydration product calcium silicate hydrate (C–S–H) phases, which lead to damage the concrete and loss of strength. [11].

$Ca(OH)_2 + H_2SO_4 = CaSO_4.2H_2O.$

$3CaO.2SiO_2.3H_2O+H_2SO_4= CaSO_4 .2H_2O + Si(OH)_4.$

$3CaSO_4 + 3Cao.Al_2O_3.6H_2O+25H_2O=3CaO.Al_2O_3.3CaSO_4 +31 H_2O$ (Ettringite).

The present study has been performed for evaluating the durability performance of concrete with different types of cement like Portland cement CEM-I , Portland Composite cement CEM-II/A-M & CEM-II/B-M , Partial replacement of Portland Cement CEM-I by Fly As & GGBFS concrete in 5% Sulphuric acid solution . An accelerated laboratory test was conducted for three months Sulphuric acid exposure to different types of concrete samples & subsequent physical test with internal microstructure analysis been performed by Scan Electron microscope (SEM) & Energy dispersive Spectrum (EDS) method.

2. MECHANISM OF H_2SO_4 ATTACK ON CONCRETE

Concrete is alkaline in nature due to presence of hydration product $Ca(OH)_2$ in concrete. In case acid concrete is attacked by an acid HX (X is negative ion of the acid), the reaction product with hydrated cementitious product in concrete [13] are as.

$Ca(OH)_2 + 2\ HX = CaX_2 + 2H_2O$

The decomposition of concrete is depend on the permeability of concrete & also amount of $Ca(OH)_2$ generated in concrete. The sulphuric acid attack on concrete too much damaging due to combined effect of acid attack & Suphate attack [12]

3. MATERIAL USED FOR EXPERIMENT

The materials used for experimentation in this research include; Ordinary Portland cement (CEM-I, 52.5 N Class as per BSEN-197-1), Portland Composite Cement (CEM-II/A-M

& CEM-II/B-M as per BSEN-197-1), Fly Ash (F-type) , GGBFS (As per BS6699), Fine aggregate (FM=2.7) ,Coarse aggregate (Crushed Basalt stone aggregate) of 19mm nominal size and PC based super plasticizer . The test properties of all the materials used in research samples are tabulated here. The physical & chemical composition of different types of cement, SCM like Fly Ash & GGBFS used for experiment are tabulated here.

Table-1: Physical properties of different types of cement.

Test Parameter	Portland cement CEM-I Class 52.5N	Portland composite cement CEM-II/A-M	Portland composite cement CEM-II/B-M
Sp. gr	3.15	2.7	2.8
Blaine-fineness (Cm^2 /gm)	3630	3230	3670
Sulphate Resistance at 14 days % expansion	0.014	0.011	0.01
Soundness (Le- Chat.) mm	0.7	2	1.5
Compressive strength at 7 Days	47.3	38.5	36.5
Compressive strength at 28 Days	55.2	48.4	48.4

Table-2: Chemical composition of different types of cement.

Component %	Portland cement CEM-I class 52.5N	Portland composite cement CEM-II/A-M	Portland composite cement CEM-II/B-M
CaO	63.9	62.6	57.6
SiO_2	21.7	20.3	23.3
Al_2O_3	5.19	4.23	6.31
Fe_2O_3	3.86	3.2	3.57
MgO	1.8	2.52	1.41
SO_3	1.21	3.0	2.37
Na_2O	0.172	0.338	0.098
K_2O	0.439	1.02	1.08

Table-3: Physical properties of Fly Ash & GGBFS.

Test Parameter	Fly Ash	GGBFS
Sp Gravity	2.2	2.8
Blaine-Fineness (cm^2/gm)	2240	2950

Table-4: Chemical composition of Fly Ash & GGBFS.

Component %	Fly Ash	GGBFS
CaO	2.87	38.2
SiO_2	56.3	35.5
Al_2O_3	23.6	18.7
Fe_2O_3	4.96	1.06
MgO	0.424	5.21
SO_3	1.22	0.727
Na_2O	0.33	0.245
K_2O	2.09	0.004
MnO	0.0416	0.595
TiO_2	0.476	0.400
P_2O_5	0.453	0.0172

Table-5: Physical properties of Coarse Aggregate.

Test Parameter	Test Results
Sp Gravity	2.87
Dry rodded Bulk Density in Kg/cum	1678
Water absorption in %	0.43
Aggregate Impact value in %	11.41
Loss Angel Abrasion in %	0.424
Flakiness Index in %	21.22
Elongation Index in %	23.5
Magnesium Sulphate Soundness in %	14
Grading Requirement (19-4.75 mm) as per ASTMC33	Satisfactory as per ASTMC33

Table –6: Physical properties of Fine Aggregate

Test Parameter	Test Results
Sp Gravity	2.54
75 micron passing in % by weight	1.75
Fineness Modulus	2.70
Water absorption in % by weight	1.54

Table-7: Properties of mixing water.

Test Parameter	Test Results
pH	7.5
Chloride Content in mg/l	250
Sulphate content (SO_4^{-2}) in mg/l	1.8
Total solids in mg/l	750
Total Alkalinity as $CaCO_3$ in mg/l	285

3.1 Mix proportioning & Specimen preparation

The specimen sizes of concrete150mm x 150 mm x150 mm cube were used for compressive strength as per BSEN 12390-3. The specimen sizes used for Sulphuric Acid durability test was 50mm x 50mm x 50mm cubes. The grade of concrete was used for reference Mix (M1) was C-30/37 with Portland cement (CEM-I ,52.5 N class as per

BSEN-197,Part-1) & subsequently mix by changes of Portland cement of reference mix M1 with different types of Portland composite cement of CEM-II/A-M & CEM-II/B-M (M_3 & M_4) & also mix with partial replacement of Portland cement (CEM-I) of reference mix M_1 with 15%,20%& 25% Fly Ash (M_5,M_6&M_7)& 50%,60%&70% GGBFS (M_8,M_9&M_{10}) keeping other ingredient of mixes are same as reference concrete mix (M_1)of C-30/37 grade concrete . The following are the details of different mix proportion used for research work.

I. Mix M1(Reference Mix) : Portland Cement CEM-I – 438 Kg/cum , Water content – 175 kg/cum , w/c ratio -0.40 , Superplasticizer -4.38 kg/cum (1% by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 % weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum

II. Mix M2 (With increased cement content in reference mix): Portland Cement CEM-I – 472 Kg/cum , Water content – 175 kg/cum , w/c ratio -0.40 , Superplasticizer - 4.38 kg/cum (1 % by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 % by weight of total CA)- 685 kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum .

III. Mix M3 : Portland composite Cement of type CEM-II/A-M – 438 Kg/cum , Water content – 175 kg/cum , w/c ratio - 0.40 , Super plasticizer -4.38 kg/cum (1% by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 % by weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum .

IV. Mix M4 : Portland composite Cement of type CEM-II/B-M – 438 Kg/cum , Water content – 175 kg/cum , w/c ratio - 0.40 , Super plasticizer -4.38 kg/cum (1% by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 % by weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum , The grade of concrete is C-30/37.

V. Mix M5: Cement CEM-I (85% by weight of total cemetitious materials) – 372.3 Kg/cum , Fly Ash -65.7 kg/cum (15% of total cemetitious materials) Water content – 175 kg/cum , w/c ratio -0.40 , Super plasticizer -4.38 kg/cum (1% by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 %by weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum .

VI. Mix M6 : Portland Cement CEM-I (80% by weight of total cemetitious materials of Reference mix M1) – 350.4 Kg/cum , Fly Ash -87.6 kg/cum (20% of total cemetitious materials of reference mix M1) Water content – 175kg/cum, w/c ratio -0.40 , Super plasticizer -4.38 kg/cum (1% by wt of cement) , Coarse Aggregate 19 mm nominal size (60 % by weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum .

VII. Mix M7 : Portland Cement CEM-I (75% by weight of total cemetitious materials of reference mix M1) – 328.5 Kg/cum , Fly Ash -109.5 kg/cum (25% of total cemetitious materials of reference mix M1) Water content – 175 kg/cum , w/c ratio -0.40 , Super plasticizer -4.38 kg/cum (1% by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 % by weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum .

VIII. Mix M8 : Portland Cement CEM-I (50% by weight of total cemetitious materials of reference mix M1) – 219 Kg/cum , GGBFS -219 kg/cum (50% of total cemetitious materials of reference mix M1) Water content – 175 kg/cum , w/c ratio -0.40 , Super plasticizer -4.38 kg/cum (1% by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 % by weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum .

IX. Mix M9: Portland Cement CEM-I (40% by weight of total cemetitious materials of reference mix M1) – 175.2 Kg/cum , GGBFS -262.8 kg/cum (60% of total cemetitious materials of reference mix M1) Water content – 175 kg/cum , w/c ratio -0.40 , Super plasticizer -4.38 kg/cum (1% by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 % by weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum .

X. Mix proportions of M10 : Portland Cement CEM-I (30% by weight of total cemetitious materials of reference mix M1) – 131.4 Kg/cum , GGBFS -306.6 kg/cum (70% of total cemetitious materials of reference mix M1) Water content – 175 kg/cum , w/c ratio -0.40 , Super plasticizer -4.38 kg/cum (1% by wt. of cement) , Coarse Aggregate 19 mm nominal size (60 % by weight of total CA)- 685kg/cum & , coarse aggregate 12.5 mm nominal size (40% by weight of total CA)- 456.8 kg/cum , Fine aggregate – 685 kg/cum .

3.2 Preparation of 5% Sulphuric acid Solution

To prepare 5 % H_2SO_4 solution from 98% concentrated H_2SO_4 acid solution having Sp Gravity of 1.84. Add 51 ml of 98% concentrated H_2SO_4 acid with 949 ml of distilled water the added solution is 5% H_2SO_4 . The normality of 5% H2SO4 acid solution is 1.91 N & the pH of the solution is 1.

3.3 Experimental Setup & Sample preparation

To evaluate the Sulphuric acid durability performance test of concrete against 5% H_2SO_4 acid attack HDPE plastic jar of 300 mm x 450 mm x 200 mm size were used . The samples of 50 mm x 50 mm x 50 mm sizes cube samples casted & cured for 28-days on distilled water at control room temperature of 27 degree centigrade .After completion of curing period the samples weight & sizes were measured & recorded for all the samples. On completion of weight measurement of 28-days cured samples, the specimens were put on 5% H_2SO_4 acid solution for a period of 90 days to evaluate the durability performance of different mixes of concrete. The samples were kept in a complete submerge of the specimen in 5% H_2SO_4 solution till the end of 90-days exposure. For evaluation of concrete strength of different mixes concrete specimens of cube size 150 mm x150 mm x150 mm were casted from the same mix used for evaluation of acid durability performance test & cured the casted specimen on distilled water at room temperature for 28-days.

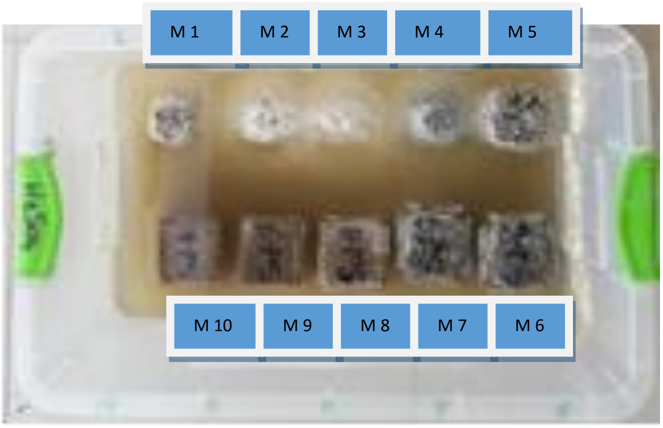

Figure 1:Durability performance of different concrete samples after 90-days exposure to 5% H_2SO_4 solution.

3. Results & Discussions

The fresh concrete & hardened concrete test results of different mix of concrete are tabulated & discussed here.

Table-8: Fresh concrete test results of different mixes.

Mix Details	Slump in mm	Consistency of Mixes
M1	170	Moderately Cohesive
M2	160	Cohesive
M3	160	Cohesive
M4	150	Cohesive
M5	180	Cohesive
M6	160	Highly Cohesive
M7	150	Highly Cohesive
M8	160	Moderately cohesive
M9	150	Highly cohesive
M10	140	Highly Cohesive

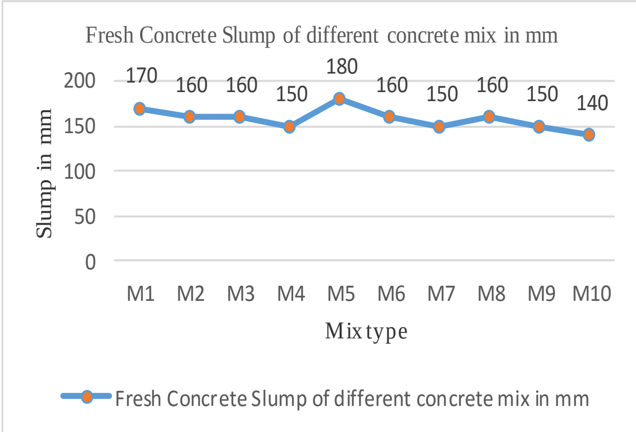

Chart -1: Comparison of concrete workability of different mix.

From the fresh concrete results it has been observed that workability of concrete mixes get decreased with Portland composite cement of type CEM-II/B-M due to high composition of mixed pozzolonic materials 21-35% [16] with same w/c ratio. However on partial replacement of Portland cement with 15% Fly Ash the workability of the concrete mixes get increased due to spherical shape of the Fly Ash particles & its ball bearing effect during plastic stage of concrete [1] & at the same time it was also noticed that when the percentage of Fly Ash was increased up to 25% the workability of mix is got reduced due to its excessive cohesiveness or adhesiveness of the mixes. On the other hand on replacement of Portland cement CEM-I with GGBFS the workability of concrete get reduced due to its long, flaky & elongated crystalline shape. The shape of the particles for both Fly Ash & GGBFS has been studied through SEM with high resolutions

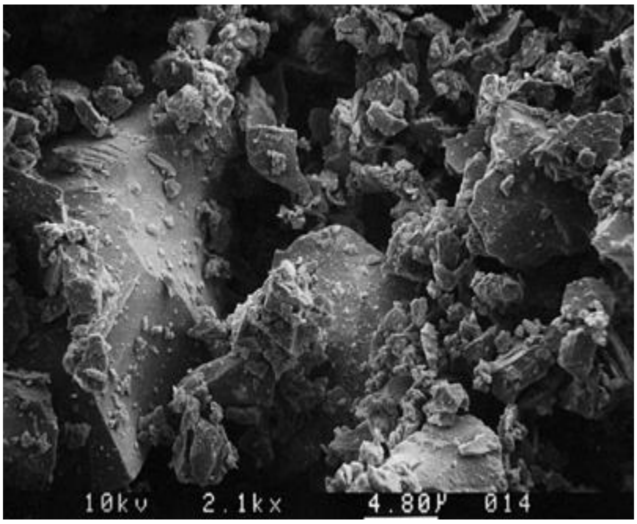

Figure 3: Scanning electron microscope micrograph of GGBFS particles at 2100X.

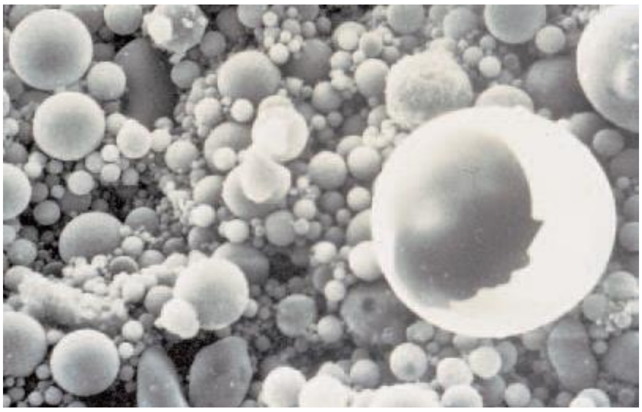

Figure 4: Scanning electron microscope (SEM) micrograph of fly ash particles at 1000X.

3.1 Hardened Concrete results: The average compressive strength of three specimen concrete cubes at 7-Days & 28-Days for different concrete mix are tabulated below in Table-9

Table-9: Concrete compressive strength of different mixes at 7-Days & 28-Days respectively.

Mix	7-Days Strength in N/mm^2	28-Days Strength in N/mm^2
M1	54.8	66.4
M2	56.4	72.4
M3	51.7	65.3
M4	43.4	61.5
M5	46.4	53.5
M6	45.0	54.2
M7	43.8	58.9
M8	44.4	54.9
M9	40.4	51.1
M10	33.2	48.8

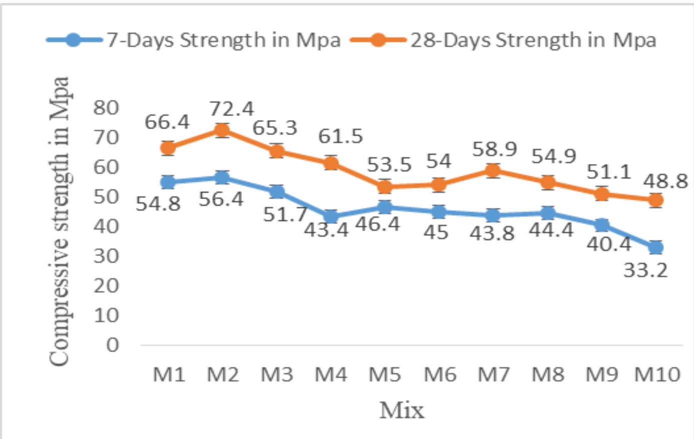

Chart -2: 7-days & 28-days compressive strength of different mixes of concrete.

The average compressive strength at 7-days for mix M_1 & M_2 with Portland Cement (CEM-I) are high as compared to other mix M_3 & M_4 with Portland Composite cement (CEM-II /A-M & CEM-II /B-M) & also with mix M5, M6 & M7 where partial replacement of Portland cement (CEM-I) with fly ash 15% , 20% & 25% respectively . It is observed that on replacement of Portland cement with 50%, 60% & 70% GGBFS in the mix M_8, M_9 & M_{10}, the early age strength development at 7-days are not significant as compared to mix with Portland cement of same quantity in mix .The initial age strength development in the Mix M_1, M_2 are high due to high content of C_3S in the Portland cement. At 28-days the strength of concrete mix (M_7) with 25% Fly ash is maximum as compared to15% & 20% Fly ash in the mix (M_5 &M_6). So with increase in Fly ash content up to 25% will increase 28-days strength but at same time early age strength is not significant as compared to mix with Portland cement (CEM-I). But at the same time by adding GGBFS in the mix 50-70% of total cemetitious materials the strength development at both 7-days & 28-days were reduced as compared to the mix (M_1, M_2) with completely Portland cement (CEM-I) due to low value of siliceous part (SiO_2) in GGBFS. However at the same time it is also observed that higher the GGBFS content in the mix its strength development at both early age 7-days & at 28-days are poor , the strength of mix with 50% GGBFS (M_8) is higher than 70% GGBFS(M_{10}) & also the strength development of GGBFS based mix is poor as compared to mix with Fly ash based due to higher siliceous compound in Fly ash helps to produce more Calcium Silicate Hydrate (C-S-H) gel on pozzolonic reaction of hydrated Calcium hydroxide & siliceous compound of Fly ash . The strength of concrete is governed by formation of C-S-H gel in concrete. The following pozzolonic reaction involve in the mechanism of strength development due to pozzolonic material.

$$Ca(OH)_2 + SiO_2 = C\text{-}S\text{-}H + H_2O$$

3.2 Physical damage of different concrete samples after 90-days exposure to 5% H_2SO_4 solution:

As per the durability performance test it has been observed that the maximum damaged occurred on sample on which maximum amount of normal Portland cement (472 kg/cum). Due higher amount of normal Portland cement the formation of $Ca(OH)_2$ is more on hydration of cement & it is being attacked by H_2SO4 easily to form forms calcium Sulphate (Gypsum) which can leached out easily. The Calcium sulphate formed on reaction is again react with calcium aluminate phase to form voluminous Calcium sulpho aluminate or ettringite, which promotes weight loss & disintegration of concrete .The calcium silicate hydrate react with sulphuric acid to form Silica gel. Which may be destroyed easily by physical force [14],[15]. However mix M_4 with Portland composite cement of type CEM-II/B-M , mix $M_7$with 25% Fly ash & mix M_{10} with 70% GGBFS shows reduce level of damage as compared to mix M_1 ,M_2 & mix M_3 with Portland composite cement of type CEM-II/A-M . The damage or detoriation of concrete mix M_4,M_7 & M_{10} shows significantly lesser damage due to formation of smaller amount of $Ca(OH)_2$ on hydration reaction due to higher amount of pozzolonic material [16] in Portland composite cement of type CEM-II/B-M & mix with partial replacement of normal Portland cement with 25% Fly ash (M_7) & 70% GGBFS (M_{10}) helps to produce smaller amount of $Ca(OH)_2$ due to reducing the level of normal Portland cement by partial replacement of normal Portland cement with pozzolonic materials of 25% Fly ash & 70% GGBFS. In addition to that reduction in formation of $Ca(OH)_2$, there is also consumption of $Ca(OH)_2$ through pozzolonic reaction between $Ca(OH)_2$ & siliceous part of Fly ash & GGBFS . The Calcium hydroxide which produced on hydration reaction of cement is susceptible to H_2SO_4 attack & by reduction & consumption of $Ca(OH)_2$ through pozzolonic reaction helps to reduce the level of damage in cement concrete against Sulphuric acid attack.

Table-10: Percentage of weight loss on different samples of concrete mix after 90 days exposure to 5% H_2SO_4.

Mix	% of weight loss at 90 days
M1	47.0
M2	57.9
M3	41.2
M4	35.5
M5	47.8
M6	36.4
M7	32.7
M8	6.0
M9	5.2
M10	3.5

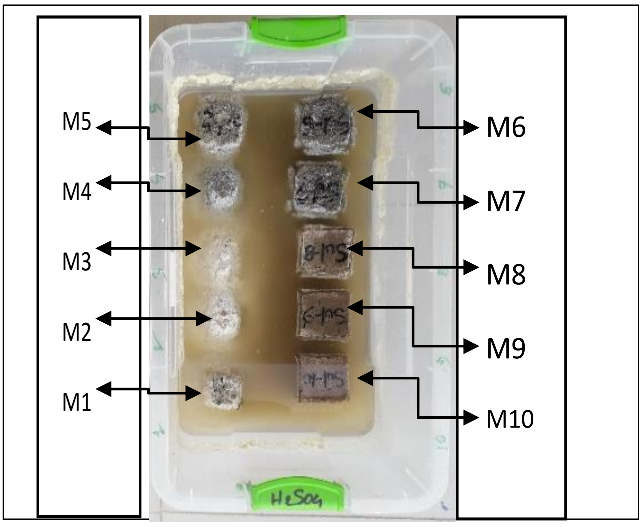

Figure 5: Physical damage of different samples of concrete mixes after 90 days exposure to 5% (v/V) H_2SO_4 exposure.

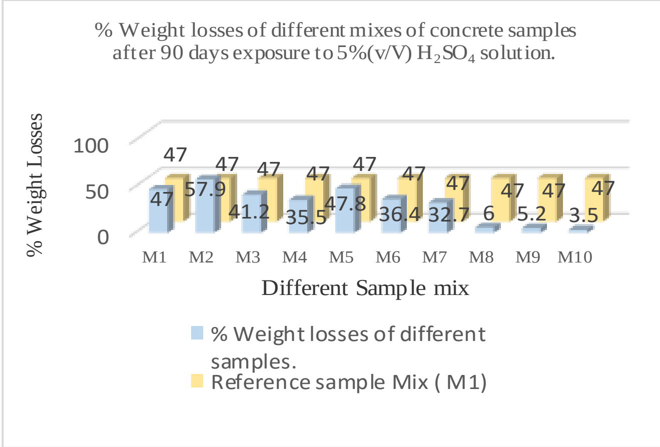

Chart -3: % Weight losses of different samples of concrete mixes with regards to reference mix after 90 days exposure to 5% H2SO4 losses of exposure.

3.3 Scanning electron microscope (SEM) & Elemental energy-dispersive spectrum (EDS) analyses:

Microstructure analyses by using Scanning electron microscope (SEM) & Energy dispersive spectrum of different concrete samples of externally exposed surface & inner core part was performed after 90-days exposure of samples to 5% H_2SO_4 solution. The following are the Micrographs & EDS analysis of the externally exposed surface & inner part of all the designated samples M1, M2, M3, M4, M5, M6, M7, M8, M9 & M10 after 90-days exposure to H_2SO_4 solution.

I. SEM & EDS Analyses of Mix M1:

a. External infected part :

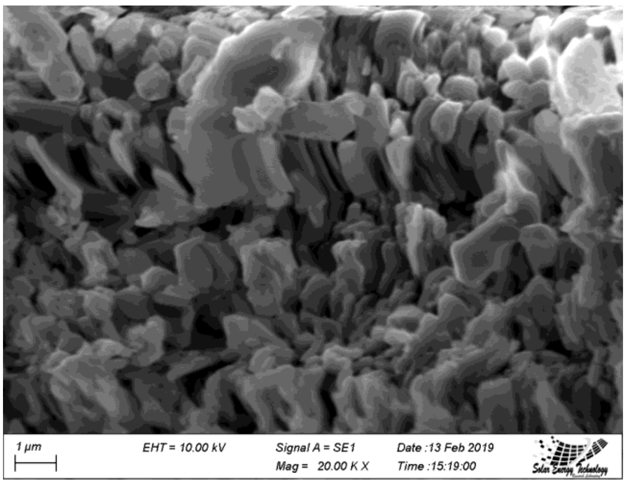

Figure 6: External infected part SEM Micrograph.

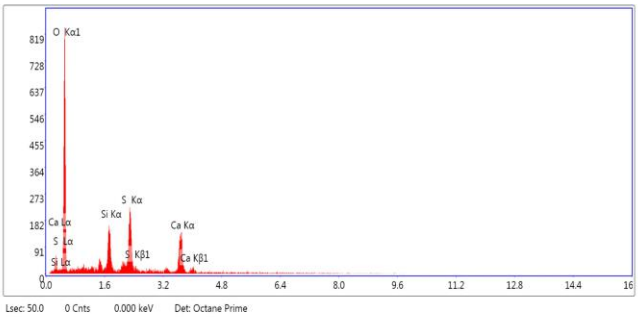

Figure 7: EDS for External infected part.

Table -11: EDS analysis for External infected part

Element	Weight %	Atomic %
O K	49.68	68.41
SiK	7.34	5.76
S K	16.05	11.03
CaK	26.93	14.81

b. Internal Part :

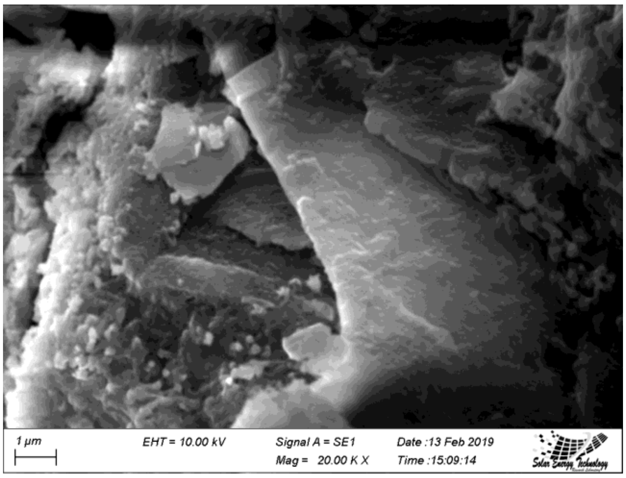

Figure 8: internal part SEM Micrograph.

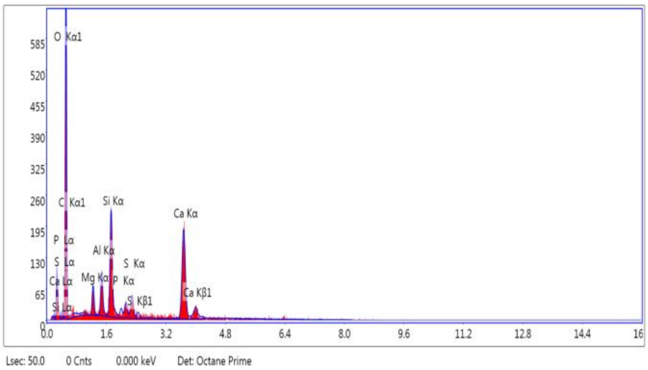

Figure 9: EDS for Internal part.

Table -12: EDS analysis for Internal part

Element	Weight %	Atomic %
C K	5.16	9.47
O K	41.15	56.71
MgK	2.13	1.93
AlK	3.22	2.64
SiK	9.12	7.16
P K	0.73	0.52
S K	2.98	2.05
CaK	35.50	19.53

II. SEM & EDS Analyses of Mix M2:

a. External infected part :

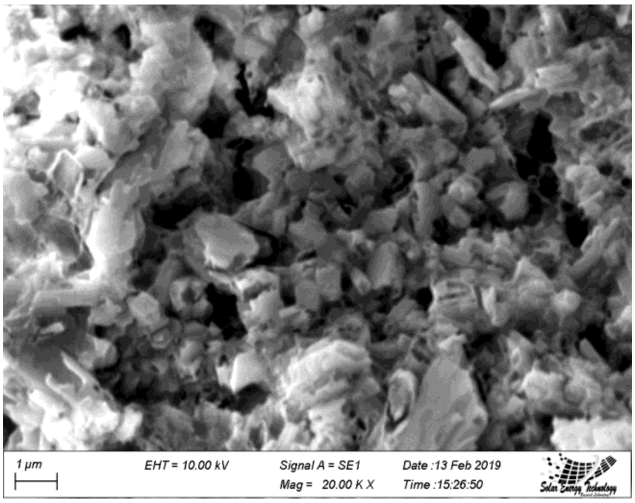

Figure 10: External infected part SEM Micrograph.

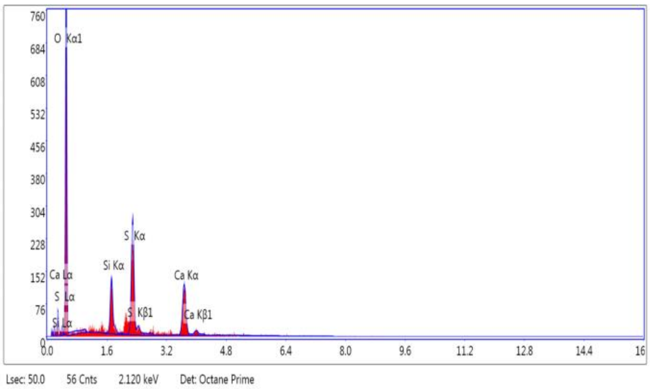

Figure 11: EDS for External infected part.

Table -13: EDS analysis for External infected part

Element	Weight %	Atomic %
O K	48.61	67.42
SiK	5.95	4.70

S K	19.65	13.60
CaK	25.79	14.28

b. Internal Part :

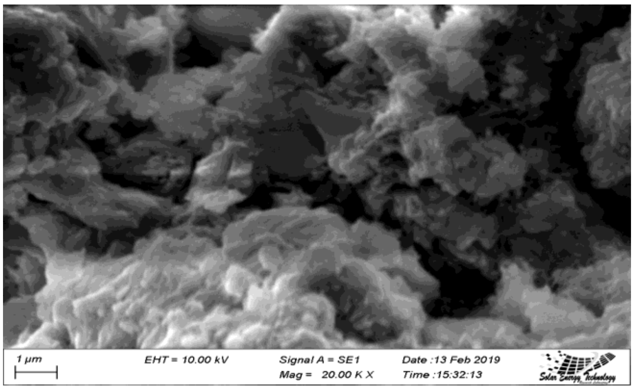

Fig.12: internal part SEM Micrograph.

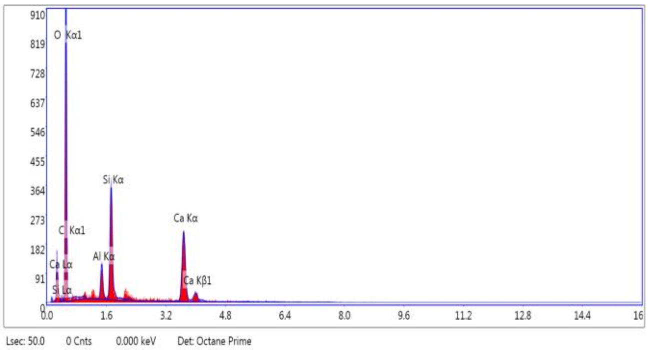

Fig-13: EDS for Internal part.

Table -14: EDS analysis for Internal part

Element	Weight %	Atomic %
C K	5.46	9.70
O K	45.36	60.50
AlK	3.33	2.64
SiK	12.12	9.21
CaK	33.73	17.96

III. SEM & EDS Analyses of Mix M3:

a. External infected part :

b.

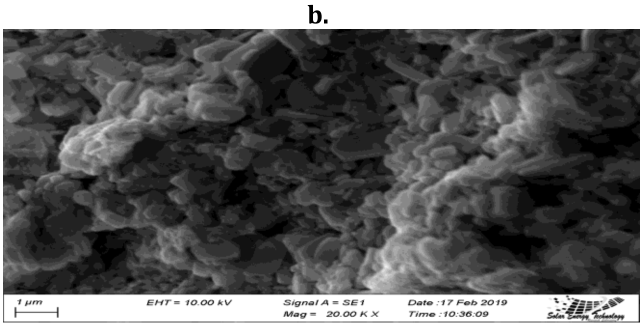

Fig14: External infected part SEM Micrograph.

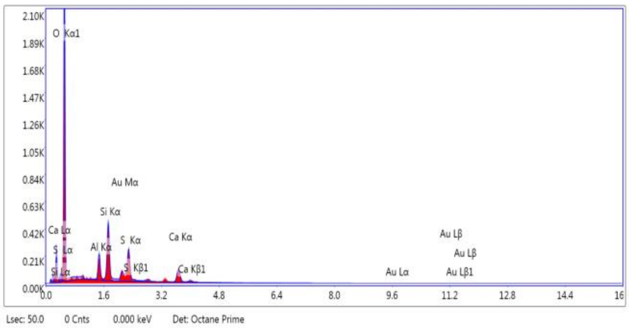

Fig15: EDS for External infected part.

Table -15: EDS analysis for External infected part

Element	Weight %	Atomic %
O K	55.67	73.65
AlK	4.72	3.70
SiK	11.51	8.67
AuM	5.38	0.58
S K	10.57	6.98
CaK	12.14	6.41

c. Internal Part :

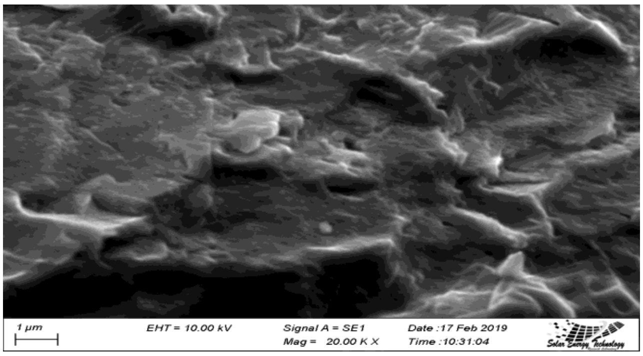

Fig16: internal part SEM Micrograph.

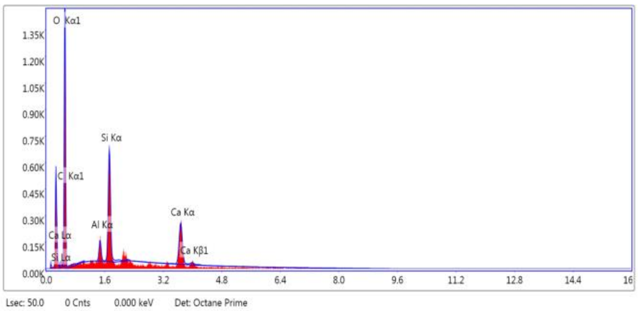

Fig17: EDS for Internal part.

Table -16: EDS analysis for Internal part

Element	Weight %	Atomic %
C K	15.10	24.24
O K	43.38	52.25

AlK	2.44	1.74
SiK	14.49	9.94
CaK	24.59	11.82

IV. SEM & EDS Analyses of Mix M4:

a. External infected part :

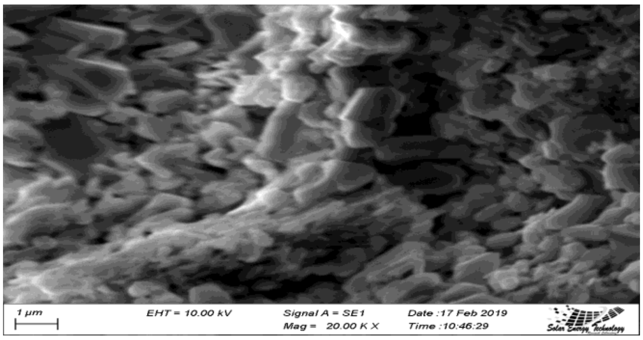

Fig18: External infected part SEM Micrograph.

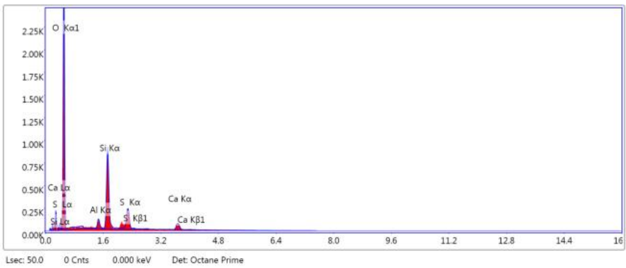

Fig19: EDS for External infected part.

Table -17: EDS analysis for External infected part

Element	Weight %	Atomic %
O K	58.85	73.31
AlK	2.25	1.66
SiK	21.36	15.16
S K	9.21	5.72

b. Internal Part :

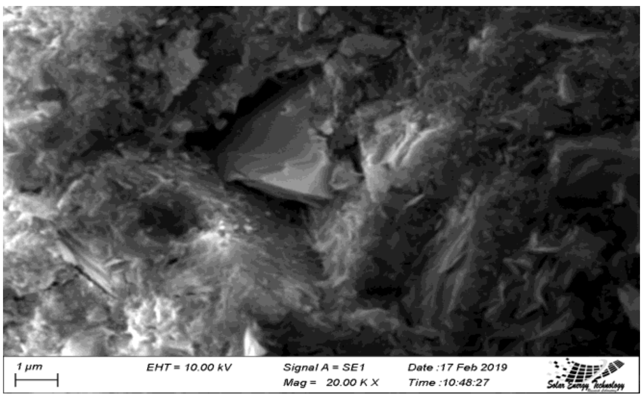

Fig20: internal part SEM Micrograph.

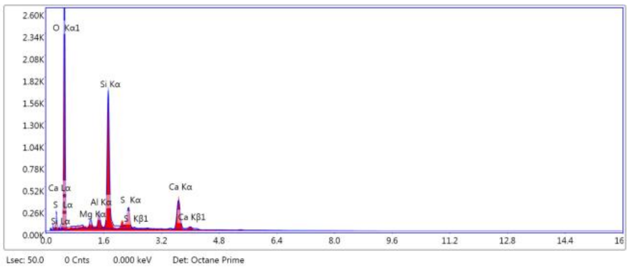

Fig21: EDS for Internal part.

Table -18: EDS analysis for Internal part

Element	Weight %	Atomic %
O K	45.64	62.95
MgK	1.21	1.10
AlK	2.36	1.93
SiK	22.44	17.64
S K	5.60	3.86

V. SEM & EDS Analyses of Mix M5:

a. External infected part :

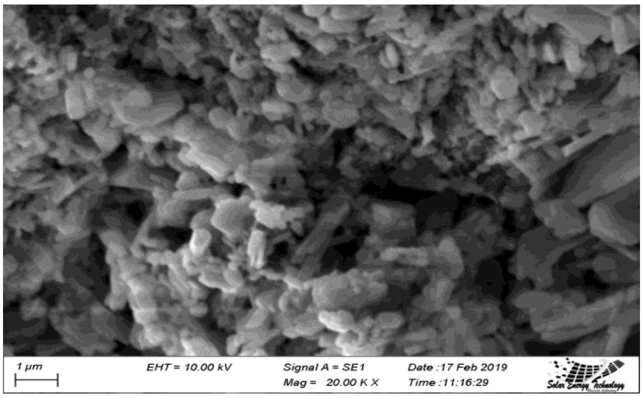

Fig22: External infected part SEM Micrograph.

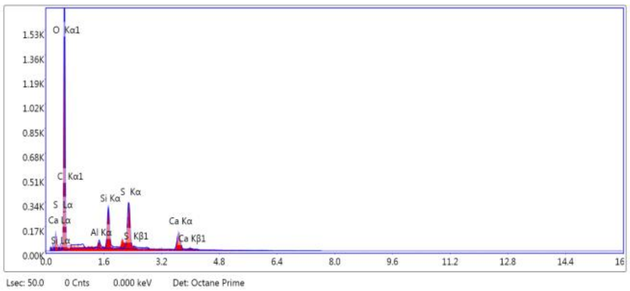

Fig23: EDS for External infected part.

Table -19: EDS analysis for External infected part

Element	Weight %	Atomic %
C K	5.76	9.47

O K	54.41	67.11
AlK	1.25	0.92
SiK	7.97	5.60
S K	14.91	9.18
CaK	15.70	7.73

b. Internal Part :

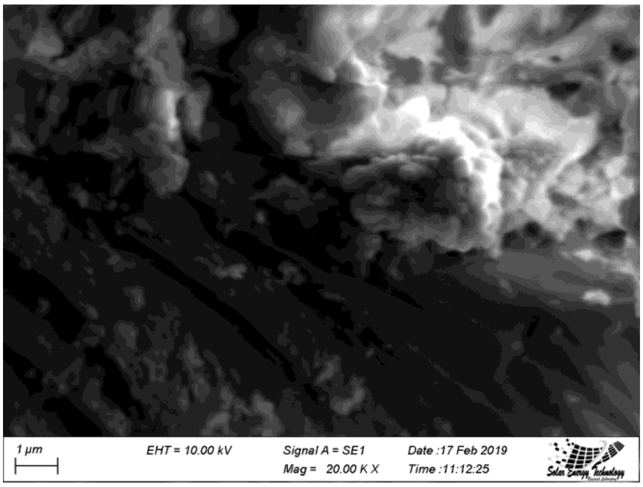

Fig24: internal part SEM Micrograph.

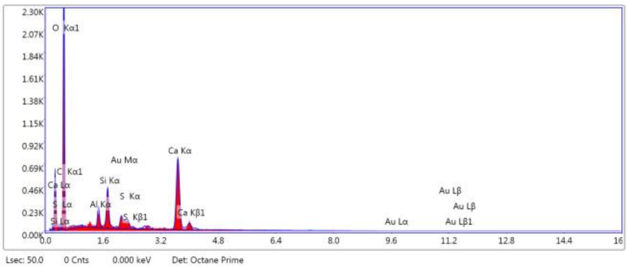

Fig25: EDS for Internal part.

Table -20: EDS analysis for Internal part

Element	Weight %	Atomic %
C K	6.52	12.18
O K	42.24	59.24
AlK	2.13	1.77
SiK	4.63	3.70
AuM	4.52	0.52
S K	1.64	1.15
CaK	38.31	21.45

VI. SEM & EDS Analyses of Mix M6:

a. External infected part:

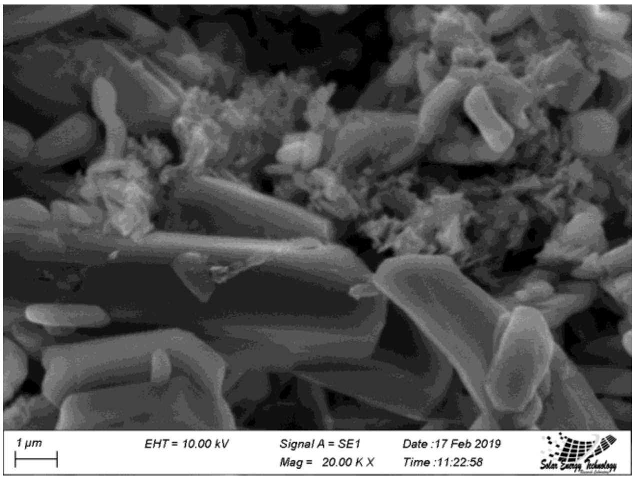

Fig26: External infected part SEM Micrograph.

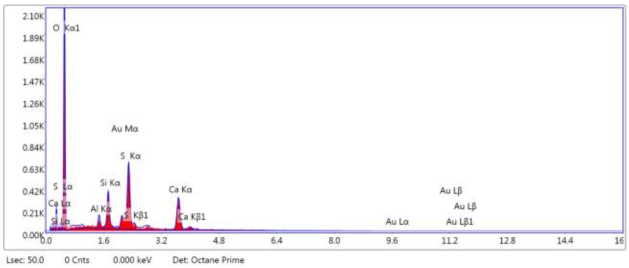

Fig27: EDS for External infected part.

Table -21: EDS analysis for External infected part

Element	Weight %	Atomic %
O K	45.91	66.91
AlK	1.74	1.50
SiK	5.78	4.80
AuM	6.00	0.71
S K	17.09	12.43
CaK	23.47	13.65

b. Internal Part :

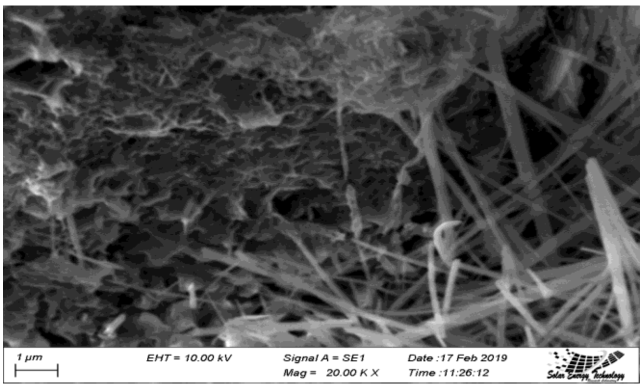

Fig28: internal part SEM Micrograph.

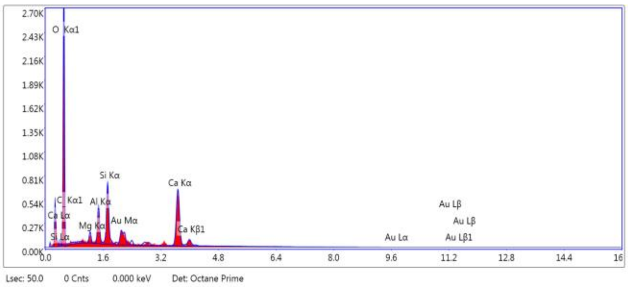

Fig 29: EDS for Internal part.

Table -22: EDS analysis for Internal part

Element	Weight %	Atomic %
C K	5.97	11.04
O K	43.10	59.82
MgK	1.18	1.08
AlK	4.31	3.54
SiK	7.61	6.02
AuM	5.57	0.63
CaK	32.27	17.88

VII. SEM & EDS Analyses of Mix M7:

a. External infected part :

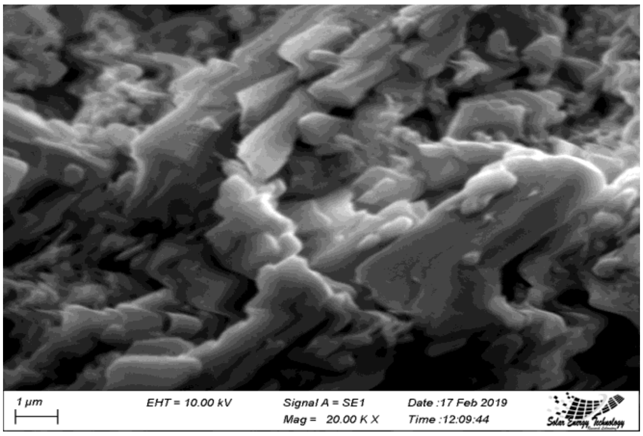

Fig 30: External infected part SEM Micrograph.

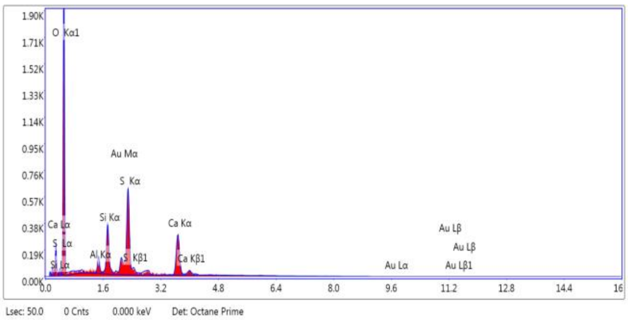

Fig31: EDS for External infected part.

Table -23: EDS analysis for External infected part

Element	Weight %	Atomic %
O K	44.83	65.81
AlK	1.73	1.51
SiK	6.10	5.10
AuM	5.88	0.70
S K	17.69	12.96
CaK	23.76	13.92

b. **Internal Part :**

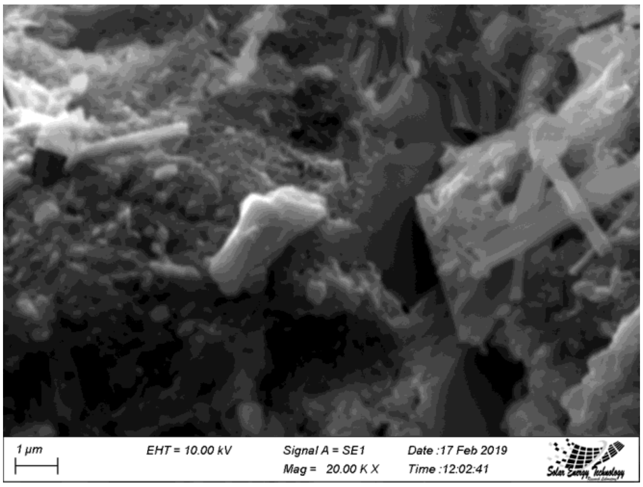

Fig32: internal part SEM Micrograph.

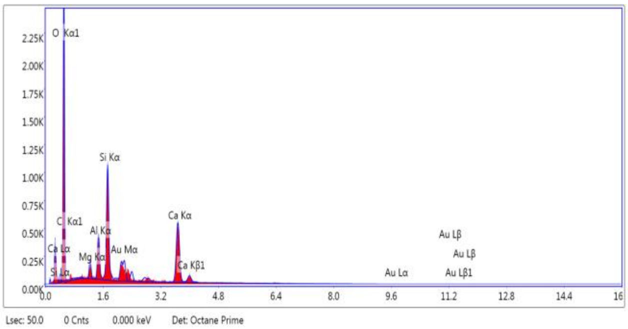

Fig33: EDS for Internal part.

Table -24: EDS analysis for Internal part

Element	Weight %	Atomic %
C K	5.26	9.93
O K	40.70	57.64
MgK	1.65	1.54
AlK	4.26	3.58
SiK	12.23	9.87
AuM	6.31	0.73
CaK	29.58	16.72

VIII. SEM & EDS Analyses of Mix M8:

a. External infected part :

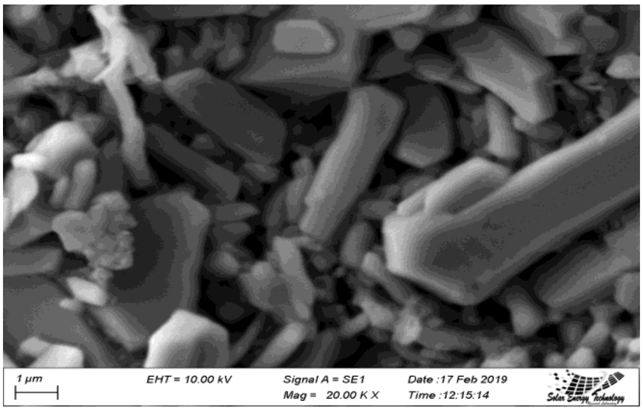

Fig34: External infected part SEM Micrograph.

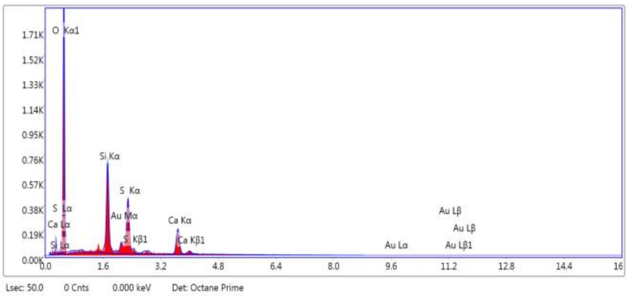

Fig35: EDS for External infected part.

Table -25: EDS analysis for External infected part

Element	Weight %	Atomic %
O K	47.14	66.58
SiK	14.66	11.79
AuM	4.47	0.51
S K	14.84	10.46
CaK	18.89	10.65

b. Internal Part :

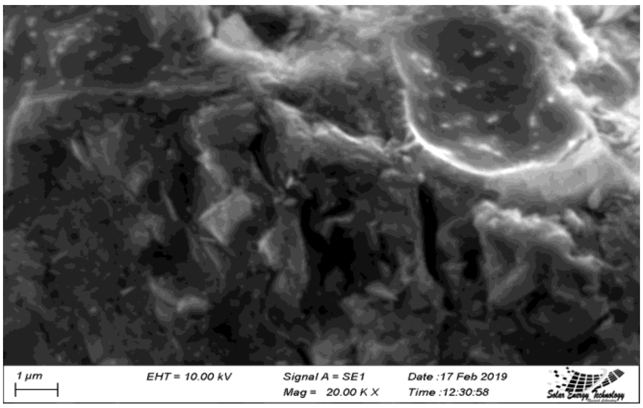

Fig36: internal part SEM Micrograph.

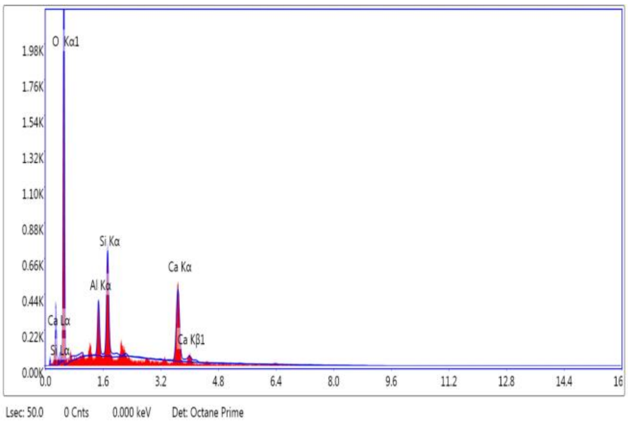

Fig37: EDS for Internal part.

Table -26: EDS analysis for Internal part

Element	Weight %	Atomic %
O K	50.08	68.76
AlK	5.07	4.12
SiK	10.79	8.44
CaK	34.06	18.67

IX. SEM & EDS Analyses of Mix M9:

a. External infected part :

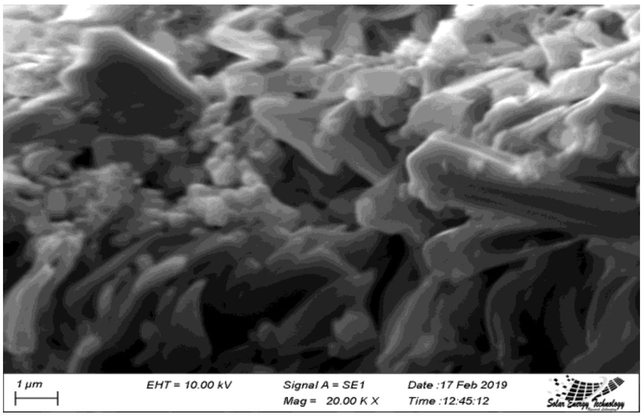

Fig38: External infected part SEM Micrograph.

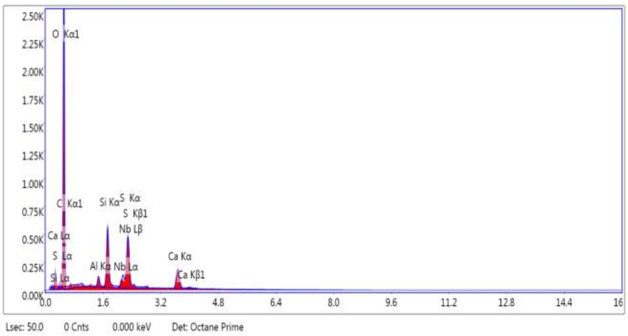

Fig39: EDS for External infected part.

Table -27: EDS analysis for External infected part

Element	Weight %	Atomic %
C K	5.18	8.82
O K	52.24	66.80
AlK	1.41	1.07
SiK	9.19	6.69
NbL	4.67	1.03
S K	12.91	8.24
CaK	14.42	7.36

b. Internal Part :

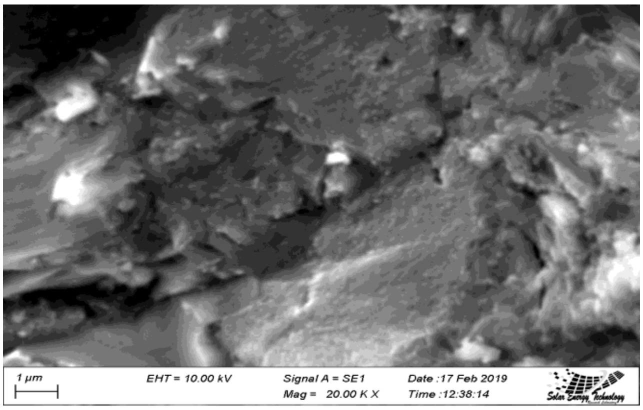

Fig40: internal part SEM Micrograph.

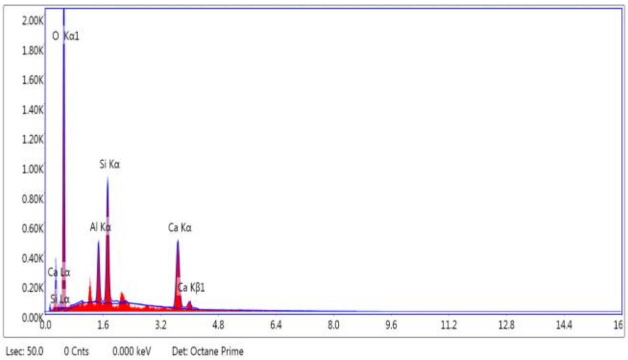

Fig41: EDS for Internal part.

Table -28: EDS analysis for Internal part

Element	Weight %	Atomic %
O K	47.40	66.01
AlK	5.90	4.87
SiK	13.27	10.53
CaK	33.43	18.59

X. SEM & EDS Analyses of Mix M10:

a. External infected part :

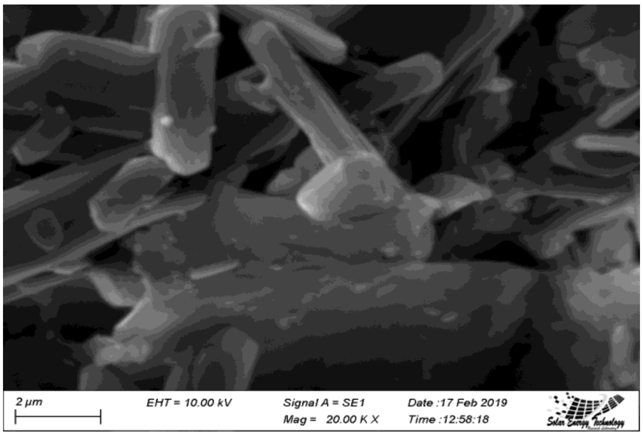

Fig42: External infected part SEM Micrograph.

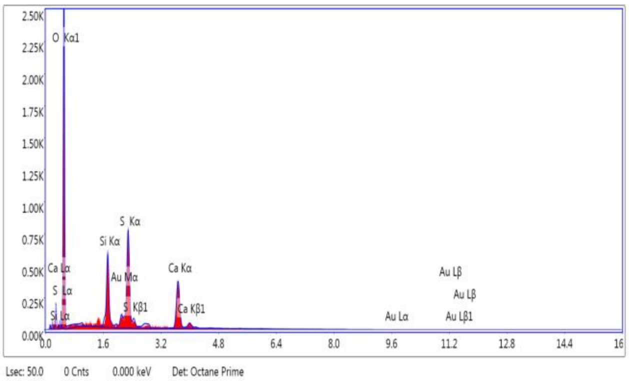

Fig43: EDS for External infected part.

Table -29: EDS analysis for External infected part

Element	Weight %	Atomic %
O K	46.10	66.20
SiK	8.07	6.60
AuM	3.57	0.42
S K	17.79	12.75
CaK	24.48	14.04

b. Internal Part :

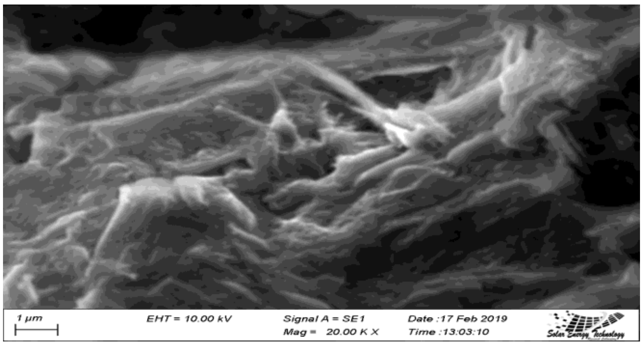

Fig44: internal part SEM Micrograph.

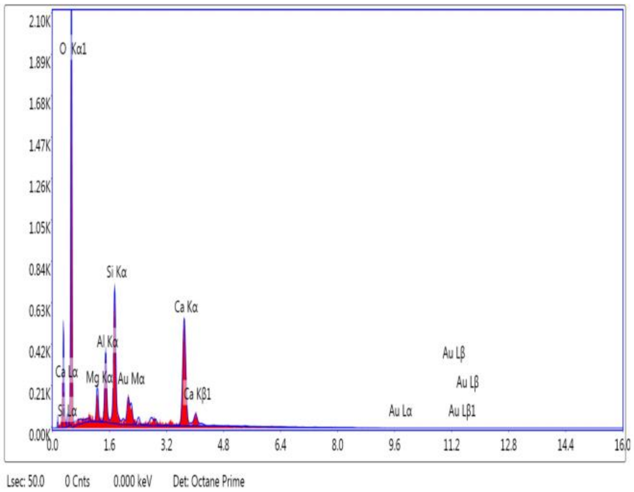

Fig45: EDS for Internal part.

Table -30: EDS analysis for internal part

Element	Weight %	Atomic %
O K	42.61	63.82
MgK	2.18	2.15
AlK	4.65	4.13
SiK	9.64	8.23
AuM	5.86	0.71
CaK	35.06	20.96

Table -31: Sulphur concentration, % wt for external surface part & inner core part after 90 days exposure to 5% H_2SO_4.

Mix	Sulphur Concentration, % wt	
	External Surface	Inner Core part
M1	19.6	2.98
M2	16.0	0
M3	10.5	0
M4	9.2	5.6
M5	14.9	1.6
M6	17	0
M7	17.6	0
M8	14.8	0
M9	12.9	0
M10	17.7	0

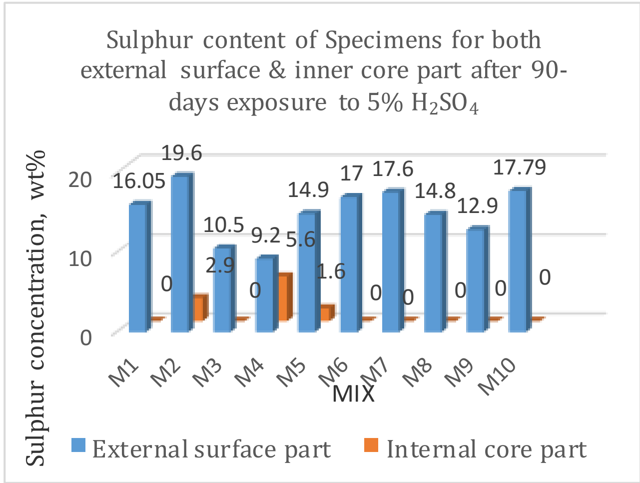

Chart-4: Sulphur concentration, wt % for external surface part & Inner core part of exposed specimen.

Typical energy-dispersive spectra obtained from the quantitative elemental analysis of Sulphur concentration , % wt of different concrete samples for both externally exposed surface & interior part are shown in Chart-4 after 90 days exposure to 5% H_2SO_4 solution . Since sulfur compounds are formed as a result of the reaction between sulfuric acid and cement paste, sulfur components of the spectra are of primary interest in these figures for different concrete samples .The figures show that the sulfur content of the external surface specimen is higher than that of the internal core specimen.

Sulfur concentrations obtained from the elemental spectra of Mix-2 which is having maximum quantity of Portland cement 472 kg/cum, shows maximum concentration of Sulphur peak in the external exposed surface part of the sample mix M_2 & also it is noticed that maximum physical damage (weight loss) occurred in this mix. Also from EDS studies of other samples it has been observed that mix with Portland composite cement of type CEM-II/B-M shows lower sulphur concentration in the external exposed surface than mix with other type of Portland composite cement CEM-II/A-M & also mix with Portland cement M_1, M_2. As the sulfur concentration in the region near the exposed surface approaches an optimum value, the concentration in the adjacent region increases rapidly, while the concentration in the region farthest from the acid-exposed surface increases less rapidly. This result suggests that the concrete deterioration starts at the surface and progresses inward. For both the external and internal specimens, the sulfur concentration is higher in the region near the acid-exposed surface than in the interior regions farther from the acid-exposed surface. The higher sulfur concentrations for external surface correspond to maximum expansion and weight loss when it is compared to specimen of interior region.

3. CONCLUSIONS

The following conclusions can be drawn within the scope of this research work:

- Workability of mix with composite cement CEM-II/B-M shown slightly lower workability than mix of same quantity of Portland cement CEM-I with same w/c ratio.
- Concrete mix with 15% replacement of Portland cement with Fly Ash shown slightly improve workability than mix of normal Portland cement with same w/c ratio. However on further increase of Fly Ash quantity in the mix with same w/c ratio the workability of the mix get reduced.
- On replacement of Portland cement with 50-70% GGBFS the workability of the mix shown lower value than mix with same quantity of Portland cement & same w/c ratio.
- The mix with Portland composite cement CEM-II/A-M shown slightly higher strength than mix with CEM-II/B-M at 28-days.
- The mix with 25% Fly ash shown higher strength than mix with 15% & 20% Fly ash.
- The mix with 50%GGBFS shown higher strength than mix with 60%&70% GGBFS.
- The mix with maximum Portland cement (M_2) shows maximum damage against Sulphuric acid attack as compared to other mixes.
- The mix with same quantity of Portland composite cement of type CEM-II/B-M shows comparatively lesser damage than mix with Portland cement (CEM-I) & Portland composite cement of type CEM-II/A-M against Sulphuric acid attack .
- The mix of concrete (M_7) where maximum 25% quantity of Portland cement were replaced with Fly ash shows significantly lesser damage against Sulphuric acid attack.
- The mixes (M_8, M9, M10) where Portland cement (CEM-I) were replaced with 50-70% GGBFS shows negligible damage against Sulphuric acid attack.
- The mixes with 70% GGBFS shows strong enough against Sulphuric acid attack & the damage shows a negligible damage.
- The sulphur concentration in the sample of external exposed surface is more than the inner part of the sample.
- Higher the sulphur concentration more is the physical damage or weight losses of the samples.

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