

By-Products of Steel Industry as a Complementary Material in Construction

DEEPAK^{1,*}, DAYANANDA H. S², VIJAYA KUMAR M. S³ and SOWMYA P. T⁴

¹Research Scholar, Department of Civil Engineering, Vidyavardhaka College of Engineering, Mysore, Karnataka, India,

²Dean Academics, Professor Department of Civil Engineering, Vidyavardhaka College of Engineering, Mysore, Karnataka, India,

³Assistant Professor, Department of Chemistry, JSS Science and Technology University, Mysore, Karnataka, India,

⁴Assistant Professor, Department of Chemistry, Vidyavardhaka College of Engineering, Mysore, Karnataka, India.

Abstract

This study has been ventured to envisage the viability of replacing Slag Sand to River Sand and Slag to Ordinary Portland Cement (OPC) individually and amalgamated in varied mix proportions. The 3, 7, 28, 56 and 90 days cured mortar cubes were subjected to compression and microstructural analysis. The 30% blended Slag Sand to River Sand yielded 38.71N/mm², 35% Slag to OPC yielded 41.84N/mm² and blending Slag and Slag Sand yielded 39.37N/mm² compressive strength for 90 days curing, which were 17%, 23% and 18% higher than the reference. The EDS results of slag, slag sand and stabilized matrix cured for 3 and 7 days confirmed the presence of Mg, Al, Si, S, Ca, C, O and Fe. The sample composition consisted of CaO, SiO₂, Al₂O₃ and MgO. SEM micrograph shows some larger particles embedded in the matrix with partial reaction during the activation process which indicates that the particle size distribution has a main role in completing the process. The XRD result of short-range order of CaO-SiO₂-Al₂O₃-MgO was observed. In addition to the common C-S-H phase, the formation of α -C₂SH was also observed in hydration product of slag sand and slag. From the Raman spectra's, low intensity bands can be found at +316 cm⁻¹ (lattice vibrations of Ca-O) and at -443 cm⁻¹ (symmetric bending ν_2 (Si-O). Small band at 365 cm⁻¹ ascribed to residual portlandite Ca(OH)₂. Partial replacement of OPC and River Sand by Slag and Slag Sand eliminates the waste management problems and impacts on the environment.

Keywords: Slag, Slag Sand, Compressive strength, XRD, SEM, EDS, Raman Spectroscopy

1. INTRODUCTION

Slag and slag sand are the by-products of iron and steel manufacturing industry. The total number of steel industries in India is approximately 3647. India is the second largest crude steel producers in the world. While

producing three tons of stainless steel, approximately one ton of stainless steel slag is generated. 50 million tons/year of steel slag is generated as a by-product in the world [2]. Major steel plants in India generate 7.76 million ton of BFS (Blast Furnace Slag) per annum. The main constituents of BFS include CaO, SiO₂, and Al₂O₃. It also contains a small amount of MgO, FeO and sulfide as CaS, MnS and FeS [3].

Cement industry consumes high energy industry, and CO₂ emission accounts about 7% of global CO₂ emissions [1]. When compared with cement, Slag requires less than a fifth of energy produced and emits less than a tenth of the CO₂. The main constituent material in concrete production is aggregate, which makes up 70% of the concrete volume. To meet the coveted demand of aggregates, many mountains and rivers have been exhaustingly exploited, which destroy the environment disastrously.

Due to higher cost of natural sand used as a fine aggregate and the rising emphasis on sustainable construction, there is a need for construction industry to search for alternative materials [5].

Research studies on utilization of industrial wastes and by-products in different fields have been carried out in recent years [4]. Industrial wastes are used as mineral admixtures to replace some part of cement. Utilizing mineral admixtures reduces the emission of greenhouse gases and improves the mechanical properties of cement [3]. Fly-ash, a by-product of thermal power plants bearing pozzolanic property is widely used as a partial replacement to cement [2]. The properties of cement concrete using fly ash, silica fume and BFS as cement replacement materials have been evaluated. Nevertheless, not much work has been carried out on the mechanical properties of mortar using supplementary materials like Slag sand and Slag.

This study intends to explore the possibility of utilizing Slag sand and Slag as a partial replacement to binder material and fine aggregate in cement mortar. The mechanical behaviour and morphological changes in solidified matrix are evaluated at different curing ages employing XRD, SEM and Raman Spectroscopy.

2. MATERIALS AND METHODS

The materials used and the methodology adopted in this research work complies with Bureau of Indian Standards specifications. OPC of 43 Grade (Brand - Coromandel) was used. The properties of OPC and Slag (source - JSW Cement Ltd) are furnished in Table 1 & 2. Natural river bed sand and Slag Sand were used as fine aggregates. The cement was analysed for routine parameters. The cubes were cast using CM 1:3. Laboratory tap water (Source-Borewell) was used for mixing and curing. The mortar cubes (Dimension - 7.5cmX7.05cmX7.05cm) were tested using compression testing machine (2000kN, Aimil, 2014), at the curing ages of 3, 7, 28, 56 and 90 days. For each curing, cubes were tested in triplicate to get the concordant values.

X-Ray diffraction studies were carried out using Powder X-Ray Diffraction instrument (MAC Science Co. Ltd). The XRD patterns were recorded at a scanning speed of 2°/min, and 2θ ranging from 60 to 10 degree. The peaks were compared with standard pattern of JCPDS data bank. SEM images of the synthesized Slag, Slag Sand, 3 and 7 Day cured reference, 3 and 7 Day cured M6 was captured using HITACHI (S-3400 N, Japan) with 10 kV acceleration voltages. For image analysis, samples were placed on a carbon-coated copper in a tiny amount and allowed to air dry and images of samples were taken. Raman shift recordings were carried out using the instrument Horiba scientific (Model Xplora Plus).

TABLE 1: Characteristics of Slag

Sl No.	Characteristics	Specification as per IS: 12089 -1987	Test Results
1	SiO ₂ (%)	-	33.30
2	Al ₂ O ₃ (%)	-	21.74
3	Fe ₂ O ₃ (%)	-	0.80
4	CaO (%)	-	34.50
5	MgO (%)	17.0 (Max)	8.30
6	Loss on Ignition (%)	-	0.33
7	IR (%)	5.0 (Max)	0.31
8	Manganese Content (%)	5.5 (Max)	0.09

9	Sulphide Sulphur (%)	2.0 (Max)	0.45
10	Glass Content (%)	85 (Min)	90
11	Moisture Content (%)	-	11.74
12	Particle Size Passing 50.0 mm	95%	100%
13	Chemical Moduli (CaO + MgO + Al ₂ O ₃) / SiO ₂	≥ to 1.0	1.93

(Source: JSW Cement Ltd)

3. RESULTS AND DISCUSSIONS

a. Basic properties

The materials used in mortar specimens had diverse properties and behaviour. The properties of materials were determined as per BIS specifications and the results obtained are represented in Table 2. Referring to Table 3, it can be observed that all the parameters are well within the threshold limits. Nevertheless, the Initial and final setting time of Slag exceeded the threshold value. It is almost double the value of that of cement. This may be due to lack of calcium chloride content. Based on the sieve analysis results of fine aggregates, the River Sand and Slag Sand belongs to zone II.

TABLE 2: Basic test results of OPC, Slag, River Sand and Slag Sand

Property	OPC	Slag	Fine Aggregate		Threshold Value	Specification
			River Sand	Slag Sand		
Sp. Gravity	3.14	3.24	2.57	2.61	Fine Aggregate : 2.6-2.8	IS 383(1970) IS 2386-3(1963)
Std. consistency (%)	32.3	30.3	-	-	26-33	IS 4031-4 (1988)
Initial setting time (min.)	39.7	80.3	-	-	30 (Minimum)	IS 4031-5 (1988)
Final setting time (min.)	497	1080	-	-	600 (Maximum)	IS 4031-5 (1988)

Fineness Modulus	-	-	2.76	2.7	Fine sand: 2.2-2.6 Medium sand: 2.6-2.9 Coarse sand: 2.9-3.2	IS: 383(1970)
Water absorption (%)	-	-	0.41	0.56	Coarse aggregate: <1.4 Fine Aggregate: <2	IS 2386-3(1963)
Bulk density, (g/cc)	-	-	1.6	1.4	-	IS 2386-3(1963)
% air voids	-	-	34.1	2.9	-	IS 2386-3(1963)

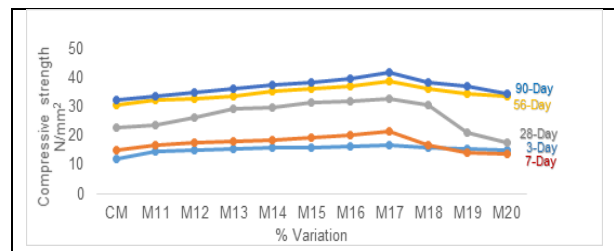


Figure 2: Compressive strength of partially replaced Slag to OPC

TABLE 3: EDS Results of Slag, Slag Sand, CM and M6 (3 and 7 Day cured)

Element Line	Amount %					
	Slag	Slag Sand	CM-3Day	CM-7Day	M6-3Day	M6-7Day
C K	50.69	35.52	40.99	32.76	43.14	46.57
O K	39.51	50.70	49.09	55.71	48.18	44.39
Mg K	0.95	0.96	0.35	0.36	0.24	0.22
Al K	2.16	2.58	0.73	0.72	0.58	0.51
Si K	3.10	4.24	3.07	3.80	1.98	2.74
Si L	---	---	---	---	---	---
S K	---	0.34	0.26	0.26	0.33	0.26
S L	---	---	---	---	---	---
Ca K	3.59	5.65	5.50	6.40	5.54	4.93
Ca L	---	---	---	---	---	---
Fe K	---	---	---	---	---	0.39
Fe L	---	---	---	---	---	---
Total	100	100	100	100	100	100

b. Compressive strength

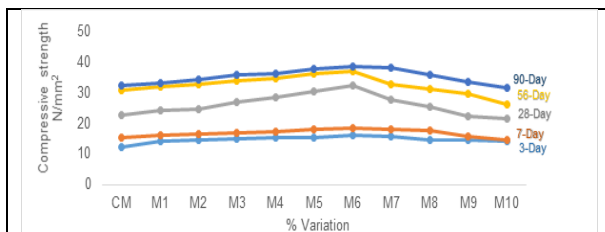


Figure 1: Compressive strength of partially replaced Slag Sand to River Sand

Figure 1 represents the compressive strength of partially replaced Slag Sand to River Sand. With the increase in replacement level of Slag Sand to River Sand, gain in strength was observed. This increment in strength was observed up to 30% replacement of Slag Sand. Then onwards, it started showing a declining profile for all the curing ages. The maximum value of compressive strength obtained at the end of 90-day curing was 38.71 N/mm² which was 17% higher than the reference. Nevertheless, it can be observed that for all the curing ages, the values obtained were higher compared with reference cube.

The compressive strength results obtained for partial replacement of Slag to OPC is indicated in Figure 2. For Slag replacement to OPC, delay in setting time was observed. With every increase in replacement percent for a constant W/C ratio of 0.5%, the setting time got increased. When the replacement level was 35%, maximum gain in strength was observed for all the curing periods. For 90-day curing, a maximum compressive strength of 41.8N/mm² was observed. Further for all the replacement levels the strength declined.

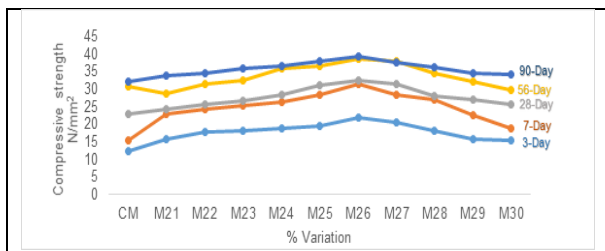


Figure 3: Compressive strength of replacement of Slag

Sand & Slag for River Sand & OPC

XRD result. The seven days cured M6 sample was also showed the same feature. These results confirmed that the crystallinity increases with increasing the curing period. The comprehensive strength decreases when the composition increases from 30% (16.18 N/mm²) to 35% (15.52 N/mm²).

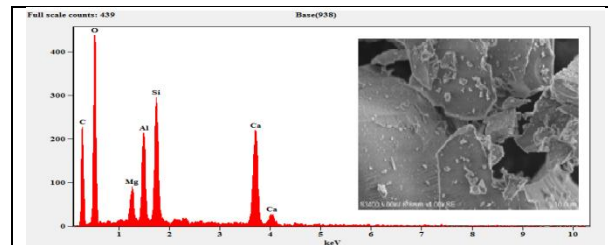


Figure 4: EDS and SEM of Slag

Figure 3 represents the compressive strength results of partial replacement of Slag and Slag Sand to River Sand and OPC. The maximum gain in strength was observed at 30% (M26) was 39.73N/mm² at the end of 90 day curing when compared to controlled specimens. Further increase in replacement decrease in strength was observed.

c. Microstructural Analysis

- Energy Dispersive Spectroscopy (EDS)**

The sample composition was analysed by EDS (EDAX) and the results obtained are summarized in Table 3. The EDS results confirm the presence of Mg, Al, Si, S, Ca, C, O and Fe. As expected, the sample composition mainly consists of CaO, SiO₂, Al₂O₃ and MgO. etc. The Fe content was observed only in M6 cured for 7 days and the cured sample are with high degree of purity.

- Scanning Electron Microscopy (SEM)**

Microstructural development is most important factor that affect the engineering and mechanical properties of stabilized matrix. The surface morphology of the slag and other samples were investigated by SEM analysis as shown in Figure 4-9. The SEM observation revealed that the samples consists of aggregates of particles with cluster like structure. Figure 4 show the amorphous phase as confirmed from the XRD results of Figure 10 whereas the GBFSS shows slight betterment in the crystalline phase with showing a slight peaks of quartz and C₂S. As the curing time increases, the optimum compressive strength also increases from 16.8 N/mm² to 38.71 N/mm². The agglomerated structure can be seen in the reference materials shown in Figure 6 and 7 but the three days cured M6 sample showed a good compact and needle like structure. The better crystallinity with the maximum intensity of a quartz peak was also observed in the

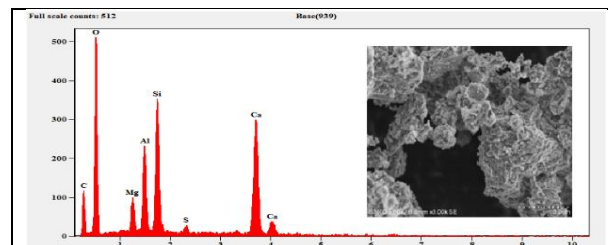


Figure 5: EDS and SEM of Slag Sand

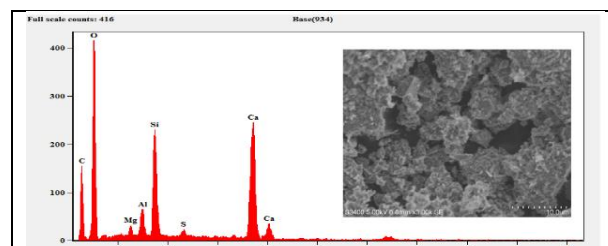


Figure 6: EDS and SEM of 3-Day Cured CM

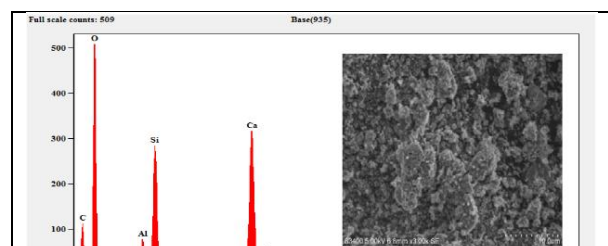


Figure 7: EDS and SEM of 7-Day Cured CM

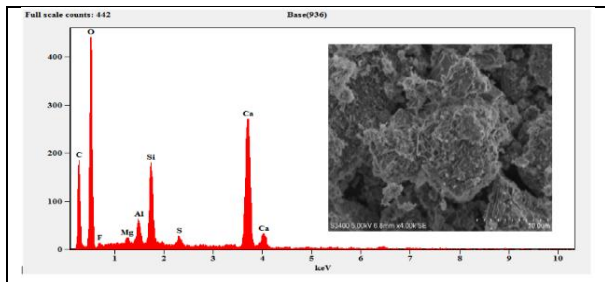


Figure 8: EDS and SEM of 3-Day Cured M6

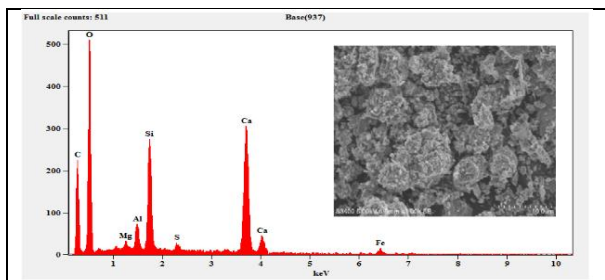


Figure 9: EDS and SEM of 7-Day Cured M6

• X-Ray Diffraction (XRD)

The raw Slag, Slag Sand and hardened solidified matrix were carried out using Powder X-ray Diffraction) to confirm the crystalline nature. XRD patterns of Slag Sand, Slag, CM (3 and 7 Day cured) and M6 (3 and 7 Day cured) samples are shown in Figure 10. It can be observed that the some of the peaks are overlapped. The main compositions are calcium silicate phase (C_3S , C_2S), and RO phase. However, in case of slag, no diffraction was observed and this clearly indicates that slag is amorphous in nature. There are few amounts of olivine, rhodonite and alite were observed. The XRD patterns of 3 and 7 day hydrated cement indicates the presence of Quartz, Ettringite, Alite (C_3S), Belite (C_2S), Gehlenite (C_2AS) and portlandite (CH) phase. The variation of characterises peak of C_3S was consumed in the hydration reaction.

The broad and diffuse background peak with maxima around $2\theta \approx 26.6$ & 28.04 in the hydrated sample of slag sand and slag. The result of short-range order of $CaO-SiO_2-Al_2O_3-MgO$ was observed. In addition to the common C-S-H phase, the formation of $\alpha-C_2SH$ was also observed in the hydration product of slag sand and slag. These data confirms the increase in crystallinity by increasing the curing period. The best crystalline phase was observed for the M6 sample cured for a period of three days. The highest intensity peak was observed at around 2 Theta of 26 indicating the presence of quartz and the sample is crystalline. This might be because of initial hydration of cement and slag.

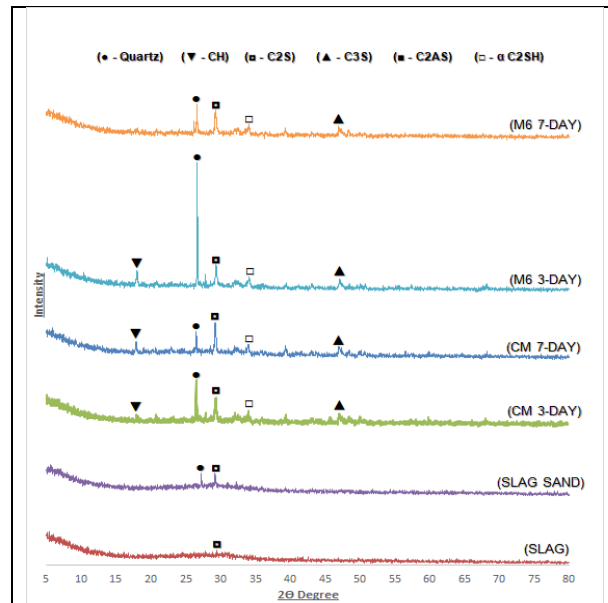


Figure 10: XRD of Slag Sand, Slag, CM and M6 (3 and 7 Day cured)

• Raman Spectroscopy

It is difficult to analyse Slag (Figure 11) by Raman spectroscopy due to its highly disordered amorphous phases. Raman spectra of River Sand, Slag Sand, OPC and Slag pastes at the depth of 0–2 mm, clearly showed an intense sharp peak at about $1500-2500\text{ cm}^{-1}$ (From Figure 13 to 16). This is due to the symmetrical stretching vibration of CO_3 of the $CaCO_3$ phases, the intensity of CO_3 band of the OPC blend was much weaker than those of Slag and OPC. In addition to the weak Raman scatter nature of River Sand and Slag Sand, the weak intensity of River Sand, Slag Sand, OPC and Slag when blended could also be attributed to the dark colour of River Sand. This is because, as well-established, the phases with dark colour can absorb more illuminating light energy. As a result, the scattered light intensity could be reduced due to reduced incident light energy. This could partly explain the much reduced Raman intensity of the River Sand/OPC blend although the intensity of the CO_3 band of Slag and OPC was not reduced, a stronger fluorescence background could be recognized. As the peak height is normally used to quantify the phases in a Raman analysis, the interference caused by River Sand and Slag to the fluorescence background of the Raman spectra could cause concerns about the quantification of $CaCO_3$ formed in the different type of mixes before establishing the carbonation profiles. Nevertheless, a strong background could be identified by Raman spectra in particular for the stabilized matrix blend with Slag Sand, Slag and pure OPC samples.

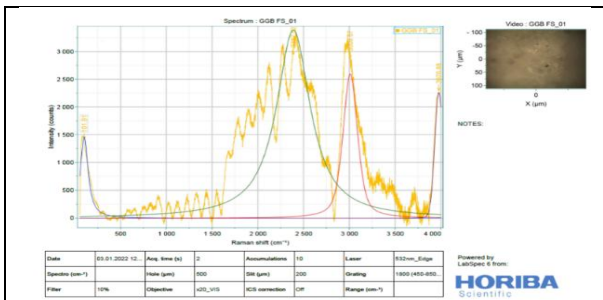


Figure 11: Raman spectroscopy of Slag

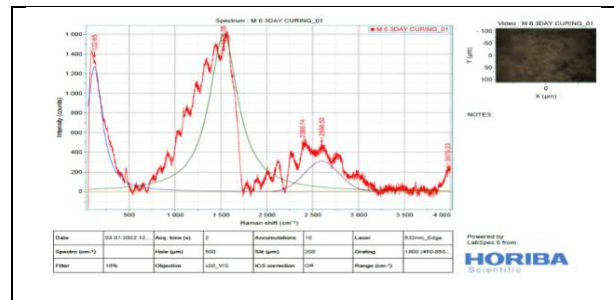


Figure 15: Raman spectroscopy of 3-Day Cured M6

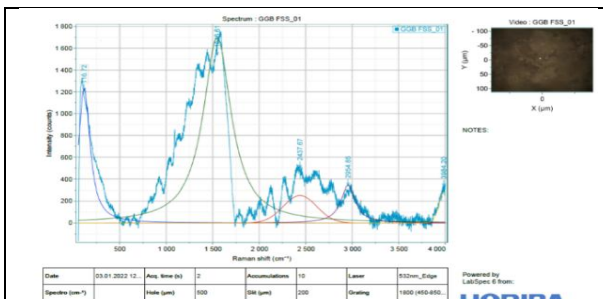


Figure 12: Raman spectroscopy of Slag Sand

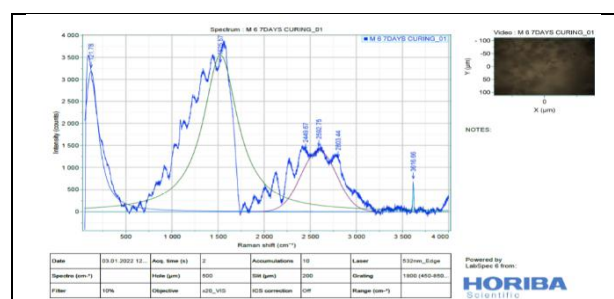


Figure 16: Raman spectroscopy of 7-Day Cured M6

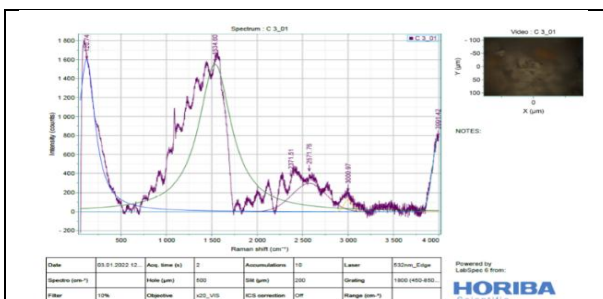


Figure 13: Raman spectroscopy of 3-Day Cured CM

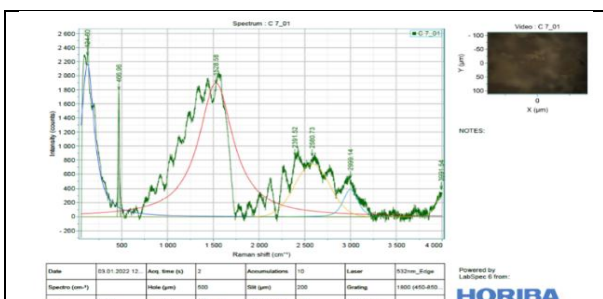


Figure 14: Raman spectroscopy of 7-Day Cured CM

4. CONCLUSION

Based on experimental investigations conducted in this research paper following conclusions and recommendations were made for the potential use of Slag and Slag Sand.

- Slag Sand when partially replaced (30%) to River sand the optimum compressive strength results for 3, 7, 28, 56 and 90 day curing were 16.8N/mm², 18.57N/mm², 32.20N/mm², 36.98N/mm² and 38.71N/mm² on par with that of control mix.
- Slag when partially replaced (35%) to OPC optimum compressive strength results for 3, 7, 28, 56 and 90 day curing were 16.88 N/mm², 18.71N/mm², 32.88N/mm², 38.67N/mm² and 41.84 N/mm² when compared to controlled mix.
- Slag Sand and Slag when partially replaced (30% and 30%) to River sand and OPC in blending, the optimum compressive strength results for 3, 7, 28, 56 and 90-day curing were 21.94N/mm², 31.36N/mm², 32.44N/mm², 38.73N/mm² and 39.37N/mm² when compared to controlled mix.

4. The crystallinity increases with increasing the curing period and also the comprehensive strength decreases when the composition increases from 30% (16.18 N/mm²) to 35% (15.52 N/mm²).
5. As the curing time increases, the optimum compressive strength also increases from 16.8 N/mm² to 38.71 N/mm².
6. The EDS results confirm the presence of Mg, Al, Si, S, Ca, C, O and Fe.
7. The XRD result of short-range order of Cao-Sio₂-Al₂O₃-MgO was observed. In addition to the common C-S-H phase, the formation of α -C₂SH was also observed in the hydration product of slag sand and slag.
8. As the percentage increased beyond optimum the compressive strength declined.
9. From the Raman spectra's, low intensity bands can be found at 316 cm⁻¹ (lattice vibrations of Ca-O) and at -443 cm⁻¹ (symmetric bending ν_2 (Si-O) and Small band at 365 cm⁻¹ ascribed to residual portlandite - Ca(OH)₂.
10. Finally, it can be concluded that replacement of Slag as cementitious material and Slag Sand as fine aggregate in construction industry, not only solves the waste management problems and impacts on environment, but also reduces the carbon foot print and consumption of natural resources leading towards sustainable development.

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BIOGRAPHIES



Mr. DEEPAK, is presently research scholar of Civil Engineering, Vidyavardhaka College of Engineering, Mysore.



Dr. DAYANANDA H S, is a Professor of Civil Engineering and Dean-Academics & VTU Examination, Vidyavardhaka College of Engineering, Mysore. He has 34 Years of teaching experience. He has published more than 40 research papers including Scopus indexed Journals with H and I index. He is a Fellow of IEI(I) & IEE(I). He is member of five professional bodies. He is presently guiding 2 research scholars for Ph.D. and one has submitted thesis to VTU.



Dr. VIJAYA KUMAR M S, currently working as Assistant Professor Department of Chemistry, JSS Science and Technology University, Mysore. He has completed his Masters in Chemistry from the University of Mysore and Doctoral degree from the Tokyo Metropolitan University, Japan. He has worked at ISAS, JAXA, Japan and Tufts University, USA. He is interested in Ceramics, Glasses, High temperature materials, nanocomposites and solidification.



Dr. SOWMYA P T currently working as Assistant Professor in the Department of Chemistry, Vidyavardhaka College of Engineering, Mysuru, India. She has obtained her post-graduation (5 Year Integrated M.Sc.) and Ph.D from University of Mysore, India. She has 15 publications to her credit. She is the recipient of DST-INSPIRE fellowship from Government of India to pursue Ph.D. Her research interests are synthetic organic chemistry, synthesis and characterization of liquid crystals and natural products.