The Effect of Fly Ash and Silica Fume on the Rheology of Cement Slurries of Ordinary Portland Cement of Grade 43 and 53

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ABSTRACT

Cement slurry is the medium of dispersion of coarse and fine aggregates when preparing concrete. The flow behavior of the cement slurries is governed by rheological parameters. The lower the value of these parameters is, the better the flowability and homogeneity of the cement slurry are. Static shear stress (τ_s), dynamic shear stress (τ_d), and the thixotropic index (β) are the basic rheological parameters. The effect of fly ash and silica fume on the rheology of Ordinary Portland Concrete (OPC) 43 and OPC 53 was studied by conducting tests on a coaxial rotating-type viscometer. Fly ash dosage was increased from 10% to 30% by the weight of cement in increment steps of 5% in binary and ternary mixes. Silica fume was kept constant at 5% in the ternary mixes. It was found that τ_s increases with fly ash in the OPC 43 but remains almost constant for the OPC 53 in both binary and ternary mixes. τ_d was almost constant for both the cement slurries in both binary and ternary mixes. β increases with an increase in fly ash for OPC 43 in binary and ternary slurries but decreases in OPC 53 slurries. The increment of fly ash increases the reversible built in the OPC 43 slurries, which can be broken on the application of shear. Thus, OPC 43 is a better cement from the rheological point of view in the development of various concrete mixes.

Keywords-cement slurry; rheology; thixotropy; fly ash; silica fume; viscometer

I. INTRODUCTION

Workability in cement technology is essential to ensure the usability of a particular cement mix in certain applications. Classical tests like slump tests, flow table tests, etc. are error prone and depend on the expertise of the performer. The reological study provides a new approach to investigate the flowability based on the internal physical and chemical changes in the mix. The application of shear reduces the yield stress in thixotropic fluid while increasing the yield stress in rheopectic fluids [1, 2]. Cement slurries are generally thixotropic or shear thinning fluids with certain exceptions [3-6]. The rheological study of the behavior of cement slurry of OPC 43 and OPC 53 shows that each cement has different flow behavior. Static shear stress (τ_s) and dynamic shear stress (τ_d) are the pre-shear parameter and post-shear parameter, respectively [7, 8]. Structuration is caused due to the associations between the cement particles [9] These associations are created owing to the electrostatic forces or the weak van-Der Waal's forces, which break on the application of shear [3, 9]. These forces are negligible immediately after the application of shear as they are weak and do not involve any chemical change. The period between the mixing of water and the application of shear is known as the dormant stage [9]. The hydration reaction when the binder particles interact with water develops the chemical bond between these particles. This is an irreversible process which does not get affected by shear. The contributions from both structuration and hydration results in thixotropic built in the cement slurry [3, 9] This built is a combination of both reversible and irreversible built. τ_s is a result of both structuration and hydration. The difference between τ_s and τ_d gives the irreversible built. Thixotropic index (β) is an index which quantifies the reversible built as a percentage ratio of the irreversible built [3]:

$$\beta=\frac{\tau_s-\tau_d}{\tau_d}\times 100 \tag{1}$$

The use of Supplementary Cementitious Materials (SCMs) like fly ash and silica fume is indispensable in the cement manufacture. OPC 43 and OPC 53 manufacture releases undesirable CO_2 in the atmosphere and its current levels are already alarming [10, 11]. In this paper, OPC 43 and OPC 53 cement slurries are tested and their rheological parameters are compared. Binary and ternary cement slurries were prepared for both cements using fly ash and silica fume as SCMs. The slurries of OPC 43 and OPC 53 were tested at a constant w/c ratio of 0.4. Polycarboxyllic ether based Chryso Optima S6123 was utilized as HRWA. The HRWA was taken as 0.2% of the binder content in the cement slurries. The composition of the cements was known in advance and the only parameter which was varied was the w/c ratio of the slurry and the resting times. The intermolecular reactions between the SCMs and cement particles after encountering water control the rheology of the mix [12]. Some HRWAs work better with certain cements, whereas others require a different cement environment for optimal performance. Also, the effect of pozzolanas on the rheology can only be studied if their dosage can be controlled [13-16].

II. MATERIALS AND EXPERIMENTAL SETUP

A. Cements

OPC 43 and OPC 53 conforming with the IS codes were deployed in the tests [17, 18]. The composition and the physical properties of the cements are tabulated in Table I.

TABLE I. COMPOSITION OF USED CEMENTS

Constituents and physical properties	OPC 43	OPC 53
CaO (%)	63.4	66.7
SiO_2 (%)	17.4	18.9
Al_2O_3 (%)	5.4	4.7
Fe_2O_3 (%)	4.7	4.3
MgO (%)	0.8	0.7
SO_3 (%)	2.8	2.5
Specific gravity	3.13	3.12
Consistency (%)	27	28.5
Soundness (mm)	0.8	1.2
Fineness (m^2/g)	225	228
Initial setting time (min)	163	141
Final setting time (min)	268	228

B. Supplementary Cementitious Materials

Fly ash and silica fume in accordance with the IS codes were used as SCMs to get the desired pozzolanic effect [19, 20]. Class C fly ash from the Kahalgaon Thermal Power Plant, NTPC and condensed silica fume manufactured by Elkem Pvt. Ltd were employed in this study. The chemical composition and the physical properties of these binders are presented in Table II.

TABLE II. COMPOSITION AND PHYSICAL PROPERTIES OF BINDERS

Specifications	Fly Ash	Silica fume
CaO (%)	2.4	0.2
SiO_2 (%)	53.2	95.1
Al_2O_3 (%)	28.4	0.4
Fe_2O_3 (%)	13.4	0.6
MgO (%)	0.7	0
SO_3 (%)	0.4	0.1
Loss on ignition (%)	0.6	1.1
Alkalies (%)	0.5	0.1
Other compounds (%)	0.4	2.5
Specific gravity	2.18	2.2
Fineness(m^2/kg)	340	17000

C. Viscometer

The coaxial type viscometer shown in Figure 1 was utilized for the experimental study. It is a mechanical device containing a hollow outer cylinder of 9.9 cm diameter and a solid internal cylinder of 8.5 cm diameter and 6.33 cm height. There is a narrow space between the cylinders, which is filled with the experimental fluid. The outer cylinder is arranged to rotate with a constant angular velocity of 42.2 rpm by a motor assembly. The inner cylinder is suspended with an experimental wire with a known modulus of rigidity. The rotation of the outer cylinder of the viscometer results in breakage of the reversible thixotropic built due to the structuration of cement. The torque is transferred by the fluid to the inner cylinder causing a torsional strain on the suspending wire. A circular dial is attached to this wire and measures the angle of twist. The torque applied on the inner cylinder is equated to the torque causing strain in the suspending wire. The complete breakdown of the initial structure stops the further twisting of the suspension wire. This provides the shear stress transmitted by the fluid on the suspended inner cylinder.

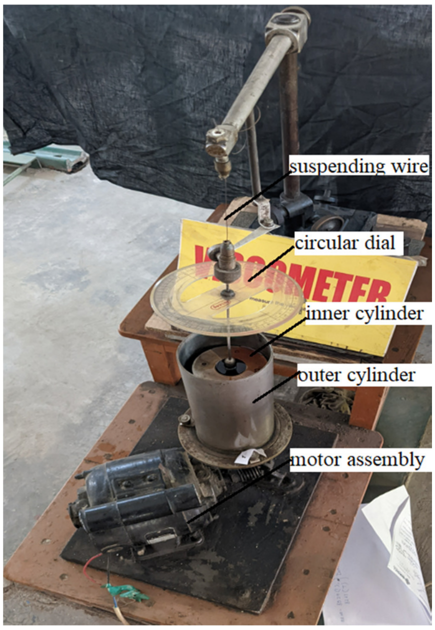

Fig. 1. Coaxial type viscometer used in the study.

III. RESULTS AND DISCUSSION

A. Static Shear Stress of OPC 43 Slurries

The increase in the fly ash dosage increases the τ_s in binary and ternary blends as observed in Figure 2. The fly ash particles act as filler and fill the pores in the slurries. The thixotropic built up due to structuration is increased in the paste as there are more associations between the binders. This filling effect has been reported in other studies as well [9]. Condensed mixes are formed with the increase of the dosage of fly ash. The increase in the resting times also increases the τ_s values. The structuration is favored by the calm conditions in the mix as particles are allowed to get in closer contact due to the attractive electrostatic forces. τ_s is a pre shear parameter and has contributions from both structuration and hydration. The extent of hydration reaction also increases the thixotropic built with increase in resting time. The increase in the fly ash dosage mainly augments the reversible built due to structuration, while the increase in resting time raises both the reversible built and the irreversible built due to hydration.

The dosage of silica fume is fixed at 5% in the ternary mixes. As a result, the τ_s values are higher in these mixes than in binary mixes with the same amount of fly ash content as noticed in Figures 2 and 3. The increase in the τ_s values is generated due to the superior filling capacity and the increase in the hydration during the initial stages of the slurry. This effect of silica fume on τ_s has also been reported in other studies [21-23].

B. Static Shear Stress of OPC 53 Slurries

In the binary slurries, the increase in the fly ash content does not increase the τ_s values as seen in Figure 3. The fine OPC 53 particles have good packing efficiency and fill the pores in the slurry. There is a minor augmentation in the τ_s values in the ternary mixes for a rise in the fly ash dosage of 15% to 20%, but the pre shear parameter is mainly controlled by the OPC 53 particles.

Figure 3 displays that the τ_s values in the OPC 53 ternary slurries are greater than their binary counterparts. The silica fume particles, being finer than the OPC 53 particles, fill up the pores in the paste. They contribute to the structuration by increasing the friction between the particles by sticking to the coarser particles, which encourages further associations between the binders. They also augment the reactivity of the paste as they are highly reactive. They get involved in the initial hydration reaction consuming the available water and increasing the density of the slurry. The rise in the resting time increases the τ_s values in all the mixes as demonstrated in case of OPC 43. The τ_s values of OPC 53 mixes are lower than those of OPC 43 for both binary and ternary slurries. The total thixotropic built in the OPC 53 is lower than that of OPC 43. The reversible and irreversible built due to structuration and hydration constitutes the τ_s. Further study of the rheological parameters is required to quantify the contributions of both builts.

C. Dynamic Shear Stress of OPC 43 Slurries

The τ_d remains constant with the increase in the fly ash content, which is illustrated in Figure 4 for the binary and the ternary mixes of OPC 43. Being a post shear parameter, τ_d mainly depends on the extent of hydration as most of the thixotropic built because structuration is lost by the application of shear. In the binary mixes the fly ash particles do not get involved in the initial stages of the reaction and hence their effect is negligible in the variation of τ_d. In the ternary blends, the τ_d values are higher than their binary counterparts due to the contribution of silica fume in the initial hydration reaction. The water demand of these slurries increases because of the high reactivity of the silica fume particles and the forming of thicker pastes. The structural built increases owing to hydration and more amount if stress is required to maintain the flow in these mixes.

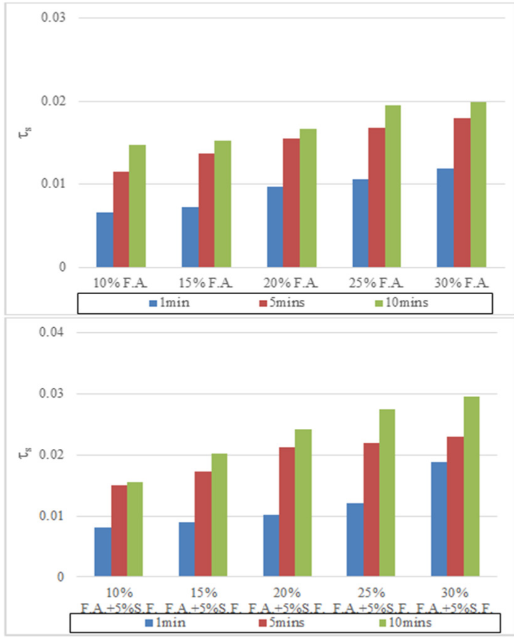

Fig. 2. τ_s for binary and ternary slurries of OPC 43.

Fig. 3. τ_s for binary and ternary slurries of OPC 53.

The increase in the resting time raises the τ_d. This is mainly due to the increase in the irreversible built caused by the hydration reaction as the contribution from structuration is neglected. More hydration products formed as the time elapses. However, this increase is not affected much from the resting time of 5 to 10 min as seen in Figure 4. The hydration rate is faster from 1 to 5 min interval and after that continues at a steady state. This behavior is spotted in the binary as well as ternary blends of OPC 43.

D. Dynamic Shear Stress in OPC 53 Slurries

The τ_d remains almost constant with the increase in the fly ash for both binary and ternary mixed blends as illustrated in

Figure 5. A significant increase in values is seen from resting time of 1 min to 5 min in all the mixes, but the values for 5 and 10 min are nearly equal. The ternary mixes display increased τ_d values due to the influence of silica fume in the thixotropic built. The overall τ_d values of OPC 53 slurries are lower than those of OPC 43 slurries. However, the contribution percentage of the structuration and hydration in the total thixotropic built cannot be ascertained by this investigation. The thixotropic index discussed in the next section gives a clearer insight in this regard.

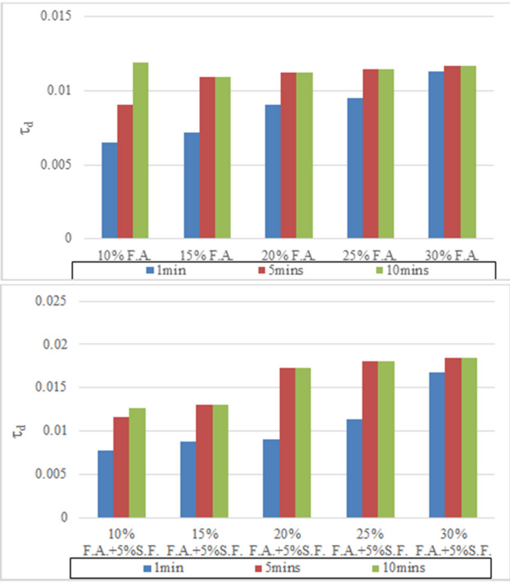

Fig. 4. τ_d for binary and ternary slurries of OPC 43.

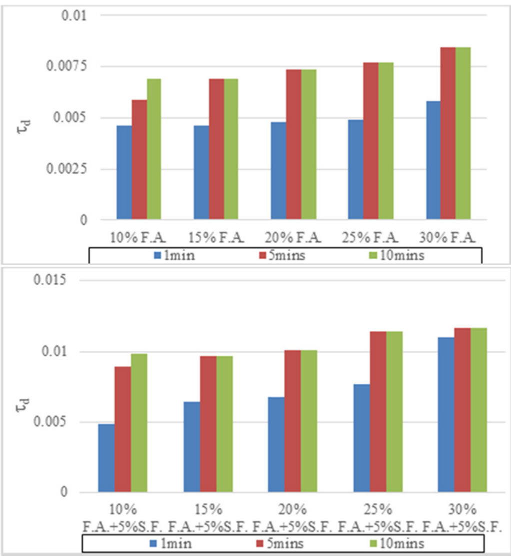

Fig. 5. τ_d for binary and ternary slurries of OPC 53.

E. *Thixotropic Index OPC 43 Slurries*

The parameter involving both the pre shear parameter τ_s and the post shear parameter τ_d is the thixotropic index β, as seen in (1). The binary OPC 43 slurries manifest an increase in the β values as portrayed in Figure 6. There is an augmentation in the structuration leading to the reversible built in these mixes. The contribution of hydration decreases as the dosage of fly ash increases. The same effect of fly ash is seen in the ternary mixes. The value of β goes on increasing as the fly ash dosage hinders the initial hydration of mixes. Silica fume does not affect the β as it increases the structuration and hydration equally during the first 10 min of the reaction. As a result, the β are nearly equal or in some cases slightly lower in the ternary mixes than the binary ones.

The increment in the fly ash dosages in OPC 43 is beneficial from the rheological perspective. The irreversible built is caused by the diminished hydration and the majority of the thixotropic built occurs due to structuration. This built, which can be broken easily by the distorting forces, is reversible. The post shear built due is low and the paste has lower hydrated products in the form of Calcium Silicate Hydrate (CSH) gel. The viscosity of the paste is low and it can be maintained at lower values for longer duration of time. Thus, the binary and ternary slurries of OPC 43 can provide a good medium of dispersion of constituents in the HPC mixes.

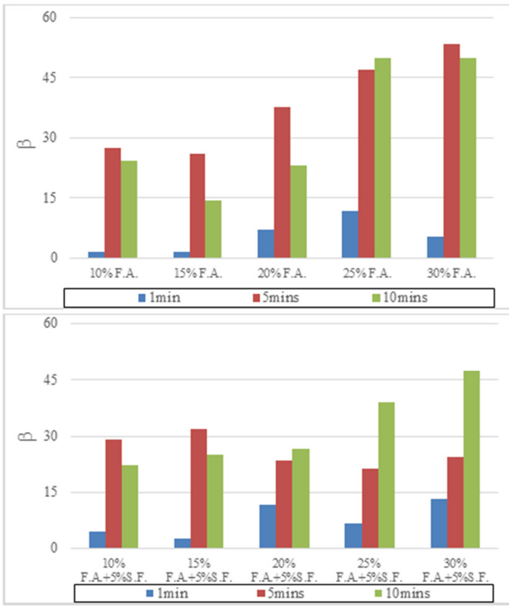

Fig. 6. β for binary and ternary slurries of OPC 43.

F. *Thixotropic Index of OPC 53 Slurries*

The β values of the OPC 53 mixes decrease on the increment of the fly ash dosages for both binary and ternary slurries as pinpointed in Figure 7. This trend means that the contribution of the irreversible built due to hydration increases when the fly ash dosage increases. The hydration reaction is accelerated in OPC 53 with the increase in the fly ash dosage with time. The augmentation in the structuration is negligible and the term (τ_s-τ_d) decreases as a result. The ternary mixes with silica fume also show the same trend but the values of β are significantly lower due to a higher rate of reaction as a consequence of the silica fume particles. The silica fume contributes more towards hydration than structuration. Thus, the rheology of the OPC 53 slurries cannot be improved by the addition of fly ash and silica fume. The values of τ_s and τ_d cannot be manipulated as required.

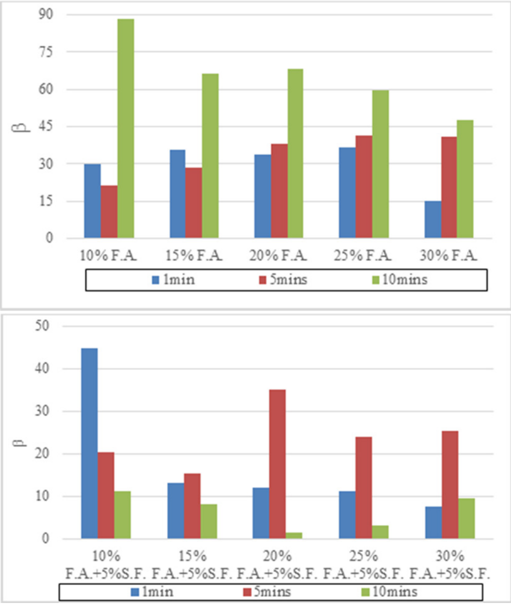

Fig. 7. β for binary and ternary slurries of OPC 53.

IV. RESULT SUMMARY

The effect of increased fly ash on the rheological parameters of the binary and ternary slurries is summarized in Table III. The fly ash dosage increased from 10% to 30% with increment steps of 5% in binary mixes. Constant silica fume addition of 5% was performed along with the given fly ash dosages in the ternary mixes. The w/b was kept at 0.4 and 0.2% HRWA was utilized as chemical admixture.

TABLE III. VARIATION OF τ_s, τ_d AND β WITH INCREASING FLY ASH CONTENT

Rheological parameters	Binary Slurries		Ternary Slurries	
	OPC 43	OPC 53	OPC 43	OPC 53
τ_s	Increase	Minor increase	Increase	Minor increase
τ_d	Constant	Minor increase	Minor increase	Minor increase
β	Increase	Decrease	Increase	Decrease

V. CONCLUSION

The increase in fly ash dosage in the OPC 43 slurries enhances the reversible built and structuration has the major contribution to the thixotropic built. Being a completely physical process, structuration does not involve any internal chemical change in the binder molecules of OPC 43. This process is reversible and does not contribute to the permanent solidification of the cement paste. OPC 43 slurries are better than the OPC 53 slurries, where hydration is the major source of the initial built, leading to permanent change due to the different compound formation. The addition of SCM alters and improves the rheology of OPC 43 cement slurry. In comparison, the OPC 53 cement slurry is comparatively passive on the addition of SCM from the rheological point of view. Thus, OPC 43 can be used as cement with fly ash and silica fume to regulate the rheology of the HPC mixes. This cement can be employed to prepare concrete with good flowability and uniform homogeneity.

REFERENCES

[1] R. Mandal, S. K. Panda, and S. Nayak, "Rheology of Concrete: Critical Review, recent Advancements, and future prospectives," *Construction and Building Materials*, vol. 392, Aug. 2023, Art. no. 132007, https://doi.org/10.1016/j.conbuildmat.2023.132007.

[2] J. Dils, V. Boel, and G. De Schutter, "Influence of cement type and mixing pressure on air content, rheology and mechanical properties of UHPC," *Construction and Building Materials*, vol. 41, pp. 455–463, Apr. 2013, https://doi.org/10.1016/j.conbuildmat.2012.12.050.

[3] J. T. Kolawole, R. Combrinck, and W. P. Boshoff, "Measuring the thixotropy of conventional concrete: The influence of viscosity modifying agent, superplasticiser and water," *Construction and Building Materials*, vol. 225, pp. 853–867, Nov. 2019, https://doi.org/10.1016/j.conbuildmat.2019.07.240.

[4] G. Ke, J. Zhang, S. Xie, and T. Pei, "Rheological behavior of calcium sulfoaluminate cement paste with supplementary cementitious materials," *Construction and Building Materials*, vol. 243, May 2020, Art. no. 118234, https://doi.org/10.1016/j.conbuildmat.2020.118234.

[5] M. Saric-Coric, K. H. Khayat, and A. Tagnit-Hamou, "Performance characteristics of cement grouts made with various combinations of high-range water reducer and cellulose-based viscosity modifier," *Cement and Concrete Research*, vol. 33, no. 12, pp. 1999–2008, Dec. 2003, https://doi.org/10.1016/S0008-8846(03)00214-X.

[6] K. H. Khayat and J. J. Assaad, "Measurement systems for determining formwork pressure of highly-flowable concrete," *Materials and Structures*, vol. 41, no. 1, pp. 37–46, Jan. 2008, https://doi.org/10.1617/s11527-006-9216-7.

[7] A. F. Omran and K. H. Khayat, "Choice of thixotropic index to evaluate formwork pressure characteristics of self-consolidating concrete," *Cement and Concrete Research*, vol. 63, pp. 89–97, Sep. 2014, https://doi.org/10.1016/j.cemconres.2014.05.005.

[8] M. V. Ghica, M. Hîrjău, D. Lupuleasa, and C.-E. Dinu-Pîrvu, "Flow and Thixotropic Parameters for Rheological Characterization of Hydrogels," *Molecules*, vol. 21, no. 6, Jun. 2016, Art. no. 786, https://doi.org/10.3390/molecules21060786.

[9] N. Roussel, G. Ovarlez, S. Garrault, and C. Brumaud, "The origins of thixotropy of fresh cement pastes," *Cement and Concrete Research*, vol. 42, no. 1, pp. 148–157, Jan. 2012, https://doi.org/10.1016/j.cemconres.2011.09.004.

[10] H. Samreen, S. Wizarat, Z. Mehdi, and R. Ahmed, "Exploring the Relationship between Foreign Investments and Carbon Emission: A Bound Test Analysis for Pakistan," *Engineering, Technology & Applied Science Research*, vol. 11, no. 5, pp. 7564–7570, Oct. 2021, https://doi.org/10.48084/etasr.4292.

[11] B. Patnaik, S. C. Swain, and U. K. Rout, "An Experimental Study of Greenhouse Gas Concentration on the Maximum Power Point of Solar PV Panels," *Engineering, Technology & Applied Science Research*, vol. 10, no. 5, pp. 6200–6203, Oct. 2020, https://doi.org/10.48084/etasr.3682.

[12] Q. Zhang *et al.*, "Advances in Organic Rheology-Modifiers (Chemical Admixtures) and Their Effects on the Rheological Properties of Cement-Based Materials," *Materials*, vol. 15, no. 24, Jan. 2022, Art. no. 8730, https://doi.org/10.3390/ma15248730.

[13] J. He, C. Cheng, X. Zhu, and X. Li, "Effect of Silica Fume on the Rheological Properties of Cement Paste with Ultra-Low Water Binder Ratio," *Materials*, vol. 15, no. 2, Jan. 2022, Art. no. 554, https://doi.org/10.3390/ma15020554.

[14] B. Uzbas and A. C. Aydin, "Microstructural Analysis of Silica Fume Concrete with Scanning Electron Microscopy and X-Ray Diffraction," *Engineering, Technology & Applied Science Research*, vol. 10, no. 3, pp. 5845–5850, Jun. 2020, https://doi.org/10.48084/etasr.3288.

[15] K. Chalah, M. Mahdad, A. Benmounah, R. Kheribet, and A. Akouche, "Effect of silica fume on cement rheology properties in presence of

superplasticisers," *Materials Today: Proceedings*, vol. 58, pp. 1246–1250, Jan. 2022, https://doi.org/10.1016/j.matpr.2022.02.006.

[16] M. Amin, A. M. Zeyad, B. A. Tayeh, and I. Saad Agwa, "Effect of ferrosilicon and silica fume on mechanical, durability, and microstructure characteristics of ultra high-performance concrete," *Construction and Building Materials*, vol. 320, Feb. 2022, Art. no. 126233, https://doi.org/10.1016/j.conbuildmat.2021.126233.

[17] *IS 8112: Specification for 43 grade ordinary Portland cement*. New Delhi, India: Bureau of Indian Standards, 2013.

[18] *IS 12269: 53 grade ordinary Portland cement*. New Delhi, India: Bureau of Indian Standards, 2013.

[19] *IS 15388: Specifications for Silica Fume*. New Delhi, India: Bureau of Indian Standards, 2003.

[20] *IS 3812-1: Specification for Pulverized Fuel Ash, Part 1: For Use as Pozzolana in Cement, Cement Mortar and Concrete*. New Delhi, India: Bureau of Indian Standards, 2013.

[21] M. Benaicha, X. Roguiez, O. Jalbaud, Y. Burtschell, and A. H. Alaoui, "Influence of silica fume and viscosity modifying agent on the mechanical and rheological behavior of self compacting concrete," *Construction and Building Materials*, vol. 84, pp. 103–110, Jun. 2015, https://doi.org/10.1016/j.conbuildmat.2015.03.061.

[22] C. K. Park, M. H. Noh, and T. H. Park, "Rheological properties of cementitious materials containing mineral admixtures," *Cement and Concrete Research*, vol. 35, no. 5, pp. 842–849, May 2005, https://doi.org/10.1016/j.cemconres.2004.11.002.

[23] P. Nanthagopalan, M. Haist, M. Santhanam, and H. S. Müller, "Investigation on the influence of granular packing on the flow properties of cementitious suspensions," *Cement and Concrete Composites*, vol. 30, no. 9, pp. 763–768, Oct. 2008, https://doi.org/10.1016/j.cemconcomp.2008.06.005.