Investigations on Pastes and Mortars of Ordinary Portland Cement Admixed with Wollastonite and Microsilica

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Abstract: Wollastonite is abundantly available in Rajasthan, Tamil Nadu, Uttarakhand, and Andhra Pradesh states of the Indian Union as a low-cost material. In this study, investigations were made on pastes and mortars to evaluate its potential as a new material for admixing with ordinary portland cement with or without microsilica. Its physical and chemical properties were analyzed. Wollastonite consists of 45.6% of CaO and 48% of SiO_2, mostly in amorphous form. It has an average specific surface area of $842.7\ m^2/kg$ and retention on 45-micron sieve of 3.20%. When ground to fine powder, it attains an average particle size of 4 microns which is about 4.5 times finer than ordinary portland cement. Scanning electron microscope images show that wollastonite particles were solid, acicular in shape, and have rough surfaces. Several cementitious mix proportions of ordinary portland cement, wollastonite, and microsilica were investigated for normal consistency, initial and final setting time of paste, and compressive strength of mortar. Test results indicate that the mortar, which contains 82.5% cement, 10% wollastonite, and 7.5% microsilica, as cementitious material attains the highest compressive strength. The mortar, which contains 77.5% cement, 15% wollastonite, and 7.5% microsilica, as cementitious material achieves compressive strength higher than the conventional OPC mortar along with rendering maximum cement replacement for better economy of concrete work. It was observed that the compressive strength of mortar varied logarithmically with the days of moist curing and linearly with the proportion of admixing. Suitable predictive models are presented accordingly.

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Introduction

Cement plants are known to consume high energy and produce a large amount of undesirable products that affect our environment. Mineral admixtures are considered as a viable solution to meet the ever increasing demand of cement as well as to prevail upon the energy consumption and CO_2 emissions (Kenai et al. 2004). They are widely used as partial substitute for ordinary portland cement (OPC) because of advantageous properties like cost reduction, reduction in heat of hydration, decreased permeability, increased chemical resistance (Mehta 1981; Massazza 1993; Tagnit-Hamou et al. 2003), improved workability (Uzal and Turanli 2003), reduced bleeding, increased compressive strength (Chai and Boonmark 2003), and lower $Ca(OH)_2$ content (Zhang et al. 1996). However, they are often identified with longer moist curing and reduction in early age strength up to 28 days. Pozzolanic reaction produces additional calcium silicate hydrates (CSHs) and calcium aluminate hydrates (CAHs) due to reaction of SiO_2 and Al_2O_3 with $Ca(OH)_2$ [American Concrete Institute (ACI) 2000]. Also, large size crystals of CSH gets converted to smaller crystals, leading to a denser concrete matrix and consequent reduction of pore size (Monteiro and Mehta 1986).

Wollastonite is a naturally occurring mineral formed due to interaction of limestone with silica in hot magmas (Paul 1977). Chemically, it is calcium-metasilicate (Ramachandran et al. 1981). It is an acicular and white mineral of high modulus of elasticity (Mathur et al. 2007). The aspect ratio varies from 3:1 to 20:1. It is abundantly available in Rajasthan, Tamil Nadu, Uttarakhand, and Andhra Pradesh states of the Indian union as a low-cost material. The present rate of extraction is about 250,000 MT per year from mines of Udaipur alone. It is being used for reduction of shrinkage cracks in ceramic tiles and refractories, improvement of tensile strength of plastics, and it is employed as a pH buffer to help resist weathering in paints, apart from finding applications in dental care, rubber, wall board, etc. (Wolkem India Limited 2003). Its chemical composition of nearly equal proportions of lime and silica along with fine particle size were viewed as favorable indicators for admixing with OPC.

Microsilica is a by-product of silicon or ferro-silicon alloy industries (Malhotra et al. 1987). Its high siliceous composition and very fine particle size were used beneficially in many works to improve the properties of fresh and hardened concrete (Bentz and Stutzman 1994).

The objective of the present work is to facilitate the utilization of wollastonite as a new material with or without microsilica for partial replacement of OPC. This is done by determining the optimal level of replacement based on compressive strength.

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Table 1. Mix Proportions of Cementitious Materials

Mix designation	OPC	Wollastonite	Microsilica	HRWR dosage
	Mix proportion (by weight)			
Control or X0	100.0	—	—	—
W0	—	100.0	—	—
W1	97.5	2.5	—	0.33
W2	95.0	5.0	—	0.38
W3	92.5	7.5	—	0.44
W4	90.0	10.0	—	0.48
W5	87.5	12.5	—	0.55
W6 or X1	85.0	15.0	—	0.60
W7	82.5	17.5	—	0.67
W8	80.0	20.0	—	0.77
W9	77.5	22.5	—	0.87
W10	75.0	25.0	—	1.00
W11	72.5	27.5	—	1.15
W12	70.0	30.0	—	1.32
M0	—	—	100.0	—
M1	97.5	—	2.5	0.32
M2	95.0	—	5.0	0.40
M3	92.5	—	7.5	0.50
M4	90.0	—	10.0	0.62
M5	87.5	—	12.5	0.75
X2	85.0	10.0	5.0	1.00
X3	82.5	10.0	7.5	1.60
X4	80.0	15.0	5.0	1.30
X5	77.5	15.0	7.5	2.00

Experimental Program

Raw Materials

OPC 43, grade fine amorphous wollastonite powder, and densified 920D-grade microsilica were used as cementitious materials. Standard Ennore sand was used as fine aggregate. Potable water was used for mixing and curing.

Chemical composition of OPC, wollastonite, and microsilica were analyzed by X-ray fluorescence spectrometer. Physical properties such as specific gravity, material retained on 45-micron sieve, specific surface of OPC by Blaine's method, and that of wollastonite and microsilica by BET method, mean grain size by Ankersmid CIS-50 laser particle size analyzer, particle shape of materials by Phillips 505 scanning electron microscope (SEM), and mineralogical analysis of materials by Rigaku make, 12-kW rotating anode X-ray diffractometer (XRD) were also investigated. The aforementioned tests are only for measuring the properties of the raw materials and not of pastes or mortars.

Mixture Proportions

Two types of mixtures—one each for pastes and mortars—were prepared. In both of them the OPC was replaced with wollastonite and microsilica to obtain new cementitious materials. The cementitious materials were prepared by replacing OPC with wollastonite at a regular interval of 2.5 up to 30% (designated from W1 to W12) and microsilica at equal increments of 2.5 up to 12.5% (designated from M1 to M5) by weight of OPC in dry condition, as shown in Table 1. Again, OPC was replaced by wollastonite and microsilica together in various combinations (designated from X2 to X5) based on the compressive strength test results of mortar obtained from the aforementioned mix proportions. X0, W0, and M0 were referred to the mix having 100% OPC (control), 100% wollastonite, and 100% microsilica, respectively, as cementitious materials. The cementitious materials were thoroughly homogenized and kept in polythene bottles.

The pastes were prepared at their normal consistency for setting time test and XRD. Mortars on the other hand were prepared with the same cementitious materials as pastes, but with a common water-cementitious material ratio (w/c).

Paste

Normal consistency was reckoned as the amount of water required to produce a cement paste to resist a specified pressure. In other words, it is that limit of water at which the cement paste resists the penetration of a standard plunger (10-mm diameter) under a standard loading of 300 g up to a distance of 10 ± 1 mm below the original surface of Vicat apparatus in a specified time of 30 s. Setting time is reckoned as the time consumed by cement paste at normal consistency to attain a hardened state by resisting a specified pressure. Periodic penetration tests were performed on paste by allowing a 1-mm-diameter Vicat needle to settle into paste. The time elapsed between initial contact of cement and water and the time when the penetration is measured or calculated to be 25 mm is the initial setting time. Final setting time is the time elapsed between initial contact of cement and water and the time when the needle does not leave a complete circular impression on the paste surface.

In the present investigation, new cementitious materials were finer than OPC due to admixing of wollastonite and microsilica. The effect of fineness on normal consistency and setting times of pastes of all cementitious materials were investigated in accordance with ASTM C187 (ASTM 2004) and ASTM C191 (ASTM 2008a), respectively, and compared with those of the control paste.

XRD analysis of cementitious materials were also conducted on pastes to reveal the hydrated compounds. The pastes had w/c of 0.32 for 100% OPC; 0.65 for 100% wollastonite; 0.76 for 100% microsilica; 0.39 for OPC:wollastonite in the proportion of 85:15; 0.37 for OPC:microsilica in the proportion of 92.5:7.5; and 0.42 for OPC:wollastonite:microsilica in the proportion of 82.5:10:7.5. The specimens were cast for a thickness of about 20 mm on a Perspex sheet plate $50\text{ mm}\times50\text{ mm}$ ensuring a level surface. They were left covered in the casting room for 24 h, and thereafter transferred to a moist closet having relative humidity of not less than 90% and temperature of $23\pm3^{\circ}$C. After 28 days, the specimens were preconditioned by drying in an oven at $50\pm2^{\circ}$C for 24 h and then allowed to cool for 3 days in a sealed container at $23\pm3^{\circ}$C. Thereafter, the specimens were powdered for XRD.

Mortar

Mortar was prepared containing one part of cementitious material to three parts of standard Ennore river sand by weight. The control mortar has the required workability at w/c of 0.50. This w/c was maintained for all admixed mortars and a high-range water reducer (HRWR) was used to compensate for the loss in workability due to an increase in surface area. Its dosage was determined by compatibility test on pastes at the w/c of 0.50 in Marsh cone apparatus.

The same procedure was adopted for preparation of admixed mortar and control mortar. Mortar cubes of 7.06 cm were cast and removed from molds after 24 h and then cured in water until the

Table 2. Chemical Composition of OPC, Wollastonite, and Microsilica

Material	Chemical composition (%)								
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	LOI
OPC	63.30	19.30	5.10	3.20	1.56	0.08	0.51	2.30	4.10
Wollastonite	45.60	48.00	1.40	0.60	—	—	—	—	4.00
Microsilica	1.00	94.00	0.70	0.62	0.52	0.30	0.42	—	2.40

time of testing. Compressive strengths of mortars were determined after the ages of 3, 7, 28, 60, 90, and 365 days of moist curing. Three cubes were tested in a hydraulically operated compression testing machine by applying steady and uniform load starting from zero at the rate of 35 $N/mm^2/min$ until the failure of the specimen.

Results and Discussions

Raw Materials

Table 2 presents the chemical composition of OPC, wollastonite, and microsilica. When considered in terms of ASTM C618 (ASTM 2008b), wollastonite may be classified as Class C pozzolan. Its loss on ignition was less than 10% which is in conformity with the code. Chemically, wollastonite comprises 45.6% CaO and 48% SiO_2. Therefore, it is likely to have some cementitious properties in addition to pozzolanic properties. Microsilica on the other hand has high SiO_2 content of 94%.

Table 3 shows the specific gravity, material passing through a 45-micron sieve (by wet sieve), specific surface and mean grain size of OPC, wollastonite, and microsilica. The mean grain sizes suggest that the wollastonite particles were about 4.5 times and microsilica particles were 30 times finer than OPC (Ransinchung et al. 2009). The fineness of microsilica was higher than that of wollastonite by about 2.5 times when considered in terms of BET method.

Fig. 1 shows the particle size and shape of OPC, wollastonite, and microsilica using SEM. It was seen that OPC particles were irregular, wollastonite particles were acicular, and microsilica particles were spherical in shape. Both OPC and wollastonite had solid particles with rough surfaces. The particle sizes of wollastonite were observed to be finer than that of OPC while microsilica comprised agglomeration of ultrafine particles with smoother surface. So, admixing of both finer materials to OPC has the effect of increasing the surface area of the cementitious materials, particularly in case of microsilica. The agglomerates of densified microsilica are designed to break up during mixing process into individual small size spheres of microsilica, while that of wollastonite are themselves capable of dispersing during mixing. This increase in surface area increases the water demand of cementitious materials and reduces workability (Neville 1995). The particle shapes and sizes in SEM images suggests that there are strong possibilities of infilling of voids between OPC particles by finer particles of wollastonite and microsilica. This may lead to a refinement of microstructure that may contribute to the higher compressive strength of mortars.

Paste

Normal Consistency

Table 4 shows the normal consistency of control and admixed pastes. The normal consistency of 100% OPC (control) paste, 100% wollastonite paste, and 100% microsilica paste were 32, 65, and 76%, respectively. When compared to the control paste, the normal consistency of OPC-wollastonite paste had increased in the range of 32.8–47% on admixing of wollastonite in equal increment of 2.5 up to 30%. Similarly, the normal consistency of OPC-microsilica paste had increased in the range of 33.5–40% on admixing of microsilica in equal increment of 2.5 up to 12.5%. In OPC-wollastonite-microsilica paste, the normal consistency had increased from 39.5 to 42% when microsilica proportion was increased from 5% in X2 to 7.5% in X3, while maintaining the uniform wollastonite proportion at 10%. It had also increased from 43 to 44.5% when microsilica proportion was increased from 5% in X4 to 7.5% in X5, while maintaining the uniform wollastonite proportion at 15%.

As much as 2.5–47% of additional water requirement over OPC paste was observed for OPC-wollastonite paste containing 2.5–30% wollastonite. Similarly, 5–25% additional water was required for OPC-microsilica paste containing 2.5–12.5% microsilica. In OPC-wollastonite-microsilica paste, the additional water requirement over OPC paste was observed to be 23% for X2, 31% for X3, 34% for X4, and 39% for X5. Additional water requirement refers to the water required by admixed pastes over and above the water required by 100% OPC paste (control) for attaining normal consistency.

The consistency of cementitious material depends on its type and fineness. More water requirement was reported for cements having higher fineness values (Rao 2003; Ganesan et al. 2007; Temiz et al. 2007). Since wollastonite and microsilica were finer than OPC, the specific surface area of resulting cementitious material increases, thereby needing more water to maintain the same normal consistency. Using the experimentally obtained results, estimation of normal consistency as a variable function $f(x)$ was

Table 3. Physical Properties of OPC, Wollastonite, and Microsilica

Material	Specific gravity	Material retained on 45-micron sieve (%)	Specific surface (m^2/kg)		Mean grain size (micron)
			Blaine	BET	
OPC	3.15	11.0	298	—	18.0
Wollastonite	2.90	3.2	—	842.7	4.0
Microsilica	2.20	0.7	—	20,000.0	0.6

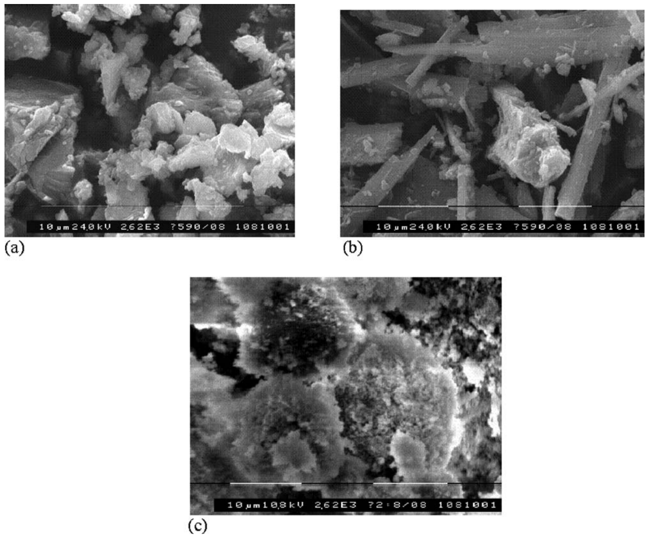

Fig. 1. SEM of materials (a) OPC; (b) wollastonite; and (c) microsilica

found to be dependent on values of variables x_1 (wollastonite proportion, %) and x_2 (microsilica proportion, %) using the following model:

$$f(x) = a + bx_1 + cx_2 \qquad (1)$$

where a=constant and b and c=coefficients of variables x_1 and x_2, respectively.

Table 4. Normal Consistency and Setting Times of Pastes

Mix designation	Normal consistency (%)	Initial setting time (min)	Final setting time (min)
Control or X0	32.0	155	221
W0	65.0	—	—
W1	32.8	160	231
W2	35.0	162	244
W3	35.8	167	258
W4	36.0	178	267
W5	38.0	180	281
W6 or X1	38.8	185	294
W7	40.5	194	310
W8	42.0	206	322
W9	43.0	208	326
W10	44.5	210	334
W11	45.6	207	337
W12	47.0	199	326
M0	76.0	—	—
M1	33.5	155	221
M2	35.5	150	219
M3	36.5	147	217
M4	38.0	140	216
M5	40.0	136	216
X2	39.5	165	256
X3	42.0	159	247
X4	43.0	182	271
X5	44.5	170	261

Table 5. Prediction Models for Normal Consistency of Pastes

Type of admixture with OPC	Prediction models	R^2	Validity range
Present work:			
Wollastonite	$31.788+0.501x_1$	0.994	$x_1 \geqslant 0$
Microsilica	$32.024+0.623x_2$	0.994	$x_2 \geqslant 0$
Wollastonite and microsilica	$31.783+0.627x_1+0.555x_2$	0.996	$x_1, x_2 \geqslant 0$
Rao (2003):			
Microsilica	$32.40+0.4x_2$	0.980	

Predictive models for normal consistency having a w/c ratio of 0.50 are presented in Table 5. It is observed that the equation obtained for microsilica in the present work have better coefficient of determination values.

Setting Times

The ability of cementitious material to make fluid mortar into hardened state is represented by setting time. Setting times of control and admixed pastes are shown in Table 4.

Initial and final setting times of OPC paste were 155 and 211 min, respectively. For OPC-wollastonite paste, the initial and final setting times had increased up to 25 and 27.5%, respectively, on admixing of wollastonite, beyond which it has decreased. Increase in setting time may be attributed to the delay in hydration reaction due to increase of wollastonite proportion in the cementitious material which has a lower CaO content as compared to OPC. After attaining a tipping point of increase, the setting times had subsequently decreased. This decrease may be due to adequate proportion of wollastonite in cementitious material, causing physical rearrangement of particles due to infilling of pores in paste, leading to densification and increased resistance to the penetration of Vicat needle. Second being Class C pozzolan, adequate quantity of wollastonite in paste may have helped hydration as well as pozzolanic reactions.

For OPC-microsilica paste, the initial setting time has decreased with the increase in microsilica proportion. However, the decrease in final setting time was largely insignificant with the increase in microsilica proportion. Similar observations were also made by Rao (2003). Some studies have reported that the pozzolanic action of microsilica was very active at early hours of hydration (Larbi et al. 1990; Bonen and Khayat 1995; Babu and

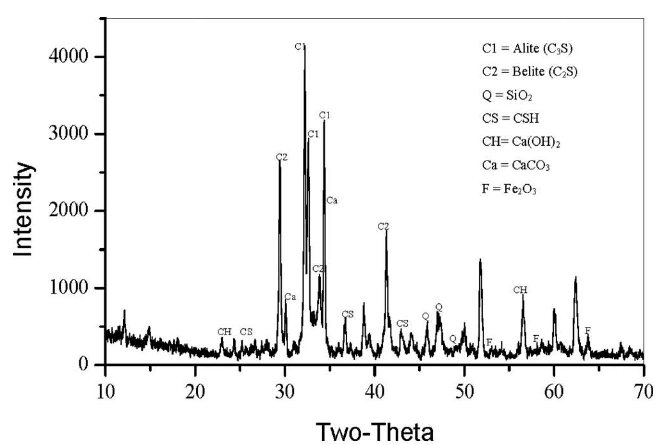

Fig. 2. XRD pattern of 100% OPC paste after 28 days of curing

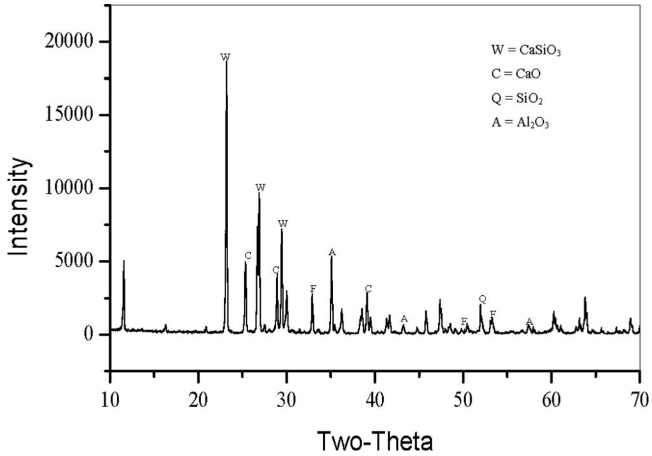

Fig. 3. XRD pattern of 100% wollastonite paste after 28 days of curing

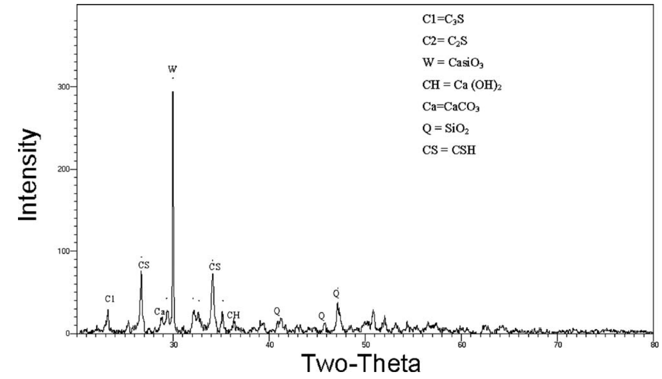

Fig. 5. XRD pattern of OPC: wollastonite paste in the proportion of 85:15 after 28 days of curing

Prakash 1995; Rao 2003). Also, microsilica was reported to accelerate the hydration of C_3A and C_3S reaction at the early hours of hydration (Cheng-yi and Feldman 1985). These might be the causative factors for decline of setting times.

In OPC-wollastonite-microsilica paste, the initial and final setting times had decreased from mix designation X2 to mix designation X3, and also from mix designation X4 to mix designation X5 with the respective increase of microsilica proportion from 5 to 7.5%. Among them the shortest setting times has occurred in paste X3 and the longest in paste X4. The results suggest that X3 was the most suitable mix proportion to obtain the optimum level of pozzolanic reaction and particle packing. Its initial and final setting times were 1.03 and 1.12 times, respectively, longer than that of control paste. The initial and final setting times for Paste X5 incorporating maximum wollastonite proportion of 15% were 1.10 and 1.18 times, respectively, longer than the control paste. The hydration reaction of CaO available in OPC and wollastonite with water may form CSH directly, while the liberated $Ca(OH)_2$ may react with the SiO_2 available in microsilica and wollastonite to form additional CSH. This illustrates the pivotal role of wollastonite in reducing the OPC and microsilica proportion which are costlier ingredients of concrete. Setting times of all cementitious materials were within the allowance specified by ASTM C150 (ASTM 2007).

Mineralogical Analysis of Paste

The XRD patterns for control and admixed pastes are shown in Figs. 2–7. Fig. 2 of control paste shows the prominence of hydrated products like CSH, $Ca(OH)_2$, and $CaCO_3$ and unhydrated compounds like alite (C_3S) and belite (β-C_2S), along with small amounts of Fe_2O_3 and quartz (SiO_2). Wollastonite paste in Fig. 3 shows the presence of $CaSiO_3$, quartz (SiO_2), and CaO prominently with small amount Fe_2O_3, while microsilica paste in Fig. 4 shows SiO_2 as the principal constituent compound.

XRD pattern of paste having cementitious mix of 85% OPC and 15% wollastonite in Fig. 5 shows that there are peaks of unhydrated compounds like alite, belite, and $CaSiO_3$ with comparatively lower contents of $Ca(OH)_2$ and $CaCO_3$ as compared to control paste. It is observed that admixing of wollastonite with OPC has reduced the peak of $Ca(OH)_2$ and $CaCO_3$ considerably. XRD pattern of paste having 92.5% OPC and 7.5% microsilica in Fig. 6 shows strong peaks of few unhydrated alite, belite, and CSH and comparatively much lower peaks of $Ca(OH)_2$ and $CaCO_3$ in comparison to control paste. The XRD pattern of paste having 82.5% OPC, 10% wollastonite, and 7.5% microsilica in Fig. 7 shows that the hydrated products like $Ca(OH)_2$ and $CaCO_3$ were considerably reduced and CSH volume has increased significantly with respect to the control paste. Few peaks of wollastonite mineral and unhydrated compounds like alite and belite

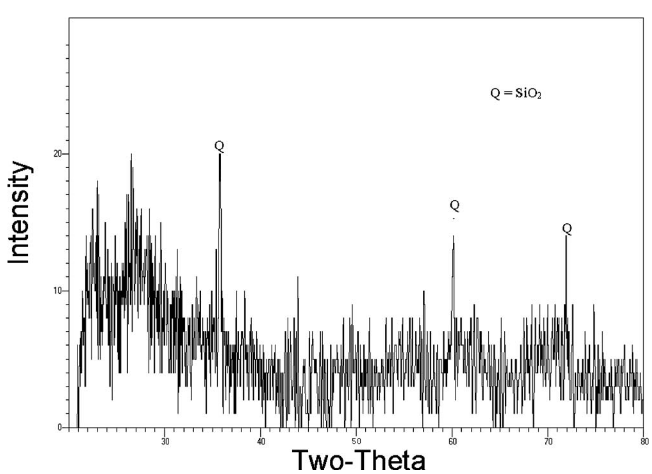

Fig. 4. XRD pattern of 100% microsilica paste after 28 days of curing

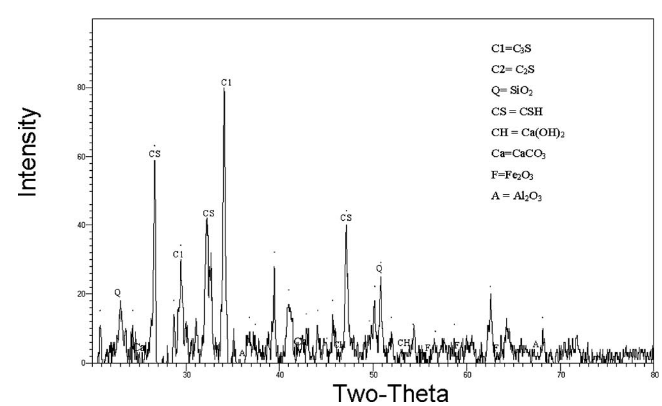

Fig. 6. XRD pattern of OPC: microsilica paste in the proportion of 92.5:7.5 after 28 days of curing

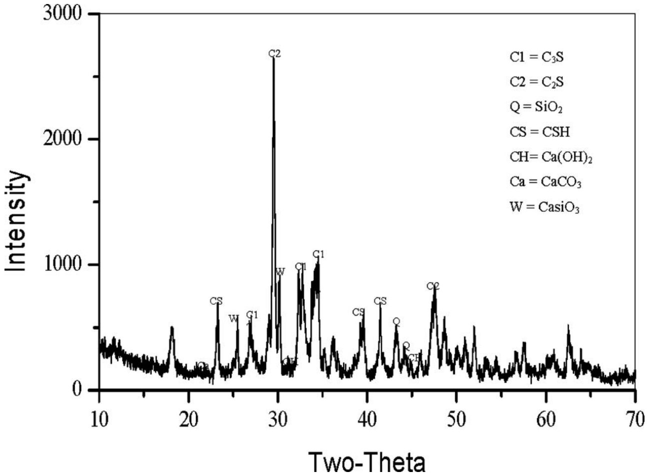

Fig. 7. XRD pattern of OPC: wollastonite: microsilica paste in the proportion of 82.5:10:7.5 after 28 days of curing

were also observed. The XRD patterns show that admixing of wollastonite and microsilica with OPC has lowered $Ca(OH)_2$ and carbonation in pastes and increased the volume of CSH.

Mortar

High-Range Water Reducer Dosage of Mortar

The HRWR dosages of mortars are shown in Table 1. It was observed that the HRWR dosage has increased in the range of 0.33–1.32% with admixing of wollastonite in equal increment of 2.5 up to 30% with OPC, while it has increased in the range of 0.32–0.75% with admixing of microsilica in equal increment of

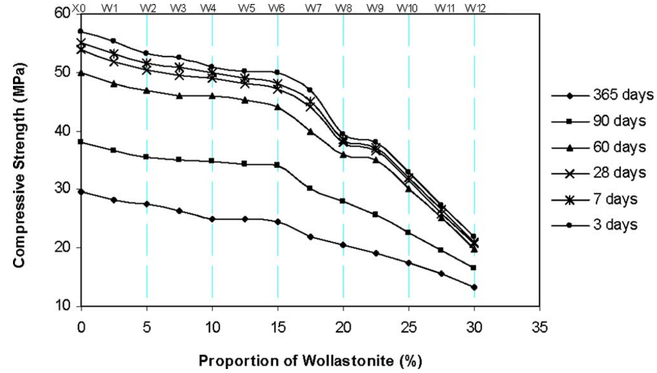

Fig. 8. Relationship between compressive strength of OPC-wollastonite mortar and proportion of wollastonite in mix

2.5 up to 12.5% with OPC. Also, admixing of both wollastonite and microsilica with OPC, the HRWR dosage has increased from 1.0% for X2 (with 5% microsilica) to 1.6% for X3 (with 7.5% microsilica) while maintaining a uniform wollastonite proportion of 10%. It has also increased from 1.3% for X4 (with 5% microsilica) to 2% for X5 (with 7.5% microsilica) while wollastonite proportion was maintained uniformly at 15%.

Compressive Strength of Mortar

Compressive strength of control and admixed mortars are shown in Table 6. Averages of five samples were used to obtain the data for compressive strength.

Compressive strength of all tested mortars has increased rapidly up to 28 days of moist curing, beyond which it was gradual up to 365 days. With the increase of wollastonite proportion in OPC-wollastonite mortar, the compressive strengths had gradu-

Table 6. Compressive Strength of Mortars

Mix designation	Compressive strength (MPa)					
	3 days	7 days	28 days	60 days	90 days	365 days
Control or X0	29.6	38.0	50.0	54.0	55.2	57.0
W1	28.2	36.6	48.2	51.8	53.3	55.4
W2	27.6	35.5	47.0	50.5	51.5	53.2
W3	26.3	35.0	46.0	49.6	51.0	52.6
W4	25.0	34.8	46.0	49.0	50.0	51.0
W5	25.0	34.2	45.2	48.0	49.0	50.3
W6 or X1	24.6	34.0	44.1	47.2	48.0	50.0
W7	22.0	30.0	40.0	44.0	45.0	47.0
W8	20.4	28.0	36.0	38.0	38.6	39.5
W9	19.0	25.6	35.0	36.6	37.0	38.0
W10	17.4	22.6	30.0	31.5	32.0	33.0
W11	15.6	19.6	25.1	26.0	26.5	27.2
W12	13.2	16.5	19.8	20.8	21.0	22.0
M1	31.5	40.3	52.5	55.6	56.6	58.5
M2	32.0	42.0	54.2	57.1	58.0	60.0
M3	34.0	45.0	58.5	63.0	64.5	66.2
M4	30.5	39.6	51.0	54.7	55.8	58.0
M5	29.8	38.6	50.4	53.8	55.4	57.6
X2	31.0	40.6	51.6	56.0	57.5	60.0
X3	31.5	42.2	54.4	60.0	61.0	63.0
X4	29.2	36.4	46.8	50.9	52.0	54.0
X5	30.1	39.0	50.3	54.9	56.2	58.6

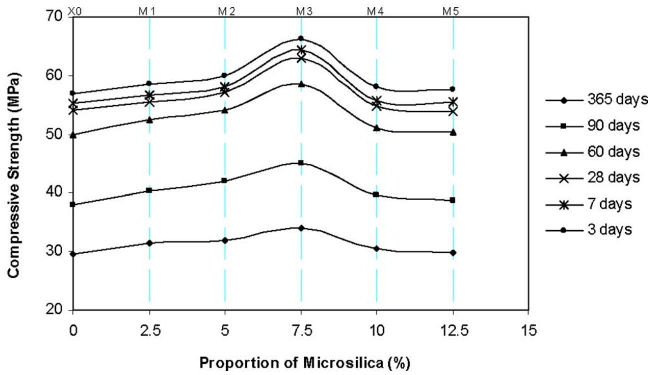

Fig. 9. Relationship between compressive strength of OPC-microsilica mortar and proportion of microsilica in mix

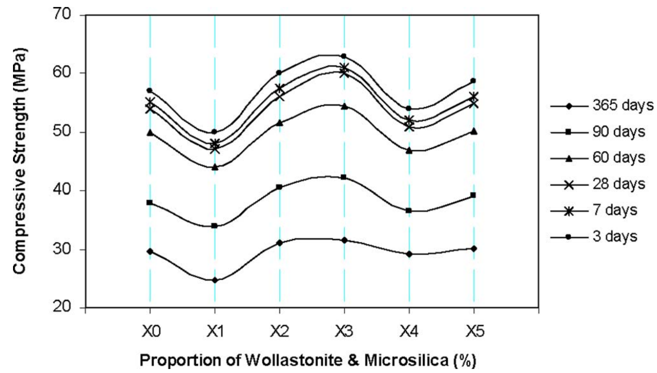

Fig. 10. Relationship between compressive strength of OPC-wollastonite-microsilica mortar and proportion of wollastonite and microsilica in mix

ally decreased with respect to the control mortar for all curing ages, as shown in Fig. 8. It was observed that up to 15% admixing of wollastonite was possible with OPC without appreciable loss of compressive strength. Up to this replacement level, the relative compressive strength of admixed mortar as compared to the control mortar was maintained between 83.1 and 89.5% for 3–365 days of curing. In case of OPC-microsilica mortar, it was observed from Fig. 9 that, with an increase in microsilica proportion up to 7.5%, the compressive strength has increased. Beyond this replacement level, the compressive strength has decreased for all days of curing. Relative compressive strength at 5% admixing was more than that of 10% admixing of microsilica at all curing ages as compared to the control mortar. Therefore, 10 and 15% of wollastonite and 5 and 7.5% of microsilica were suitable proportions for admixing with OPC to form new cementitious materials for further study.

Fig. 10 shows that the compressive strength of OPC-wollastonite-microsilica mortar has increased from mix designation X2 to mix designation X3 as compared to control (X0). This was under the respective increase of microsilica proportion from 5 to 7.5% at all ages of curing, having wollastonite proportion maintained at 10%. When wollastonite proportion was raised to 15%, admixing of 5% microsilica to OPC has lowered the compressive strength of mix designation X4 below the control. Also, admixing of 7.5% microsilica has made mix designation X5 to achieve compressive strength higher than the control mortar for 3–365 days of curing. The relative compressive strength of X3 and X5 were in the range of 106.4–111.1% and 100.6–102.8%, respectively, as compared to the control mortar. Therefore, mix designation X3 is the optimum mix proportion that has attained maximum compressive strength among all mixes at all curing ages. In the interest of economy, mix designation X5 would be preferable due to maximum utilization of low-cost wollastonite at 15% and having attained compressive strength higher than control mortar at all days of curing.

The mechanisms responsible for strength enhancement using fine grained pozzolans were identified as (1) strength enhancement by pore size refinement and matrix densification; (2) strength enhancement by reduction of $Ca(OH)_2$ content; and (3) strength enhancement by cement paste-aggregate interfacial zone refinement (Feldman and Cheng-yi 1985; Cohen and Klitsika 1986; Cohen 1990; Rao 2003). The transformation of large pores into finer pores, which is generally termed as pore refinement as a consequence of pozzolanic reaction, plays an important role in enhancing strength of admixed mortar. These findings when applied to the present work leads to infer that the presence of wollastonite and microsilica in conventional OPC mortar may cause considerable reduction in the volume of large pores at all ages, and therefore instrumental in enhancing the compressive strength.

The compressive strength of mortar as response variable $f(x)$ was found to be dependent on the days of moist curing x for the proportion of wollastonite at 10 and 15%, and the proportion of microsilica at 5 and 7.5% which was measured by a logarithmic function as follows:

$$f(x) = a + b\ \ln(x) \tag{2}$$

where a=constant and b=coefficient of variable x. The prediction models are presented in Table 7.

From the experimental data, the variation of compressive strength of mortar as responsive variable $f(x)$ was again measured at combinations of values of variables x_1 (wollastonite proportion,

Table 7. Prediction Models for Compressive Strength of Mortars from Days of Moist Curing

Admixture proportion with OPC	Prediction models	R^2	Validity range
100% OPC (no admixing)	$26.487+5.984\ \ln(x)$	0.901	$x \geqslant 0$
W4 (10% wollastonite)	$23.292+5.560\ \ln(x)$	0.864	$x \geqslant 0$
W6 or X1 (15% wollastonite)	$22.684+5.359\ \ln(x)$	0.887	$x \geqslant 0$
M2 (5% microsilica)	$29.833+5.956\ \ln(x)$	0.879	$x \geqslant 0$
M3 (7.5% microsilica)	$31.009+6.955\ \ln(x)$	0.890	$x \geqslant 0$
X2 (10% wollastonite and 5% microsilica)	$27.889+6.199\ \ln(x)$	0.916	$x \geqslant 0$
X3 (10% wollastonite and 7.5% microsilica)	$28.355+6.802\ \ln(x)$	0.900	$x \geqslant 0$
X4 (15% wollastonite and 5% microsilica)	$26.016+5.424\ \ln(x)$	0.917	$x \geqslant 0$
X5 (15% wollastonite and 7.5% microsilica)	$26.761+6.159\ \ln(x)$	0.917	$x \geqslant 0$

Table 8. Prediction Models for Compressive Strength of Mortars from the Proportions of Admixture

Type of admixture with OPC	Age (days)	Prediction models	R^2	Validity range
Wollastonite	3	$30.398-0.519x_1$	0.967	$0\leq x_1\leq 55$
	7	$40.303-0.685x_1$	0.907	$0\leq x_1\leq 55$
	28	$53.357-0.930x_1$	0.894	$0\leq x_1\leq 55$
	60	$57.546-1.031x_1$	0.900	$0\leq x_1\leq 55$
	90	$58.953-1.068x_1$	0.903	$0\leq x_1\leq 55$
	365	$60.869-1.103x_1$	0.903	$0\leq x_1\leq 55$
Microsilica	3	$29.72+0.548x_2$	0.957	$0\leq x_2\leq 7.5$
	7	$37.92+0.908x_2$	0.988	$0\leq x_2\leq 7.5$
	28	$49.72+1.088x_2$	0.964	$0\leq x_2\leq 7.5$
	60	$53.15+1.14x_2$	0.878	$0\leq x_2\leq 7.5$
	90	$54.18+1.172x_2$	0.846	$0\leq x_2\leq 7.5$
	365	$56.06+1.164x_2$	0.865	$0\leq x_2\leq 7.5$
Wollastonite and microsilica	3	$29.685-0.314x_1+0.733x_2$	0.950	$0\leq x_1\leq 15$, $0\leq x_2\leq 7.5$
	7	$38.647-0.352x_1+0.849x_2$	0.888	$0\leq x_1\leq 15$, $0\leq x_2\leq 7.5$
	28	$50.622-0.492x_1+1.019x_2$	0.915	$0\leq x_1\leq 15$, $0\leq x_2\leq 7.5$
	60	$54.698-0.568x_1+1.270x_2$	0.924	$0\leq x_1\leq 15$, $0\leq x_2\leq 7.5$
	90	$55.898-0.588x_1+1.310x_2$	0.934	$0\leq x_1\leq 15$, $0\leq x_2\leq 7.5$
	365	$57.742-0.577x_1+1.347x_2$	0.928	$0\leq x_1\leq 15$, $0\leq x_2\leq 7.5$

%) and x_2 (microsilica proportion, %) using the model stated in Eq. (1). Predictive models for estimation of compressive strength at various ages are presented in Table 8.

Conclusions

The results of this experiment lead to the following conclusions:

1. Wollastonite is a Class C pozzolan as per ASTM C618 (ASTM 2008b). When ground to fine powder, it attains an average particle size of 4 microns which is about 4.5 times finer than OPC. It has an average surface area of $842.7\ m^2/kg$ and retention on 45-micron sieve of 3.20%. SEM images show that wollastonite particles were solid, acicular in shape, and have rough surfaces.
2. Admixing of wollastonite causes increase in initial and final setting times up to 25 and 27.5% replacement of OPC, respectively, beyond which it decreases. Admixing of microsilica to OPC decreases the initial setting time, but the final setting time was mostly unaffected. Admixing of both wollastonite and microsilica to OPC caused a decrease in initial and final setting times with the increase of microsilica proportion from 5 to 7.5%. Mix designations X3 with 10% wollastonite and 7.5% microsilica and X5 with 15% wollastonite and 7.5% microsilica have setting times reasonably closer to the conventional OPC paste. Mix designation X3 has the potential to achieve the highest pozzolanic reaction and particle packing, while mix designation X5 has the potential of achieving maximum economy. Wollastonite is capable of reducing the OPC and microsilica proportion in the cementitious material which are costly ingredients of concrete.
3. Mortar mix designation X3 (82.5% cement, 10% wollastonite, and 7.5% microsilica as cementitious material) has presented the highest compressive strength of 54.4 MPa at 28 days, 61.0 MPa at 90 days, and 63.0 MPa at 365 days in the study. Mortar mix designation X5 (77.5% cement, 15% wollastonite, and 7.5% microsilica as cementitious material) has attained compressive strength of 50.3 MPa at 28 days, 56.2 MPa at 90 days, and 58.6 MPa at 365 days, which was higher than conventional OPC mortar, rendering maximum cement replacement and better economy.
4. Based on the experimental results, the cementitious material comprising OPC, wollastonite, and microsilica has a high potential for use in concrete work that requires high compressive strength. However, more research is needed on concrete and its durability aspects.
5. Strong logarithmic correlations were found to exist between days of moist curing and compressive strength of mortar. Also, strong linear correlations were found to exist between proportions of admixing of wollastonite and/or microsilica and compressive strength of mortar on specific 3, 7, 28, 60, 90, and 365 days of moist curing. Predictive equations for these correlations are presented.

References

American Concrete Institute (ACI). (2000). "ACI 232.2R use of flyash in concrete." *ACI 232.2R*, Detroit.

ASTM. (2004). "Standard test method for normal consistency of hydraulic cement." *C187*, West Conshohocken, Pa.

ASTM. (2007). "Standard specification for portland cement." *C150*, West Conshohocken, Pa.

ASTM. (2008a). "Standard test methods for time of setting of hydraulic

cement by Vicat needle." *C191*, West Conshohocken, Pa.
ASTM. (2008b). "Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete." *C618*, West Conshohocken, Pa.
Babu, K. G., and Prakash, P. V. S. (1995). "Efficiency of silica fume in concrete." *Cem. Concr. Res.*, 25(6), 1273–1283.
Bentz, D. P., and Stutzman, P. E. (1994). "Evolution of porosity and calcium hydroxide in laboratory concretes containing silica fume." *Cem. Concr. Res.*, 24(6), 1044–1050.
Bonen, D., and Khayat, K. H. (1995). "Characterization and pozzolanic properties of silica fume stored in an open pond." *Cem. Concr. Res.*, 25(2), 395–407.
Chai, J., and Boonmark, R. (2003). "Cementing material from calcium carbide residue-rice husk ash." *J. Mater. Civ. Eng.*, 15(5), 470–475.
Cheng-yi, H., and Feldman, R. F. (1985). "Hydration reactions in portland cement-silica fume blends." *Cem. Concr. Res.*, 15(4), 585–592.
Cohen, M. D. (1990). "A look at silica fume and its actions in portland cement concrete." *Indian Concr. J.*, 64(9), 429–438.
Cohen, M. D., and Klitsika, M. (1986). "Mechanisms of hydration and strength developments in portland cement composites containing silica fume particles." *Indian Concr. J.*, 60(11), 296–299.
Feldman, R. F., and Cheng-yi, H. (1985). "Properties of portland cement silica fume pastes: II. Mechanical properties." *Cem. Concr. Res.*, 15(6), 943–952.
Ganesan, K., Rajagopal, K., and Thangavel, K, (2007). "Rice hush ash blended cement: Assessment of optimal level of replacement for strength and permeability properties of concrete." *Constr. Build. Mater.*, 22(8), 1675–1683.
Kenai, S., Soboyejo, W., and Soboyejo, A. (2004). "Some engineering properties of limestone concrete." *Mater. Manuf. Processes*, 19(5), 949–961.
Larbi, J. J., Fraay, A. L. A., and Bijen, J. M. J. M. (1990). "The chemistry of the pore fluid of silica fume-blended cement systems." *Cem. Concr. Res.*, 20(4), 506–516.
Malhotra, V. M., Ramachandran, V. S., Feldman, R. F., and Aitcin, P. C. (1987). *Condensed silica fume in concrete*, CRC, Boca Raton, Fla.
Massazza, F. (1993). "Pozzolanic cements." *Cem. Concr. Compos.*, 15(4), 185–214.
Mathur, R., Mishra, A. K., and Goel, P. (2007). "Marble slurry dust and wollastonite inert mineral admixtures for cement concrete." *Indian Highways*, 35(12), 41–46.
Mehta, P. K. (1981). "Studies on blended portland cements containing Santorin earth." *Cem. Concr. Res.*, 11(4), 507–518.
Monteiro, P. J. M., and Mehta, P. K. (1986). "Improvement of the aggregate cement paste transition zone by grain refinement of hydration product." *Proc., 8th Int. Congress on the Chemistry of Cement*, Vol. 2, Rio de Janeiro, Brazil, 433–437.
Neville, A. M. (1995). *Properties of concrete*, 4th Ed., Pearson Education, Inc., and Dorling Kindersley Publishing, Inc., New Delhi, India.
Paul, F. K. (1977). "*Mineral descriptions—Wollastonite. Optical mineralogy*, 4th Ed., McGraw-Hill, New York.
Ramachandran, V. S., Feldman, R. F., and Beaudoin, J. J. (1981). *The system CaO–SiO*$_2$. *Concrete science: Treatise on concurrent research*, Heyden & Son, London.
Ransinchung, G. D., Kumar, B., and Kumar, V. (2009). "Assessment of water absorption and chloride ion penetration of pavement quality concrete admixed with wollastonite and microsilica." *Constr. Build. Mater.*, 23(2), 1168–1177.
Rao, G. A. (2003). "Investigations on the performance of silica fume-incorporated cement pastes and mortars." *Cem. Concr. Res.*, 33(11), 1765–1770.
Tagnit-Hamou, A., Pertove, N., and Luke, K. (2003). "Properties of concrete containing diatomaceous earth." *ACI Mater. J.*, 100(1), 73–78.
Temiz, H., Kose, M. M., and Koksal, S. (2007). "Effects of portland composite and composite cements on durability of mortar and permeability of concrete." *Constr. Build. Mater.*, 21(6), 1170–1176.
Uzal, B., and Turanli, L. (2003). "Studies on blended cements containing a high volume of natural pozzolans." *Cem. Concr. Res.*, 33(11), 1777–1781.
Wolkem India Limited. (2003). *Leaders in wollastonite and calcite*, "From mines to market," Wolkem India Ltd., Udaipur, India.
Zhang, M. H., Lastra, R., and Malhotra, V. M. (1996). "Rice husk ash paste and concrete: Some aspects of hydration and the microstructure of the interfacial zone between the aggregate and the paste." *Cem. Concr. Res.*, 26(6), 963–977.