CHAPTER - 4
CONCLUSIONS

This chapter deals with the conclusions drawn on the basis of results obtained by the study of effect of partial substitution of cement with MS and/or NS on fresh, hardened and durability properties & microstructure of cement mortars in comparison to control mix (CMS). The conclusions obtained have been discussed ahead for all of the studied properties in terms of effect of rate of content enhancement of micro silica and nano silica as partial substituent for cement, as well as increase in curing age. Along with the difference in the pozzolanic action of micro silica and nano silica has been considered.

4.1. NORMAL CONSISTENCY

The consistency of CMS was found to be lower as compared to MM1 (5% MS), MM2 (10% MS), MM3 (15% MS), MM4 (20% MS), MN1 (0.5% NS), MN2 (0.75% NS), MN3 (1.0% NS), MN4 (1.25% NS), MNM1 (5% MS+1% NS), MNM2 (10% MS+1% NS), MNM3 (15% MS+1% NS) and MNM4 (20% MS+1% NS) cement pastes containing finer silica particles with greater specific area as compared to cement. An increase in consistency of MM1, MM2, MM3 and MM4 cement pastes was observed with increase in content of MS due to increase in content of micro silica particles. Similar effect was found in case of MN1, MN2, MN3 and MN4 cement pastes with increase in content of NS and MNM1, MNM2, MNM3 and MNM4 cement pastes with increase in content of MS. However, the consistency of MN1, MN2, MN3 and MN4 cement pastes was lesser as compared to MM1, MM2, MM3 and MM4 cement pastes because of difference in amount of silica used for substitution. The consistency of MNM1, MNM2, MNM3 and MNM4 cement pastes was further observed to be higher as compared to
MM1, MM2, MM3, MM4, MN1, MN2, MN3 and MN4 cement pastes because of better
distribution of micro silica particles in presence of nano silica particles in the matrix.

4.2. SETTING TIME

The setting time of CMS was found to be lower as compared to MM1, MM2, MM3,
MM4 cement pastes linked to the thinning effect of micro silica particles. However, the
setting time of CMS was found to be higher as compared to MN1, MN2, MN3, MN4,
MNM1, MNM2, MNM3 and MNM4 cement pastes linked to the thickening effect of
ultra fine nano silica particles.

An increase in content of MS from 5% to 20% resulted in an increase in setting time of
MM1, MM2, MM3 and MM4 cement pastes due to increase in the thinning effect. On the
other hand, an increase in content of NS from 0.5% to 1.25% resulted in a decrease in
setting time of MN1, MN2, MN3 and MN4 cement pastes due to increase in the
thickening effect. A significant decrease in setting time of MNM1, MNM2, MNM3 and
MNM4 cement pastes was observed as compared to CMS. An increase in setting time of
MNM1, MNM2, MNM3 and MNM4 cement pastes was observed with increase in
content of MS attributed to the increased thinning effect of micro silica particles.

4.3. FLOW OR WORKABILITY

The flow of CMS was found to be higher as compared to MM1, MM2, MM3, MM4,
MN1, MN2, MN3, MN4, MNM1, MNM2, MNM3 and MNM4 mortar specimens. The
flow of cement mortar depends upon the size and packing of particles. Partial substitution
of cement by comparatively smaller sized micro silica and nano silica particles enhance
the packing of the particles by occupation of the voids in the matrix and reduce the flow
due to their stabilizing effect.
An increase in content of MS from 5% to 20% resulted in a decrease in flow of MM1, MM2, MM3 and MM4 mortar specimens due to packing promotion by finer micro silica particles and reduction of space available for water to bleed over the mortar surface. Similarly, an increase in content of NS with filler effect from 0.5% to 1.25% resulted in a decrease in flow of MN1, MN2, MN3 and MN4 mortar specimens due to increase in the homogeneity and stiffness of matrix.

A significant decrease in flow of MNM1, MNM2, MNM3 and MNM4 mortar specimens was observed as compared to CMS due to better packing of micro silica particles in matrix in presence of nano silica particles. The voids left unoccupied even by micro silica particles are occupied by nano silica particles because of their ultrafine size and filler effect. The flow of MNM1, MNM2, MNM3 and MNM4 mortar specimens was further found to decrease significantly with increase in content of MS attributed to the increased homogeneity of the matrix by occupation of the voids by micro silica and nano silica particles.

4.4. COMpressive StRENGTH

The compressive strength of CMS was found to be lesser as compared to MM1, MM2, MM3, MM4, MN1, MN2, MN3, MN4, MNM1, MNM2, MNM3 and MNM4 cement mortars indicating the pozzolanic action of micro silica and nano silica particles leading to consumption of calcium hydroxide and generation of additional CSH gel responsible for enhancement of compressive strength.

An increase in compressive strength of MM1, MM2 and MM3 mortars was obtained with increase in content of MS from 5% to 15% along with a slight reduction in strength of MM4 mortar as compared to MM3 mortar. The increase in compressive strength was because of involvement of micro silica in the pozzolanic reaction while the slight decrease was linked to the friction between micro silica particles at higher content. An increase in compressive strength of MN1, MN2 and MN3 mortars was obtained with an
increase in content of NS from 0.5% to 1% along with a slight reduction in strength of MN4 (1.25%NS) mortar as compared to MN3 (1%NS) mortar. The gain of compressive strength was linked to the filler effect and better pozzolanic behavior of NS leading to production of extra CHS gel as compared to MS. The slight decrease in compressive strength of MN4 specimen as compared to MN3 specimen was attributed to the agglomeration of nano particles at higher content in the cement matrix. Thus, 1% content of NS was designated as the optimum percentage, used further in mortars with MS+1%NS.

The MNM1, MNM2, MNM3 and MNM4 cement mortars with substitution of cement by MS+1%NS showed further enhancement in compressive strength due to the better performance of MS and NS in combination. However, the compressive strength was found to increase on substitution of cement with 5% to 10% MS, but decreased further at substitution of cement with 15% to 20% of MS. This decrease in compressive strength was because of the reduction in homogeneity of the cement matrix at higher content of MS. An empirical relationship was also developed between the compressive strength at standard curing age and the required curing age.

4.5. SPLIT TENSILE STRENGTH

The tensile strength was observed to increase with curing age for CMS, MM1, MM2, MM3, MM4, MN1, MN2, MN3, MN4, MNM1, MNM2, MNM3 and MNM4 mortar specimens with lowest value for CMS due to pozzolanic action in other specimens. The trends for tensile strength were similar to that in compressive strength studies for increase in the substitution content of MS or NS accordingly. The results not only confirmed the better pozzolanic behavior of nano silica but also the beneficiary use of micro silica in presence of optimized content of nano silica. Thus, maximum tensile strength was obtained for MNM2 (10% MS+1%NS) specimens with increased homogeneity and
densification of the matrix. An empirical relationship was also developed between the tensile strength at standard curing age and the required curing age.

4.6. RAPID CHLORIDE PERMEABILITY TEST (RCPT)

A decrease in RCPT values and hence chloride ion permeability of CMS, MM1, MM2, MM3, MM4, MN1, MN2, MN3, MN4, MNM1, MNM2, MNM3 and MNM4 specimens with increase in curing age was observed due to strength development obvious from mechanical strength studies. Least RCPT value was obtained for MM3 (15% MS) specimen in case of MM1, MM2, MM3 and MM4 specimens. On the other hand, in case of MN1, MN2, MN3 and MN4 specimens, least RCPT value was obtained for MN3 (1%NS) specimen having maximum compressive and tensile strength. Best results were obtained for MNM2 (10% MS+1% NS) specimen among all the studied specimens with overall maximum compressive and tensile strength. The results further strengthened the enhanced pozzolanic action with substituent content of 10%MS+1%NS.

4.7. CARBONATION

The depth of carbonation for CMS, MM1, MM2, MM3, MM4, MN1, MN2, MN3, MN4, MNM1, MNM2, MNM3 and MNM4 specimens was observed to increase with increasing curing age in correlation with reduction in pore structure of the cement matrix with CSH development at increased curing age. MM3 specimen exhibited least depth of carbonation and lowest value of Carbonation coefficient among MM1, MM2, MM3 and MM4 specimens. Least carbonation depth was obtained for MN3 specimens in case of MN1, MN2, MN3 and MN4 specimens in consistence with strength analysis. However, the carbonation depth of MNM2 (10% MS+1% NS) specimens was found to be least among
all the specimens indicating the enhanced durability of these specimens towards carbon dioxide.

4.8. **SULFATE ATTACK**

The compressive strength of CMS and all the other specimens in exposure to magnesium sulfate solution was found to increase with increase in age of curing, but at the same time the values were lesser as compared to that in water. The strength was reduced in comparison to the strength in water due to slight destruction of CSH gel and formation of gypsum. The trends were similar to that observed in earlier studies with best performance in terms of enhanced durability towards magnesium sulfate solution by MNM2 (10% MS+1% NS) specimens.

4.9. **CHLORIDE ATTACK**

In comparison to sulfate attack, CMS and all the specimens exhibited higher compressive strength in sodium chloride solution as compared to magnesium sulfate solutions indicating little effect of chloride attack. Otherwise the trends for compressive strength in exposure to sodium chloride solution were similar to that observed in case of sulfate attack. MNM3 specimens with 15% MS+1% NS was found to have maximum compressive strength indicating the better pozzolanic action of MS+1%NS.

4.10. **STATISTICAL ANALYSIS**

Regression model was estimated for the normal consistency and setting time with the value of $R^2$ varying from 0.8876 to 0.99915 for normal consistency and from 0.6449 to 0.9978 for setting time. The compressive and split tensile strength of specimens were optimized using Box-Behnken design. The plots revealed the maxima of strength values
for 10% MS+1% NS substitution content with maximum increase in compressive strength and confirmed the optimum content as 1% NS. The low values of p and higher value of $R^2$ in comparison to $R^2$ adjusted values obtained by ANOVA confirmed the significance of the results. Further, a good correlation was observed between the studied properties including compressive strength, tensile strength, rapid chloride permeability, sulfate attack, chloride attack with high value of $R^2$. An empirical expression was developed for the relationship between compressive and split tensile strength at the studied ages and a good validation of the results was obtained.

4.11. XRD ANALYSIS

The XRD patterns of MM1, MM2, MM3, MM4, MN1, MN2, MN3, MN4, MNM1, MNM2, MNM3 and MNM4 specimens showed an increase in the peak intensity of Q in comparison to CMS due to presence of silica in higher amount. However, the peak intensity of Q was found to decrease and that of CSH was found to increase with increase in curing age, indicating the progression of the pozzolanic reaction. The same effect was observed with increase in content of MS from 5% to 15% in MM1, MM2, MM3 and MM4 specimens with slight reversal as the content of MS was increased from 15% to 20%. The trend confirmed the loss of pozzolanic activity of MS at higher content due to friction among micro silica particles.

Similar trend in peak intensity was observed with increase in content of NS from 0.5% to 1%, with slight reversal as the content of NS was increased from 1% to 1.25% due to reduction in pozzolanic activity of nano silica particles at higher content. However, in case of MNM1, MNM2, MNM3 and MNM4 specimens, the change in trends was reported as the content of MS substitution was increased up to 10%. The trends are in consistence with strength and durability studies indicating the decrease in pozzolanic activity at higher content of MS even in presence of optimized content of NS.
4.12. SEM-EDX ANALYSIS

The microstructure of MM1, MM2, MM3, MM4, MN1, MN2, MN3, MN4, MNM1, MNM2, MNM3 and MNM4 specimens appeared comparatively more compact with progression in curing age and in comparison to CMS. The high Ca/Si ratio of 9.95 for CMS at 3 days confirmed the presence of large amount of CH produced in the hydration reaction. Higher amount of CH supported the low compressive strength of CMS. As the curing age increased, a decrease in Ca/Si was observed in confirmation of formation of CSH gel due to dissolution of $C_3S$ and $C_2S$.

The microstructure of the MM1, MM2, MM3 and MM4 specimens at 3 days showed CH Needles along with scanty pores that decreased with increase in curing age. However, the extent of CH needles got lessened while that of CSH crystals increased with increase in content of MS from 5% to 15% in support of strength enhancement of the specimens. Further increase of micro silica to 20% made the microstructure comparatively less compact possibly due to friction between the micro silica particles at higher content, decreasing the extent of pozzolanic reaction. The Ca/Si ratio was lesser for all the specimens with MS in comparison to CMS in confirmation with microstructure development. The very low Ca/Si ratio in MM3 (15% MS) specimens confirmed the increased strength in these specimens at 28 days.

The microstructures of MN1, MN2, MN3 and MN4 specimens were packed with needle like structures as well as CSH gel leading to improved pore structure and low Ca/Si value. The microstructure of the specimens developed with increase in curing age as well as content from 0.5% to 1% NS and were found to be homogeneous in correlation with strength studies. Further, comparatively less homogeneous microstructure and slightly high value of Ca/Si for MN4 specimens also confirmed the slight decrease of strength linked to the agglomeration of the finer particles. Further improvement in microstructure and a decrease in the value of Ca/Si was observed in MNM1, MNM2, MNM3 and MNM4 specimens in comparison to CMS as well as MM1, MM2, MM3, MM4, MN1,
MN2, MN3 and MN4 specimens. A slight decrease in compactness with comparatively lesser CSH phases and a slight rise in the values of Ca/Si was observed in MNM3 (15% MS+1% NS) and MNM4 (20% MS+1% NS) specimens. The observations support the enhanced strength of MNM2 (10% MS+1% NS) specimens with a slight decrease in strength of MNM3 and MNM4 specimens.

The use of micro silica and nano silica for partial substitution of cement has not only reduced the usage of cement but also improved the fresh, hardened and durability properties due to microstructural development. Further, the partial substitution of cement by 10% micro silica along with 1% nano silica enhanced the performance of cement mortars. Thus, the study reveals the beneficiary use of micro silica and nano silica to improve the microstructure and hence the strength & durability properties of cement mortar in need of sustainable construction practices.

4.13. FUTURE SCOPE OF RESEARCH

The beneficial aspects of micro silica and nano silica along with their combination in optimized content must be studied for partial substitution of cement in concretes for further use in sustainable construction. Further, study of durability properties need to be studied at later ages to explore the resistance in service life of the material. Other SCMs also need to be explored for binary and ternary blends of cement mortar and concrete as well. Although the use of nano silica has proved to be beneficial, yet its agglomeration formation tendency needs to be addressed by the use of suitable inert fillers or plasticizers to increase the feasibility and effectiveness of the binary/ternary blends. Extensive study of other durability properties such as acid resistance, water permeability and drying shrinkage should be carried out. Commercially available nano silica is quite expensive, hence cost analysis of its use for partial substitution of cement is highly recommended. Also, the researchers should design new techniques for manufacture of nano silica in interest of sustainable construction practices and reduction of carbon footprints is desired.