CHAPTER 4
RESULTS AND DISCUSSION

4.1 ANALYSIS OF PHYSICAL PROPERTIES OF CEMENT

In ordinary Portland cement and blended cement based composite binders the inclusion of refractory chemicals may modify the properties of fresh and hardened mortars. In order to investigate the effect of addition of selected refractory chemicals to OPC and blended cement, the physical properties such as setting time, consistency of the different mixes as described in Chapter 3 was determined. The water to cement ratio for obtaining the consistency was 0.3.

The results of the tests performed to determine physical property such as specific gravity, consistency, initial and final setting time conducted at room temperature showed that the variation was conforming to IS:269 and are listed in Table 4.1.

The trial results on different refractory chemicals blended with ordinary Portland cement showed that the physical properties confirmed to BIS standards. The results of compressive strength of cement mortar with the addition of different percentages of Titanium di oxide and Silicon carbide were not encouraging although their other physical characteristics confirmed to BIS standards. Hence for further investigations refractory chemicals Zirconium di oxide and alumina were considered since they indicated better performance when added to ordinary Portland cement.
Table 4.1. Physical Properties of Mixes

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<th>%TiO₂</th>
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4.2 COMpressive STRENGTH OF MORTars

The strength of heated and cooled mortar specimens is defined as residual strength for comparison the ratio of residual strength and virgin strength (unheated specimen strength) is considered and expressed as percentage.

Table 4.1 gives the results of the compressive strength of cement mortar and its respective residual strength based on the experimental investigations explained in Chapter 3, section 3.2.8. The results presented in the table 4.1 are the average values of three tested specimens. Using these results the graphs of residual compressive strength vs temperature levels and exposure conditions were plotted and are presented in figures 4.1.
Table 4.1 Compressive Strength of Cement Mortar cubes

<table>
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<th>Temperature</th>
<th>Duration of Exposure</th>
<th>Average Compressive Strength in N/mm²</th>
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4.3 PROPERTIES OF CEMENT MORTAR

4.3.1 Residual Compressive Strength vs Temperature of Cement Mortar

![Fig. 4.1. Residual compressive strength of CM at various temperatures](image-url)
It is observed from the Figures 4.1 on exposure to sustained elevated temperature 100 °C to 800 °C the compressive strength of cement mortars decreases for all the three levels of exposure conditions. When the temperature is increased to 100 °C the compressive strength is found to be increased by 17.30 % after 2 hours of exposure, by 13.28 % after 4 hours of exposure and 9.26 % for 6 hours of exposure conditions.

The increase in compressive strength is due to the additional hydration of cement grains due to auto claving effect. The water liberated during exposure to heat above 100° creates a high pressure in the paste. The conditions thus created is called as internal autoclaving [15].

On increasing the temperature to 300°C the compressive strength decreases for all durations of exposure. At 300 °C the strength is reduced by 37.65 % for 2 and 4 hours of exposure, by 36.30 % for 6 hours of exposure.

The decrease in compressive strength between 400°C and 800°C is drastic. When the sustained elevated temperature is increased to 400 °C the strength is reduced by 15.35% for 2 hours of exposure, by 23.99% for 4 hours and by 16.04% for 6 hours of exposure. At 400°C there is greater reduction in compressive strength as the duration of exposure increases.

When the sustained elevated temperature is at 500 °C strength is reduced by 22.91 % for 2 hours of 20.50 % for 4 hours of exposure and 20.66 % for 6 hours of exposure conditions. The reduction is compressive strength is almost uniform for all durations of exposure. Further when the sustained elevated temperature is increased to 600 °C the reduction in strength is found to be 20.32 % for 2 hours of exposure, 16.67 % for 4 hours of exposure and 20.30 % for 6 hours of exposure conditions. When the sustained elevated temperature is at 800 °C the reduction in strength is 28.53 % for 2 hours of exposure, 32.0 % for 4 hours of exposure and 30.10 % for 6 hours of exposure conditions.

On increasing the temperature of exposure between 300-800°C a decrease in compressive strength is observed. Beyond 500°C the reduction is drastic. The strength
loss up till 300°C is mainly due to loss of evaporable water leading to coarsening of pore structure. At 300°C the decomposition of portlandite and C-S-H begins causing a reduction in compressive strength. Beyond 300°C the drastic reduction in strength, between 400-600°C, is mainly due to the decomposition of C-S-H to C2S and C3S and portlandite (CH) to calcium oxide. CaO. (Peng).

4.3.2 Thermal Conductivity

![Graph showing thermal conductivity vs temperature](attachment:image.png)

**Fig. 4.2. Variation of thermal conductivity of CM with temperature**

The thermal conductivity of cement mortar is 0.54 W/m/K at 30°C as seen in figure 4.2. The thermal conductivity of ordinary Portland cement mortar is found to be 0.541 W/m/K. The thermal conductivity was found to decrease on subjecting the specimens to elevated temperatures in the range 100-800°C. For 2 hour duration of exposure at 100°C, the thermal conductivity decreases from 0.541 to 0.583 W/m/K. Not much change in thermal conductivity is seen in the temperature range of 100-400°C. But on increasing the temperature from 500-800°C the thermal conductivity decreases further by 15% and is 0.263 W/m/K at 600°C. A sharp decrease in thermal conductivity is seen on further heating to 800°C. The decrease in thermal conductivity is linked to the deterioration of microstructure of the cement matrix. The deterioration is caused due to
the dehydration of hydration products leading to increase in air voids. The formation of air voids causes a decrease in thermal conductivity and increase in total porosity and water absorption.

The thermal conductivity decreases by 57.71%, 43.88 % and 18.64% after exposure to 100°C for 2, 4, 6 hours respectively. The decrease is due to the loss of evaporable water present in the cement paste. Between 200°C and 300°C the decrease in thermal conductivity is rapid. The thermal conductivity decreases by nearly 25-40% for the three duration of exposure. This is because the thermal conductivity is related to the mineral crystallinity and with rise in temperature the well crystallized structure changes to poorly crystallized structure caused by commencement of the dehydration of CH and CSH at these temperatures

4.3.3 Water Absorption and Porosity

![Graph](image)

**Fig. 4.3. Variation of water absorption of CM with temperature**
The variation in water absorption and porosity in CM with temperature is shown in figure 4.3 and 4.4 respectively. The water absorption of the specimens after exposure to 100°C increases to 51.73 % for 2 hours of exposure, 72.58 % for 4 hours of exposure and 77.95 % for 6 hours of exposure conditions. This indicates that as the duration of exposure increases the water absorption capacity of the specimens also increases due to the increase in pores.

At 200°C, water absorption of the specimens increases to 76.01 % after 2 hours of exposure, 81.03 % after 4 hours of exposure and 84.95 % after 6 hours of exposure conditions. The percentage increase in the porosity is highest in specimens heated for are 6 hours. This shows that as the duration of exposure increases the water absorption capacity of the specimens also increases due to the increase in pores.

After exposure to 300°C, Water absorption of the specimens is observed to be increased to 79.33 % for 2 hours of exposure, 82.21 % for 4 hours of exposure and 87.73 % for 6 hours of exposure conditions. This shows that the residual strength decrease is directly proportional to the percentage increase in its water absorption capacity and porosity.
After exposure to 400 °C, water absorption of the specimens is observed to be increased to 81.47 % for 2 hours of exposure, 83.07 % for 4 hours of exposure and 89.96 % for 6 hours of exposure conditions.

Water absorption of the specimens exposed to 500 °C was found to increase to 82.96 % for 2 hours of exposure, 84.10 % for 4 hours of exposure and 91.50 % for 6 hours of exposure. This shows that as the sustained temperature is increased, the volume of pores inside the mortar specimens is also increased substantially.[41]

Water absorption of the specimens is observed to be increased to 84.82 % for 2 hours of exposure, 85.64 % for 4 hours of exposure and 92.82 % for 6 hours of exposure at 600 °C.

The maximum increase is observed when the temperature of exposure is maintained at 800 °C. The increase in water absorption of the specimens is 87.78 % for 2 hours of exposure, 88.28 % for 4 hours of exposure and 93.85 % for 6 hours of exposure conditions. This shows that as the sustained temperature is increased, the volume of pores inside the mortar specimens is also increased substantially.

4.3.4 Microstructure Studies

4.3.4.1 XRD Analysis

Fig. 4.5. XRD of CM at room temperature
XRD of Cement Mortar at Room Temperature

The above Figure 4.5 represents XRD cement mortar, peaks of hydration products of ordinary Portland cement at ambient temperature. The peaks in the graph at displacements $2\theta=26^\circ,32-34^\circ,41-43^\circ,59-60^\circ$, shows the formation of hydration products such as calcium silicate hydrate, quartz. The counts of these compounds in terms of height of the peaks are 19407, 430, 1307, 641, 2706, 1971, 1684, being higher than any other compound present in the specimen. The next higher counts is alunino silicates and portlandite having displacements of $2\theta=17-19^\circ,18-20^\circ,33-35^\circ,45-47^\circ$. They have heights of 13,286, 575 with relative intensities of 0.07, 2.96, 1.47.

XRD CM 200 °C

![XRD CM 200 °C](image)

**Fig. 4.6. XRD CM at 200 °C**

Figure 4.6 shows the diffraction peaks in CM after exposure to elevated temperature of 200 °C for 4 hours. This figure clearly indicates the peaks of portlandite at $2\theta=17.7$, 28.6 and 46.8. The portlandite has counts in terms of height of peaks 355.6, 121.4 and 330.54 respectively. The peaks representing CSH can be observed at $2\theta=29.0$, 50.5 with intensities of 441.4 and 153.36.
Fig. 4.7. XRD CM at 400 °C

The peaks in the graph at displacements 2θ=18, 26, 32-34, 41-43, 59-60, shows the formation of hydration products such as portlandite, calcium oxide, C₃S.

The counts of portlandite in terms of height of the peaks at 2θ = 33.8, 46.9 are 275.95 and 400.76 are being higher than any other compound present in the specimen.

The next higher counts are for CSH having displacements of 2θ = 29.1 and 31.77. They have height of 736 and 307 with relative intensities of 247.69 and 236.47.

The peak observed at 2θ = 31.8, 32.2 corresponds to that of C₂S and C₃S having an intensity of 275.95 in terms of height in counts. The peaks representing CaO are observed at 2θ = 32.22 and d=2.77 having 275.95 counts, in terms of height of the peak and the intensity being 32.61.
The peaks in the Figure 4.8 at displacements $2\theta=18$, 26, 32-34, 41-43, 59-60, shows the formation of hydration products such as portlandite, calcium oxide, C$_3$S.

The height of peak of portlandite in terms of counts of the peaks at $2\theta =17.9$, 47.09 are 69.15 and 153.11. The next higher counts is for CSH having displacements of $2\theta = 29.1$. They have height in terms of counts of 558.94.

The peak observed at $2\theta=32.2$ corresponds to that of CaO having an intensity of 347 counts in terms of in height.
The peaks in the graph at displacements $2\theta = 18, 26, 32-34, 41-43, 59-60$, shows the formation of hydration products such as portlandite, calcium oxide, $C_3S$.

The counts of portlandite in terms of height of the peaks at $2\theta = 17.9, 47.09$ are 69.15 and 153.11. The next higher counts is for CSH having displacements of $2\theta = 29.1$. They have height in terms of count of 558.94.

The peak observed at $2\theta = 32.2$ corresponds to that of CaO having an height in terms of count as of 347.
Fig. 4.10. XRD of CM at different temperatures for 2 hour duration of exposure
CH – calcium hydroxide, CSH – calcium silicate hydrate, A – C₃S (Alite), B – β-C₂S (Belite)
The XRD diffraction of CM at 200 °C shows the presence of CH and C-S-H and it was observed that the intensity of portlandite corresponds to 2θ = 18° and 34.1° increases temperature of the exposure conditions increased. The peak corresponding to that of CSH at 29.5° increases at 200 °C due to enhanced hydration.

The peak intensity of CH, CSH decreases in specimens exposed to the temperature range of 400-600°C. This may be due the decomposition of portlandite and CSH which begins around 400 °C. The main peaks of Alite (C2S) and belite (C3S) which are observed at 32.2° and 32.5° respectively and therefore as the temperature of exposure increases, the intensity of the peaks corresponding to C2S and C3S increase, but the peak at 2θ = 29.5° begins to decrease due to decomposition of CSH.

The reduction in portlandite content is rapid beyond 500 °C. Simultaneously the content of C2S and C3S increases due to the decomposition of calcium silicate hydrates. These factors explain the reduction of compressive strength and thermal conductivity of the cement mortars when exposed to elevated temperatures. It was also observed that the longer the durations of exposure, the extent of decomposition of portlandite and CSH increases and the strength loss is greater. A similar trend was observed by J. Piasta et al., [15] in their study on changes in microstructure of hardened cement paste when exposed to elevated temperatures. The XRD peaks corresponding to portlandite, C-S-H and calcium carbonate remains even after 8 Hours of exposure at 400 °C. The decomposition of portlandite and calcium carbonate is initiated in the temperature range of 430-530 °C and the peaks corresponding to C2S and C3S begins to increase from 560 °C due to decomposition of C-S-H [16].

### 4.3.4.2 SEM Analysis

SEM investigations on the hardened cement mortars shows distinct changes in morphology as a consequence of exposure to elevated temperatures. Figures 4.11 to 4.17 shows the SEM micrograph of OPC mortar before exposure to elevated temperature and after exposure to temperatures of 300°C and 800°C.

SEM micrographs of hardened cement mortar at ambient temperatures reveal formation of well-developed hydrated phases such as Ca(OH)₂ and C-S-H.
micrograph of cement mortar exposed to 300 °C shows the formation of voids due to decomposition of hydration products and deformation of Ca(OH)₂. Further SEM investigation on mortar samples exposed to 800°C reveal massive changes in the morphology due to formation of cracks and voids and increased porosity.

Fig. 4.11. SEM Micrograph CM at Room Temperature

Fig. 4.12. SEM Micrograph CM at Room Temperature
Fig. 4.13. SEM Micrographs of CM at Room Temperature

Fig. 4.14. SEM Micrograph CM at 300 °C
Fig. 4.15. SEM Micrograph CM at 400 °C

Fig. 4.16. SEM Micrograph CM at 300 °C
Fig. 4.17. SEM micrograph of CM at 800 °C[5]

4.3.4.3 FTIR Analysis

Fig. 4.18. FTIR Analysis of hydrated CM at room temperature
The IR spectra of cm hydrated for 28 days as shown in figure 4.18. A peak observed at 3645 cm\(^{-1}\) is assigned to the O-H vibrations in Ca(OH)\(_2\) formed. The band observed in the 3100-3400 cm\(^{-1}\) is caused due to symmetric and asymmetric stretching of O-H present in water molecules. The band at 1650 cm\(^{-1}\) is due to deformation mode H-O-H of the molecular water absorbed. The carbonate peaks can be observed at 1480 cm\(^{-1}\), 872 cm\(^{-1}\), and 712 cm\(^{-1}\), due to reaction of atmospheric CO\(_2\) with calcium hydroxide the main characteristics of the hydrated sample is the presence of peak at 970 cm\(^{-1}\). This accounts for the polymerization of SiO\(_4\) limits in C\(_3\)S and C\(_2\)S and this result in formation C-S-H. The band arrangements are in good agreement with previously reported studies [89, 90, 91].

The IR spectra of CM heated at different temperatures is shown in the Figure 4.19. The peaks corresponding to portlandite does not change in intensity in the specimens heated at 200 °C and 400 °C. This indicates that the decomposition of CH has
not begun, but the peak 3440 cm\(^{-1}\) and 1630 cm\(^{-1}\) associated with water molecules are weakened completely. This indicates that the water molecules having evaporated leading to the pore structure coarsening and decrease in compressive strength.

For the band 970-986 cm\(^{-1}\)(CSH) as shown in the Figure 4.19. The intensity of these peaks decreases in samples after exposure to elevated temperatures in the range 400-800 °C. This confirms the decomposition of CSH at higher temperatures.

Further in all the samples after exposure to elevated temperature the CSH peak between 970-990 cm\(^{-1}\) had decreased in intensity after thermal treatment and a strong peak at 890cm\(^{-1}\) corresponding to Si-O band in C\(_2\)S appears. This is due to dehydration of C-S-H. In the sample CM after exposure to 800 °C the band at 1540 cm\(^{-1}\) decreases in intensity indicating the decomposition of calcium carbonate.

4.4 PROPERTIES OF CEMENT MORTAR WITH ADDITION OF 2% ALUMINA

4.4.1 Residual Compressive Strength Vs Temperature

Referring to Figure 4.20 when cement mortars with addition of 2 % alumina are under compression at room temperature it is observed that the compressive strength is 55.17 MPa which is 14.32% higher than control specimens. From Figure 4.20 it is observed that for cement mortars with 2% alumina exposed to sustained elevated temperature of 100 °C the residual compressive strength is found to be increased by 5.78 % for 2 hours of exposure, 2.45 % for 4 hours of exposure and 1.62 % for 6 hours of exposure. This clearly shows that there is an increase in residual compressive strength of cement mortar with 2% alumina at 100 °C sustained elevated temperature and at all the three levels of duration of exposures. It is observed that the percentage increase in strength is not constant for all the three levels of duration of exposure. The percentage increase observed is maximum for 2 hours duration of exposure and is minimum for 6 hours duration of exposure.

Further beyond 100 °C to 800 °C there is a decrease in the residual compressive strength for all the three levels of duration exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the residual compressive
strength decreases. When the sustained elevated temperature is increased to 200 °C it is observed that the residual compressive strength is decreased by 6.65 % for 2 hours of exposure, 15.0 % for 4 hours of exposure and 34.09 % for 6 hours of exposure conditions in comparison with that of the room temperature values. This shows that the percentage variation in strength is found to vary from 6.65 % to 34.09 % of its original strength.

At 300 °C sustained elevated temperature the percentage decrement is found to be 31.23 % for 2 hours of exposure, 35.79 % for 4 hours of exposure and 38.25 % for 6 hours of exposure conditions in comparison with that of the room temperature values which shows that there is a rapid retention in the rate of reduction in residual compressive strength. From Figure 4.20 it is evident that the percentage variation in the residual compressive strength with an interval of 100 °C is ranging from 1.62 % to 35.70 % decrement for 2, 4, 6 hours of exposure conditions. The maximum reduction in the residual compressive strength of 74.70 %, 78.68 %, 91.19 %, is noticed at 800 °C elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate strength loss is at 800 °C elevated temperature sustained upto 6 hours duration of exposure.

![Fig. 4.20. Residual compressive strength of CM 2A at various temperatures](image)
4.4.2 Thermal Conductivity

The thermal conductivity of the cement mortars containing 2% alumina is represented in Figure 4.21. It shows the variation of thermal conductivity at elevated temperatures for all levels of exposure. For two hour duration of exposure at 100°C causes a decrease in thermal conductivity by 19% due to loss of evaporable water. On increasing the exposure temperature from 300-800°C the thermal conductivity decreases gradually from 0.388 W/m/K to 0.173 W/m/K. The decrease in thermal conductivity is caused due to the dehydration of hydration products such as portlandite and CSH at these temperatures causing a decrease in crystallinity in the cement matrix and thus causing an increase in air voids contents.

For 4 hour duration of exposure the thermal conductivity is higher at 100°C than that observed for 2 hour duration of exposure. This could be due to enhanced hydration of cement grains in the presence of alumina at high temperature. But beyond 300 °C the reduction in thermal conductivity is greater by 8% when the duration of exposure is increased to 4 hours.
The thermal conductivity of the CM2A at all elevated temperatures for 6 hour duration of exposure are lower than that for 2 hour and 4 hour duration of exposure. This is because the degradation of cement matrix increases with increase in duration of exposure to elevated temperature.

4.4.3 Water Absorption and Porosity

When 2 % of Alumina is added to blended cement mortar and subjected to various sustained elevated temperatures it is observed from figure 4.22 that the water absorption is 6.16 % at room temperature which is higher by 0.88 % in comparison with the control specimens. The variations in the water absorption of 2% Alumina added specimens with respect to various sustained elevated temperatures are plotted in figure 4.22. The variation of porosity is represented in figure 4.23.

![Fig. 4.22. Variation of water absorption of CM 2A with temperature](image-url)
Fig. 4.23. Variation of porosity of CM 2A with temperature

In CM2A it is noticed that the water absorption is increase with increase in temperature. From fig 4.22 it is observed that the increase in water absorption is 11.36 % for 2 hours of exposure, 12.87 % for 4 hours of exposure and 14.18 % for 6 hours duration of exposure which is higher compared to those of blended cement mortar specimens.

Similar to control specimens beyond 100°C to 800°C there is an increase in the water absorption for 2% Alumina added specimens which are subjected to 2, 4, 6 hours of sustained elevated temperatures. Rapid variation in water absorption is noticed for the temperature range between room temperature and 100°C which is increasing.

When the sustained elevated temperature is at 200 °C it is observed that the water absorption is increased by 2.34 % for 2 hours of exposure, 1.60 % for 4 hours of exposure and 0.95 % for 6 hours of exposure conditions.

It is observed that when the temperature is elevated from 200°C to 300°C the rate of variation in increment of water absorption is changed drastically for which the
increase in water absorption is noted as 14.22 % for 2 hours of exposure, 17.62 % for 4 hours of exposure and 20.80 % for 6 hours of exposure conditions.

The maximum increase in the water absorption of 22.68 %, 29.03 % & 34.26 %, is noticed at 800 °C elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate increase in water absorption at 800 °C is reduced by 1.53 % in comparison with the control specimens.

4.4.4 Microstructure Studies

4.4.4.1 XRD Analysis

XRD of CM2A Room Temperature

Figure 4.24 represents the XRD pattern of the hydration products formed on the hydration of cement mortars with 2 % alumina. The main hydration products CSH, CASH and portlandite are observed. The main peaks of CASH are observed at 23.1, 35.6 and 47.9. These peaks have height in terms of counts as 106.82, 110.27, 112.88. The peaks of CSH observed at 2θ=29.06,32.3,49.8,59.6 The height of peak in
terms of counts is 853,189,1727,1256. The next higher count is for peaks corresponding to portlandite at $2\theta = 46.8$ and 54.5. the counts in terms of height being 138 and 673 respectively.

**XRD OF CM2A 400**

![CM2A XRD graph](image)

**Fig. 4.25. XRD OF CM2A at 400 °C**

Figure 4.25 represents the XRD of CM4A after thermal treatment at 400°C. At 400°C the intensity of CH peak decreases this is due to the partial conversion of Ca(OH)$_2$ to CaCO$_3$ and decomposition of CaO. The formation of calcium alumino silicate hydrate is observed (gismondine). The XRD also shows the presence of tobermorite which is still present at 400°C and has not decomposed. This can be due to reduction of thermal stresses in the mortar with the addition of 2% alumina.

This shows that the addition of alumina to OPC has favoured the formation of calcium alumino silicate hydrate which is otherwise not seen in OPC mortar at 400°C.
4.4.4.2 SEM analysis

Fig. 4.26. SEM Micrograph CM 2A at Room Temperature

Fig. 4.27. SEM Micrograph CM 2A at 400 °C
Figure 4.26 represents the SEM micrograph of CM2A at ambient temperature, while Figures 4.27 and 4.28 represent the SEM micrograph of CM2A at 400 and 800 °C. As seen in above mentioned figures, the addition of alumina to cement mortar samples leads to the formation of more CSH gel. A denser structure with lesser number of pores as compared to cement mortar can be observed at 300 and 600 °C. The decomposition of CSH is reduced at 600°C with the addition of alumina as compared to cement mortar. Hence fewer number of voids and microcracks are seen.
4.5 PROPERTIES OF BLENDED CEMENT MORTAR WITH ADDITION OF 4% ALUMINA

4.5.1 Residual Compressive Strength Vs Temperature

Fig. 4.29. Residual compressive strength of CM 4A at various temperatures

When 4% of Alumina is added to blended cement mortar and subjected to various sustained elevated temperatures it is observed that the compressive strength is 52.12 MPa at room temperature which is higher than 7.46% in comparison with the control specimens. The variations in the residual compressive strength of 4% Alumina added specimens with respect to various sustained elevated temperatures are plotted in Figure 4.29.

In case of 4% Alumina added specimens it is noticed that at 100 °C the residual compressive strength is increased in comparison with that of the room temperature strength. From Figure 4.29 it is observed that the increase in strength is 10.16% for 2 hours of exposure, 7.24% for 4 hours of exposure and 2.49% for 6 hours duration of exposure. Though the strength at 100 °C is increased for all the specimens the percentage of increase is not the same for different duration of exposure. The least
percentage of increase in strength is found in 6 hours duration of exposure, whereas the maximum increase in strength is noticed in 2 hours duration of exposure specimens.

Similar to control specimens beyond 200 °C to 800 °C except for 200 °C there is a decrease in the residual compressive strength for 4% Alumina added specimens which are subjected to 2, 4, 6 hours of sustained elevated temperatures. Rapid variation in residual compressive strength is noticed for the temperature range between 200 °C and 300 °C which is decreasing, and between 500 °C to 600 °C which is decreasing.

When the sustained elevated temperature is at 200 °C it is observed that the residual compressive strength is increased by 21.20 % for 2 hours of exposure, 12.82 % for 4 hours of exposure and 6.49 % for 6 hours of exposure conditions in comparison with that of the room temperature values. This shows that the percentage increase in strength is found to be not same for 2, 4 and 6 hours duration of exposure. And the percentage variation in strength for 4 and 6 hours is similar.

It is observed that when the temperature is elevated from 200 °C to 300 °C the rate of variation in reduction of strength is changed drastically for which the decrease in residual strength is noted as 0.91 % for 2 hours of exposure, whereas reduction in residual strength is noted as 9.11 % for 4 hours of exposure and 11.46 % for 6 hours of exposure conditions in comparison with that of the room temperature.

From figure 4.29, for sustained elevated temperature increment of 100 °C it is observed that the percentage reduction in the residual compressive strength is between 1.55 % to 24.99 % for 2, 4, 6 hours of exposure conditions. The maximum reduction in the residual compressive strength of 61.03 %, 67.75 % and 71.46 %, is noticed at 800 °C elevated temperature sustained up to 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate strength loss at 800 °C is high by 1.13 % in comparison with the control specimens.
4.5.2 Thermal Conductivity

Figure 4.30 represents the variation of thermal conductivity of CM4A with temperature for all durations of exposure. The addition of 4% alumina to cement mortar increases the thermal conductivity to 0.567 W/m/K as compared to 0.541 W/m/K at room temperature. This could be due to enhanced hydration of cement grains in the presence of alumina. On exposing the specimens to elevated temperatures between 100°C to 400°C for a duration of 2 hours the thermal conductivity decreases from 0.425 W/m/K to 0.284 W/m/K. There is no change in thermal conductivity when the temperature of exposure is increased to 800°C.

When the duration of exposure is increased to 4 hours the thermal conductivity drops to 0.45 W/m/K at 100°C. The thermal conductivity decreases gradually on increasing the temperature from 100°C to 800°C. A similar trend is observed when the duration of exposure is increased to 6 hours. It is observed that the decrease in thermal conductivity is greater when the duration of exposure is increased.
Fig. 4.31. Variation of water absorption of CM 4A with temperature

Fig. 4.32. Variation of porosity of CM 4A with temperature
4.5.3 Water Absorption and Porosity

On addition of 4% alumina to the cement mortars at room temperature it is observed that the water absorption is 4.78%. From figure 4.31 it is observed that when these specimens are exposed to sustained elevated temperature of 100 °C the water absorption is found to be increased by 11.16% for 2 hours, 12.40% for 4 hours and 14.18% for 6 hours of exposure. It is observed that the percentage increase in water absorption increases as the duration of exposure increases.

Further on increasing the temperatures from 100 °C to 800 °C there is an increase in the water absorption for all the three levels of duration exposure. When the sustained elevated temperature is increased to 200 °C it is observed that the water absorption is increased by 15.28% for 2 hours of exposure, 17.65% for 4 hours of exposure and 18.61% for 6 hours of exposure conditions. This shows that the percentage variation in water absorption is found to vary between 4.12% to 5.25%. When the sustained elevated temperature is successively increased, it is observed that the percentage variation in the water absorption is ranging from 2.25% to 9.39%. The maximum increase in water absorption of 37.86%, 40.18%, 47.01%, is noticed at 800 °C when sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the water absorption at 800 °C is reduced by 13.13% in comparison with the control specimens.

Since porosity is directly related to water absorption it’s variation is similar to that of water absorption as seen in figure 4.32.
4.5.4 Microstructure Studies

4.5.4.1 XRD Analysis

XRD CM4A Room Temperature

The XRD pattern of the hydration products formed on the hydration of cement mortars with 4% alumina is represented in figure 4.33. The main hydration products being CSH, CASH and portlandite. The main peaks of CASH are observed at 23.1, 35.6 and 47.9. These peaks have a height in terms of count as 106.82, 110.27, 112.88. The peaks of CSH observed at 2θ=29.06, 32.3, 49.8, 59.6. The height of peak in terms of counts is 853, 189, 1727, 1256. The next higher count is for peaks corresponding to portlandite at 2θ= 46.8 and 54.5, the intensity counts in terms of height being 138 and 673 respectively.

Fig. 4.33. XRD of CM4A at room temperature
The Figure 4.34 represents the XRD of CM4A at 600 °C. The XRD pattern represents the hydration products formed on the hydration of cement mortars with 4% alumina. The main hydration products being CSH, CASH, CaO and portlandite. The height of peak of CaO in terms of count at 2θ= 32.22 has count of 363.4. The height of the peaks of CSH at 2θ=29.0 is 610.26. The height of the peak of portlandite in terms of counts is 156.47.
The Figure 4.35 represents the XRD of CM4A at 800 °C. The XRD pattern represents the hydration products formed on the hydration of cement mortars with 4% alumina. The main hydration products being CSH, CASH and portlandite. The intensity of portlandite peak at 2θ= 34.1 has reduced in intensity. The peaks has intensity of 474 counts. But the intensity of CASH peaks has increased. The intensity of the peak at 47.9 is 134 counts.

4.5.4.2 FTIR Analysis
The FTIR spectra of CM blended with 4% alumina are shown in the figure 4.36. Only specific sample have been chosen for FTIR analysis. These samples have shown to posses better residual properties after exposure to elevated temperature. It can be observed that the peak at 990cm\(^{-1}\) corresponding to CSH appears in CM4A after thermal treatment at 600 °C and 800 °C.

Generally CH should decompose when cement mortars are subjected to temperatures above 800 °C, but a peak of small intensity is observed in CM4A specimens after being subjected to elevated temperatures of 600 °C and 800 °C. Hence the band at 3638 cm\(^{-1}\) can be assigned to calcium alumino silicate hydrates. The band occurring at 892, 1122 cm\(^{-1}\), can be assigned to stretching vibration of Si-O-Si, and Al-O-Si. Even though these peaks have smaller intensity they are absent in samples of CM after thermal treatment. This proves the presence of alumina in CM in 4% exhibits better thermal resistant property [92].

### 4.6 PROPERTIES OF CEMENT MORTAR WITH ADDITION OF 2% ZIRCONIUM DI OXIDE

#### 4.6.1 Residual Compressive Strength Vs Temperature

![Graph](image)

**Fig. 4.37. Residual compressive strength of CM 2Z at various temperatures**
When 2% of Zirconium di oxide is added to cement mortar and subjected to various sustained elevated temperatures it is observed that the compressive strength is 50.67 MPa at room temperature which is higher than 4.99% in comparison with the control specimens. The variations in the residual compressive strength of 2% Zirconium di oxide added specimens with respect to various sustained elevated temperatures are plotted in Figure 4.37.

In case of 2% Zirconium di oxide added specimens also it is noticed that at 100 °C the residual compressive strength is increased in comparison with that of the room temperature strength. From figure 4.37 it is observed that the increase in strength is 13.80% for 2 hours of exposure, 12.38% for 4 hours of exposure and 7.16% for 6 hours duration of exposure. Though the strength at 100 °C is increased for all the specimens the percentage of increase is not the same for different duration of exposure. The least percentage of increase in strength is found in 6 hours duration of exposure, whereas the maximum increase in strength is achieved for 2 hours duration of exposure specimens.

Similar to control specimens beyond 100 °C to 800 °C there is a decrease in the residual compressive strength for 2% Zirconium di oxide added specimens which are subjected to 2, 4, 6 hours of sustained elevated temperatures. Rapid variation in residual compressive strength is noticed for the temperature range between room temperature and 100 °C which is increasing, and between 100 °C to 200 °C which is decreasing.

When the sustained elevated temperature is at 200 °C it is observed that the residual compressive strength is decreased by 17.43% for 2 hours of exposure, 17.38% for 4 hours of exposure and 20.17% for 6 hours of exposure conditions in comparison with that of the room temperature values. This shows that the percentage decrease in strength is found to be same for both 2 and 4 hours duration of exposure. And the percentage variation in strength for 6 hours is similar to that of control specimens.

It is observed that when the temperature is elevated from 200 °C to 300 °C the rate of variation in reduction of strength is changed drastically for which the reduction in residual strength is noted as 18.65% for 2 hours of exposure, 23.81% for 4 hours of
exposure and 24.52 % for 6 hours of exposure conditions in comparison with that of the room temperature.

For sustained elevated temperature increment of 100 °C it is observed that the percentage variation in the residual compressive strength is ranging from 4.35 % to 31.32 % decrement for 2, 4, 6 hours of exposure conditions. The maximum reduction in the residual compressive strength of 53.50 %, 62.87 % and 64.87 %, is noticed at 800 °C elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate strength loss at 800 °C is enhanced by 12.93 % in comparison with the control specimens.

### 4.6.2 Thermal Conductivity

![Thermal Conductivity Graph](image)

**Fig. 4.38. Variation of thermal conductivity of CM 2Z with temperature**

The thermal conductivity of the OPC mortars containing 2% Zirconium di oxide at different temperatures for all levels of duration of exposure is represented in the figure 4.38. It was observed that the thermal conductivity decreases at room temperature on addition of Zirconium di oxide. This is because Zirconium di oxide naturally is a material of low thermal conductivity.
When subjected to elevated temperature of 100 °C for two hours the thermal conductivity decreases by 7.5%. This can be attributed to the loss of evaporable water present in the cement matrix. Between 100-200 °C of exposure temperature, the thermal conductivity decreases by further 13%. A steep reduction in thermal conductivity is observed in the temperature range of 300-600°C. the thermal conductivity falls to 0.283 W/m/K. For two hour duration of exposure the thermal conductivity does not change much in the temperature range of 600-800°C. The thermal conductivity decreases in the temperature range 300-600°C due to the pore structure coarsening of hydrated cement paste [17]. Beyond 600°C there is decrease in crystallinity due to the decomposition of calcium hydroxide and calcium carbonate and hence the pore structure degrades further. As compared to 4 hours of exposure, the decrease in thermal conductivity is only 2% greater for 6 hours of exposure at all elevated temperatures.

4.6.3 Water Absorption and Porosity

![Diagram of water absorption and porosity](image)

Fig. 4.39. Variation of water absorption of CM 2Z with temperature
Figure 4.39 and figure 4.40 represents the water absorption and porosity of CM2Z at different temperatures. The increase in the total porosity with thermally treatment is attributed to the formation of air voids and enlargement of micro-cracks and thus increase in the degree of deterioration of the decomposed hydrates. This effect leads to opening the pore system, consequently, the total porosity increases. The porosity increases rapidly due to the decomposition of Ca(OH)$_2$ between 400 and 600 °C. The slight rate of increase in the total porosity after 600 °C up to 800 °C is due to the decomposition of CaCO$_3$ on bulky CaO and gaseous CO$_2$ releasing out of the matrix as well as some carbonated C-S-H.

After exposure to 100 °C the water absorption of the specimens being increased by 62% for 2 hours of exposure, 86 % for 4 hours of exposure and 113 % for 6 hours of exposure conditions. This indicates that as the duration of exposure increases the water absorption capacity of the specimens also increases due to the increase in pores.

Between 300 to 600°C the water absorption capacity increases drastically for all levels of duration of exposure the water absorption and porosity increases by nearly 250 -300%. The decomposition of free Ca(OH)$_2$ and CaCO3, which occurred from 300 to 600 °C, affected the porosity and pore structure coarsening. Beyond 600°C the water absorption increases slightly for 2 hours and 4 hours of exposure, but increases by another 400% for 6 hours duration of exposure due to the decomposition of hydrates.
The water absorption capacity is directly related to total porosity. The increase in the total porosity with thermally treatment is attributed to the formation of air voids and enlargement of micro-cracks and increase in the degree of deterioration of the decomposed hydrates. This effect leads to opening the pore system, consequently, the total porosity increases. The porosity increases rapidly due to the decomposition of Ca(OH)$_2$ between 400 and 600 °C. The slight rate of increase in the total porosity after 600 °C up to 800 °C is due to the decomposition of CaCO$_3$ on bulky CaO and gaseous CO$_2$ releasing out of the matrix as well as some carbonated C-S-H [16].

On exposure to elevated temperatures between 30 and 200°C for 2 hour duration, the porosity increased from 8% to 20% and between 200-400°C the porosity increased from 20% - 25%. The maximum increase in porosity is as expected in the temperature range of 500-800°C. The porosity was 33% at 500°C and 45 % at 800°C.

As the duration of exposure increase the porosity also increased linearly. This is in line with the thermal conductivity results obtained.

4.6.4 Microstructure Studies

4.6.4.1 XRD Analysis

XRD CM2Z Room Temperature

![XRD CM2Z Room Temperature](image)

Fig. 4.41. XRD of CM2Z at room temperature
Figure 4.41 shows the XRD of CM2Z at room temperature. Diffraction peaks corresponding to CH was observed at 2θ = 18°, 34.1° and that C-S-H between 2θ = 32°, -34°. The intensity of these peaks is more as compared to CM at room temperature. This indicates the enhanced hydration due to the presence of Zirconium di oxide.

XRD CM2Z 300

Figure 4.42 shows the XRD pattern of CM2Z at 300 °C. The XRD diffraction of CM2Z at 300 °C shows the presence of CH and C-S-H and it was observed that the intensity of portlandite corresponds to 2θ = 18° and 34.1° increases as temperature of the exposure conditions increased. The peak corresponding to that of CSH at 29.5° increases at 300 °C due to enhanced hydration.

Fig. 4.42. XRD CM2Z at 300 °C
The peak intensity of CH, CSH decreases in specimens exposed to the temperature of 800°C as indicated in Figure 4.43. The main peaks of Alite (C₃S) and belite (C₃S) which are observed at 32.2° and 32.5° respectively and therefore as the temperature of exposure increases, the intensity of the peaks corresponding to C₂S and C₃S increase, but the peak at 2θ = 29.5° begins to decrease due to decomposition of CSH.
Figure 4.44 represents the XRD pattern of portland cement mortars with 2% Zirconium oxide at different temperature. The main phases identified are portlandite (CH), calcium silicate hydrate (CSH) exists in the form of rosenhanite, hillebrandite. The diffraction lines corresponding to portlandite can be seen at 2θ = 18°, 28.6°, 34.1°. The lines representing CSH can be seen at 2θ = 32-34°. The intensity of the portlandite
peak is more in CM2Z mortar at room temperature and at 100 °C. This is due to increase hydration of cement in the presence of Zirconium di oxide. The intensity of the peaks of CSH also increases. The presence of these phases improves the compressive strength to 53 MPa as compared to that of OPC mortars which possessed a strength of 35 MPa at temperatures 100-300 °C. But as the temperature of exposure is increased the intensity of the CSH peak decreases.

At 500°C intensity of the diffraction line due to CH is still present which is not observed as in the case of CM. This is also reflected in observed thermal conductivity values. Thus the replacement of refractory chemicals like Zirconium di oxide in 2 to 6% to cement mortars increases the thermal endurance of cement at elevated temperatures. The presence of small amount of tobermerite in Figure 4.43, after exposure to 800°C explains the better residual strength of CM2Z at 800 °C.

4.6.4.2 SEM Analysis

![SEM Micrograph CM 2Z at Room Temperature](image-url)
Fig. 4.46. SEM Micrograph CM 2Z at Room Temperature

Fig. 4.47. SEM Micrograph CM 2Z at 300 °C
Fig. 4.48. SEM Micrograph CM 2Z at 300 °C

Fig. 4.49. SEM Micrograph CM 2Z at 300 °C
Fig. 4.50. SEM Micrograph CM 2Z at 600 °C

Fig. 4.51. SEM Micrograph CM 2Z at 600 °C
Figures 4.45 to 4.50 represent the SEM micrographs of CM2Z at room temperature, 300 °C, 600 °C. The SEM micrograph of the specimen before thermal treatment is represented by Figures 4.45 and 4.46. The formation of fibrous and ill crystalline CSH and well defined plate like CH is indicated. The addition of Zirconium di oxide has led to the formation of additional hydration products and hence a dense microstructure.

Figures 4.47 and 4.49 shows SEM micrographs of CM2Z after heating to 300 °C. A dense closed texture with lower number of voids and pore size is noticed as compared to CM at the same temperature.

Figure 4.50 and 4.51 shows the SEM micrographs of CM2Z specimens thermally treated at 600 °C. The micrographs shows the presence of CSH in the pores. The appearance of cracks and voids is due to the dehydration reactions and shrinkage of the hydrates.

The CM2Z specimens after exposure to all elevated temperatures shows to have a denser structure as compared to CM. This could be due to the presence of Zirconium di oxide in the mortar. Zirconium di oxide mortars have shown to possess high thermal conductivity and thereby reduce the thermal stresses by quicker dissipation of heat. This indicates that CM2Z has better resistance to heat and crack formation and therefore has a better compressive strength to CM at the same temperatures.

4.7 PROPERTIES OF CEMENT MORTAR WITH ADDITION OF 4% ZIRCONIUM DI OXIDE

4.7.1 Residual Compressive Strength Vs Temperature

Further addition of Zirconium di oxide by 4% to cement mortar specimens increases the compressive strength at room temperature to 51.43 MPa at room temperature which is 3.17 % higher than the control specimens. When the cement mortars with 4% Zirconium di oxide addition specimens are subjected to sustained elevated temperatures at regular intervals of 100 °C it is observed that the residual
compressive strength is found to be increased for the temperatures ranging from room temperature to 100 °C and beyond 100 °C up to 800 °C there is a decrease in its strength.

It is observed from figure 4.52 for the sustained elevated temperature of 100 °C the residual compressive strength is found to be increased to 16.04 % for 2 hours of exposure, 14.87 % for 4 hours of exposure and 12.44 % for 6 hours of exposure. This clearly shows that there is an increase in residual compressive strength of cement mortar at 100 °C sustained elevated temperature in comparison with the room temperature values. This increment is 1.59 % higher than the control specimens for 4 hours of exposure and 3.17% higher for 6 hours of exposure. It is observed that beyond 100 °C to 800 °C there is a decrease in the residual compressive strength for all the three levels of duration of exposure.

For the temperature increment from 100 °C to 200 °C the strength loss is 17.70 % for 2 hours of exposure, 17.66 % for 4 hours of exposure and 19.47 % for 6 hours of exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the residual compressive strength decreases. It is noticed that with 4% Zirconium di oxide addition about 1.19 % of strength loss is retained in case of 6 hours of sustained duration of exposure.

When the sustained elevated temperature is successively increased further at a regular increment of 100 °C it is observed that the percentage variation in the residual compressive strength is ranging from 2.34 % to 33.73 %. The maximum reduction in the residual compressive strength of 62.02 %, 64.21 % and64.21 %, is noticed at 800 °C elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate strength loss at 800 °C is enhanced by 13.59 % in comparison with the control specimens which is higher than the 2% Zirconium di oxide specimens.
4.7.2 Thermal Conductivity

Fig. 4.52. Residual compressive strength of CM 4Z at various temperatures

Fig. 4.53. Variation of thermal conductivity of CM 4Z with temperature
The variation of thermal conductivity with temperature of CM2Z is shown in figure 4.53. With the addition of 4% Zirconium dioxide the thermal conductivity of the mortar decreases to 0.49 W/m/K. This is because Zirconium dioxide is amorphous in nature and has lower thermal conductivity value.

On being subjected to elevated temperature of 100 °C for 2 hours, the thermal conductivity reduces from 0.463 to 0.375 W/m/K. When the temperature of exposure is raised to 300°C the thermal conductivity decreases to 0.325 W/m/K. On further heating to 600°C the thermal conductivity dropped to 0.275 W/m/K and remained constant on heating to 800°C.

When the duration of exposure is increased to 4 hours the thermal conductivity reduced to 0.425 W/m/K at 100°C which is slightly higher than that observed for 2 hour duration of exposure. Also increasing the duration of exposure causes a further reduction in the thermal conductivity values. The reduction in thermal conductivity values was 12% at 100°C for 4 hour duration of exposure and 32% at 400 for 4 hour duration of exposure, while the reduction in thermal conductivity value at 400 °C was only 19% for 2 hour duration of exposure. Increasing the duration of exposure caused an increased reduction in thermal conductivity.

4.7.3 Water Absorption and Porosity

![Graph showing water absorption vs temperature](image)

Fig. 4.54. Variation of water absorption of CM 4Z with temperature
The variation of water absorption and porosity of CM4Z with temperature is shown in figures 4.54 and 4.55 respectively. The water absorption cement mortars with addition of 4% Zirconium di oxide at room temperature is observed that 4.18%. From figure 4.54 it is observed that for cement mortars with 4% Zirconium di oxide exposed to sustained elevated temperature of 100°C the water absorption is found to be increased by 2.84% for 2 hours of exposure, 3.57% for 4 hours of exposure and 4.28% for 6 hours of exposure. This clearly shows that there is an increase in water absorption of cement mortar with 4% Zirconium di oxide at 100°C sustained elevated temperature and at all the three levels of duration of exposures. The percentage increase observed is maximum for 6 hours duration of exposure and is minimum for 2 hours duration of exposure.

Further beyond 100°C to 800°C there is an increase in the water absorption for all the three levels of duration exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the water absorption decreases. When the sustained elevated temperature is to 200°C it is observed that the water absorption is increased by 9.05% for 2 hours of exposure, 9.47% for 4 hours of exposure.

**Fig. 4.55. Variation of porosity of CM 4Z with temperature**

![Graph showing the variation of porosity with temperature.](image-url)
exposure and 11.96 % for 6 hours of exposure conditions. This shows that the percentage variation in water absorption is found to vary from 0.98 % to 2.45 %.

At 300 °C sustained elevated temperature the percentage increment is found to be 11.96 % for 2 hours of exposure, 12.44 % for 4 hours of exposure and 15.33 % for 6 hours of exposure conditions. This shows that there is a rapid variation in the rate of increment in water absorption for 2 and 4 hour exposure. It is observed that the percentage variation in the water absorption with an interval of 100 °C is ranging from 0.67 % to 5.89 % increment for 2, 4, 6 hours of exposure conditions. The maximum increase in the water absorption of 21.69 %, 23.01 %, 31.89 %, is noticed at 800°C elevated temperature sustained up to 2, 4, 6 hours duration of exposure respectively.

The water absorption capacity is directly related to total porosity. The increase in the total porosity with thermally treatment is attributed to the formation of air voids and enlargement of micro-cracks and/or increase in the degree of deterioration of the decomposed hydrates. This effect leads to opening the pore system, consequently, the total porosity increases. The porosity increases rapidly due to the decomposition of Ca(OH)₂ between 400 and 600 °C. The slight rate of increase in the total porosity after 600 °C up to 800 °C is due to the decomposition of CaCO₃ on bulky CaO and gaseous CO₂ releasing out of the matrix as well as some carbonated C-S-H.

On exposure to elevated temperatures between 30 and 200°C for 2 hour duration, the porosity increased from 8% to 20% and between 200-400°C the porosity increased from 20% - 25%. The maximum increase in porosity is as expected in the temperature range of 500-800°C. The porosity was 33% at 500°C and 45 % at 800°C.

As the duration of exposure increase the porosity also increased linearly. This is in line with the thermal conductivity results obtained.
4.7.4 Microstructure Studies

4.7.4.1 XRD Analysis

XRD CM4Z 100 °C

Figure 4.56 represents the XRD pattern of portland cement mortars with 4% Zirconium di oxide at 100°C. The main phases identified are portlandite (CH), calcium silicate hydrate (CSH) exists. The diffraction lines corresponding to portlandite can be seen at 2θ = 18°, 28.6°, 34.1°. The lines representing CSH can be seen at 2θ = 32-34°. The intensity of the portlandite peak is more in CM4Z mortar at 300 °C. This is due to increase hydration of cement in the presence of Zirconium di oxide. The presence of ettringite indicated that the hydration reaction has proceeded towards the formation of secondary products.
Figure 4.57 represents the XRD pattern of portland cement mortars with 4% Zirconium di oxide at 300°C. The main phases identified are portlandite (CH), calcium silicate hydrate (CSH) exists. The diffraction lines corresponding to portlandite can be see at 2θ= 18°,28.6°,34.1°. The lines representing CSH can be seen at 2θ =32-34°.The intensity of the portlandite peak is more in CM4Z mortar at 100 °C. This is due to increase hydration of cement in the presence of Zirconium di oxide. The presence of ettringite indicated that the hydration reaction has proceeded towards the formation of secondary products.
4.7.4.2 SEM Analysis

Fig. 4.58. SEM Micrograph CM 4Z at Room Temperature

Fig. 4.59. SEM Micrograph CM 4Z at Room Temperature
Fig. 4.60. SEM Micrograph CM 4Z at 300 °C

Fig. 4.61. SEM Micrograph CM 4Z at 600 °C
Figures 4.58 and 4.59 are the SEM micrographs of CM4Z before exposure to elevated temperature. The figure 4.60 and 4.61 represent the SEM micrographs at 300 °C. While figure 4.62 represents SEM micrograph at 600 °C. The addition of Zirconium di oxide to cement mortar samples leads to the formation of more CSH gel. A denser structure as compared to cement mortar can be observed at 300 °C and 600 °C. The decomposition of CSH is reduced at 600 °C with the addition of Zirconium di oxide as compared to cement mortar. Hence the number of voids and microcracks is also reduced as seen the SEM micrographs.
4.7.4.3 FTIR Analysis

The FTIR spectra of CM4Z after thermal treatment at 400 °C and 600 °C is shown in the figure 4.63. The peak due to O-H vibrations at 3643 cm\(^{-1}\) and 1643 cm\(^{-1}\) are present in the sample CM4Z after exposure to 400 °C. The peak of CSH can also be noticed at 967 cm\(^{-1}\) and 473 cm\(^{-1}\). A broad band corresponding -OH vibrations in CSH at 3437 cm\(^{-1}\) can also be noticed. The FTIR spectra of CM4Z after exposure to elevated temperature of 800 °C indicates that the peak at 3643 cm\(^{-1}\) has decreased in intensity and the peak at 976 cm\(^{-1}\) has broadened. This is due to dehydration of CSH but the intensity of peaks is greater than the intensity of peaks in CM after thermal treatment at 400 °C and 800 °C normally the carbonates are expected to decompose at 800 °C but the peaks of carbonate at 1427 and 874 cm\(^{-1}\) are still visible. These observations indicate that the presence of CH and CSH at 600 °C. Therefore, the addition of 4% ZrO2 has improved thermal resistance of cement mortar.
### 4.8 COMPRESSION STRENGTH OF BLENDED CEMENT MORTAR

The values of compressive strength for blended cement mortar specimens blended with refractory chemicals at elevated temperatures are given in Table 4.2.

#### Table 4.2 Compressive Strength of Blended Cement Mortar

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Duration of Exposure</th>
<th>Average Compressive Strength in N/mm²</th>
<th>BLEND CEMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hours</td>
<td>BM</td>
<td>BM2 A</td>
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<tr>
<td>0°C Room Temperature</td>
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<td>4</td>
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<td></td>
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<td></td>
<td>6</td>
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<td></td>
<td>6</td>
<td>14.39</td>
<td>10.57</td>
</tr>
</tbody>
</table>
4.9 PROPERTIES OF BLENDED CEMENT MORTAR

4.9.1 Residual Compressive Strength Vs Temperature

When the blended cement mortars are at room temperature it is observed that the compressive strength is 48.50 Mpa. From Figure 4.64 it is observed that for blended cement mortars exposed to sustained elevated temperature of 100 °C the residual compressive strength is found to be decreased by 4.23 % for 2 hours of exposure, 5.88 % for 4 hours of exposure and 9.86 % for 6 hours of exposure. This clearly shows that there is a decrease in residual compressive strength of blended cement mortar at 100 °C sustained elevated temperature and at all the three levels of duration of exposures. It is observed that the percentage decrease in strength is not constant for all the three levels of duration of exposure. The percentage decrease is maximum for 6 hours duration of exposure and is minimum for 2 hours duration of exposure.

Further beyond 100 °C to 800 °C there is a decrease in the residual compressive strength for all the three levels of duration exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the residual compressive strength decreases. When the sustained elevated temperature is increased to 200 °C it is...
observed that the residual compressive strength is decreased by 11.26 % for 2 hours of exposure, 14.97 % for 4 hours of exposure and 17.61 % for 6 hours of exposure conditions in comparison with that of the room temperature values. This shows that the percentage variation in strength is found to vary from 4.23 % to 17.61 % of its virgin strength.

At 300 °C sustained elevated temperature the percentage decrement is found to be 16.43 % for 2 hours of exposure, 21.92 % for 4 hours of exposure and 26.76 % for 6 hours of exposure conditions in comparison with that of the room temperature values which shows that there is a rapid retention in the rate of reduction in residual compressive strength. From Figure 1.4 it is evident that residual compressive strength at 100 °C varies from 4.23 % to 20.70 % for 2, 4 & 6 hours of exposure conditions. The maximum reduction in the residual compressive strength of is noticed at 800 °C which 66.97 %, 65.20 %, 70.33 %, for 2, 4, 6 hours duration of exposure respectively.

4.9.2 Thermal Conductivity

![Graph showing thermal conductivity variation with temperature](image)

Fig. 4.65. Variation of thermal conductivity of BM with temperature

With the replacement OPC with 20% fly ash, the thermal conductivity of mortar decreases from 0.54 to 0.397 W/m/K at room temperatures. The reduction in thermal conductivity is due to reduction in density in the presence of fly ash and partly due to
amorphous nature of the minerals [44]. On exposure to elevated temperatures the thermal conductivity of BM decreases gradually as shown in figure 4.65.

The thermal conductivity of blended cement mortar is found to be 0.397 W/m/K. The thermal conductivity was found to decrease on subjecting the specimens to elevated temperatures in the range 100-800°C. For 2 hour duration of exposure at 100° C, the thermal conductivity decreases from 0.397 to 0.361 W/m/K. Thermal conductivity decreases from 0.385-0.292 W/m/K in the temperature range of 100-400°C. On increasing the temperature from 500-800°C the thermal conductivity decreases further by 20% and is 0.233 W/m/K at 800°C. The decrease in thermal conductivity is linked to the deterioration of microstructure of the cement matrix. The deterioration is caused due to the dehydration of hydration products leading to increase in air voids. The formation of air voids causes a decrease in thermal conductivity and increase in total porosity and water absorption as the duration of exposure to elevated temperature increases the thermal conductivity also decreases. With increasing duration of exposure the extent of reactions occurring at the particular temperatures also increases hence greater degradation and greater increase in voids.

4.9.3 Water Absorption and Porosity

![Fig. 4.66. Variation of water absorption of BM with temperature](image-url)
As seen in figure 4.66 the water absorption at room temperature for blended cement mortar specimens is 5.28%. It can be observed from the graph that at 100 °C the water absorption is increased to 10.32% in case of 2 hours of exposure, 10.4% for 4 hours and 11.28% for 6 hours duration of exposure. With this it is clear that as the duration of exposure is increased the water absorption capacity also increases. The percentage variation at 100 °C is ranging from 5.03% to 6.0% in comparison with that of control specimens.

When the sustained elevated temperature is at 200 °C the water absorption capacity further increases for all the three levels of duration of exposures. The increase is found to be 11.48% for 2 hours, 12.18% for 4 hours and 13.83% for 6 hours of exposure. The percentage variation is observed to be ranging from 1.16% to 2.55%.

At 300 °C sustained elevated temperature the percentage increment is found to be 12.13% for 2 hours of exposure, 14.18% for 4 hours of exposure and 18.69% for 6
hours of exposure conditions which shows that there is a rapid retention in the rate of increase in water absorption.

It is also observed that the percentage variation in the water absorption with an interval of 100 °C is ranging from 0.64 % to 6.0 % increment for 2, 4, 6 hours of exposure conditions. The maximum increase in the water absorption of 21.42 %, 27.97 %, 35.80 %, is noticed at 800 °C elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate water absorption is at 800 °C elevated temperature sustained upto 6 hours duration of exposure. Figure 4.67 indicates the variation of porosity of BM with temperature.

4.9.4 Microstructure Analysis

4.9.4.1 XRD Analysis

XRD BM Room Temperature

Fig. 4.68. XRD BM at room temperature
The XRD pattern for BM at room temperature as shown in figure 4.68 indicates predominant peaks of CH at $2\theta=54.4, 59.6$ having intensity in terms of counts as 198.36, 2247.31. The major peaks of CSH at $2\theta = 29.0, 42.3, 49.8$ have counts of 1076, 4331, 2191 respectively. The lower intensity peaks correspond to calcium aluminosilicate hydrates.

**Figure 4.69. XRD BM at 200 °C**

Figure 4.69 indicates the XRD pattern of BM at 200 °C. The XRD pattern of BM at 200 °C indicates the presence of CH, CASH, CSH as the main hydration products. The predominant peaks of CH are observed at $2\theta = 28.6, 34.1, 47.2, 50.9, 54.5$ with peak intensities in terms of height in counts are 66, 496, 208, 167, 70 respectively. The next higher intensity peaks are seen at $2\theta=32.2, 49.6, 55.4$ having height in terms of count 115, 32, 311 respectively which corresponds to CSH. The CSH phases observed are Tobermerite and Hillebrandite. Low intensity of CASH can be observed at 29.5 and 35.6.
The XRD pattern of BM at 600 °C as shown in figure 4.70 indicates the predominant peaks of CSH at 2θ=29.1 with intensity having a count of 571.8. The next peak predominant is of C₃S at 2θ=32.2 with peak count of 330.62.
The XRD pattern of BM at 800 °C as seen in figure 4.71 indicates the presence of CH, CASH, CSH as the main hydration products. The predominant peaks of CH are observed at 2θ = 28.6, 34.1, 47.2, 50.9, 54.5 with peak intensities in terms of height in counts are 66, 651, 165, 167, 70 respectively. The next higher intensity peaks are seen at 2θ = 30.9 having height in terms of count 218 which corresponds to CSH. The CSH phases observed are Tobermerite and Hillebrandite. High intensity peaks of CASH can be observed.
Fig. 4.72. XRD of CM20FA at different temperatures

Figure 4.72 represents the XRD of CM20FA at different temperatures. A progressive reduction of the intensity of the peak at $2\theta = 18^\circ$, $34.1^\circ$ representing portlandite and the presence of calcium alumino silicate are noticed at all temperature range studied. With increase in temperature the intensity of diffraction peaks of CASH increases. This could be due to increased pozzolanic reaction. The presence of calcium alumino silicate contribute to the retention of mechanical strength. Similar observations have been found in the mixes containing mineral admixtures at 800 °C as reported by Hosam. El_Din H. Seleem [93].
4.9.4.2 SEM Analysis

Fig. 4.73. SEM Micrograph BM at Room Temperature

Fig. 4.74. SEM Micrograph BM at Room Temperature
Fig. 4.75. SEM Micrograph BM at Room Temperature

Fig. 4.76. SEM Micrograph BM at 800 °C
Fig. 4.77. SEM Micrograph BM at 800 °C

Fig. 4.78. SEM Micrograph BM at 800 °C
SEM investigations on the hardened blended cement mortars shows distinct changes in morphology as a consequence of exposure to elevated temperatures. Figures 4.73 to 4.79 shows the SEM micrograph of blended cement mortar at ambient temperature and after exposure to temperature of 800°C.

SEM micrographs of hardened cement mortar at ambient temperatures reveal formation of well-developed hydrated phases such as Ca(OH)$_2$ and C-S-H. SEM micrograph of cement mortar exposed to 300 °C shows the formation of voids and deformation of Ca(OH)$_2$. Further SEM investigation on mortar samples exposed to 800°C reveal massive changes in the morphology due to formation of cracks and voids and increased porosity. The crystallinity increases due to the presence of CASH (calcium alumino silicate hydrate).
4.9.4.3 FTIR Analysis

Figure 4.80 shows the FTIR spectra of BM at different temperatures. The bands corresponding to vibrations of carbonate can be observed in all samples at around 876, 1445, 2951, 2500 cm\(^{-1}\). This could be due to the reaction between CaO and atmospheric carbon dioxide. A weak band at 3665 cm\(^{-1}\) with a small shoulder at 3620 cm\(^{-1}\) indicates the presence of calcium alumino silicate hydrates in BM at room temperature and after exposure to elevated temperature [94].
4.10 PROPERTIES OF BLENDED CEMENT MORTAR WITH 2% ALUMINA

4.10.1 Residual Compressive Strength Vs Temperature

As shown in Figure 4.81 on addition of 2 % alumina to blended mortars it is observed that the compressive strength is 49.21 MPa which is 1.46 % higher than control specimens at room temperature. It is observed that for blended cement mortars with 2% alumina on exposure to sustained elevated temperature of 100 °C the residual compressive strength increases by 10.99 % for 2 hours of exposure, 6.25 % for 4 hours of exposure and 3.96 % for 6 hours of exposure. It is observed that the percentage increase in strength is not constant for all the three levels of duration of exposure. The percentage increase observed is maximum for 2 hours duration of exposure and is minimum for 6 hours duration of exposure.

Further beyond 300 °C to 800 °C there is a decrease in the residual compressive strength for all the three levels of duration exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the residual compressive strength decreases. When the sustained elevated temperature is increased to 200 °C it is observed that the residual compressive strength is increased by 21.83 % for 2 hours of exposure, 14.47 % for 4 hours of exposure and 8.93 % for 6 hours of exposure conditions in comparison with that of the room temperature values. This shows that the
percentage variation in strength is found to vary between 3.96 % to 10.99 % of its virgin
strength.

At 300 °C sustained elevated temperature the percentage decrement is found to be
5.14 % for 2 hours of exposure, 15.12 % for 4 hours of exposure and 17.67 % for 6
hours of exposure conditions in comparison with that of the room temperature values
which shows that there is a rapid change in the rate of variation in residual compressive
strength of 2 hour duration of exposure. From Figure 4.81 it is evident that the
percentage variation in the residual compressive strength with an interval of 100 °C is
ranging from 3.96 % to 29.59 % decrement for 2, 4, 6 hours of exposure conditions. The
maximum reduction in the residual compressive strength of 59.14 %, 65.78 %, 66.99 %,
is noticed at 800 °C elevated temperature sustained upto 2, 4, 6 hours duration of
exposure respectively. This shows that the ultimate strength loss is at 800 °C elevated
temperature sustained upto 6 hours duration of exposure.

4.10.2 Thermal Conductivity

Fig. 4.82. Variation of thermal conductivity of BM 2A with temperature
At room temperature the thermal conductivity of blended mortars containing 2% alumina increases by 27%. This could be due to the increase hydration of cement grains which contributes to the increase in compressive strength on addition of alumina. On exposure to elevated temperatures for 2, 4 and 6 hours the thermal conductivity decreases gradually with increasing temperature as represented in figure 4.82.

The thermal conductivity of blended cement mortar with 2% alumina is found to be 0.505 W/m/K. The thermal conductivity was found to decrease on subjecting the specimens to elevated temperatures in the range 100-800°C. For 2 hour duration of exposure at 100°C, the thermal conductivity decreases 0.481 W/m/K. Thermal conductivity decreases from 0.481-0.346 W/m/K in the temperature range of 100-400°C. On increasing the temperature from 500-800°C the thermal conductivity decreases further by 19% and is 0.251 W/m/K at 800°C.

The decrease in thermal conductivity with temperature can be attributed to the variation of moisture content [95]. The decrease in thermal conductivity is linked to the deterioration of microstructure of the cement matrix. The deterioration is caused due to the dehydration of hydration products leading to increase in air voids. The formation of air voids causes a decrease in thermal conductivity and increase in total porosity and water absorption. As the duration of exposure to elevated temperature increases the thermal conductivity also decreases. With increasing duration of exposure the extent of reactions occurring at the particular temperatures also increases hence greater degradation and greater increase in voids.

As the duration of exposure is increased the thermal conductivity also decreased linearly. But it was observed that at levels of elevated temperatures and for all durations the thermal conductivity of BM2A was greater than BM. This indicates that the higher thermal conductivity allow faster dissipation of heat and thus reducing the thermal gradients and thermal stresses in the mortar. This reduces the mechanical property degradations [96].
4.10.3 Water Absorption and Porosity

Fig. 4.83. Variation of water absorption of BM 2A with temperature

Fig. 4.84. Variation of porosity of BM 2A with temperature
The variations in the water absorption of 2% Alumina added specimens with respect to various sustained elevated temperatures are plotted in figure 4.83. It is observed that the water absorption is 6.16 % at room temperature which is higher by 0.88 % in comparison with the control specimens. In case of 2% Alumina added specimens also it is noticed that at 100 °C the water absorption is increased in comparison with that of the room temperature. It is also observed that the increase in water absorption is 11.36 % for 2 hours of exposure, 12.87 % for 4 hours of exposure and 14.18 % for 6 hours duration of exposure which is higher compared to those of blended cement mortar specimens without addition of alumina. Though water absorption at 100 °C is increased for all the specimens the percentage of increase is not the same for different duration of exposure. The least percentage of increase in strength is found in 2 hours duration of exposure, whereas the maximum increase in strength is achieved for 6 hours duration of exposure specimens.

Similar to control specimens beyond 100° c to 800°c there is an increase in the water absorption for BM2A when subjected to sustained elevated temperatures for 2, 4, 6 hours. Rapid variation in water absorption is noticed for the temperature range between room temperature and 100°C. When the sustained elevated temperature is at 200°C it is observed that the water absorption is increased by 2.34 % for 2 hours of exposure, 1.60 % for 4 hours of exposure and 0.95 % for 6 hours of exposure conditions. And the percentage variation in water absorption for 6 hours is much lesser than that of control specimens. It is observed that when the temperature is elevated from 200°c to 300° c the rate of variation of water absorption is changed drastically for which the increase in water absorption is noted as 14.22 % for 2 hours of exposure, 17.62 % for 4 hours of exposure and 20.80 % for 6 hours of exposure conditions. From Figure-4.83 for sustained elevated temperature increment of 100°C it is observed that the percentage variation in the water absorption is ranging from 0.27 % to 8.02 % increment for 2, 4, 6 hours of exposure conditions. The maximum increase in the water absorption of 22.68 %, 29.03 % and 34.26 %, is noticed at 800°c elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. Figure 4.84 shows the variation of porosity with temperature for BM2A.
4.10.4 Microstructure Analysis

4.10.4.1 SEM Analysis

Fig. 4.85. SEM Micrograph BM 2A at 200 °C

Fig. 4.86. SEM Micrograph BM 2A at 200 °C
Figures 4.85 and 4.86 represent the SEM micrograph of BM2A after exposure to 200°C. While Figures 4.87 and 4.88 represent the micrographs of BM2A after exposure...
to 400°C. It can be noticed that the microstructure of blended mortars is more dense with the addition of 2% alumina both at 200°C and 400°C. This can be attributed to the fact that alumina particles are smaller in size thus act as nucleating sites for enhanced hydration of cement grains.

4.11 PROPERTIES OF BLENDED CEMENT MORTAR WITH ADDITION OF 4% ALUMINA

4.11.1 Residual Compressive Strength Vs Temperature

![Graph showing residual compressive strength vs temperature]

**Fig. 4.89. Residual compressive strength of BM 4A at various temperatures**

When 4% of Alumina is added to blended cement mortar and subjected to various sustained elevated temperatures it is observed that the compressive strength is 52.12 MPa at room temperature which is higher than 7.46% in comparison with the control specimens. The variations in the residual compressive strength of 4% Alumina added specimens with respect to various sustained elevated temperatures are plotted in Figure 4.89.
In case of 4% Alumina added specimens it is noticed that at 100 °C the residual compressive strength is increased in comparison with that of the room temperature strength. From Figure 4.89 it is observed that the increase in strength is 10.16 % for 2 hours of exposure, 7.24 % for 4 hours of exposure and 2.49 % for 6 hours duration of exposure. Though the strength at 100 °C is increased for all the specimens the percentage of increase is not the same for different duration of exposure. The least percentage of increase in strength is found in 6 hours duration of exposure, whereas the maximum increase in strength is noticed in 2 hours duration of exposure specimens.

Similar to control specimens beyond 200 °C to 800 °C except for 200 °C there is a decrease in the residual compressive strength for 4% Alumina added specimens which are subjected to 2, 4, 6 hours of sustained elevated temperatures. Rapid variation in residual compressive strength is noticed for the temperature range between 200 °C and 300 °C which is decreasing, and between 500 °C to 600 °C which is decreasing.

When the sustained elevated temperature is at 200 °C it is observed that the residual compressive strength is increased by 21.20 % for 2 hours of exposure, 12.82 % for 4 hours of exposure and 6.49 % for 6 hours of exposure conditions in comparison with that of the room temperature values. This shows that the percentage increase in strength is found to be not same for 2, 4 and 6 hours duration of exposure. And the percentage variation in strength for 4 and 6 hours is similar.

It is observed that when the temperature is elevated from 200 °C to 300 °C the rate of variation in reduction of strength is changed drastically for which the decrease in residual strength is noted as 0.91 % for 2 hours of exposure, whereas reduction in residual strength is noted as 9.11 % for 4 hours of exposure and 11.46 % for 6 hours of exposure conditions in comparison with that of the room temperature.

From Figure 4.89 after exposure to elevated temperature of 100 °C it is observed that the percentage variation in the residual compressive strength reduces from 1.55 % to 24.99 % for 2, 4, 6 hours of exposure conditions. The maximum reduction in the residual compressive strength of 61.03 %, 67.75 % and 71.46 %, is noticed at 800 °C elevated temperature sustained up to 2, 4, 6 hours duration of exposure respectively.
This shows that the maximum strength loss is at 800 °C as compared with the control specimens.

4.11.2 Thermal Conductivity

![Graph showing thermal conductivity vs. temperature]

**Fig. 4.90. Variation of thermal conductivity of BM 4A with temperature**

Figure 4.90 shows the variation of thermal conductivity of BM4A with temperature. At room temperature the thermal conductivity of blended mortars containing 4 % alumina almost doubles on the addition of 4% alumina as compared to blended mortar. This could be due to the increase hydration of cement grains which contributes to the increase in compressive strength on addition of alumina. On exposure to elevated temperatures for 2, 4 and 6 hours the thermal conductivity decreases gradually with increasing temperature.

The thermal conductivity of blended cement mortar with 4% alumina is found to be 0.777 W/m/K. The thermal conductivity of the specimens was found to decrease on subjecting the specimens to elevated temperatures in the range 100-800°C. For 2 hour duration of exposure at 200°C, the thermal conductivity decreases to 0.506 W/m/K. Thermal conductivity decreases from 0.506-0.390 W/m/K in the temperature range of 200-400°C. On increasing the temperature from 500-800°C the thermal conductivity decreases to 0.289 W/m/K at 800°C.
The decrease in thermal conductivity with temperature can be attributed to the variation of moisture content. The decrease in thermal conductivity is linked to the deterioration of microstructure of the cement matrix. The deterioration is caused due to the dehydration of hydration products leading to increase in air voids. The formation of air voids causes a decrease in thermal conductivity and increase in total porosity and water absorption. As the duration of exposure to elevated temperature increases the thermal conductivity also decreases. With increasing duration of exposure the extent of reactions occurring at the particular temperatures also increases hence greater degradation and greater increase in voids [95].

As the duration of exposure is increased the thermal conductivity also decreased linearly. But it was observed that at levels of elevated temperatures and for all durations the thermal conductivity of BM4A was greater than that of BM and BM2A. This indicates that the higher thermal conductivity allow faster dissipation of heat and thus reducing the thermal gradients and thermal stresses in the mortar. This reduces the mechanical property degradations [96].

4.11.3 Water Absorption and Porosity

![Graph showing water absorption over temperature for BM4A](Fig. 4.91. Variation of water absorption of BM 4A with temperature)
When the blended cement mortars with addition of 4% alumina are at room temperature it is observed that the water absorption is 6.16%. From Figure 4.91 it is observed that when these specimens are exposed to sustained elevated temperature of 100°C the water absorption is found to be increased by 9.94% for 2 hours of exposure, 11.86% for 4 hours of exposure and 12.66% for 6 hours of exposure. This clearly shows that there is an increase in water absorption of blended cement mortar with 4% alumina at 100°C sustained elevated temperature and at all the three levels of duration of exposures in comparison with that of 2% alumina specimens. It is observed that the percentage increase in water absorption is not constant for all the three levels of duration of exposure. The percentage increase is maximum for 6 hours duration of exposure and is minimum for 2 hours duration of exposure. Further beyond 100°C to 800°C there is an increase in the water absorption for all the three levels of duration exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the water absorption increases. When the sustained elevated temperature is increased to 200°C it is observed that the water absorption is increased to 12.45% for 2 hours of exposure, 16.49% for 4 hours of exposure and 18.95% for 6
hours of exposure conditions. This shows that the percentage variation in water absorption is found to vary between 2.51% to 6.29%. When the sustained elevated temperature is successively increased further at a regular increment of 100°C it is observed that the percentage variation in the water absorption is ranging from 0.45% to 7.40%. The maximum increase in water absorption of 18.16%, 42.49%, 50.97%, is noticed at 800°C elevated temperature sustained up to 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate water absorption at 800°C is increased by 15.17% in comparison with the control specimens which is higher by 16.70% with that of 2% alumina specimens. The variation of porosity is shown in figure 4.92.

4.11.4 Microstructure Studies

4.11.4.1 XRD Analysis

The above figure 4.93 represents the peaks of hydration products of BM2A at 200°C.

The peaks in the graph at displacements 2θ=26°, 32-34°, 41-43°, 59-60°, shows the formation of hydration products such as calcium silicate hydrate, quartz. The XRD also shows the formation of gismondine (2θ =22°, 28.4°, 36°) and ettringite.
Fig. 4.94. XRD BM 4A at 400 °C

Fig. 4.95. XRD BM 4A at 600 °C

Fig. 4.96. XRD BM 4A at 800 °C
Figures 4.94 to 4.96 represents the XRD of BM4A at, 400, 600, 800 °C for four hours duration of exposure. The intensity of the diffraction peaks corresponding to gismondine 2θ=28.4 is found to increase with temperature upto 400°C and decreases in samples after exposure to 600° and 800°. The compressive strength of blended cement mortars increases with the addition of alumina. The increase in strength even at elevated temperature is due to the formation of Gismondine. (Ca,Al₂,₅,Si₂,₀₈,₄H₂O). Gismondine a calcium alumino silicate hydrate is formed by the pozzolanic reaction between fly ash and ordinary portland cement. The formation of gismondine begins at elevated temperature at 200 °C, is because of accelerated hydration due to the presence of Ca(OH)₂ obtained by the enhanced hydration of cement in the presence of alumina in 4% and these crystals fills up the pores and account for better strength of these mixes [98, 99].

Figure 4.97 represents FTIR of BM4A at room temperature and after exposure to elevated temperature. The FTIR spectra of BM4A at room temperature indicates distinct band observed at 877cm⁻¹ due to Al-O stretching vibration of silicate and alumina group the spectra showed the appearance of bands at 877 1071 1489 3729 3034 cm⁻¹ the peak at 1489 represents CO₃ the peak at 1071 cm⁻¹ are due to asymmetric vibration of O-Si-O, O-Al-O in alumina silicates. A band 3729 cm⁻¹ indicates the presence of the calcium alumino silicate hydrates which is confirmed by XRD analysis it can be observed that on BM4A on exposure to elevated temperature of 200, 400 °C the intensity of the peak 3709 cm⁻¹ increases in intensity up to 600 °C. At 800 °C it intensity decreases but CASH is still present. The peak of C-S-H at 970 cm⁻¹ is also present up to 600 °C which disappears at sample exposed to 800 °C. The addition of 4% alumina to BM has favored the formation of CASH. The hydration product is gismondine as identified by XRD.
4.11.4.2 FTIR Analysis

Fig. 4.97. FTIR of BM 4A at different temperatures
4.12 PROPERTIES OF BLENDED CEMENT MORTAR WITH ADDITION OF 2% ZIRCONIUM DI OXIDE

4.12.1 Residual Compressive Strength Vs Temperature

![Graph showing residual compressive strength vs temperature for BM 2Z at various temperatures.]

**Fig. 4.98. Residual compressive strength of BM 2Z at various temperatures**

When 2% of Zirconium di oxide is added to blended cement mortar and subjected to various sustained elevated temperatures it is observed that the compressive strength is 53.03 MPa at room temperature which is higher than 7.26% in comparison with the control specimens and 8.99% higher in comparison with cement mortar control specimens. The variations in the residual compressive strength of 2% Zirconium oxide added specimens with respect to various sustained elevated temperatures are plotted in Figure 4.98.

In case of 2% Zirconium oxide added specimens also it is noticed that beyond 300 °C the residual compressive strength is decreased in comparison with that of the room temperature strength. From figure 4.98 it is observed that at 100 °C the increase in strength is 7.26% for 2 hours of exposure, 4.14% for 4 hours of exposure and 0.37% for 6 hours duration of exposure. Though the strength at 100 °C is increased for all the specimens the percentage of decrease is not the same for different duration of exposure.
The least percentage of increase in strength is found in 6 hours duration of exposure, whereas the maximum increase in strength is achieved for 2 hours duration of exposure specimens.

Similar to control specimens beyond 300 °C to 800 °C there is a decrease in the residual compressive strength for 2% Zirconium di oxide added specimens which are subjected to 2, 4, 6 hours of sustained elevated temperatures. Rapid variation in residual compressive strength is noticed for the temperature range between room temperature and 100 °C which is decreasing.

When the sustained elevated temperature is at 200 °C it is observed that the residual compressive strength is increased by 10.33 % for 2 hours of exposure, 8.66 % for 4 hours of exposure and 3.44 % for 6 hours of exposure conditions in comparison with that of the room temperature values.

It is observed that when the temperature is elevated from 200 °C to 300 °C the rate of variation in reduction of strength is changed drastically in comparison with that of cement mortar specimens for which the reduction in residual strength is noted as 20.25 % for 2 hours of exposure, 24.19 % for 4 hours of exposure and 27.59 % for 6 hours of exposure conditions in comparison with that of the room temperature.

From figure 4.98 for sustained elevated temperature increment of 100 °C it is observed that the percentage variation in the residual compressive strength is ranging from 0.37 % to 32.85 % decrement for 2, 4, 6 hours of exposure conditions. The maximum reduction in the residual compressive strength of 63.42 %, 65.48 % and 71.59 %, is noticed at 800 °C elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate strength loss at 800 °C is decreased by 4.62 % in comparison with the control specimens.
4.12.2 Thermal Conductivity

Fig. 4.99. Variation of thermal conductivity of BM 2Z with temperature

On addition of 2% Zirconium di oxide to the blended cement mortar the thermal conductivity is found to increase to 0.49 W/m/K as compared to blended mortar, before exposure to elevated temperature. This increase can be attributed to the enhanced hydration of cement grains due to the presence of Zirconium di oxide which is acting as an inert filler and the crystallinity therefore increases.

The thermal conductivity was found to decrease on subjecting the specimens to elevated temperatures in the range 100-800°C. For 2 hour duration of exposure at 100°C, the thermal conductivity decreases from 0.49 to 0.45 W/m/K. Thermal conductivity decreases from 0.45 to 0.329 W/m/K on increasing the temperature of exposure to 400°C from 100°C. On increasing the temperature from 500 to 800°C the thermal conductivity decreases to 0.246 W/m/K at 800°C. The decrease in thermal conductivity is linked to the deterioration of microstructure of the cement matrix. The deterioration is caused due to the dehydration of hydration products leading to increase in air voids. The formation of air voids causes a decrease in thermal conductivity and increase in total porosity and water absorption. As the duration of exposure to elevated...
temperature increases the thermal conductivity also decreases. With increasing duration of exposure the extent of reactions occurring at the particular temperatures also increases hence greater degradation and greater increase in voids.

4.12.3 Water Absorption and Porosity

Fig. 4.100. Variation of water absorption of BM 2Z with temperature

Fig. 4.101. Variation of porosity of BM 2Z with temperature
Figures 4.100 and 4.101 represent the variation of water absorption and porosity with temperature for all durations of exposure. On addition of Zirconium dioxide by 2% to blended cement mortar specimens, the water absorption at room temperature is found to be 4.60% which is 0.68% lesser than the control specimens. When the blended cement mortars with 2% Zirconium dioxide addition specimens are subjected to sustained elevated temperatures at regular intervals of 100 °C it is observed that the water absorption is found to be increased for the temperatures ranging from room temperature to 800 °C. It is observed from Figure 4.100 for the sustained elevated temperature of 100 °C the water absorption is found to be increased to 9.76% for 2 hours of exposure, 10.14% for 4 hours of exposure and 12.39% for 6 hours of exposure. This clearly shows that there is an increase in water absorption of blended cement mortar with 2% Zirconium dioxide at 100 °C sustained elevated temperature in comparison with the room temperature values. For the temperature increment from 100 °C to 200 °C the water absorption is 10.28% for 2 hours of exposure, 11.19% for 4 hours of exposure and 14.35% for 6 hours of exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the water absorption also increases.

When the sustained elevated temperature is successively increased further at a regular increment of 100 °C it is observed that the percentage variation in the water absorption is ranging from 0.52% to 7.80%. The maximum increase in the water absorption of 22.40%, 25.11% and 34.82%, is noticed at 800°C elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate water absorption at 800°C is reduced by 0.97% in comparison with the control specimens for 6 hour duration of exposure which is higher by 0.55% in comparison with that of 2% alumina specimens.
4.12.4 Microstructure Studies

4.12.4.1 XRD Analysis

XRD BM2Z 200

![Fig. 4.102. XRD BM2Z 200](image)

XRD BM2Z 600

![Fig. 4.103. XRD BM2Z 600](image)
The XRD diffractograms obtained for the hydrated BM2Z after exposure to elevated temperature of 200 and 600 is shown in figure 4.102 and 4.103 respectively. The main phases identified in the mortar is gismondine at \( \theta_2 = 20.77, 26.65, 49.92, 67.43 \). These peaks are found along with peaks for portlandite. On exposure to an elevated temperature of 600 °C, the intensity of the portlandite peak decreases. This is due to the decomposition of calcium hydroxide which begins after 500°C. The effect of addition of 2% Zirconium di oxide is indicated by the fact gismondine is formed at 200 °C. At 600 °C the intensity of diffraction peaks of gismondine increases and also peaks tobermorite and calcium alumino silicate hydrate can also be seen. The diffraction line corresponding to calcite can also be noticed. This shows that the blended mortars with the addition of 2% Zirconium di oxide exhibit better thermal resistance property. Although the main peaks of gismondine are masked by quartz, a comparative examination of the intensity of reflections at different temperatures of exposure times shows that a peak of gismondine at 28.49°. Based on this observation, gismondine is the main cementitious product that contributes to the long term strength development.

4.12.4.2 SEM analysis

![SEM Micrograph BM 2Z at 200 °C](image)

Fig. 4.104. SEM Micrograph BM 2Z at 200 °C
From the micrographs it is clear that the mixes containing ZrO₂ have a dense well structured C-S-H and sheets of Ca(OH)$_2$ at room temperature. This is due to enhanced hydration of cement in the presence of Zirconium di oxide [11]. The dense structure of cement gel is destroyed which has lead to the reduction in strength at higher temperature. The hydrated phases and these the products of hydration C-S-H are not completely destroyed even after exposure upto 800 °C. The micro-structure of blended cement mortars containing 2% and 4% of Zirconium di oxide indicted compact cement phase with very low porosity. This indicates that the hydrated phases are not decomposed completely in the presence of refractory chemical Zirconium di oxide and pore coarsening is not observed. The non-decomposition of crystalline hydrated phases and the formation of Gismondine, supported by XRD, explains the better residual compressive strength of the mortars blended with fly ash and Zirconium di oxide at elevated temperatures.
4.13 PROPERTIES OF BLENDED CEMENT MORTAR WITH ADDITION OF 4% ZIRCONIUM DI OXIDE

4.13.1 Residual Compressive Strength Vs Temperature

Further addition of Zirconium di oxide by 4% to blended cement mortar specimens the compressive strength at room temperature is found to be 51.21 MPa at room temperature which is 5.58 % higher than the control specimens. When the blended cement mortars with 4% Zirconium di oxide addition specimens are subjected to sustained elevated temperatures at regular intervals of 100 °C it is observed that the residual compressive strength is found to be increased for the temperatures ranging from room temperature to 200 °C and beyond 300 °C up to 800 °C there is a decrease in its strength except for 2 hour duration of exposure specimens.

It is observed from Figure 4.106 for the sustained elevated temperature of 100 °C the residual compressive strength is found to be increased to 17.73 % for 2 hours of exposure, 13.44 % for 4 hours of exposure and 7.32 % for 6 hours of exposure. This clearly shows that there is an increase in residual compressive strength of cement mortar at 100 °C sustained elevated temperature in comparison with the room temperature values. This increment is 12.34 % higher than the control specimens for 2 hours of exposure, 10.53 % for 4 hours of exposure and 7.37 % higher for 6 hours of exposure. It
is observed that beyond 300 °C to 800 °C there is a decrease in the residual compressive strength for 4 and 6 hours of duration of exposure.

For the temperature increment from 100 °C to 200 °C the strength gain is 29.03 % for 2 hours of exposure, 24.16 % for 4 hours of exposure and 14.41 % for 6 hours of exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the residual compressive strength increases.

When the sustained elevated temperature is successively increased further at a regular increment of 100 °C it is observed that the percentage variation in the residual compressive strength is ranging from 7.09 % to 40.25 %. The maximum reduction in the residual compressive strength of 60.70 %, 63.79 % and 65.32 %, is noticed at 800 °C elevated temperature sustained upto 2, 4, 6 hours duration of exposure respectively. This shows that the ultimate strength loss at 800 °C is enhanced by 5.01 % in comparison with the control specimens for 2 hour duration of exposure which is higher than the 2% Zirconium di oxide specimens.

### 4.13.2 Thermal Conductivity

![Thermal Conductivity Graph]

**Fig. 4.107. Variation of thermal conductivity of BM 4Z with temperature**

Figure 4.107 represents the variation of thermal conductivity with temperature for BM2Z.
On addition of 4% Zirconium di oxide to the blended cement mortar the thermal conductivity is found to increase to 0.64 W/m/K, before exposure to elevated temperature. This increase can be attributed to the enhanced hydration of cement grains due to the presence of Zirconium di oxide which acts as a nucleating agent. The crystallinity of the matrix therefore increases.

The thermal conductivity was found to decrease on subjecting the specimens to elevated temperatures in the range 100-800°C. For 2 hour duration of exposure at 100°C, the thermal conductivity decreases from 0.64 to 0.541 W/m/K. Thermal conductivity decreases from 0.54 to 0.331 W/m/K on increasing the temperature of exposure to 400°C from 100°C. On increasing the temperature from 500 to 800°C the thermal conductivity decreases to 0.285 W/m/K at 800°C.The decrease in thermal conductivity is linked to the deterioration of microstructure of the cement matrix. The deterioration is caused due to the dehydration of hydration products leading to increase in air voids. The formation of air voids causes a decrease in thermal conductivity and increase in total porosity and water absorption. As the duration of exposure to elevated temperature increases the thermal conductivity also decreases. With increasing duration of exposure the extent of reactions occurring at the particular temperatures also increases hence greater degradation and greater increase in voids.

4.13.3 Water Absorption and Porosity

![Fig. 4.108. Variation of water absorption of BM 4Z with temperature](image-url)
Fig. 4.109. Variation of porosity of BM 4Z with temperature

Referring to Figure 4.108 it is observed that the water absorption of BM4Z is 5.22 %. It is observed that for blended cement mortars with 4% Zirconium di oxide exposed to sustained elevated temperature of 100 °C the water absorption increases by 4.81 % for 2 hours of exposure, 5.44 % for 4 hours of exposure and 6.42 % for 6 hours of exposure. The percentage increase observed is maximum for 6 hours duration of exposure and is minimum for 2 hours duration of exposure. Further beyond 100 °C to 800 °C there is an increase in the water absorption for all the three levels of duration exposure. This indicates that as the sustained elevated temperature and the duration of exposure increases the water absorption decreases. When the sustained elevated temperature is increased to 200 °C it is observed that the water absorption is increased by 1.01 % for 2 hours of exposure, 1.70 % for 4 hours of exposure and 1.87 % for 6 hours of exposure conditions. This shows that the percentage variation in water absorption is found to vary between 1.01 % to 1.87 %. At 300 °C sustained elevated temperature the percentage increment is found to be 3.54 % for 2 hours of exposure, 2.58 % for 4 hours of exposure and 3.90 % for 6 hours of exposure conditions.
4.13.4 Microstructure Studies

4.13.4.1 XRD Analysis

XRD BM4Z 100

![XRD BM4Z 100 graph](image1.png)

Fig. 4.110. XRD BM4Z 100

XRD BM4Z 800

![XRD BM4Z 800 graph](image2.png)

Fig. 4.111. XRD BM4Z 800
The XRD diffractograms obtained for the hydrated BM4Z after exposure to elevated temperature of 100, and 800 is shown in Figures 4.110 and 4.111 respectively. The main phases identified in the mortar is gismondine at $2\theta = 20.77, 26.65, 49.92, 67.43$. These peaks are found along with peaks of calcite. After exposure to an elevated temperature of 800 °C, the intensity of the calcite peak is expected to disappear since calcite starts to. This is due to the decomposition of calcium hydroxide which begins after 500°C. The effect of addition of 2% Zirconium di oxide is indicated by the fact gismondine is formed at 200 °C. At 600 °C the intensity of diffraction peaks of gismondine increases and also peaks tobermorite and calcium alumino silicate hydrate can also be seen. This shows that the blended mortars with the addition of 2% Zirconium di oxide exhibit better thermal resistance property. As in the case of BM2Z the main peaks of gismondine are masked by quartz, a comparative examination of the intensity of reflections at different temperatures of exposure times shows that a peak of gismondine at 28.49° Based on this observation, gismondine is the main cementitious product that contributes to the long term strength development [99].

4.13.4.2 SEM Analysis

Fig. 4.112. SEM Micrograph BM 4Z at 100 °C
Fig. 4.113. SEM Micrograph BM 4Z at 100 °C

Fig. 4.114. SEM Micrograph BM 4Z at 800 °C
The Figures from 4.112 to 4.115 represents the SEM micrographs of BM4Z after thermal treatment at 100 and 800 °C. From the micrographs it is clear that the mixes containing ZrO$_2$ have a dense well structured C-S-H and sheets of Ca(OH)$_2$ at room temperature. This is due to enhanced hydration of cement in the presence of Zirconium di oxide. The dense structure of cement gel is destroyed which has lead to the reduction in strength at higher temperature. The hydrated phases and these the products of hydration C-S-H are not completely destroyed even after exposure upto 800 °C. The micro-structure of blended cement mortars containing 2% and 4% of Zirconium di oxide indicted compact cement phase with very low porosity. This indicates that the hydrated phases are not decomposed completely in the presence of refractory chemical Zirconium di oxide and pore coarsening is not observed. The non-decomposition of crystalline hydrated phases and the formation of Gismondine, supported by XRD, explains the better residual compressive strength of the mortars blended with fly ash and Zirconium di oxide at elevated temperatures. The filling effect of the hydration products decreased the pores, altered the morphological characteristics of the formed hydrates and thus efficiently hardened the mortars. This observation was valid for the superior residual strength of the blended mortars containing 4% zirconium di oxide.
4.13.4.3 FTIR Analysis

Fig. 4.116. FTIR of BM 4Z
The FTIR of BM4Z at room temperature shows a very strong peak at 3643 cm\(^{-1}\) as compound to BM. This indicates that the addition of 4\% ZrO\(_2\) enhanced the hydration of cement which increases the CH content. The peak at 3452 cm\(^{-1}\) and 1641 cm\(^{-1}\) corresponds to water molecules present in CSH and the peak present at 923 cm\(^{-1}\) corresponds to O-Si-O vibration spectra in C-S-H. The peak representing O-H of Ca(OH)\(_2\) disappears on increasing the temperature of exposure but increases at 1081 cm\(^{-1}\) representing –O-Si-O, O-Al-O vibrations of calcium alumino silicates. It can be noticed that a band width maximum at 3442 and 1641.9 cm\(^{-1}\) in BM4Z after thermal treatment at 400 °C. These peaks diminish in intensity on increasing the temp of exposure to 800 °C but they don’t disappear. These vibrations generally corresponding to O-H water molecules these bands are absent in Cm at these temperatures to dehydration of CSH and evaporation of absorbed water. Hence these vibrations of the functional groups of OH type must be zeolitic in nature. Similar peaks has also been seen near 680 and 745 cm\(^{-1}\) which are assigned to symmetric Si-O-Si and Al-O of zeolite framework [100].

4.14 COMPARISON OF PROPERTIES OF CEMENT MORTARS WITH DIFFERENT REFRACTORY CHEMICALS AT ELEVATED TEMPERATURE

4.14.1 Compressive Strength

The investigations shows the variation of compressive strength of cement mortar when exposed to different levels of elevated temperature it is observed from the figures 4.117 and 4.118 the percentage residual compressive strength is increased in cement mortar and also for CM2Z, CM2A, CM4Z & CM4A at 100 °C for all durations of exposure it can be seen from the figures 4.117 and 4.118 that when the temperature level increases beyond 100 °C upto 800 °C there will be a decrease in strength. At all levels of temperature it can be observed that the percentage strength retained in mortar is higher in case of CM2Z, CM2A, CM4Z & CM4A. Thus it shows that the refractory chemicals have a definite role in improving the performance of cement mortar when subjected to elevated temperature.
Fig. 4.117. % Residual compressive strength v/s Temperature (2%)

Fig. 4.118. % Residual compressive strength v/s Temperature (4%)
4.14.2 % Calcium Oxide

Fig. 4.119. CaO % v/s Temperature (2%)

Fig. 4.120. CaO % v/s Temperature (4%)
The variations in calcium oxide content as shown in the figure 4.119 and 4.120 in cement mortar implies the role of refractory chemicals in cement mortar. The calcium oxide content is gradually increased as the level of temperature is increased in CM, CM2Z, CM2A, CM4Z & CM4A. The increase is high in the case of CM compared to CM2Z, CM2A, CM4Z & CM4A for 2, 4 & 6 hours of exposure.

4.14.3 Porosity (%)

The porosity has also increased in CM, CM2A, CM2Z, CM4A & CM4Z. From the figures 4.121 and 4.122 it can be observed that the increase in percentage porosity is very high in CM as compared to CM2Z, CM2A, CM4Z & CM4A. This results in the retention of higher percentage of strength in CM2Z, CM2A, CM4Z & CM4A as compared to CM.
The variations in calcium oxide and the porosity is shown in figures 4.119 to 4.120 has reflected in the percentage strength retained of the cement mortar. It has also been observed that cement mortar with Zirconium dioxide has performed marginally better than with alumina.

Similar observations have been made with respect to BM, BM2Z, BM2A, BM4Z & BM4A.