Mechanical properties of blended cement mortar systems exposed to ammonium chloride environment

Sheba Babu¹,², Mohammed Sahad¹, Vijeesh K P¹, Syamjith C K¹, Mohammed Raneesh¹, Ramaswamy K P¹, Nazeer M¹ and Mohammed Thowsif¹

¹Department of Civil Engineering, TKM College of Engineering, Kollam-691005, India.
²Email: shebababu447@gmail.com

Abstract. There are number of areas where cement composites can be exposed to ammonium based compounds such as agricultural land, chemical fertilizer plants, waste waters, polluted and industrial environments, which can induce severe and premature deterioration of concrete systems. Based on the review of literature, the most common and deleterious ammonium based salts were found to be ammonium nitrate, ammonium chloride and ammonium sulphate. The cementitious systems with Ordinary Portland Cement (OPC) may be attacked easily by these ammonium based chemicals as the OPC hydrates such as Portlandite and C-S-H gel are considered to be unstable in these aggressive media. Thus, it is necessary to understand the alteration kinetics of cementitious systems and the effectiveness of Supplementary Cementitious Materials (SCMs) in improving the resistance when exposed to ammonium based environments for developing more durable and sustainable concrete systems. The aim of this experimental study was to investigate the durability aspects in terms of the changes in mechanical properties of cement mortar specimens made with OPC and different combinations of various Supplementary Cementitious Materials (SCMs) exposed to ammonium chloride solution prepared using chemical grade ammonium chloride (NH₄Cl). The mortar specimens were exposed to ammonium chloride solution in two different concentrations (1.25 M and 2.5 M) for a maximum exposure duration of two and half months. The SCMs used for the study include Class F Fly ash (FA), Ground Granulated Blast Furnace Slag (GGBS), and Silica fume (SF). The changes in the mechanical properties were evaluated on the basis of visual assessment, depth of penetration, changes in the compressive strength, changes in Ultrasonic Pulse Velocity (UPV) and relative dynamic modulus of elasticity. From all the test results, it can be concluded that the ternary blended mix with OPC, GGBS and Silica fume (OPC-GGBS-SF) has higher resistance to ammonium chloride attack. The results stress the need to include SCMs and the importance to tailor make the concrete for structures exposed to aggressive environment like ammonium chloride.

1. Introduction

Since cement concrete is the one of the most widely used construction material, it can come in contact with aggressive aqueous environments in many situations. Thus the concrete systems are more vulnerable to chemical attack by these aggressive environments. The understanding of the alteration kinetics and mechanisms of degradation of cementitious matrices by these aggressive media is an essential step in
making concrete systems more durable which will then increase the service life of the concrete structures. The incorporation of Supplementary Cementitious Materials (SCMs) along with cement were found to be more effective in improving the durability of cement composites in aggressive chemical environments as it imparts a compact microstructure with low penetrability [2, 15, 16]. The replacement of cement with SCMs can also be considered as the most viable solution to make the cement concrete more sustainable.

The resistance of cementitious systems in ammonium environment and the effectiveness of SCMs in improving the durability can be considered as the one of the most important durability indices to be studied, as they can be exposed to ammonium based compounds in various areas such as chemical fertilizer plants, agricultural land, industrial environments, waste waters, ground waters and polluted environment [1, 3, 5, 10, 17]. Based on the review of literature, the most common and deleterious ammonium based compounds were found to be ammonium nitrate, ammonium chloride and ammonium sulphate [2, 4-17].

There are number of studies reported on the deterioration of cementitious matrices exposed to ammonium sulphate and ammonium nitrate solutions. The deterioration by ammonium sulphate \((\text{NH}_4\text{H}_2\text{SO}_4)\) is the one of the most aggressive corrosion, characterised by the intensive dissolution of cement hydrates, cracking and expansion due to the formation of gypsum and ettringite [7, 14]. It is caused by the combined action of acid hydrolysis, sulphate and ammonium corrosion with the formation of gypsum crystals on the surface of specimens [4, 6, 8, 12].

The mechanism of ammonium nitrate \((\text{NH}_4\text{NO}_3)\) attack is characterised by the leaching, decalcification and the dissolution of hydration products [11]. The deterioration leads to the formation of soluble calcium nitrate, calcium nitro aluminate salt and ammonia emanation with rhombic calcite as surface deposits on the specimens [2, 12, 13].

But the studies reported on the deterioration of cementitious systems in ammonium chloride \((\text{NH}_4\text{Cl})\) environment is very limited, characterised by the dissolution of portlandite and crystallization of thaumasite salt. Another intermediate phase is characterized by the formation of Friedel’s salt. The final reaction products formed were found to be gypsum, calcite and vaterite [14]. The formation of calcium chloro aluminate hydrate and calcium hydroxychloride hydrate results in considerable increase in volume leading to expansion and disruption of hardened concrete [9]. However, the mechanism of ammonium chloride attack is not well understood and more micro-analytical characterization studies are to be performed to understand the mechanism in a better way.

Since there are very few works reported on the deterioration kinetics of cementitious matrices exposed to various concentrations of \(\text{NH}_4\text{Cl}\) solution over different exposure duration, the objective of this experimental study was to investigate the effect of \(\text{NH}_4\text{Cl}\) solution on the durability properties of cement mortar specimens with various combinations of SCMs over an exposure duration of two and half months on the basis of visual examinations, changes in compressive strength, degradation depth, Ultrasonic Pulse Velocity (UPV) and changes in the dynamic modulus of elasticity of mortar specimens.

2. Materials used
The various materials used in this experimental study include Ordinary Portland Cement (OPC) 53 Grade conforming to IS: 12269-1987, Manufactured Sand (M Sand) as fine aggregates conforming to IS 383, SCMs such as Class F Fly ash (FA), Ground Granulated Blast Furnace Slag (GGBS) and Silica fume (SF). The specific gravity of OPC, Fly ash, GGBS and Silica fume is 3.15, 2.20, 2.90 and 2.05 respectively. The
ammonium based salt used in this experimental study was chemical grade ammonium chloride (NH₄Cl) in two different concentrations of 1.25 and 2.5 M (mol/L) respectively.

Six different mixes of cement mortar specimens made with OPC and different combinations of SCMs (shown in Table 1) of 1:1.5 (binder: sand) mix proportion with water-binder ratio 0.50 were selected for the study. Mix 1 is kept as the reference or control mix. Mixes 2 to 4 are binary mixes whereas mixes 5 and 6 are ternary blended mixes. Fine aggregate (M Sand) which passed through 2.36 mm sieve and retained on 90 micron sieve were used for the study. Polycarboxylate Ether (PCE) admixture was used as superplasticizer with optimum dosage as 0.5% of weight of binder in order to improve the workability of the mortar mix. PCE was used only for Silica fume based mixes.

| Mix             | OPC (%) | FA (%) | GGBS (%) | SF (%) |
|-----------------|---------|--------|----------|--------|
| Mix 1 (OPC)     | 100     | -      | -        | -      |
| Mix 2 (OPC+FA)  | 70      | 30     | -        | -      |
| Mix 3 (OPC+GGBS)| 50      | -      | 50       | -      |
| Mix 4 (OPC+SF)  | 90      | -      | -        | 10     |
| Mix 5 (OPC+FA+SF)| 70     | 20     | -        | 10     |
| Mix 6 (OPC+GGBS+SF)| 50   | -      | 40       | 10     |

3. Methodology
The degradation kinetics of cement mortar specimens made with OPC and different combinations of SCMs exposed to two different concentrations 1.25 M and 2.5 M of ammonium chloride (NH₄Cl) solution were evaluated on the basis of changes in the mechanical properties of mortar specimens before and after exposure. The performance were evaluated periodically on the basis of visual assessment, depth of penetration, changes in the compressive strength and changes in the UPV and relative dynamic modulus of elasticity of specimens over an exposure duration of two and half months.

The raw materials required for the casting of mortar specimens were weighed accurately using precise weighing balance as per the mix proportion. All the ingredients were mixed well using a Hobart mixer for about 5 minutes, filled in the oiled plastic cylindrical moulds (diameter 25 mm and height 50 mm) and allowed to set for 24 hours. After 24 hours, the specimens were demoulded and kept for lime saturated curing for a duration of 14 days. For lime saturated curing, 3g/L of calcium hydroxide (Ca(OH)₂) solution was used. Cylindrical specimens having 25 mm diameter and 50 mm height were used for performing all the tests.

The initial appearance, compressive strength and UPV of the specimens (in saturated but surface dry condition) were noted before immersion in NH₄Cl solution to determine the changes in these parameters after the exposure. Then these specimens were exposed in two concentrations; 1.25 M and 2.5 M NH₄Cl solution. The NH₄Cl solution was replenished every 2 weeks in order to maintain the aggressiveness of the solution. The ratio of volume of ammonium solution to that of specimens was kept fixed at five for the evaluation of degradation kinetics for the entire exposure period. Thus, an accelerated immersion based
leaching test is adopted in this experimental investigation in order to understand the degradation kinetics of various binders upon exposure to ammonium based solutions.

After each week of exposure, the specimens were then taken out of the solution and tested to determine the changes in the physical appearance, altered depth, compressive strength and UPV of the mortar specimens. The tests were carried out for a maximum exposure duration of 10 weeks for 1.25 M and 7 weeks (due to rapid deterioration) for 2.5 M NH₄Cl solution. The changes in the physical appearance of specimens were identified by taking digital photographs of specimens of various mixes. For measuring altered depth, 1% phenolphthalein solution was used as the indicator. Compressive strength test was carried out on the modified Marshall testing machine with testing rig. Ultrasonic Pulse Velocity (UPV) test were carried out as per the guidelines of IS 13311(Part I)-1992 using transducers having a frequency of 150 kHz. The mean value of the three specimens from each mix was taken for the each test result.

4. Results and discussions
4.1 Visual examinations
The cylindrical mortar specimens were visually examined to identify the changes in the physical appearance upon exposure in 1.25 M and 2.5 M NH₄Cl solution. The typical photographs of the specimens in (saturated and surface dry condition) taken on a weekly basis before and after exposure over the entire exposure duration is as shown in Table 2. It was observed that the specimens of all the six mixes exposed to both concentrations (1.25 M and 2.5 M) of NH₄Cl solution undergone only minimal changes in their physical appearance upon the exposure. The physical deterioration on the specimens was found to be minimal and they remained structurally intact. The variations in the physical appearance were found to be similar for all the mixes studied.

Table 2. Visual examination of mortar specimens in NH₄Cl solution (1.25 M and 2.5 M).

| Before exposure | After exposure in NH₄Cl solution |
|-----------------|---------------------------------|
|                 | 1.25 M (10th week)             |
|                 | 2.5 M (7th week)               |
| ![Before exposure](image1.png) | ![After exposure in NH₄Cl solution](image2.png) | ![After exposure in NH₄Cl solution](image3.png) |

4.2 Altered depth
In this test, the altered depth was determined by spraying 1% phenolphthalein indicator solution on the freshly cut and exposed surfaces of mortar specimens. The degradation depth measurement was started only after third week of exposure and continued for the entire exposure duration. A magenta coloured portion and a colourless portion were observed on the freshly cut surface. The altered depth is taken as the sum of depth of leaching and depth of reaction. The depth of leaching is taken as the half of the changes in
The diameter of specimens before and after exposure and the depth of reaction is taken as the half of the depth of colourless portion obtained on the specimens after exposure in ammonium chloride solution. It was found that the degradation depth increased with the increase in the concentration (the altered depth higher for 2.5 M as compared to 1.25 M) of NH₄Cl solution. Table 3 shows the photographs of the freshly cut surface of specimens after spraying the phenolphthalein solution. The variations in the altered depth of specimens of all the six mixes obtained after exposure in 1.25 M (for 10 weeks) and 2.5 M (for 7 weeks) NH₄Cl solution is as shown in Figure 1 and 2 respectively.

Table 3. Images showing altered depth in NH₄Cl solution (1.25 M and 2.5 M).

| Mortar mix          | After exposure in NH₄Cl solution |
|---------------------|---------------------------------|
|                     | 1.25 M  | 2.5 M  |
|                     | (10th week) | (7th week) |
| OPC                 | ![Image](image1) | ![Image](image2) |
| OPC+FLYASH          | ![Image](image3) | ![Image](image4) |
| OPC+GGBS            | ![Image](image5) | ![Image](image6) |
| OPC+SF              | ![Image](image7) | ![Image](image8) |
| OPC+FLYASH+SF       | ![Image](image9) | ![Image](image10) |
| OPC+GGBS+SF         | ![Image](image11) | ![Image](image12) |

The degradation depth was found to be higher for fly ash based mixes (Mix 2 and Mix 5) and lower for control mix OPC (Mix 1) in both the concentrations. Among the two mixes incorporated with flyash, the altered depth was found to be higher for binary blended mixes with OPC and Flyash as compared to ternary mix with OPC, Flyash and SF. For binary blended mix OPC-FLYASH (Mix 2), the altered depth
in 1.25 M and 2.5 M was found to be 11.6 mm and 12.83 mm respectively. But for the mix OPC-FLYASH-SF (Mix 5), the degradation depth was found to be 10.02 mm and 12.80 mm respectively in 1.25 M and 2.5 M concentrations. The altered depth for control mix OPC was found to be only 7.90 mm and 11.06 mm respectively in 1.25 M and 2.5 M concentrations of NH_4Cl solution. After the control mix OPC, the altered depth was found to be higher for GGBS based mixes (Mix 3 and Mix 6). For binary mix with OPC and GGBS, the altered depth was found to be 8.31 mm and 11.94 mm respectively and for ternary mix with OPC, GGBS and SF, the altered depth was found to be 8.30 mm and 11.58 mm respectively in 1.25 M and 2.5 M concentrations of NH_4Cl solution. From this result, the altered depth of Fly ash based mix (both binary and ternary) was found to be almost same in both 1.25 M and 2.5 M NH_4Cl solution. Similarly, the altered depth of GGBS based mix (both binary and ternary) was also found to be same in 1.25 M and 2.5 M NH_4Cl solution. Based on the degradation depth, it can be ascertained that the performance of control mix OPC was better compared to the other mixes. But among the blended mixes with SCMs, the performance of OPC-GGBS-SF based mix was found to be better.

![Figure 1. Altered depth in 1.25 M NH_4Cl solution.](image1)

![Figure 2. Altered depth in 2.5 M NH_4Cl solution.](image2)

### 4.3 Compressive strength test

The compressive strength variation of cylindrical mortar specimens of all the six mixes of mortar specimens when exposed to 1.25 M (maximum duration 10 weeks) and 2.5 M (maximum duration 7 weeks) NH_4Cl solution is presented in Figure 3 and 4 respectively. It was found that the initial compressive strength (after 14 days of curing) of control mix OPC was found to be higher when compared to other binary and ternary blended mixes. Among the binary blended mixes, the initial compressive strength was found to be higher for mix with OPC and SF as compared to GGBS and FLYASH based mixes. Among ternary blended binder mixes, the high initial compressive strength was obtained with Mix 5 (OPC-FLYASH-SF) when compared with Mix 6 (OPC-GGBS-SF). It was found that specimens of all the mixes have undergone significant reduction in strength when exposed to both 1.25 M and 2.5 M NH_4Cl solution. After exposure in NH_4Cl, all the specimens have undergone a reduction in compressive strength. The strength loss was found to be higher for the control mix OPC and lower for GGBS based mixes. The strength loss for OPC exposed in 1.25 M and 2.5 M NH_4Cl solution was found
to be about 77.58% and 79.24% respectively. It was found that the compressive strength of both the binary (OPC-GGBS) and ternary (OPC-GGBS-SF) blended mixes with GGBS was reduced by about 70% in both concentrations at the end of the exposure duration. Based on the strength loss, it can be ascertained that the performance of OPC-GGBS-SF blended mix was better compared to the other mixes.

4.4 Ultrasonic Pulse Velocity (UPV) test
The UPV test, being a non-destructive test helps in assessing the strength and quality of specimens by measuring the changes in the pulse velocity. The changes in the UPV of specimens of various mixes before and after exposure in ammonium chloride solution are as shown in Table 4. Before exposure, the velocities of specimens of all the six mixes were found to be above 3.5 km/sec, which indicates the good quality specimens as per IS 13311(Part I)-1992. Among the various mixes, the initial pulse velocity was found to be high for the control mix OPC. The pulse velocities of binary blended mixes was high as compared to ternary mixes. The higher velocities indicates good quality and homogeneity of the material while lower velocities indicates the presence of micro cracks or voids or deterioration in microstructure. After exposure in the ammonium chloride solution, a significant reduction in the pulse velocities were observed on all the specimens of various mixes in both concentrations (1.25 M and 2.5 M) which gives information about the microstructural deterioration. The reduction in pulse velocity was found to be higher for the control mix OPC and lower for GGBS based mixes (both binary and ternary). Among the GGBS mixes, the velocity reduction was found to be lower for ternary blended mix OPC, GGBS and SF as compared to binary mix with GGBS and SF.

From these changes in the pulse velocity, the changes in the dynamic modulus of elasticity of specimens can be determined as per the codal provisions. Since the poisson’s ratio of the specimens were not known, the changes in the relative dynamic modulus of elasticity of specimens were analysed and shown in Figure 5 and 6 respectively. Relative dynamic modulus of elasticity was calculated as the ratio of dynamic modulus of elasticity at a particular age of exposure to the dynamic modulus of elasticity just before the exposure. Here also, the variation was found to be similar as in the case of changes in pulse velocity.
velocity. The relative dynamic modulus of elasticity of control mix OPC was found to be 0.730 and 0.674 respectively in 1.25 M and 2.5 M NH₄Cl solution. For the ternary blended mix OPC-GGBS-SF, the relative dynamic elastic modulus was about 0.853 and 0.756 respectively in 1.25 M and 2.5 M concentrations and this higher value indicates better resistance. But for the binary mix OPC-GGBS, it was about 0.776 and 0.746 respectively in 1.25 M and 2.5 M NH₄Cl solution. Thus based on the changes in the UPV and relative dynamic modulus of elasticity, the performance of ternary blended mix with GGBS and SF as SCM (OPC-GGBS-SF) was found to be better as compared to other mixes.

Table 4. Changes in the UPV of specimens in NH₄Cl solution (1.25 M and 2.5 M).

| Mortar Mix          | Ultrasonic Pulse Velocity (km/sec) | After exposure in NH₄Cl solution |
|---------------------|------------------------------------|---------------------------------|
|                     | Before exposure                     | 1.25 M (10th week) | 2.5 M (7th week) |
| OPC                 | 3.89                               | 3.43                          | 3.38              |
| OPC+FLYASH          | 3.77                               | 3.38                          | 3.29              |
| OPC+GGBS            | 3.75                               | 3.48                          | 3.43              |
| OPC+SF              | 3.74                               | 3.43                          | 3.36              |
| OPC+FLYASH+SF       | 3.73                               | 3.32                          | 3.28              |
| OPC+GGBS+SF         | 3.73                               | 3.49                          | 3.46              |

Figure 5. Changes in relative dynamic modulus of elasticity in 1.25 M NH₄Cl solution.  
Figure 6. Changes in relative dynamic modulus of elasticity in 2.5 M NH₄Cl solution.
5. Conclusions

Concrete systems exposed to the chemical fertilizer plants, agricultural land, sewage plants and many other industrial applications are more prone to chemical attacks by ammonium based compounds. Thus the resistance of cementitious systems in ammonium environment has to be comprehensively investigated as the exposure to these aggressive environments can induce severe and premature deterioration of cementitious systems.

In this experimental programme, NH₄Cl solution in two different concentrations (1.25 M and 2.5 M) was used to study the effect of ammonium based salt solution on the mechanical properties of OPC cement mortar specimens made with different combinations (both binary and ternary) of various SCMs. The degradation kinetics was evaluated in terms of visual examinations, changes in the compressive strength, degradation depth and changes in the dynamic modulus of elasticity of mortar specimens before and after the exposure.

From the test results, it was found that specimens of all the mixes have undergone a significant reduction in their compressive strength when exposed to 1.25 M and 2.5 M NH₄Cl solution. Based on the compressive strength loss, it can be ascertained that the performance of OPC-GGBS-SF blended mix was better compared to the other mixes. The reduction in compressive strength may be ascribed to the leaching phenomenon and decalcification of hydrates such as Portlandite and CSH gel.

The measurement of degradation depth helps in identifying the degraded zone from the sound zone, as the magenta coloured portion indicates unattacked sound portion (pH above 9) and colourless portion indicate deteriorated region (pH below 9). In terms of the depth of degradation, it can be ascertained that the performance of control mix OPC was better compared to the other mixes. But among the blended mixes with SCMs, the performance of OPC-GGBS-SF based mix was found to be better.

It was found that specimens of all the mixes have also undergone a significant reduction in their pulse velocities and relative dynamic modulus when exposed to 1.25 M and 2.5 M NH₄Cl solution. Based on the changes in the UPV and relative dynamic modulus, the performance of ternary blended mix with GGBS and SF as SCM (OPC-GGBS-SF) was found to be better as compared to the other mixes. The changes in UPV gives information about the variations in the quality and microstructural deterioration that the specimens have undergone upon exposure to NH₄Cl solution.

Based on all the test results, it can be concluded that the ternary blended mix with OPC, GGBS and Silica fume (OPC-GGBS-SF) possess better mechanical properties after the exposure, and has higher resistance to ammonium chloride attack. The results stress the need to include SCMs in concrete mixture formulations and the importance to tailor make the concrete for structures exposed to aggressive environment like ammonium chloride. The changes in mechanical properties shall be further validated by conducting a detailed microanalytical characterization study.

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6. References

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