Influence of Calcium Sulphate on Cement Motor and Characteristics Behaviour at Different Proportions

[1] Md. Jalal Uddin, [2]Md. Quayyum
[1, 2] Assistant Professor-Civil Engineering
Jaya Prakash Narayan College of Engineering
Mahabubnagar 509 001
Andhra Pradesh

Abstract

Cement is considered one of the most important building materials around the world. It is mainly used for the production of concrete. Concrete is a mixture of inert mineral aggregates, e.g. sand, gravel, crushed stones, and cement. Cement consumption and production is closely related to construction activity, and therefore to the general economic activity. Cement is one of the most produced materials around the world. Due to the importance of cement as a construction material, and the geographic abundance of the main raw materials, i.e. limestone, cement is produced in virtually all countries.

Many cement concretes have been found to be susceptible to deterioration in soils, ground waters, or seawaters that contain high levels of sulphates. Sulphates react with the aluminium-containing phases of portland cement concrete-mortar-paste, causing internal expansion. It has been found that the resistance of a concrete to sulphate attack is related to the C_3A content of the cement and to the total amount of aluminate compounds, C_3A and C_4AF. Sulphate attack is consider one of the major deteriorative problems occurred when the cement based materials, such as concrete, mortars and buildings, are exposed to this environment. Sulphate ions in soil, ground water and sea water may cause deterioration of reinforced concrete structures by provoking expansion and cracking due to factors such as type of cement, sulphate cation type, sulphate concentration and the period of exposure. Many structures affected by sulphate degradation often need to be repaired or, in most severe cases, they need to be reconstructed.

In this investigation the work is carried out to examine calcium sulphate particularly effecting the different parameters , such as strength , setting times, soundness, consistency etc. the sand used is ennore sand of three different grades. Calcium sulphate is added in different proportions to cement and its effect is studied at different ages.

Keywords: Cement mortar, calcium sulphate ($caso_4$), strength, soundness.

Literature Review

Amer Rashed Shalal[9] had carried out his work on the effect of sulphate in cement .Sulphates may be found in any of the raw materials of cement. Sand contaminated with sulphates is currently a local problem because of the difficulty in obtaining well- graded sand which could be used in concrete that has an acceptable sulphate content regarding to overcome from this problem he carried out his work on the effect of sulphate in cement with 5% pozzolana and in sand correlation between compressive strength and ultrasonic pulse velocity (U.P.V) of concrete of different mixes such as 1:1.5:3, 1:2::4, and 1:3:6 is studied in order to asses the degree of the correlation of different mixes and its resistance to sulphate attack. He showed that the (U.P.V) seem to be a good method for assessing the quality and strength of the concrete specimens. This work is carried out in the engineering Journal of Qatar University Al- Mustansiryah.**Yutaka Nakajima and Kazuo Yamada[10]**The research work carried out in this project is on The effect of the kind of calcium sulphate in cements on the dispersing ability of poly β-naphthalene sulphonate super plasticizer (PNS) It is problematic that not all cement–PNS combination is compatible. In this study, the influence of the kind of calcium sulphate on the dispersing ability of PNS was examined by measuring paste flow. The kind of calcium sulphates influences flow loss of cement paste. Flow loss of cement paste is lower when cement containing a higher ratio of hemihydrate as compared to gypsum is used. The mechanism was investigated, considering composition of solution phase and amount of adsorbed PNS per unit surface area. As a result, the following are clarified. Alkali sulphate affects the SO_4^{2-} concentration all through the ages. On the other hand, the kind of calcium sulphate affects the initial value only. When the cement containing hemiydrate mainly is used, initial SO_4^{2-} concentration is higher; however, it decreases rapidly with time elapse. The adsorbed amount of PNS can be calculated by assuming the Langmuir type competitive adsorption of PNS with SO_4^{2-} onto the surface of hydrated cement particle .it was found that the difference in flow loss between two cement containing different kinds of calcium sulphate could be explained by the effect of SO_4^{2-} concentration on the adsorbed amount of PNS. When the cement containing mainly hemihydrate is used, a rapid decrease of SO_4^{2-} concentration with time elapse affects the adsorption equilibrium. Adsorbed PNS increases as SO_4^{2-} concentration is decreased. As a result, the flow loss of cement paste becomes less. This work is carried out in the Cement and Concrete Development Research Centre, Taiheiyo Cement Corporation, Sakura, Chiba .

Mustafa Tuncan and Kadir Kılınç [14] Had carried out the work on the effect of sulphates on the physical properties of portland cement mortars Concrete is produced by mixing cement, aggregate and water. The aggregates are inert materials and the chemical reactions take place between cement and water. Therefore, the properties of mixing water are very important for the behaviour of fresh and hardened concrete. Practically, the water used for drinking is suitable for the concrete production. In any case, the mixing water which is planned to be used in concrete should be tested since the presence of impurities affects significantly the properties of the concrete. In this investigation, magnesium sulphate, sodium sulphate and sodium sulphide were used in various proportions for the preparation of salty solutions. Portland cement pastes and mortars were produced by using these solutions as mixing water. The initial and final setting times of cement pastes, unit weights of fresh mortars and the drying shrinkage values of hardened mortar specimens were determined according to relevant standards. The results showed that the initial setting times accelerated and final setting times delayed generally by the addition of salts. There was no significant effect of mixing water on the unit weights of fresh mortars. It was also observed that the drying shrinkage values increased by magnesium and sodium sulphate and decreased by sodium sulphide. Materials of Construction Division, Istanbul Technical University, Istanbul, Turkey

What Is Sulphate Attack?

Sulphate attack is a common form of concrete deterioration. It occurs when concrete comes in contact with water containing sulphates (SO4). Sulphates can be found in some soils (especially when arid conditions exist), in seawater, and in wastewater treatment plants.

- Sulphate attacks are of two types 'external' or 'internal'.

A. **External**:

Sulphates entering the pore structure of concrete from the surrounding environment can cause four chemical processes, depending on which sulphates and hydrates are involved. For further information regarding what the various terms in the chemical formulas mean, see the definitions section. Due to penetration of sulphates in solution, in groundwater for example, into the concrete from outside.

B. **Internal:**

Internal sulphate attack is a phenomenon that has been identified relatively recently, and is thus less understood that external sulphate attack. Internal sulphate attack is commonly characterized as any sulphate attack caused by sulphate originating from within the concrete (i.e. hydration products, aggregate). Due to a soluble source being incorporated into the concrete at the time of mixing, gypsum in the aggregate, for example.

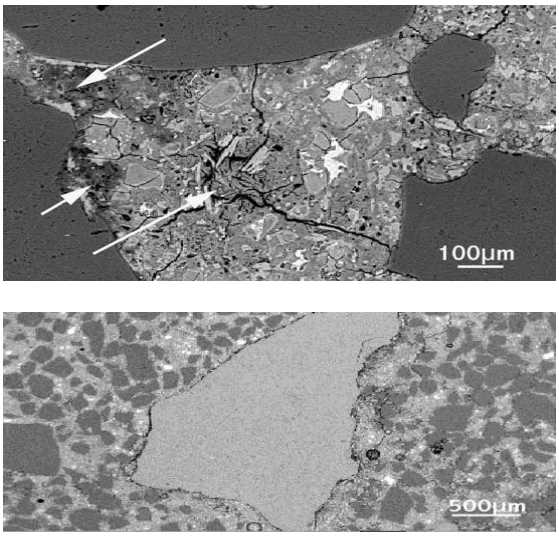


Fig 1 Sulphate attack on cement mortar

Waterborne sulphates react with hydration products of the tri-calcium aluminate (C_3A) phase of Portland cement, and with calcium hydroxide ($Ca(OH)_2$) to form an expansive crystalline product called ettringite. Expansion due to ettringite formation causes tensile stresses to develop in the concrete. When these stresses become greater than the concrete's tensile capacity, the concrete begins to crack. These cracks allow easy ingress for more sulphates into the concrete and the Deterioration accelerates. Sulphates also cause chemical disintegration of some of the cement hydration products.

Fig 2 Severity of sulphate attack depends on type and concentration of the sulphate and increases with wetting and drying

1.1.1. What Happens When Sulphates Get Into Concrete?

- It combines with the C-S-H, or concrete paste, and begins destroying the paste that holds the concrete together. As sulphate dries, new compounds are formed, often called ettringite.
- These new crystals occupy empty space, and as they continue to form, they cause the paste to crack, further damaging the concrete.

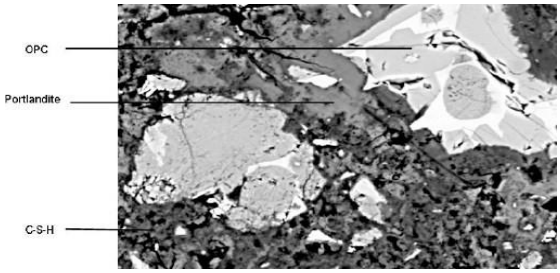


Fig 1.1.1 Sulphates Get Into Concrete

- Both chemical and physical phenomena observed as sulphate attack, and their separation is inappropriate.
- Spalling due sulphate attack.

Fig 1.1.2 Spalling due to sulphate attack

1.2.2 Sulphate Attack Mechanism:

Caused by exposure of concrete to sulphate ions and moisture, sulphate attack is due to a series of chemical reactions between sulphate ions and principle components of the cement paste microstructure. The chemistry of sulphate attack is complex and involves numerous overlapping reactions, mechanisms, and internal or external sources. In external sulphate attack, the migration of sulphate ions into concrete may be accompanied by a gradual dissolution of portlandite (CH) and decomposition of the C-S-H phase. In the latter case, the C/S ratio of this phase eventually declines as increasing amounts of Ca2+ are removed from the structure, thus resulting in a strength loss of the hardened cement paste. Simultaneously, the formation of ettringite crystals and consequent volumetric strains in the hardened material are also considered to be responsible for expansive forces and micro-cracking

Mechanism of Sulphate Attack:

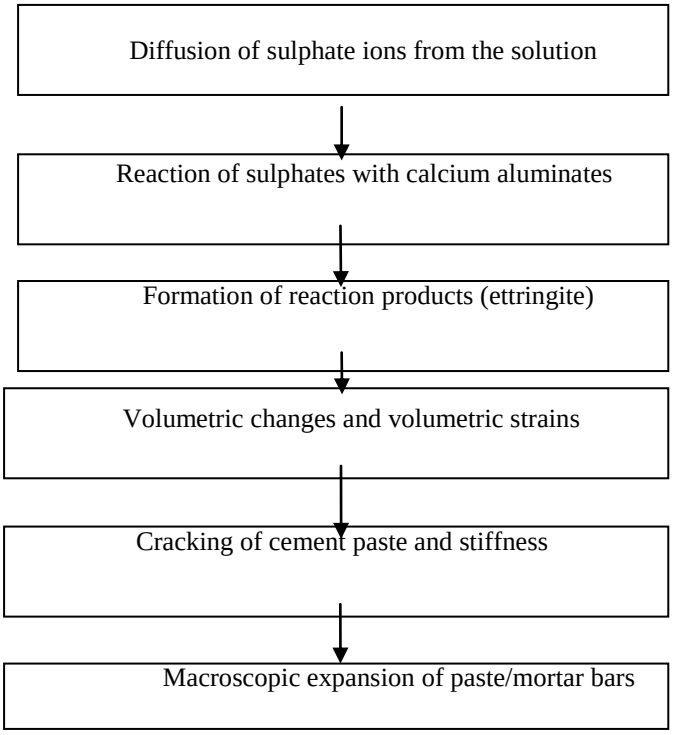


Fig 1.2.2 Mechanism of sulphate Attack

1.2.3 Prevention Measures:

- Internal sulphate attack can be avoided by selecting cement, aggregate, and admixtures that do not contain sulphate-bearing compounds.
- It is important to closely monitor the materials being used in the concrete. Also important is that the water/cement ratio of the mix be kept as low as possible (roughly 0.4).
- Since a concrete with a high ratio has a more expansive and easily traversed pore structure, it is easier for dissolved forms of sulphate to infiltrate the concrete.
- To prevent external sulphate attack, it is vital to understand the soil and ground water conditions of the site where the concrete is to be poured.
- If the environment contains a high level of sulphate-bearing compounds, the concrete mix can be designed to better handle it with proper w/c ratio and admixtures. Sulphate-resistant cements

1.2.4 Control of Sulphate Attack

The quality of concrete, specifically a low permeability, is the best protection against sulphate attack.

- Adequate concrete thickness
- High cement content
- Low w/c ratio
- Proper compaction and curing

1.3. Calcium sulphate ($caso_4$):

- It forms as evaporates from marine waters and is usually found collectively with other mineral deposits such as quartz, sulfur, and clays. Other applications of calcium sulphate are as a soil additive, as a food and paint filler, and a component of blackboard chalk, medicines, and toothpaste $caso_4$ is also found in lakes, seawater, and hot springs as deposits from volcanic vapors. sources are centered near California, the Great Lakes, and the Texas-Oklahoma area

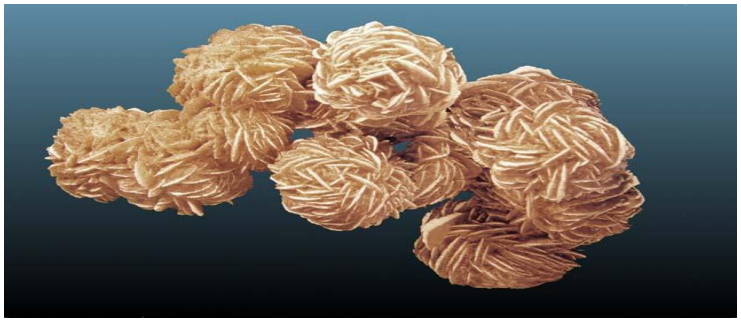


Fig 1.3 (a) Natural Form Of Calcium Sulphate

➢ Calcium sulphate [$CaSO_4$] has several forms, ie, calcium sulphate dihy-drate (commercially known as gypsum), calcium sulphate anhydrous (anhydrite),calcium sulphate hemihydrate, present in two different structures,*a*-hemihydrate and*b*-hemihydrate

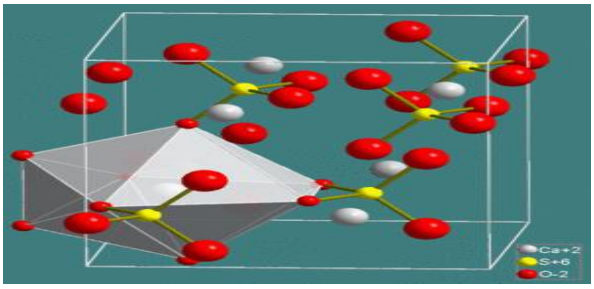


Fig 1.3 (b) Molecular Structure of Calcium Sulphate

➢ Calcium sulphate ($CaSO_4$) occurs in nature in both the anhydrous and the hydrated form. The former is found primarily as the mineral known as anhydrite, while the latter is probably best known as alabaster or gypsum. Calcium sulphate also occurs in forms known as selenite, terra alba, satinite, satin spar, and light spar.

➢ Calcium sulphate was well known to ancient cultures. Theophrastus of Eresus (about 300 B.C.), for example, described its natural occurrence, its properties, and its uses. The Persian pharmacist Abu Mansur Muwaffaq is believed to have first described one of the major products of gypsum, plaster of Paris, around 975 A.D

1.3.1 Characteristics of Calcium Sulphate (Gypsum) ($CaSO_4.2H_2O$)

- solubility in water at 25°C :
- 2.1 g $CaSO_4$/litre
- 2.6 g $CaSO_4 . 2H_2O$/litre
- Ks ($CaSO_4$) : 2.38 x 10^{-4}
- corresponding with 1.45 g $SO4^{2-}$/litre
- hardness : 1.5 tot 2 Mohs;
- specific weight : 2.32 g/cm³
- pH : neutral
- crystal form : monoclinic
- very stable molecule

1.3.2. Manufacture of calcium sulphate:

➢ Calcium sulphate is also known as gypsum. Gypsum is a sedimentary rock, which settled through the evaporation of sea water trapped in lagoons. According to the nature of its impurities, gypsum can show various_colours, ranging from white to brown, yellow, Gray and pink.

➢ Gypsum selection and preparation (cleaning, classifying) are key factors to produce the best plasters. The chemical reaction is :

(CaSO4, 2 H2O) + Heat = (CaSO4, ½ H2O) + 1.5 H2O

➢ Controlling some critical calcination parameters is essential to master the growth of the plaster crystals. And the performance of the plaster depends a lot on its crystals' sizes and shapes.

Process:

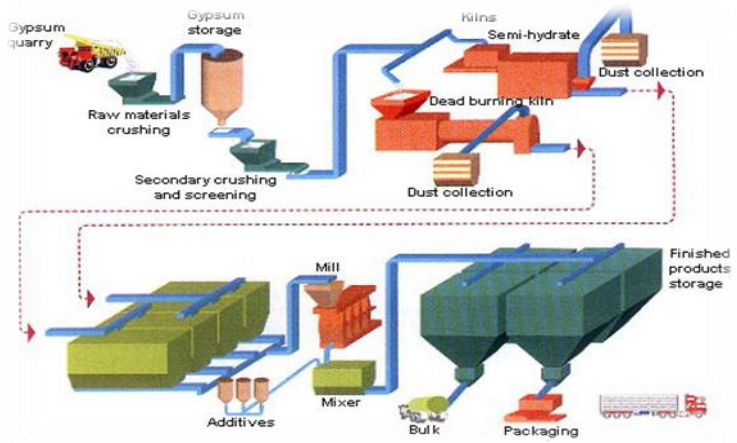
➢ Grinding plaster will determine the particle size distribution of the powder. Different applications call for different granulometrical distributions, and Lafarge Prestia uses different types of grinding processes which enable to serve of markets.

➢ Finally, the plasters will be mixed with additives and fillers, in order to adjust their rheological characteristics (setting times, fluidity, viscosity), their hardening kinetics, their permeability (through pore size distribution), their mechanical strengths, their resistance to abrasion, etc…

➢ Lafarge Prestia knows not only how to formulate for all types of applications, but also which additives to choose in order to delay the ageing process of the plaster in bags, a distinctive competitive-edge

➢ The efficiency of fully automated production lines and the flexibility of manufacturing cycles that allow to reduce batch sizes and shorten production lead-times, thus enabling us to respond to order requirements with increased rapidity.

Fig 1.3.2 (a) Manufacture Of($CaSO_4$) Gypsum



➢ Gypsum is a naturally occurring mineral that is made up of calcium sulphate and water (CaSO4+2H2O) that is sometimes called hydrous calcium sulphate.It is the mineral calcium sulphate with two water molecules attached. By weight it is 79% calcium sulphate and 21% water. Gypsum has 23% calcium and 18% sulfur and its solubility is 150 times that of limestone, hence it is a natural source of plant nutrients. Gypsum naturally occurs in sedimentary deposits from ancient sea beds. Gypsum is mined and made into many products like drywall used in construction, agriculture and industry. It is also a by-product of many industrial processes.

1.3.3. Sources of Gypsum ($CaSO_4$):

Mined gypsum is found at various locations around the world. In North America there are gypsum deposits from Canada to Texas and in many Western States. Chemically raw mined gypsum is primarily calcium sulphate hydrated with water molecules in its chemical structure. Other materials and chemicals in mined gypsum may be small amounts of sand or clay particles and a few trace elements. The trace elements may be boron or iron to arsenic and lead and varies with each deposit. Many deposits in Canada have arsenic while those in Texas may have very little. Primarilymined gypsum is very safe to use and a great amendment for many soil.

Calcium Sulphate (CaSO4) :

- In aqueous conditions, calcium sulphate reacts with calcium aluminate hydrate($4CaO{\cdot}Al_2O_3{\cdot}13H_2O$) to form ettringite (Bensted 1983): $3\ CaSO_4 + 4CaO{\cdot}Al_2O_3{\cdot}13H_2O + 20\ H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O + Ca(OH)_2$
- When the supply of calcium sulphate becomes insufficient to form additional ettringite, calcium aluminate hydrate ($4CaO{\cdot}Al_2O_3{\cdot}13H_2O$) reacts with ettringite already produced to form mono sulphate (Bensted 1983):$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O + 2\ (4CaO{\cdot}Al_2O_3{\cdot}13H_2O) \rightarrow 3\ (3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O) + 2\ Ca(OH)_2 + 20\ H_2O$ From MS Shetty[1]

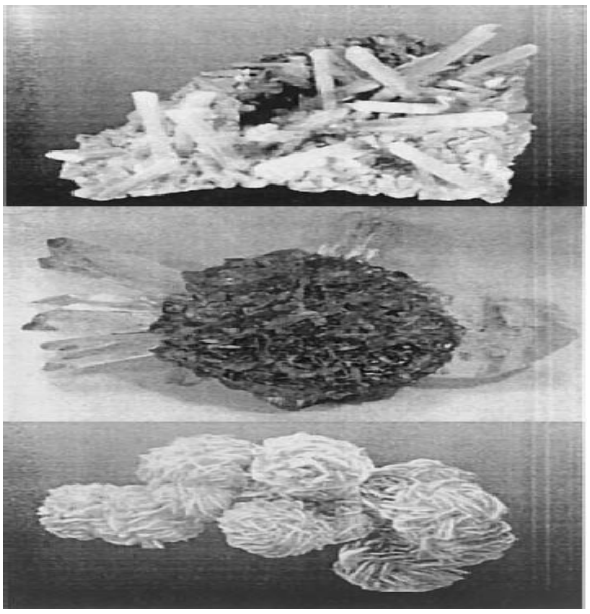
1.3.4. Physical Description:

- Gypsum is a naturally occurring form of calcium sulphate. We market two grades of Gypsum, both being light brown in colour. "Soil Life" which is a fine powder and Gypsum Natural (previously known as "Soil Break") which is a combination of larger chips and powder.

1.3.3 Fig. Calcium Sulphate ($CaSO_4$)

Use of Calcium Sulphate:

Among the many other uses of calcium sulphate are as a pigment in white paints, as a soil conditioner, in Portland cement, as a sizer, filler, and coating agent in papers, in the manufacture of sulphuric acid and sulphur, in the metallurgy of zinc ores, and as a drying agent in many laboratory and commercial processes



i) Five centimetre pencil-sized acicular crystals of gypsum

ii) Six centimetre bladed rosettes of gypsum

iii) Gypsum rose Red River Floodway

OBJECTIVES OF THE STUDY

1. The effect of sulphate on cement is studied for different proportions of calcium sulphate at different ages is carried out in this project, by carrying out in this project, by carrying out experimental tests for a different parameters.
2. Normal consistency of cement with calcium sulphate is tested and compared with standard values.
3. Similarly effect of calcium sulphate on setting time of cement is calculated.
4. Fineness of cement (53 grade) is calculated by sieve analysis.
5. Soundness of cement is studied on addition of calcium sulphate.
6. Workability is tested using flow table test.
7. Cubes of 70.7 x 70.7 x 70.7mm to be casted and immersed in water and there pH variations at different ages are tabulated.
8. Curing should be properly employed to ensure cementitious materials gain their full potential strength. Any other technique is open to variation unless fully controlled and monitored.
9. At every age the weight of cubes and its corresponding compressive strength recorded.

RESULTS AND DISCUSSION

- The Standard consistency of cement paste is defined as the consistency which will permit a vicat plunger having 10mm diameter and 50mm length to penetrate to a depth of 33-35 mm from the top of the mould.
- Initial setting time of cement is the limit within which comment mortar or concrete made from it shall be placed or compacted without loss of its plasticity. According to IS: 4031 part4 the initial setting time should not be less than 30 minutes for ordinary Portland cement. In this work the values has been exceeded above 30 minutes for different concentrations so the loss plasticity is more (plasticity time is more). Final setting is the time limit beyond which moulds can be removed for ordinary Portland cement of 33, 43 and 53 grades the following limits according to code. The final setting time should not be less than 600 minutes..As per IS: 4031- (Part- iv) 1988 and IS: 12269 – 1987.
- The initial and final setting time calculated in the test differs in penetrating as for different concentrations.
- The soundness test of cement is calculated in a le-chatlier test the expansion should not be more than 10mm so in this work the soundness values are below 10mm by adding magnesium sulphate to the cement it is unsoundness. More soundness results in cracks that are expansion. As per IS: 4031- (Part- III) 1988 and IS: 12269 – 1987.
- For different concentrations such as 400 and 300 the soundness is increased reamimg other concentrations is constant.
- Similarly the workability of the cement is varies in the 400 and 300 concentrations And reaming are constant

Conclusions

- Based on the present study, the following conclusions, with respect to influence of calcium sulphate on cement mortar and its compressive strength behaviour are as follows.
- The fineness of cement is done by sieve analysis after continuously sieving 15 minutes the residue in IS: 90 micron is 10% or 10 grams of 100 grams. If it is finer the strength will be more and the surface area will be more
- The average compressive strength of cement mortar cubes varies as per IS code specifications.

- The cement which is used for normal reference cubes the workability is 16mm and for the concentration of $CaSO_4$ cubes the workability increases.
- The values for 3days increased 44% 7 days 53% and 28 days 44% for concentrations of 400mg mixed with calcium sulphate.
- Similarly for 300mg the 3 days value increased 33%, for 7 days 36% and 28 days 38%
- The values are varying according to IS: 12269 – 1987. should be for 3days 50%, 7 days 70%, and 28 days 100%

- The value of pH is neutral for reference cube but the values of the concentration of $CaSO_4$ ie, for 10mg, 50mg, 100mg, 200mg, 300mg and 400mg the pH value has increased, with the increase in the $CaSO_4$ concentration. (pH 6 to 9 neutral, but 9 to 14 are acidic in nature).
- So we concluded that the effect of calcium sulphate on cement mortar is sever according to the different concentrations with low exposure
- The effect of sulphate is a major problem causing to the constructions of structures.
- Laboratory prepared specimens were tested to investigate the mechanisms of calcium sulphate attack on different ages.
- Sulphate attack is consider one of the major deteriorative problems occurred when the cement based materials, such as concrete, mortars and buildings, are exposed to this environment.
- The role of Sulphate ions in causing deterioration of concrete has been investigated intensively. Based on the literature available

Future Scope For Study

- For present study the age can be prolonged up to 2 years to find out detailed results.
- Present study can be further carried out by testing effect of different acids on durability.
- These studied was for only one sulphate i.e., calcium sulphate $caso_{4,}$ a combination of different sulphates such as magnesium, calcium, sodium can be studied.
- In this work the concentrations has been taken with low exposures it can further taken as high exposure with prolonged results .By increase and decrease in water cement ratios and cement proportions

References:

1. Concrete Technology : MS Shetty
2. Concrete Technology : Surendra Singh 5th Edition
3. IS: 4031(part I) 1996: methods of physical test for hydraulic cement is referred for determination of fineness by dry sieving.
4. IS :4031(part IV) 1988: methods of physical test for hydraulic cement is referred for determination of consistency of standard cement paste.
5. IS: 4031(part VI) 1988: methods of physical test for hydraulic cement is referred for determination of compressive strength.
6. Concrete Technology: Surendra Singh 5th Edition.
7. IS: 4031(part IV)1988: methods of physical test for hydraulic cement is referred for determination of initial and final setting time.
8. 4031(part III) 1988: methods of physical test for hydraulic cement is referred for determination of soundness
9. Amer Rashed Shalal This work is carried out in the engineering Journal of Qatar University Al- Mustansiryah.
10. Yutaka Nakajima and Kazuo Yamada This work is carried out in the Cement and Concrete Development Research Center, Taiheiyo Cement Corporation, Sakura, Chiba.
11. Tae-Ho Ahn and Toshiharu Kishi This project work is carried out in the Journal of Advanced Concrete Technology Vol. 8
12. Dunja Mikulić and Bojan Milovanović This research work is done in the concrete Testing research Nantes, France, June 30th 2009
13. Jorgomai Ceesa This work is carried out in Fairbank Highway Research Center (FHWA) in McLean, Virginia.
14. Mustafa Tuncan and Kadir Kılınç This work is carried out at Materials of Construction Division, Istanbul Technical University,Istanbul, Turkey.