The Effect of Cement and Admixture Types on the Resistance of High Performance Concrete to Internal Sulphate Attack

Prof.Nada Mahdi Al-galawi
Department of Civil Engineering
College of Engineering
Baghdad University
Email : naljalawi @yahoo.com.

Samaa Ali Hassooni
Department of Civil Engineering
College of Engineering
Baghdad University
Email : samaali706 @yahoo.com.

ABSTRACT

This work is concerned with the study of the effect of cement types, particularly OPC and SRPC, which are the main cement types manufactured in Iraq. In addition, study the effect of mineral admixtures, which are HRM and SF on the resistance of high performance concrete (HPC) to internal sulphate attack. The HRM is used at (10%) and SF is used at (8 and 10)% as a partial replacement by weight of cement for both types. The percentages of sulphate investigated are (1,2 and 3)% by adding natural gypsum as a partial replacement by weight of fine aggregate. The tests carried out in this work are: compressive strength, flexural strength, ultrasonic pulse velocity, and density at the age of 7, 28, 90 and 120 days.

The results indicated that the SRPC mixes showed lower reduction in the properties of concrete compared to OPC mixes at all ages of test. The greatest reduction in compressive strength was at the age of (90) days for OPC mixes and the age of (28) days for SRPC mixes. After that, the concrete showed the lower reduction for all percentages of sulphate in fine aggregate. The results also indicated that the performance of HRM showed better results than the SF, and the replacement of 10% SF exhibits better results than 8% SF for both types of cement.

Key words: high performance concrete , internal sulphate attack , ordinary portland cement, sulphate resisting portland cement , high reactivity metakaolin , silica fume.

تأثير أنواع السمنت والمضافات على مقاومة الخرسانة عالية الأداء لهجوم الكبريتات الداخلية

أ. ندى مهدي الجيلاوي
قسم الهندسة المدنية
كلية الهندسة / جامعة بغداد

سماء علي حسوني
قسم الهندسة المدنية
كلية الهندسة / جامعة بغداد

الخلاصة

يتناول البحث دراسة تأثير أنواع السمنت وخاصة السمنت البورتلاندي الاعتيادي والسمنت البورتلاندي المقاوم وهي من الانواع الرئيسية المصنعة في العراق، بالأضافة الى دراسة تأثير المضافات المعدنية وهما الميتاكاؤولين عالي الفعالية ودقيق السليكا على مقاومة الخرسانة عالية الاداء لهجوم الكبريتات الداخلية. تم استعمال الميتاكاؤولين عالي الفعالية بنسبة (10) % ودقيق السليكا بنسبة (10,8)% كأستبدال جزئي من وزن السمنت لكلا النوعين. وللحصول على المستويات الملحية بنسبة (1 ,3,2)% ،تم أضافة جبس طبيعي كأستبدال جزئي من وزن الركام الناعم.

في إطار هذا البحث تم إجراء أربعة أنواع من الفحوص هي: مقاومة الأنضغاط ، مقاومة الأنثناء، سرعة الموجات فوق الصوتية، والكثافة في أعمار(7 ,28 ,90 ,120) يوم. وأشارت النتائج بأن خلطات السمنت البورتلاندي المقاوم أظهرت نقصان أقل في خصائص الخرسانة مقارنة بخلطات السمنت البورتلاندي الأعتيادي ولكافة أعمار الفحص. حيث كان أعظم نقصان بمقاومة الأنضغاط بعمر (90) يوم لخلطات السمنت البورتلاندي الأعتيادي وعمر (28) يوم لخلطات السمنت البورتلاندي المقاوم. ولكن بعد ذلك أظهرت الخرسانة نقصان أقل لكل نسب الكبريتات في الركام الناعم. كما بينت النتائج بأن الخلطات الحاوية على الميتاكاؤولين عالي الفعالية أظهرت نتائج أفضل من الخلطات الحاوية على دقيق السليكا، وإن أستبدال (10)% من دقيق السليكا كانت أفضل من (8)% من دقيق السليكا ولكلا النوعين من السمنت.

- **الكلمات الرئيسية** : خرسانة عالية الأداء، هجوم الكبريتات الداخلية، السمنت البورتلاندي الأعتيادي، السمنت البورتلاندي المقاوم، الميتاكاؤولين عالي الفعالية ، دقيق السليكا.

1. INTRODUCTION

High performance concrete (HPC) is concrete with properties or attributes which satisfy the performance criteria. The improved pore structure of high performance concrete is mainly achieved by the use of chemical and mineral admixtures. HRWRA allow substantial reduction in the mixing water. Mineral admixtures provide additional reduction to porosity and improve the interface with the aggregate and hence enhanced durability performance.

Most applications of high performance concrete to date have been in high rise building, long span bridges and some special structures. Generally, concretes with higher strength and attributes superior to conventional concretes are desirable in the construction industry and result economical advantages. Therefore high performance concrete can be considered a logical development of concretes in which the constituents are proportioned and selected to contribute efficiently to the various properties of concrete in fresh as well as in hardened states. **Prassad & Jha, 2005**.

Concrete durability is important, it may deteriorates due to several causes among them are: sulphate attack, corrosion of the reinforcement, alkali- aggregate reactivity, freezing and thawing. Sulphate attack which is the subject of this research and it seems to be the most common cause of concrete deterioration in Iraq. Sulphate attack can be external or internal. This work focuses on the durability of HPC to internal attack related to sulphate within the fine aggregate for both types of cement (OPC and SRPC). This type of attack occurs in different types of concrete structures which justifies the purpose of the use of OPC in the resistance of internal sulphate attack.

2. Internal Sulphate Attack

Sulphates are found in concrete mix from internal sources such as aggregates, cement, and water. These sulphate react with cement paste to form calcium sulphoaluminate. Calcium sulphate (gypsum) is considered more important for this type of attack, because of the addition of gypsum to the cement at the grinding stage to control the hydration speed and the setting of cement paste. Calcium sulphate is about 95% of the total sulphate in the Iraqi sand. **Al-Khalaf, 1983**.

Al-Rawi, 1981 stated that the presence of sulphates in sand or in any concrete constituent will cause reaction with some cement compounds, mainly C_3A. Such a reaction was associated with considerable increase in solid volume. This may be harmful to concrete structure because of the large stresses induced. This harmful effect was demonstrated by a larger reduction in compressive strength which was apparent at early ages (as early as 3 days). This reduction will increase with time if the sulphate content was high, but it will be minimized by autogenous healing if the sulphate content was low, as in this case it depleted within a short period after casting concrete.

Al-Rawi, 1985 pointed out that, a major cause of failure of concrete structures in the Middle East was the contamination of sand with sulphates in the form gypsum. The research pointed that the gypsum is normally added to cement to retard early hydration and prevent quick set. The total sulphate in concrete may, therefore, be high enough to cause internal sulphate attack. This may led to deterioration and possibly cracking and failure of concrete structures. To avoid the adverse effects of sulphates, several specifications put an upper limit on sulphate content in aggregates or on total sulphates in concrete. In some countries, however, it is difficult to find aggregates with the required low sulphates content. In other countries, the supply of sulphate free aggregate may not be indefinite.

This investigation shows that it is possible to reduce the gypsum added to cement and consequently raise the upper limit of sulphate content in aggregate. This will allow the use of huge reserves of sand, hitherto not allowed, with no durability risk or undue loss in concrete strength. The reduction in gypsum, however, will reduce the grinding efficiency. But this may be overcome by the addition of a small percentage of pozzolan or lime. Reduction of gypsum will also cause a slight decrease in setting time of cement, but pozzolan addition will restore the original setting time.

Al-Robayi, 2005 investigated the resistance of normal and high performance concrete exposed to external and internal sulphate attack. The research used high reactivity metakaolin as a partial replacement by weight of cement. The research reached the following conclusions:

- HPC showed better resistance to both external and internal sulphate attack than normal concrete.
- In internal sulphate attack, there was a reduction in strength at early ages (less than 28 days) for normal and HPC. The reduction was positively correlated to the SO_3 presented in fine aggregate. At later ages (more than 28 days) in HPC, the reduction in strength decreased while in normal concrete increased continuously. The pozzolanic action of HRM could be the cause of strength improvement.

Al-Janabi ,2007 investigated the behavior of high performance concrete exposed to internal sulphate attack. Two types of pozzolans were used HRM and FA with OPC and one type of pozzolan was used HRM with SRPC, as a partial replacement by weight of cement. Results indicated that the SRPC gave the same reduction in strength of OPC, and the reduction in strength was increased with the increase of (SO_3)% in fine aggregate, but they regained strength after the consumption of C_3A. The study also showed that HRM gave higher strength than FA in all ages of the tests because of the higher reactivity of metakaolin compared to fly ash.

3. EXPERIMENTAL WORK

3.1 Materials

3.1.1 Cement

Two types of Portland cement are used in this work. The first is ordinary Portland cement (OPC) and the second is sulphate resisting Portland cement (SRPC). Both are produced in Iraq commercially known as (**TASLUJA**) for OPC and (**Al-JESER**) for SRPC. The chemical analysis of the two types of cement are given in **Tables 1 and 2** respectively. The results conform to the Iraqi specification **IQS No.5/1984**.

3.1.2 Fine aggregate

Natural sand from **Al-Ekhadir** region is used for concrete mixes of this work. The grading and physical properties within the limit specified by Iraqi standard **IQS No.45/1984**, as shown in **Table 3**.

3.1.3 Coarse aggregate

Crushed gravel has been used as a coarse aggregate with a maximum size of (10 mm). It is obtained from Al-Nibaee region. The grading and physical properties within the limit specified by Iraqi standard **IQS No.45/1984**, as shown in **Table 4**.

3.1.4 Mixing water

Tap water is used in preparing all mixes.

3.1.5 High range water reducing admixture (HRWRA)

A high range water reducing admixture (superplasticizer) commercially known as **EUCOBET SUPER VZ** manufactured by Swiss Chemistry Company. This type of admixture conforms to the **ASTM C494 type G**.

3.1.6 Mineral admixtures

- **High reactivity metakaolin (HRM)**

Kaolin is a local Iraqi material. It has been grinded by air blast to obtain high fineness of kaolin, then burned in a controlled temperature furnace for one hour at 700C°. The chemical composition and physical properties of HRM are shown in **Table 5**. HRM used in this work conforms to the requirements of **ASTM C618-03**.

- **Silica fume (SF)**

The chemical composition and physical properties of SF are shown in **Table 6**. SF used in this work conforms to the requirements of **ASTM C1240-03.**

- **Strength activity index**

The strength activity index for HRM is performed according to **ASTM C311-02** and for SF according to **ASTM C1240-03. Table 7** shows the strength activity index for mortars.

3.1.7 Natural gypsum

The natural gypsum (**$CaSO_4.2H_2O$**) has been grinded by the hammer and passed through the same sieves of sand, and then added. The natural gypsum contains (43.73%) of SO_3, which quantity added to the sand is measured according to this equation:

$$W=(R-M\%)\times S/N \quad \textbf{(1)}$$

Where:
W: the required weight of natural gypsum (kg);
R: the percentage of SO_3 desired in sand;
S: the weight of sand in mix (kg);
M: the actual SO_3 in sand (0.32%);
N: the percentage of SO_3 in the used natural gypsum (43.73%).

The sand has been reduced relative to gypsum added in the mix.

3.2 Mix Design

Design of HPC mixes to achieve characteristic compressive strength of 50 MPa at 28 days, are made according to the American Method **ACI 211.4R-93** as shown in **Table 8**. The cement content is (513 kg/m³) and the W/C is 0.32. The slump required for all mixes is (100 mm). According to the mix design procedure, the mix proportion is (**1: 1.21: 2.03**). Then These mixes have been studied by adding different percentages of sulphate in fine aggregate of (1, 2 and 3)%, at the age of 7, 28, 90, and 120 days.

3.3 Preparation of Concrete Mixes

The mixing process is performed by hand mixing according to **ASTM C192-02.** Firstly, the sand is well mixed with the gypsum to attain a uniform mix. After that the cement is mixed with required quantity of HRM or SF powder then added to the mix. Finally, the gravel is added to the mix and the whole dry materials are well mixed for about 2 minutes. The required amount of tap water and HRWRA will be added gradually and the whole constituents are mixed for further 2 minutes to get a homogenous mix.

After mixing, the concrete mix is placed in the steel moulds after lubricating them with oil to avoid adhesion with concrete after hardening. The specimens are compacted using a vibrating table for sufficient period, in addition to the use of a metal rod to remove any entrapped air as much as possible. Then the concrete surface is leveled and smoothed by means of trowel, and the specimens are covered with nylon sheet for 24 hrs. After that the moulds are opened and cured until testing date.

3.4 Measurement of Workability of Concrete

A slump test is a suitable test to determine the workability for all types of concrete mixes; the test is performed according to **ASTM C143-00**.

Many attempts of slump test have been carried out to choose the appropriate dose of HRWRA to give equal workability of (100 mm) slump for all mixes, which is (1%) by weight of cement for mix containing (10%) HRM and (1.4 and 1.6)% by weight of cement for mixes containing (8 and 10)% SF respectively, as shown in **Table 8**.

3.5 Testing of Hardened Concrete

3.5.1 Compressive strength: The compressive strength test is performed according to the **British Standard B.S. 1881-part 116-1989** , on 100 mm cubes as shown in **Figs.1and 2**. (No. of specimens are 324)

3.5.2 Flexural strength: (100*100*400) mm concrete beams are used for testing as shown in **Fig.3**. The test is carried out according to **ASTM C293-02.** (No. of specimens are 192)

3.5.3 Ultrasonic pulse velocity (U.P.V.): Concrete cubes (100*100*100) mm are used in this test according to **ASTMC597-02,** using a device commercially known of (PUNDIT) as shown in **Fig.4**. (No. of specimens are 288)

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3.5.4 Density: (100*100*100) mm concrete cubes are used for density test. The density of concrete cubes is determined in dry air by measuring the dimensions and weight of specimens using the measurement feet (vernier) and the electrical scale. The test is performed according to **ASTM C642-97.** (No. of specimens are 288)

4. RESULTS

4.1 Compressive strength

The results indicate that the compressive strength decreases with the increase of sulphate content compared to the reference HPC (0.32%) SO_3 for OPC and SRPC mixes at all ages of test, as shown in **Figs. 5 to 11**.

The results of OPC mixes can be explained as follows:

For mix (MI10), which contains (10%) HRM with OPC, the greatest reduction is (8.20, 13.81, 17.54)% at (90) days and the reduction decreases after that age of (1, 2 and 3)% SO_3 in fine aggregate respectively. While for the mixes (SI8) and (SI10), containing (8%) SF and (10%) SF with OPC respectively, the greatest reduction is (13.66, 20.25, 23.87)% and (10.85, 16.67, 19.51)% at (90) days for (SI8) and (SI10), but the reduction decreases after that age of (1, 2 and 3)% SO_3 in fine aggregate respectively.

Concerning the results of SRPC mixes, they are shown as follows:

For mix (MV10), which contains (10%) HRM with SRPC, the greatest reduction is (7.51, 12.44, 15.03)% at (28) days, but the reduction decreases after that age at 90 and 120 days of (1, 2 and 3)% SO_3 in fine aggregate respectively.

Whereas for the mixes (SV8) and (SV10), containing (8%) SF and (10%) SF with SRPC respectively, the greatest reduction is (11.30, 16.34, 19.25)% and (9.33, 14.20, 18.01)% at (28) days for (SV8) and (SV10) respectively. The reduction decreases after that age at 90 and 120 days of (1, 2 and 3)% SO_3 in fine aggregate respectively.

4.2 Flexural strength

The results indicate that the flexural strength decreases with the increase of sulphate content compared to the reference HPC (0.32%) SO_3 for OPC and SRPC mixes at all ages of test as shown in **Figs. 12 to 18**.

The results of OPC mixes can be explained as follows:

For mix (MI10), the greatest reduction is (3.21, 6.54, 8.57)% at (28) days. After that age of the test, in (90, 120) days there is an improvement in the regain of the flexural strength of (1, 2 and 3)% SO_3 in fine aggregate respectively.

Whereas for the mixes (SI8) and (SI10), the greatest reduction is (7.44,9.88, 10.78)% and (5.72, 7.43, 9.50)% at (28) days for (SI8) and (SI10) respectively. The reduction decreases after that age at 90 and 120 days of (1, 2 and 3)% SO_3 in fine aggregate respectively.

Concerning the results of SRPC mixes, they are shown as follows:

For mix (MV10), the greatest reduction is (2.27, 4.77, 7.38)% at (28) days, but the reduction decreases after that age of (1, 2 and 3)% SO_3 in fine aggregate respectively.

While for the mixes (SV8) and (SV10), the greatest reduction is (5.86, 7.33, 9.16)% and (4.52, 6.26, 7.88)% at (28) days for (SV8) and (SV10) respectively. The reduction decreases after that age of (1, 2 and 3)% SO_3 in fine aggregate respectively.

4.3 Ultrasonic pulse velocity

The results demonstrate a slight decrease in pulse velocity with the increase of sulphate content compared to the reference HPC (0.32%) SO_3 for OPC and SRPC mixes at all ages of test. The ultrasonic pulse velocity results for mixes of OPC show the greatest reduction at (90) days and the reduction improve after that age at (120) days. Whereas the ultrasonic pulse velocity results for mixes of SRPC show a greatest reduction at (28) days and the reduction improve in (90 and 120) days. **Fig. 19** shows the effect of sulphate content in fine aggregate on UPV at 120 days for OPC and SRPC mixes.

4.4 Density

The results show that the mixes of OPC and SRPC exhibit an increase in density with the increase of sulphate content in fine aggregate at all ages of the test. Generally, the results show a slight increase in density relative to reference HPC (0.32%) SO_3.

Fig. 20 shows the effect of sulphate content in fine aggregate on density at 120 days for OPC and SRPC mixes.

5. DISCUSION

There are many variables that affect the strength development of different mixes. These variables are: type of portland cement (OPC and SRPC), the effect of pozzolanic materials (HRM and SF), and SO_3 in fine aggregate.

5.1 Effect of Cement Composition

The cement composition difference and relative amounts of hydration products between the OPC and SRPC are likely to be responsible for the differences in strength results.

The durability in a sulphate attack depends mainly on C_3A content of cement. Thus, it can be considered the chief contributor to volume change in sulphate attack. **Shanahan, and Zayed, 2007**.

As shown in **Tables 1 and 2**, the C_3A of OPC and SRPC are (10.04, 2.00)% respectively. The greater C_3A content will influence the relative amounts of ettringite and monosulphate (calcium aluminate hydrates) initially formed on hydration, and hence the propensity for expansion by ettringite formation upon sulphate. In addition, any unhydrated C_3A remaining may also result in ettringite formation and expansion. Because the high C_3A content, OPC contains more ettringite and monosulphate than the SRPC. **Naik et al., 2006**

The low C_3A leads to an increase in other compounds of cement (C_3S, C_2S). These two compounds are responsible for strength on the one hand and the high fineness of SRPC which increases the surface area of the (C_3S, C_2S) on the other hand. **Neville, 2002, Shanahan, and Zayed , 2007**

The result of the reaction of C_3A with gypsum depends on the C_3A content of cement by forming: **Al-Khalaf, 1983**

a. Calcium sulphoaluminate (ettringite), containing a high sulphate ($C_3A.3CaSO_4.32H_2O$), when the content of C_3A is high.

b. Calcium sulphoaluminate, containing a low sulphate ($C_3A.CaSO_4.12H_2O$), when the content of C_3A is low.

In spite of that the durability in sulphate attack is not dependent on the C_3A content of cement only. **Shanahan, and Zayed, 2007** have mentioned that the other chemical components in the cement that control permeability such as C_3S/C_2S ratio, help to control the rate and severity of sulphate attack. Increasing C_3S content or C_3S/C_2S ratio in cement generates more $Ca(OH)_2$ on hydration. This has possibly two effects. First, higher lime content in cement limits the solubility of aluminates and retards hydrated calcium aluminates. Second, lime availability increases formation of ettringite. While, cement containing lower amounts of C_3S show improvement of sulphate resistance.

Odler, and Jawed, 1991, have explained that C_4AF also produces ettringite, but at a reaction rate much slower than C_3A, and the resulting ettringite crystals contain iron along with aluminum in the lattice.

As noted in **Tables 1 and 2**, C_4AF of OPC and SRPC are (9.97, 14.47)% respectively. The effect of the greater relative amount of C_4AF in SRPC as compared to the OPC needs to be considered. Due to the greater quantity of C_4AF, ettringite formed in SRPC during sulphate attack is likely to be Fe-substituted. The iron-substituted ettringite is not expansive or less expansive. However, in order to achieve this, the Al_2O_3/Fe_2O_3 ratio in C_4AF is decreased by the addition of iron, which in turn raises the C_4AF content. **Naik et al., 2006, Tikalsky et al., 2002.**

Neville, 2002 has stated that the C_4AF reacts with gypsum to form calcium sulphoferrite as well as calcium sulphoaluminate, and its presence may accelerate the hydration of the silicate. In addition, this compound may form a protective film over C_3A; thus, the reaction of C_3A with sulphate ions will be reduced therefore, this compound is more resistance to sulphate attack than C_3A.

Tikalsky et al., 2002 have reported that the C_3A content is not the primary factor controlling sulphate attack, but C_4AF is the most beneficial in controlling sulphate attack.

5.2 Effect Type of Pozzolan

The HRM provides higher strength results compared to SF for both types of cement. This may be either due to the HRM consumes a significant proportion of the lime produced by the cement hydration to form more (C-S-H) gel than SF, or due to the lower surface area of HRM than SF. The possibly, high surface area of SF leads to more increase in the surface reaction between C_3A and sulphate ions.

In addition, the mix containing (10%) SF has higher strength results than (8%) SF for both types of cement. Generally, this can be explained by the following mechanisms. First, the replacement of a more portion of Portland cement with SF reduces the total amount tricalcium aluminate hydrate. Thus, the quantity of expansive ettringite will be less in the cement paste of concrete. The second mechanism is through the pozzolanic reaction between the SF and $Ca(OH)_2$ released during the hydration of cement, which consumes part of the $Ca(OH)_2$. Furthermore, the formation of secondary (C-S-H) by the pozzolanic reaction produces a film or a coating on the alumina-rich and other reactive phases thereby hindering the formation of ettringite**., Zelic et al., 2007.**

The different components of the two pozzolanic materials can be the direct reason for the difference in strength activity. The major components responsible for the pozzolanic reaction of HRM are silica (SiO_2) and alumina (Al_2O_3). **Headwater resources, 2005**, as the pozzolanic reaction of SF depends mainly on amorphous SiO_2. **ACI 234R-96**

From the chemical analysis of pozzolanic materials, the sum percentage of Al_2O_3 and SiO_2 for HRM is 93.12%, more than the percentage of SiO_2 in SF which is 88.30%. The pozzolanic reaction take place between the components mentioned above in pozzolanic material (HRM and SF) and calcium hydroxide formed during the hydration process. This leads to the more cementitious compound produced from the reaction of HRM than SF and leads to densification of the concrete matrix resulting increase in strength for the same type of cement.

The C_3A content of cement should be regarded when discussing the effect of pozzolanic materials on the type of cement as **Lea, 1970** has reported that the pozzolanic cements prove resistant in the test if made of Portland cement of low C_3A content but not exceptionally high content of reactive silica.

Neville, 2002 has indicated that the replacement of low C_3A content cement (i.e. sulphate resisting cement) with pozzolan, provide a better performance in sulphate resistance.

Kalousek et al., 1972 have reported that partial pozzolana replacement of sulphate resisting cement is very effective in making the concrete resistant to sulphate attack but that is related to SiO_2: R_2O_3 ratio in the pozzolana.

According to **Lea, 1970** the pozzolan containing high SiO_2 nearly (90%) and low R_2O_3 (Al_2O_3 + Fe_2O_3) can increase the sulphate resistance of SRPC.

As reported by **Cao, et al., 1997** that the sulphate resistance of pozzolanic materials is dependent on its composition.

In spite of that the SF has a high SiO_2 and low Al_2O_3, but it does not prove an effective subsistent for enhancing the sulphate resistance than HRM for the same type of cement.

Concerning the results of density and ultrasonic pulse velocity, SF has higher results than HRM for both types of cement due to the higher fineness of SF than HRM that leads to filling the pores and to cut the continuity of capillary pores.

The density results increase with the increase of (SO_3%) in fine aggregate. This can be attributed to the presence of ettringite which leads to a denser structure as a result of precipitation of ettringite within voids and microspores. **Zelic et al., 2007.**

5.3 Effect of sulphate content in fine aggregate

Gypsum ($CaSO_4.2H_2O$) is the main source of sulphate in cement, sand, and coarse aggregate. It has significant effect on the concrete strength.

The increase of (SO_3%) in fine aggregate causes an increase in the reduction of strength results and the reduction decreases at later ages. Generally, this can be attributed to the pozzolanic reaction which increases the amount of hydration products and reduces the tricalcium aluminates in cement. As reported by **Al-Rawi, 1981** that the autogenuous healing may take place in internal sulphates at later ages when pozzolan replaces Portland cement and result in an improving in compressive strength. In addition to the pozzolanic reactions, they also have possibly another reason either due to the consumption of calcium sulphate while the C_3A is still hydration. Thus, the ettringite decomposes into the more stable compound, monosulphate, or due to the consumption of C_3A while calcium sulphate is still in free state (with no reaction that causes expansion and deterioration in HPC. **Al-Khalaf, 1983, Minard et al., 2007**

But the reaction will be slow over time due to the consumption of salts. Thus, the effect of salts on the strength of concrete is more clearly in the early ages than the later ages for this type of attack. **Al-Nakshabandy, 2005**.

The purpose of adding (SO_3%) to fine aggregate is because of its high surface area compared to coarse aggregate. This leads to more increase in the surface reaction between C_3A and sulphate ions. As **Al-Salihi, 1994** has stated that SO_3 from sand has more effect than SO_3 from coarse aggregate. The difference between the effects is quite large as in the case of cement and sand.

While the work done by **Ali**, **1981** has shown that SO_3 from cement has more destructive effect on concrete strength compared to the effect of the same amount of SO_3 from sand. This is attributed to the finer cement grains compared to sand grains. Finer grains mean higher surface area and higher rate of solubility and reaction of SO_3 in the form of gypsum in cement or sand.

The adopted percentages of (SO_3%) in the present work are (1, 2 and 3)%, all of the percentages have been compared to the reference of (0.32%) SO_3, which is less than the allowable (SO_3%) in Iraqi specification (**IQS**).

In addition, the internal resistance of concrete depends on the total SO_3 content and must not exceed certain upper limit. (SO_3Tot.) of HPC is calculated according to (IQS No.45/1984). IQS indicate that the maximum content of SO_3 in concrete mixes is (4%) by weight of cement, when cement content (≥ 300 kg/m³) and SO_3 in fine aggregate is (0.5%).

$$\mathbf{SO_{3Tot.}} = A + (Y/X)\times B + (Z/X)\times C + (L/X)\times D \qquad \mathbf{(2)}$$

Where:
A: SO_3 content in cement.
B: SO_3 content in fine aggregate.
C: SO_3 content in coarse aggregate.
D: SO_3 content in pozzolan.
X: weight of cement.
Y: weight of fine aggregate.
Z: weight of coarse aggregate.
L: weight of pozzolan.

6. CONCLUSIONS

1. High reactivity metakaolin shows higher strength than the silica fume in all ages of the test for both types of cement (OPC and SRPC).

2. The employment 10% of SF as a partial replacement by weight of cement exhibits higher strengths at all ages of test than 8% of SF. However, the 10% of HRM indicates superior performance in the resistance of HPC to internal sulphate attack than (8 and 10)% SF for both types of cement.

3. In ultrasonic pulse velocity and density tests, the maximum results in ultrasonic pulse velocity and density are noted with 10% SF followed by 8% SF and 10% HRM for both types of cement. However, there is not much of a difference between the performance of 8% SF and 10% HRM.

4. Sulphate resisting portland cement shows the lower reduction in strength than ordinary portland cement for mixes containing of 10% HRM and SF at (8 and 10)%.

5. The reduction in strength tests increases with the increase of (SO_3%) in fine aggregate at all ages of test, but the reduction decreases at later ages because the pozzolanic reactions can be the cause of strength improvement for OPC and SRPC mixes. There is an improvement in the regain of strength after age of (28 and 90) days for SRPC and OPC mixes respectively.

6. The resistance of HPC to internal sulphate attack depends mainly on the chemical composition of cement.

7. The alumina in pozzolanic material has not its effect on the resistance of HPC to (SO_3%) in fine aggregate. Thus, it cannot be considered as additional source to react with SO_3. Whereas HRM has higher alumina if compared with SF (Al_2O_3 for HRM =34.65%, and for SF= 0.35%), but it gives higher resistance of HPC to internal sulphate attack than SF for both types of cement.

8. Under the sulphate within the fine aggregate up to about 3%, HPC mixes of OPC and SRPC does not suffer significantly deterioration in all its properties. (SO_3Tot.) generally is not much higher than the allowable limit of (SO_3) in concrete. The (SO_3Tot.) for high sulphate content of (3%) SO_3 in fine aggregate is (5.64, 5.69, 5.71)% for mixes containing 10% HRM, 8% SF and 10% SF with OPC, and (5.46, 5.51, 5.53)% for mixes containing 10% HRM, 8% SF and 10% SF with SRPC respectively.

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NOMENCLATURE

Notation	Description
HPC	High Performance Concrete
HRM	High Reactivity Metakaolin
SF	Silica Fume
HRWRA	High Range Water Reducing Admixtures
OPC	Ordinary Portland Cement
SRPC	Sulphate Resisting Portland Cement
U.P.V.	Ultrasonic Pulse Velocity
SO_3Tot.	Total Sulphate Content in Concrete
MI10	Mix of OPC and 10% Metakaolin
SI8	Mix of OPC and 8% Silica fume
SI10	Mix of OPC and 10% Silica fume
MV10	Mix of SRPC and 10% Metakaolin
SV8	Mix of SRPC and 8% Silica fume
SV10	Mix of SRPC and 10% Silica fume

Table 1. Chemical composition and main compounds of ordinary portland cement.

Oxide composition	**Abbreviation**	**by weight%**	**Limits of Iraqi spec. No.5/1984**
Lime	CaO	61.30	-
Silica	$SiO2$	20.54	-
Alumina	Al_2O_3	5.88	-
Iron oxide	Fe_2O_3	3.28	-
Sulphate	SO_3	1.87	≤ 2.8%
Magnesia	MgO	1.93	≤ 5%
Loss on Ignition	L.O.I.	2.45	≤ 4%

Lime saturation Factor	L.S.F.	0.90	0.66-1.02
Insoluble residue	I.R.	0.15	≤ 1.5%
Main compounds (Bogues eq.)		**by weight of cement%**	
Tricalcium silicate (C_3S)		43.85	
Dicalcium silicate (C_2S)		25.88	
Tricalcium aluminate (C_3A)		10.04	
Tetracalcium aluminoferrite (C_4AF)		9.97	

Table 2. Chemical composition and main compounds of sulphate resisting portland cement.

Oxide composition	**Abbreviation**	**by weight%**	**Limits of Iraqi spec. No.5/1984**
Lime	CaO	60.63	-
Silica	SiO_2	21.63	-
Alumina	Al_2O_3	3.79	-
Iron oxide	Fe_2O_3	4.76	-
Sulphate	SO_3	1.69	≤ 2.5%
Magnesia	MgO	2.72	≤ 5%
Loss on Ignition	L.O.I.	1.94	≤ 4%
Lime saturation Factor	L.S.F.	0.87	0.66-1.02
Insoluble residue	I.R.	0.77	≤ 1.5%
Main compounds (Bogues eq.)		**% by weight of cement**	
Tricalcium silicate (C_3S)		45.28	
Dicalcium silicate (C_2S)		27.93	
Tricalcium aluminate (C_3A)		2.00	
Tetracalcium aluminoferrite (C_4AF)		14.47	

Table 3. Grading and Physical Properties of Fine aggregate

Sieve size (mm)	Passing %	Limits of Iraqi spec. No.45/1984/Zone 2
10	100	100
4.75	100	90-100
2.36	85	75-100
1.18	65	55-90
0.6	50	35-59
0.3	15	8-30
0.15	4	0-10
Physical properties		**Limits of Iraqi spec. No.45/1984**
Fineness modulus: 2.81		-
Specific gravity: 2.5		-
Absorption: 1.6%		-
SO_3: 0.32 %		≤ 0.5%
Dry rodded density: 1780 kg/m³		-

Table 4. Grading and Physical Properties of Coarse aggregate

Sieve size (mm)	Passing%	Limits of Iraqi spec. No.45/1984
37.5	100	100
20	100	95-100
10	48	30-60
4.75	3	0-10
Physical properties		**Limits of Iraqi spec. No.45/1984**
Specific gravity: 2.65		-
Absorption: 0.5%		-
SO_3: 0.06%		≤ 0.1%
Dry rodded density: 1600 kg/m³		-

Table 5. Chemical analysis and physical properties of HRM.

Oxide Composition	Oxide content %	Pozzolan class N ASTM C618-03
SiO_2	58.47	Σ = 94.52% Min. 70%
Al_2O_3	34.65	
Fe_2O_3	1.40	
MgO	0.21	
CaO	0.38	
SO_3	0.21	Max. 4%
Na_2O	0.66	
L.O.I	2.47	Max. 10%
Physical properties		
Specific gravity	2.32	
Fineness (Blaine)	865 m²/kg	
Physical form	powder	
Color	off-white	

Table 6. Chemical analysis and physical properties of SF.

Oxide Composition	Oxide content %	ASTM C1240-03
SiO_2	88.30	Min. 85%
Al_2O_3	0.35	
Fe_2O_3	1.17	
MgO	2.40	
CaO	1.25	
SO_3	0.91	
Na2O	1.37	
L.O.I	3.78	Max. 6%
Physical properties		
Specific gravity	2.016	
Fineness (Blaine)	16000 m²/kg	
Physical form	powder	
Color	grey	

Table 7. Strength activity index for tested mortars.

Mix symbol	Cementitious material content		Fine agg. kg/m³	SO_3 % by wt. of Fine agg.	Coarse agg. kg/m³	Water kg/m³	HRWRA by wt. of cement %	W/Cm	Compressive strength (MPa)	
	Cement kg/m³	Pozzolan kg/m³							7d.	28d.
MI10	461.70	51.30	622	0.32	1040	164	1	0.32	47.54	61.46
SI8	471.96	41.04	622	0.32	1040	164	1.4	0.32	44.36	56
SI10	461.70	51.30	622	0.32	1040	164	1.6	0.32	45	58.60
MV10	461.70	51.30	622	0.32	1040	164	1	0.32	50.36	67.50
SV8	471.96	41.04	622	0.32	1040	164	1.4	0.32	45.43	57.50
SV10	461.70	51.30	622	0.32	1040	164	1.6	0.32	46.53	60.40

Table 8. The details of HPC mixes used throughout this investigation prior addition of sulphate.

Index	Strength activity index%
R	-
HRM	140
SF	108

Figure 1: Specimens of cubes for compressive strength test.

Figure 2: Compressive strength test devise.

Figure 3: Specimens of prism for flexural strength test.

Figure 4: Ultrasonic pulse velocity test.

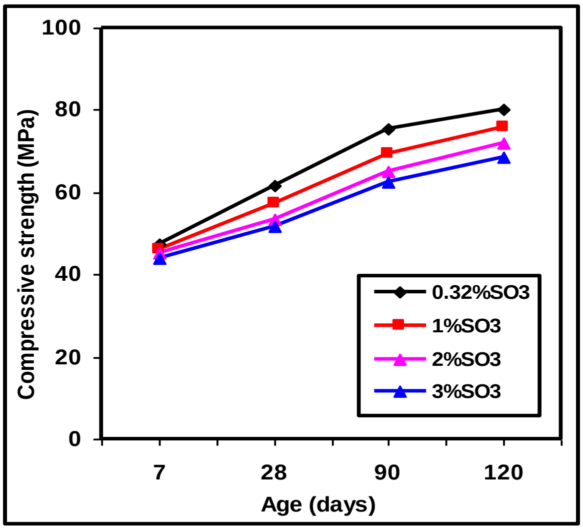

Figure 5. Effect of age on compressive strength with different sulphate content for mix (MI10).

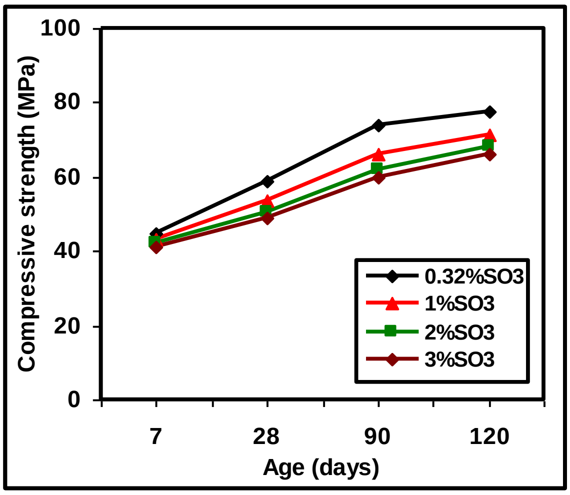

Figure 7. Effect of age on compressive strength with different sulphate content for mix (SI10).

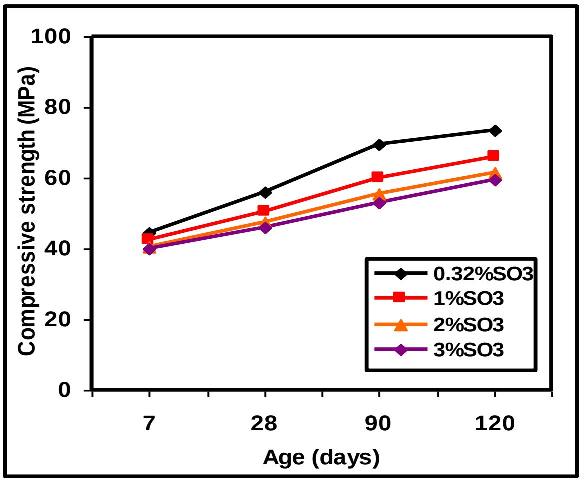

Figure 6. Effect of age on compressive strength with different sulphate content for mix(SI8).

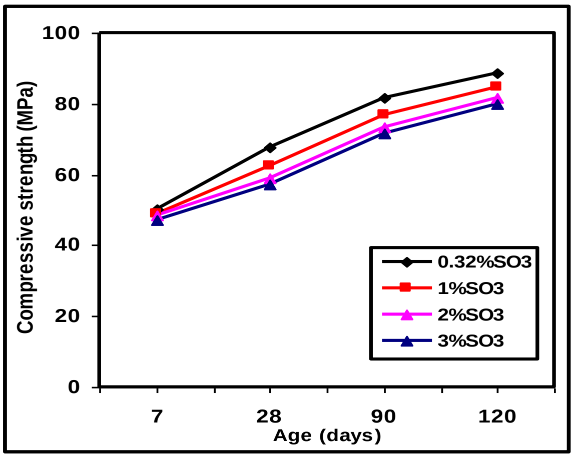

Figure 8. Effect of age on compressive strength with different sulphate content for mix (MV10).

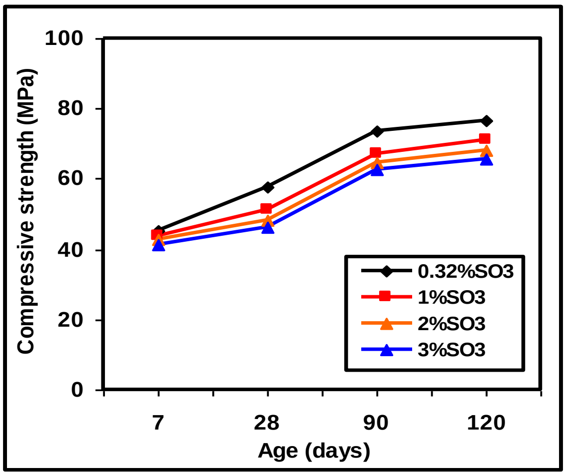

Figure 9. Effect of age on compressive strength with different sulphate content for mix (SV8).

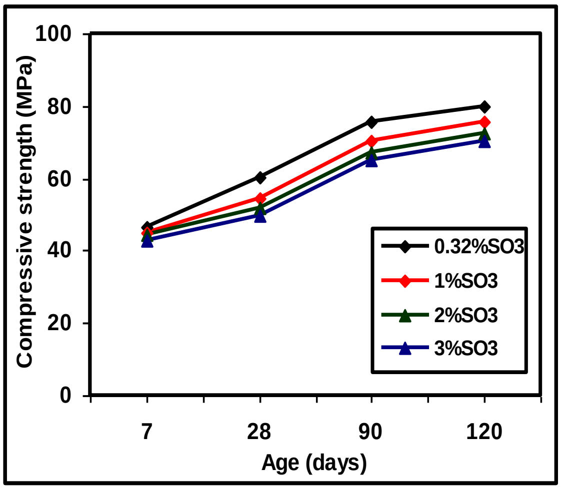

Figure 10. Effect of age on compressive strength with different sulphate content for mix (SV10).

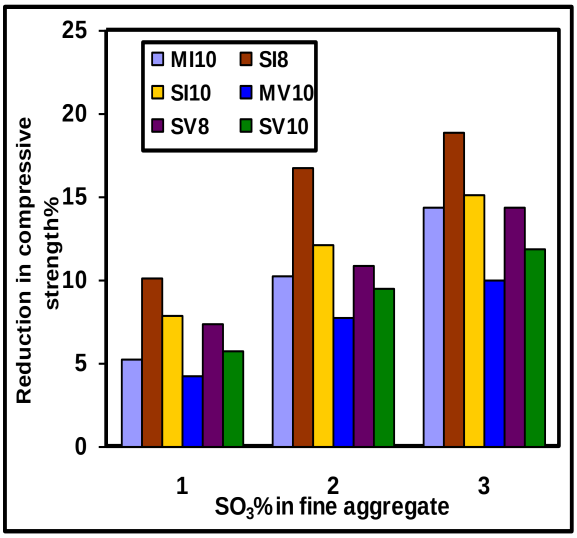

Figure 11. Effect of sulphate content on reduction in comp. strength at 120 days for OPC and SRPC mixes.

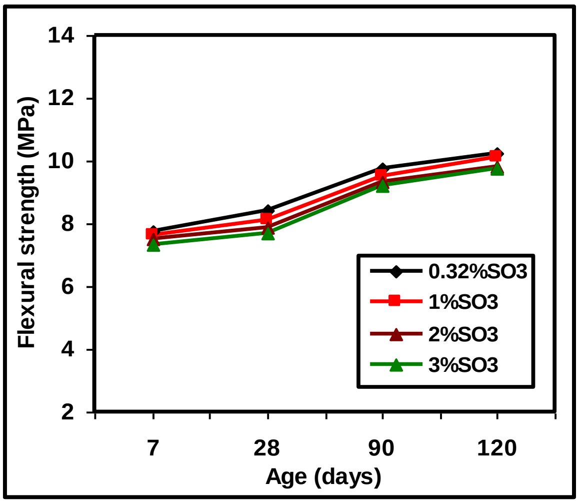

Figure 12. Effect of age on flexural strength with different sulphate content for mix (MI10).

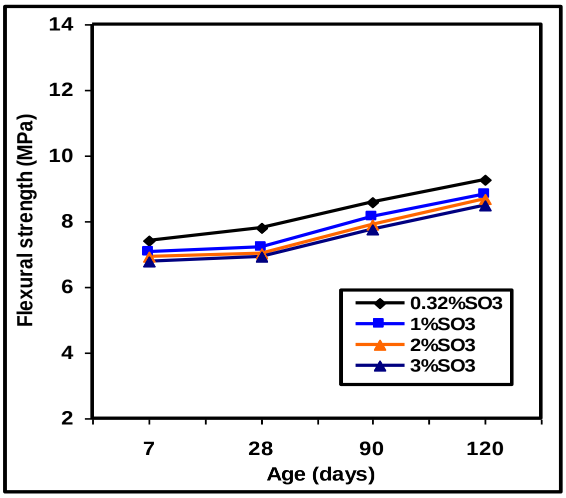

Figure 13. Effect of age on flexural strength with different sulphate content for mix (SI8).

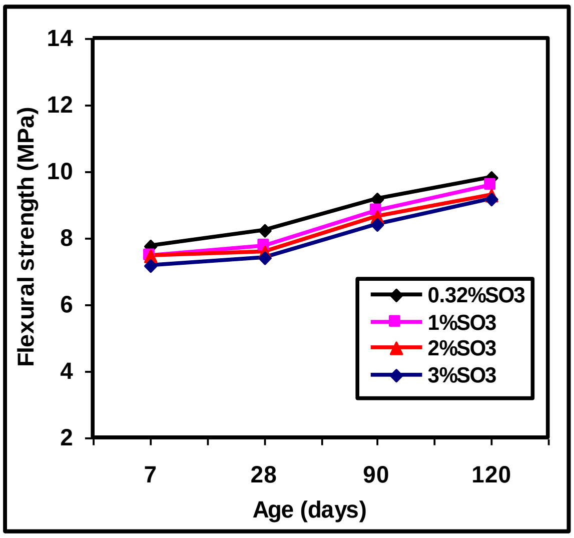

Figure 14. Effect of age on flexural strength with different sulphate content for mix (SI10).

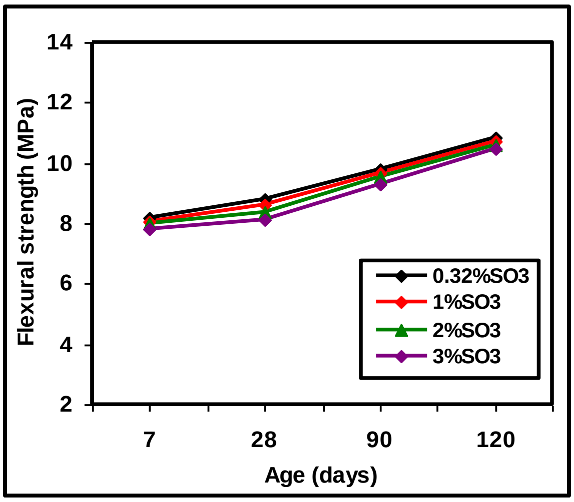

Figure15. Effect of age on flexural strength with different sulphate content for mix (MV10).

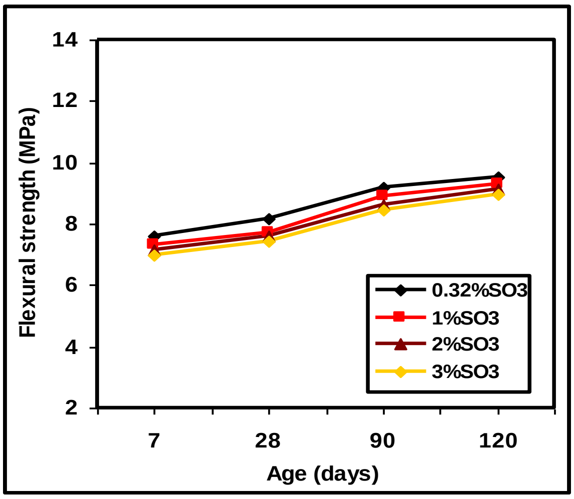

Figure 16. Effect of age on flexural strength with different sulphate content for mix (SV8).

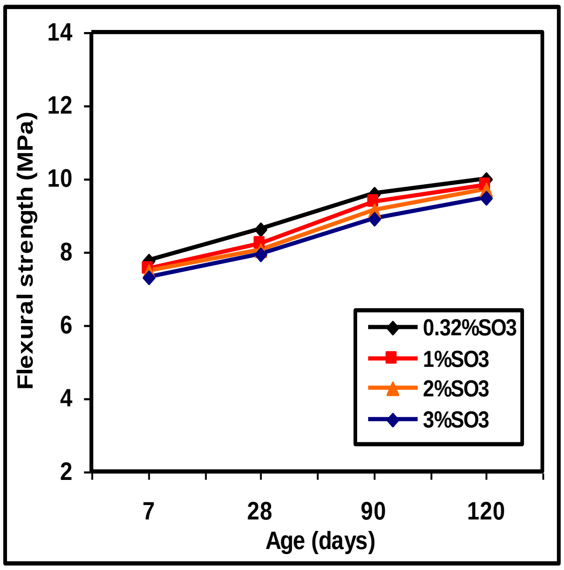

Figure 17. Effect of age on flexural strength with different sulphate content for mix (SV10).

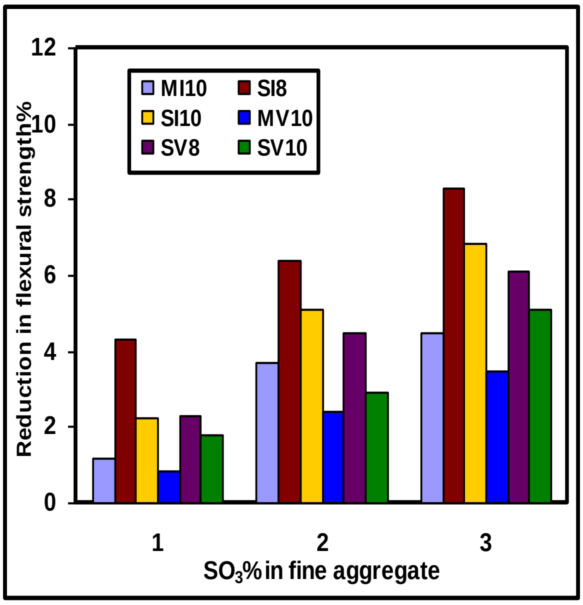

Figure 18. Effect of sulphate content on reduction in flexural strength at 120 days for OPC and SRPC mixes.

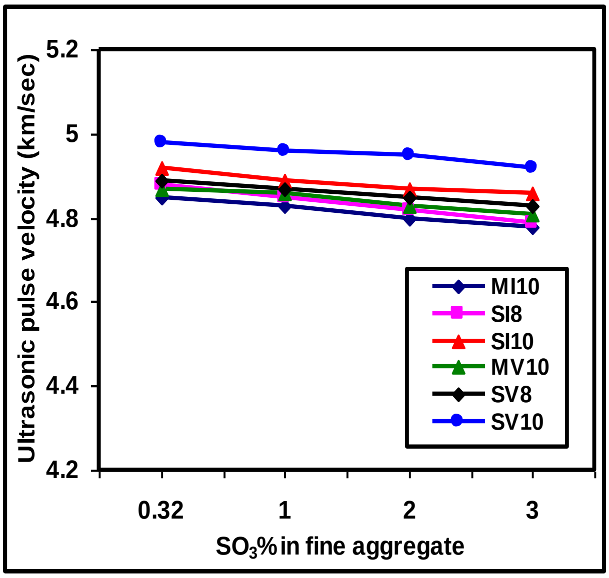

Figure 19. Effect of sulphate content in fine agg. on UPV at 120 days for OPC and SRPC mixes.

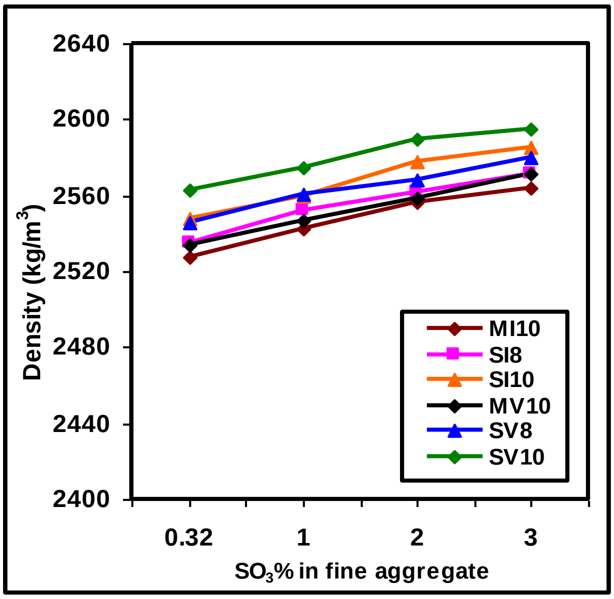

Figure 20. Effect of sulphate content in fine agg. on density at 120 days for OPC and SRPC mixes.