

# ASSESSMENT OF SETTING TIMES AND COMPRESSIVE STRENGTH BY USING METAL IONS WASTEWATER OF PAINT INDUSTRY

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## ABSTRACT:

The feasibility of treated industrial wastewater as mixing water and effect of its constituents on cement mortar was experimentally evaluated. The cement mortar specimens were casted by using deionised water, treated paint industry wastewater, and presence of zinc, lead, cooper, nickel, chromium. The characteristics of the deionised water tap water and treated effluent of paint industry used in this experimental study. The impurities present in PITE are different concentrations and each one react differently with the constituents of the cement. Not all impurities will have adverse effects on the properties of the cement. Some react in such a way that the net result may be harmless or may even improve the concrete properties. The setting times are found to significantly retard with PITE, as metal concentration increased setting times are accelerated. So, there are no adverse effects on resulting compressive strength, when cement mortar specimens are cured in PITE. Therefore, the present experimental study confirms the feasibility of using PITE in cement mortar and metal ions also are interacted friendly with cement matrix.

## 1.INTRODUCTION:

Water is life that is why it is called “Jeevan” in Sanskrit. Water sustains all biological life, ecosystems and human activities. It makes up 65% of our bodies and covers 70% of the area of our planet “earth”. It is essential for all food production from fields or healthy. Although water seems to be a common commodity, it is actually scarce on the earth and it has no substitute. Most of the world’s water is saline and is contained in the oceans. Only about 2% of it is fresh and of its 97% is tied up in the polar caps in the form of permanent snow and in deep depths below ground. The remainder (i.e. 3%) is renewable through the cycle of precipitation and evaporation from the oceans and the surface sources on earth and even this is often not available where or when required.

As against the problem of increased demand for water, the availability of usable quality of water is again getting diminished every year all over the world and particularly in the developing countries, on account of the discharge of different types of industries discharging of treated and untreated wastewater into the environment, which are polluting the surface and subsurface sources of water. Particularly Industrial activities, which are growing rapidly, are also leading to generation of large quantities of wastewater and are also adversely polluting various segments of the environment.

As per Central Statistical Organization (CSO), there are about 32 lakhs industries in India in the year 1998-99, out of which 1,35,551 are registered manufacturing industries. Remaining industries like taxi stands, restaurants, hotels, tailoring etc. As per the latest inventory of Central Pollution Control Board (CPCB), there are about 8432 large and medium polluting industries in India. The number of small scale industries, which are established in unplanned areas and in an unsystematic manner.

Such industries are located even in residential areas. A large number of them are not even registered.

As per Central Water Commission (CWC, 2005), the total wastewater generated from all major industrial sources is about 82,446 million liters per day. Water demand for industries in the year 2000 was 30 billion cubic meters, but water demand for industries is projected to be as high as 120 billion cubic meters in the year 2025. As against the problem of increased demand for water, the availability of limited usable quality of water is again getting diminished every year all over the world and particularly in the developing countries. Hence, the demand for the use of treated wastewater from industries and domestic is bound to increase in the future. Efforts towards wastewater reuse have lately gained world wide consideration and attention in both the agricultural and industrial fields.

All consequences are certainly being emphasized that Recycling and Reuse of wastewater will have to be practiced extensively for the sustainable development. In this connection, the present

experimental studies are intended to use of treated industrial wastewater as mixing water in cement works.

Present study conducting experiments on cement cubes making with **Paint Industry Treated Effluent (PITE)** for finding Setting times and Compressive strength at different ageing periods (3 day, 7 day and 28 day).

## 2.LITERATURE REVIEW:

### 2.1 GENERAL

This chapter presents a review of literature concerning the investigation and analysis of cement and its constituents, their phase relationship, structure of hydrated cement paste, physical properties of Portland cement and influence of wastewater and its constituents on cement.

### 2.2 CEMENT AND ITS CONSTITUENTS

Portland cement is manufactured by igniting a mixture of calcareous and argillaceous materials, at a very high temperature. These two types of materials occur in nature with varying quantities of chemical constituents. Calcium carbonate predominates in calcareous materials and clay constituents in argillaceous materials. The Portland cement is expected to contain some of the constituents which include calcium oxide, silicon dioxide, aluminum oxide, ferric oxide, magnesium oxide, sulphuric anhydride, gypsum, alkalis, some constituents lost on ignition and insoluble residue.

Calcium oxide or oxide of lime (quick lime) is an essential ingredient of all the cements. It is mainly derived from thermal decomposition of calcium carbonate. It is a white, amorphous and friable material with a specific gravity ranging from 3.08 to 3.30. Its chemical activity depends on the temperature at which it is oxidized by thermal action. It slakes vigorously, when water is added. High quantity of CaO makes the cement unsound and causes expansion and thereby leads to disintegration. Low content of CaO lowers the compressive strength of cement and simultaneously makes the cement to set quickly. Hence the optimum level of CaO is very much required.

Silicon dioxide or Silica is the most important and abundantly available mineral in nature. It is abundantly present in clay, shale, quartz and sand stone. The specific gravity of SiO<sub>2</sub> is 2.65. It is completely insoluble in water and is not attacked by acids except by hydrofluoric acid. When heated, silica undergoes a series of changes in the crystalline structure, which is accompanied by appreciable volume changes. When heated further to a high temperature, silica becomes chemically reactive. The best example for this is strong alkalis, i.e. potassium or sodium hydroxide, which react with silica at high temperature to give a water soluble product. It imparts strength to cement by forming dicalcium and tricalcium silicates. Even though excess silica imparts strength to cement, it prolongs the setting time. It reacts with lime and water to form limesilica gel.

Pure aluminum oxide commonly known as alumina is an abundantly available mineral in nature in the forms of corundum (Al<sub>2</sub>O<sub>3</sub>), clay and bauxite. Pure clay has the chemical formula Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.2H<sub>2</sub>O. But clay is not suitable for the manufacture of pure alumina as it contains SiO<sub>2</sub> in its composition. Pure bauxite is a common raw material for manufacturing alumina. It is quite useful in cement industry as it reacts with lime and water to form gel like products.

Ferric oxide is also an important constituent in cement though it is required in a small quantity for cement production. It is an important constituent of iron ores. It behaves as a fluxing agent in the process of clinker burning.

Magnesium oxide or Magnesia is present in small quantities in Portland cement. It is derived from magnesium carbonate present in the original limestone in the form of dolomite (CaCO<sub>3</sub>MgCO<sub>3</sub>). It has distinct hydraulic properties. It is the main agent, which imparts greenish gray colour to cement.

Sulphuric anhydride is also an important constituent of cement. It is mainly derived from CaSO<sub>4</sub>. It imparts soundness to cement. Higher quantity of SO<sub>3</sub> makes the cement unsound during hardening of cement in the presence of excess moisture.

Gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) has great significance in regulating the setting time of cement. A limited quantity of gypsum present in cement has greater importance, as it is capable of preventing flash setting of cement. A higher quantity of gypsum will cause expansion during subsequent hardening in the presence of moisture, ultimately leading to unsoundness of cement.

The alkali compounds i.e. potassium oxide and sodium oxide are invariably associated with raw materials of cement described above. They have been found to react with some aggregates, the products of the reaction causing disintegration of the concrete, and have also been observed to affect the rate of the gain of strength of cement.

The components lost on ignition are only a minor fraction. Ignition loss is defined as the percentage of weight loss suffered by sample of cement after heating to 1000<sup>o</sup>C. This ignition loss in

cement is due to the expulsion of carbon dioxide and water from free lime and free magnesia from cement at higher temperatures.

A certain degree of moisture absorption cannot be avoided during the manufacturing process of cement. Clinkers absorb moisture from the atmosphere during storage. Finally, the gypsum added to cement during grinding of clinkers contains over 18% of chemically bound water, which is additional to the moisture associated with gypsum in the dry condition.

The insoluble residue representing that fraction of cement, which is insoluble in hydrochloric acid, is a measure of adulteration of cement, largely arising from impurities in gypsum. This quantity can be determined only after reaction of all minerals, present in clinker, with hydrochloric acid and become soluble. BS 12:1978 limits this insoluble residue to 1.5% of the weight of cement. Its content shall be less than 2% as per BIS recommendations. The ASTM specification gives the upper limits as 2.5% (ASTMC-150-78a, 1955).

A general idea of composition of cement can be obtained from Table 2.1, which gives the composition of Portland cement.

**Table 2.1: Chemical Composition of Typical Portland Cement**

Sl. No.	Constituents	Normal range (%)
1	Lime, CaO	60-67
2	Silica, SiO <sub>2</sub>	17-25
3	Alumina, Al <sub>2</sub> O <sub>3</sub>	3-8
4	Iron oxide, Fe <sub>2</sub> O <sub>3</sub>	0.5-6.0
5	Magnesia, MgO	0.1-4.0
6	Sulphur trioxide, SO <sub>3</sub>	1-3
7	Alkalis, K <sub>2</sub> O and Na <sub>2</sub> O	0.2-1.3
8	Ignition loss	<5
9	Insoluble residue	<2

Most of the standard specifications specified the percentage of constituents with the following ratios.

**Silica Ratio:** Silica ratio is the ratio of percentage by weight of silica to that of the sum of the alumina and ferric oxide.

Mathematically it is expressed as

$$\text{Silica ratio} = \frac{\text{SiO}_2}{(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)}$$

The significance of this ratio is that it shows whether the cement is rich or poor in silica in Portland cement. An average value of this ratio should be between 1.7 to 3.5. High silica ratio means a value from 2.5 to 3.5 and a low silica ratio ranges between 1.7 to 2.0 approximately.

**Alumina Ratio:** Alumina ratio is the ratio of alumina to ferric oxide. Mathematically it is expressed as

$$\text{Alumina ratio} = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$$

With a high value of this ratio we have an alumina rich and ferric oxide free Portland cement. On the other hand for iron ore, which contains no alumina, this ratio is practically zero.

**Lime Saturation Factor (L.S.F):** L.S.F. has very high significance in the technology of Portland cement. It is the ratio of the quantity of lime present by weight to that required by the acidic oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) to form the main mineralogical clinker compounds.

$$\text{L.S.F.} = \frac{\text{CaO} - 0.7(\text{SO}_3)}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3}$$

The cause for the deduction of SO<sub>3</sub> from the total lime percentage is due to the addition of gypsum during grinding of clinker, which is added to regulate the setting process of cement. The CaO derived from this addition of gypsum enters into the total lime percentage when determined analytically during chemical analysis of cement. The extra CaO induced into cement by addition of gypsum must therefore be subtracted from the total lime content. The actual extra CaO content is obtained by multiplying the quantity of SO<sub>3</sub> obtained by the chemical analysis of cement by a factor 0.70.

BIS 12:1978 specifies that the Portland cement shall have the L.S.F. corresponding to a high proportion of dicalcium silicate and also a value corresponding to a high proportion of tricalcium silicate. Bureau of Indian Standards Specifications IS 8112:1989 specifies the chemical composition of ordinary Portland cement of 43-grade variety and the same has been presented in the Table 2.2.

Tricalcium aluminate content  $C_3A$  is calculated by the formula

$$C_3A = 2.65 Al_2O_3 - 1.69 Fe_2O_3$$

Where each symbol refers to the percent by mass of total oxide present in cement, excluding any contained in insoluble residue referred at SL. No. (3).

### 2.3 CEMENT CONSTITUENTS AND THEIR PHASE RELATIONSHIP

The discussions held above refer only to the raw materials and their constituents present in cement. If these raw materials are made to burn in a kiln at fixed proportions to temperature up to  $1450^{\circ}C$ , clinkers are formed in the manufacturing process. In this burning process raw materials undergo chemical changes and form the main constituents of cement. The mineralogical constituents of Portland cement, known as Bogue compounds are formed during the burning of raw materials at high temperatures for a fixed period are shown in Table 2.3.

**Table 2.2: BIS Specification for Chemical Analysis of 43-Grade Portland Cement as per IS 8112:1989**

Sl. No.	Characteristics	Requirements
1	Ratio of percentage of lime to the percentage of silica, alumina and iron oxide when calculated by the formula $L.S.F. = \frac{CaO - 0.7(SO_3)}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3}$	Not less than 0.66 and not more than 1.02.
2	Ratio of percentage of alumina to that of iron oxide	Not less than 0.66
3	Insoluble residue percent by mass	Not more than 2
4	Magnesia percent by mass	Not more than 6
5	Total sulphur content calculated as sulphuric anhydride ( $SO_3$ ) percent by mass	Not more than 2.5 and 3.0 when tricalcium aluminate percent by mass is 5 or less and greater than 5 respectively
6	Total loss on ignition	Not more than 5.0%
7	Chlorides	Not more than 0.05%

**Table 2.3: Hydrated Products of Cement**

Sl. No.	Name of the compounds	Formula	Abbreviation
1	Tricalcium silicate	$(3CaO \cdot SiO_2)$	$C_3S$
2	Dicalcium silicate	$(2CaO \cdot SiO_2)$	$C_2S$
3	Tricalcium aluminate	$(3CaO \cdot Al_2O_3)$	$C_3A$
4	Tetracalcium alumino ferrite	$(4CaO \cdot Al_2O_3 \cdot Fe_2O_3)$	$C_4AF$

The mineralogical composition of Portland cement can be determined approximately from chemical analysis data of cement (Bogue, 1955).

Bogue (1955), in his book 'The Chemistry of Portland Cement', derived special conversion formulae for determining analytically the percentages of the mineral components present in the Portland cement and they are given below.

- $3CaO \cdot SiO_2 = 4.07 CaO - 7.60 SiO_2 - 6.72 Al_2O_3 - 1.43 Fe_2O_3 - 2.85 SO_3$
- $2CaO \cdot SiO_2 = 2.87 SiO_2 - 0.754 (3CaO \cdot SiO_2)$
- $3CaO \cdot Al_2O_3 = 2.65 Al_2O_3 - 1.69 Fe_2O_3$
- $4CaO \cdot Al_2O_3 \cdot Fe_2O_3 = 3.04 Fe_2O_3$

The above equations give the approximate amount of various mineral components formed in the cement. The reaction of cement with water is exothermic and the heat liberated is called heat of hydration. The rate of hydration of pure cement compounds is shown in Fig. 2.1 and the contribution of cement compounds to the strength of cement is shown in Fig. 2.2.

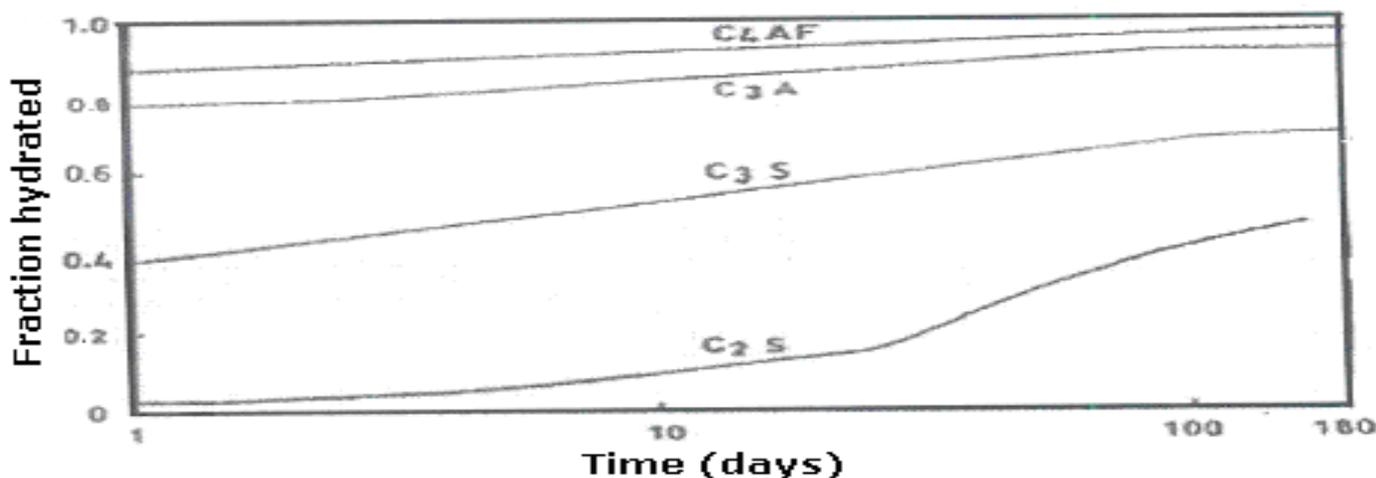


Fig 2.1 Rate of hydration of pure cement compounds

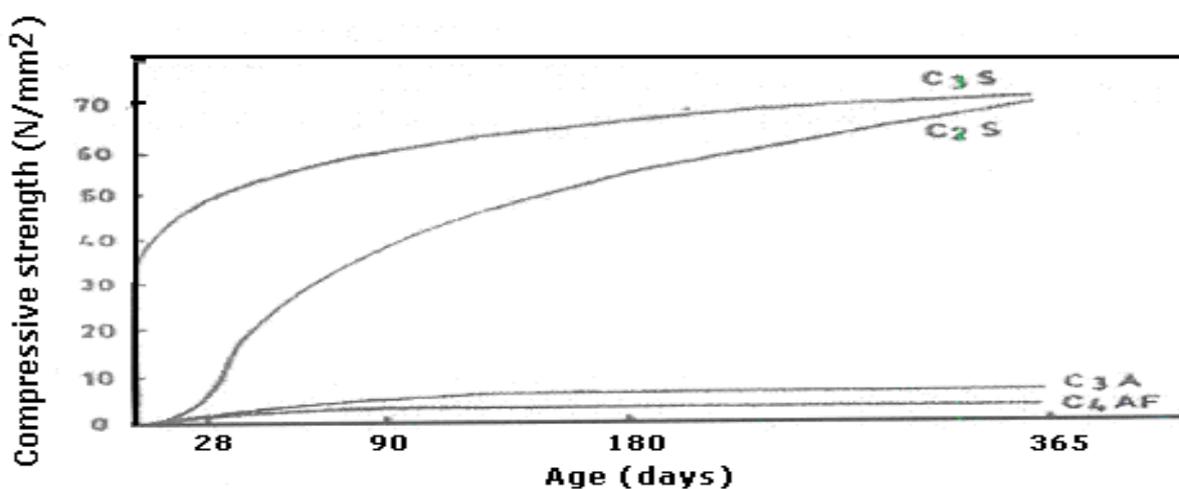


Fig 2.2 Strength contribution of cement compounds

#### 2.4 PHYSICAL PROPERTIES OF PORTLAND CEMENT

The cement to be used must have certain specified qualities in order to play its part effectively. Based on these properties, it is possible to compare the quality of cement and to carry out frequent tests on cement either on dry powder or on hardened paste and sometimes on the mortar or concrete made from the cement to maintain quality within specified limits. The important physical properties of cement are

i) Fineness ii) Setting times iii) Compressive strength iv) Soundness.

The fineness of cement is a measure of the size of the particles of cement and is expressed in terms of specific surface of cement. The finer the cement, the higher is the rate of hydration as more surface area is available for chemical reaction.

Cement, when mixed with water forms slurry, which gradually becomes less plastic and finally a hard mass is obtained. In this process, a stage is reached when the cement paste is sufficiently rigid to withstand a definite amount of pressure. The time to reach this stage from the instant the water is added to the cement is termed as 'setting time'.

Setting time is divided into two parts, viz., initial setting time and final setting time. The time at which the cement paste loses its plasticity is termed as initial setting time. The time taken to reach the stage at which the paste becomes a hard mass is known as final setting time. In practice, the terms initial and final set are used to describe arbitrarily chosen stages of setting. The unsoundness of cement is caused by undesirable expansion of some of its constituents, sometime after setting, which might result in disintegration and severe cracking. It is due to the presence of free lime and magnesia in cement.

It is essential that a cement paste, once it has set, does not undergo a large change in volume. In particular, there must be an appreciable expansion, which under conditions of restraint could result in a disruption of the hardened cement paste. Such expansion may take place due to the delayed or slow hydration or other reaction of some compounds present in the hardened cement, namely free lime, magnesia, and calcium sulphate.

The compressive strength of hardened cement is the most important of all the properties. Strength tests are not made on neat cement paste because of difficulties of excessive shrinkage and subsequent

cracking of neat cement. Strength of cement is found indirectly on cement sand mortar is specific proportion. The standard sand is used for finding the strength of cement. IS 8112:1989 specified certain values for important physical properties of 43-grade ordinary Portland cement and these are presented in Table 2.4.

**Table 2.4: Important Physical Properties of 43-Grade Ordinary Portland Cement**

Sl. No.	Particulars	Requirements
1	Physical requirements: a) Fineness ( $m^2/kg$ )	Not less than 225
2	Setting time (minutes) :a)Initial b)Final	Not less than 30 Not greater than 600
3	Soundness: a) Le – Chatlier’s expansion (mm) b) Autoclave (%)	Not less than 10 Not less than 0.8
4	Compressive strength ( $N/mm^2$ ): a) 72 $\pm$ 1 hrs. b) 168 $\pm$ 2hrs. c) 672 $\pm$ 4 hrs.	Not less than 23 Not less than 33 Not less than 43

## 2.5 USE OF WASTEWATER IN CEMENT MORTAR AND CONCRETE MIX

Ever since concrete began to be used as a construction material, potable water has been and is being used as the mixing water. The present study has shown, however, that water not fit for human consumption might also be used for mixing cement. Water from streams or rivers that was not subjected to pollution by domestic sewage, and that did not have a brackish or salty taste, has been found to be suitable for concrete mixing. It has been found that pond or lake water having low contents of silt, organic matter or other impurities has little or no adverse effect on concrete properties.

Potable water resources are not inexhaustible. For urbanized cities with limited potable water resources coupled with rapid industrial and construction growth, the need to conserve potable water becomes more urgent with each passing year. Therefore, efforts towards wastewater reuse have lately gained worldwide consideration and attention in both the agricultural and industrial fields (Metcalf and Eddy, 1991).

The suitability of using treated wastewater for mixing concrete was experimentally evaluated in Kuwait. Concrete cube specimens were cast using tap water, preliminary treated wastewater, secondary treated wastewater and tertiary treated wastewater obtained from the local Raqqa wastewater treatment plant. This type of water used for mixing did not affect concrete slump and density. However, setting times were found to increase with deteriorating wastewater quality. Preliminary treated wastewater and secondary treated wastewater were found to have the most effect on retarding setting time and were showed slower strength development for ages up to 1 year. At early concrete age up to 7 days, the strength of concrete made with tertiary treated wastewater was higher than that of concrete made with tap water. The possibility of steel corrosion increased with the use of preliminary treated wastewater and secondary treated wastewater, especially when a thinner cover to the reinforcing steel was used.

In summary, tertiary treated wastewater from wastewater in Kuwait, is found to be suitable for mixing concrete with no adverse effects.

As per the IS 456:2000 specifications, water used for mixing and curing shall be clean and free from injurious amounts of oils, acids, alkalis, salts, sugar, organic materials or other substances which may be deleterious to concrete or steel. Permissible limits for solids shall be given in Table 2.5 of IS 456:2000.

**Table 2.5: Permissible Limits for Solids**

Sl. No.	Solids in water	Tested as per	Permissible limits, maximum
1	Organic	IS 3025 (Part 18)	200 mg/L
2	Inorganic	IS 3025 (Part 18)	3000 mg/L
3	Sulphates (as $SO_4$ )	IS 3025 (Part 24)	400 mg/L
4	Chlorides (as Cl)	IS 3025 (Part 32)	2000 mg/L for concrete not containing embedded steel 500 mg/L for R.C.C. work

5	Suspended matter	IS 3025 (Part 17)	2000 mg/L
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## 2.6 EFFECT OF WASTEWATER CONSTITUENTS ON CEMENT MORTAR AND CONCRETE MIX

Water, being the most abundant solvent, may contain any number of impurities that are soluble in water even in very large concentrations. Water available in the arid regions or the regions which are susceptible to saline water intrusion may contain very high amounts of Sodium chlorides, some times even up to 20,000 mg/L. Some uncontaminated natural waters are found to be acidic due to the presence of carbon dioxide in solution. Mixing water sometimes contains even industrial wastewater, which are mainly inorganic in nature. Of these, Zn, Pb, Cu, Ni and Cr are known to be deleterious.

A search of literature indicates that constituents of water have both positive and negative effects on the quality of concrete. Many research workers have investigated the suitability of water for mixing concrete. An over view of some of the available literature on the effect of quality of water upon the mortar and concrete is presented in subsequent sections.

Using a large number of waters, many of which were highly un-potable, cast concrete cylinders and tested them in compression at ages upto twenty eight days and found that despite the wide variation in the origin and types of waters used, most of the samples gave good results in concrete and none caused unsoundness. The few waters that Abrams reported as unsuitable contained, with one exception, total dissolved solids exceeding 6000 mg/L. The solitary exception was a highly carbonated mineral water with only 2140 mg/L of total solids.

Has investigated the effect of sea water upon concrete and found that sea water containing upto 35,000 mg/L dissolved solids can make good concrete, provided the tricalcium aluminate ( $C_3A$ ) level of the Portland cement is about 8 percent. It was also found that although seawater may give enough early strength, its use often results in reduction in strength at latter ages.

The engineering properties of cement mortar and concrete specimen prepared by using a mixture of treated effluent and potable water in various proportions were studied in Qatar, an arid region where and fresh water resources are scarce. The total dissolved solids, chloride and sulphate content in the mixing water containing up to 40% treated effluent lie within the threshold limit for mixing water in concrete in mixing. About 90% of the compressive strength is retained in the cement mortar and concrete specimens when the proportion of treated effluent does not exceed 20% in the mixing water. The tensile strength, as well as the ratios of compressive strength to tensile strength and setting time for the cement mortar were found to be within the limits prescribed by BIS 12:1978, BIS 3148:1980.

The formation of tricalcium silicate phase in cement would be enhanced by the introduced heavy metals. While owing to a high level of heavy metals concentrations ( $> 1.5\%$  w/w) in cement raw mix,  $C_3S$  crystalline in cement would be inhibited by a large sludge replacement. The results of leaching test shows that the trapped elements in hydrated samples would not leach out under acidic conditions. The reuse of heavy metals such as Zn, Pb, Cu, Ni, and Cr containing sludge as cement raw material would not cause leaching hazard from sintered clinkers. Heavy metals contains sludge should have the potential to be utilized as alternative raw materials in cement production.

The dry sludge is used an additive for concrete for which it must be guaranteed that the resulting concrete has the appropriate mechanical strength and durability. The only difference noted is a slowing of the hydration process, shown by the presence of un-hydrated  $C_2S$  in the concretes with higher concentrations of sludge.

The effect of lead-rich waste forms generated using Portland cement has been investigated. The presence of lead was observed to produce lead carbonate sulphate hydroxide ( $Pb_4 SO_4 (CO_3)_2(OH)_2$ ), lead carbonate hydroxide hydrate ( $3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$ ) and two other unidentified lead salts in cavity areas, and was observed to significantly retard the hydration of cement.

The influence of metal oxides like  $ZnO$ ,  $Cr_2O_3$  and  $PbO$  was studied on cement properties. These metal oxides were shown that zinc oxide retards setting time with respect that of the cement, it also decreases compressive strength at short ages (7 day, 28 day), but its effect decreases with the sample age.  $Cr_2O_3$  and  $PbO$  have given same strength that of cementations products, but they retard the setting with respect to cement.

The performance of products arising from the stabilization / solidification of slag from lead batteries recycle into a Portland cement matrix has been evaluated not only in order to get a stabilized waste to be disposed of according to the current legislation, but also to obtain a recyclable material, with both economic and environmental benefits. The constituents of slag (Zn, Pb, Cu, Ni and Cr etc) are shown slow down of the hydration reactions, the initial set times are prolonged. The both tricalcium and dicalcium silicates, the hydration reactions are markedly retarded. The hardening of the final waste forms is less influenced and mechanical characteristics after 28 days curing are acceptable, as reported by.

### 3. MINERALS AND METHODS

#### 3.1 GENERAL

The physico-chemical properties of cement, sand and wastewater used in the investigation and also the standard experimental procedures laid down in IS codes, ASTM and BIS, which were adopted for the determination of normal consistency, initial and final setting times and compressive strength of cement mortar cubes are presented in this chapter.

#### 3.2 MATERIALS

The materials used in the experimental investigation include:

1. 43-Grade Ordinary Portland Cement (OPC)
2. Fine Aggregate (Ennore sand)
3. Deionised Water (DW), Paint Industry Treated Effluent (PITE), Tap Water (TW)
4. Zn, Pb, Cu, Ni and Cr with different selected concentrations in mixing water.

The properties of these materials are given in the following sub-sections.

##### 3.2.1 Cement

Initial experiments like initial setting time, final setting time and compressive strength on mortar cubes were conducted on 43-grade cement with regard to various water quality parameters. However, no significant variations were observed in the trends of the experimental results. Hence, 43-grade ordinary Portland cement was used in the construction works. The chemical composition of the cement was analyzed according to the standard procedures laid down in IS 4032:1968. The results of the analysis of the cement are presented in Table 3.1.

**Table 3.1: Chemical Composition of Cement**

Sl. No	Oxides	Percentage of contents
1	CaO	65.49
2	SiO <sub>2</sub>	21.67
3	Al <sub>2</sub> O <sub>3</sub>	5.97
4	Fe <sub>2</sub> O <sub>3</sub>	3.85
5	SO <sub>3</sub>	1.66
6	MgO	0.78
7	K <sub>2</sub> O	0.46
8	Na <sub>2</sub> O	0.12

The percentage composition of the major compounds (known as the Bogue compounds) present in the cement are calculated and presented in Table 3.2 (Bogue and Lerch, 1934).

**Table 3.2: Percentage Composition of the Major Compounds Present in the Test Cement**

Sl. No.	Name of the compounds	Conversion formulas	% Present in cement
1	Tricalcium silicate (3CaO.SiO <sub>2</sub> )	4.07 (CaO) -7.60 (SiO <sub>2</sub> ) -6.72 (Al <sub>2</sub> O <sub>3</sub> )-1.43 (Fe <sub>2</sub> O <sub>3</sub> )-2.85 (SO <sub>3</sub> )	51.49
2	Dicalcium silicate (2CaO.SiO <sub>2</sub> )	2.87 (SiO <sub>2</sub> ) -0.754(3CaO.SiO <sub>2</sub> )	23.37
3	Tricalcium aluminate (3 CaO.Al <sub>2</sub> O <sub>3</sub> )	2.65 (Al <sub>2</sub> O <sub>3</sub> ) -1.69 (Fe <sub>2</sub> O <sub>3</sub> )	9.31
4	Tetracalcium alumino ferrite (4CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub> )	3.04 (Fe <sub>2</sub> O <sub>3</sub> )	11.70

##### 3.2.2 Ennore Sand

The sand used through out the experimental work was obtained from the Ennore, near Chennai (Ennore sand IS 650:1991). The sand was obtained from Tamilnadu minerals limited, Chennai. It is the only organization in India, approved by Indian Standard Institution to manufacture and supply of sand conforming to IS 650:1991. The sand used in the experimental work has the following particle size distribution.

1. Passing through 2mm X retained in 1mm
2. Passing through 1mm X retained in 0.5 mm
3. Passing through 0.5mm X retained in 0.09mm

The properties of sand were analysed in accordance with the procedures laid down in IS 2386:1963 and were presented in Table 3.3.

**Table 3.3: The Properties of Ennore Sand**

Sl. No.	Properties	Unit	Results
1	Specific gravity	-	2.64
2	Bulk density	KN/m <sup>3</sup>	15.54
3	Fineness modulus	-	2.72
4	Particle size variations	mm	0.09 to 2.0
5	Colour	Hazan	Grayish white
6	Absorption in 24 hours	-	0.8%
7	Shape of grains	-	Sub angular

### 3.2.3 Deionised Water

The characteristics of deionised water, tap water, treated wastewater of paint industry were analysed according to the standard methods for the examination of water and wastewater, and presented in the Table 3.4.

**Table 3.4: Characteristics of Deionised Water (DW), Paint Industry Treated Effluent (PITE) Standards as per CPCB and Existing Characteristics of Treated Wastewater of Paint Industry.**

Impurity (mg/L)	Deionised water (DW)	PITE Standards as per CPCB
pH	7.3	6-9
TSS	-	100
TDS	15	-
Alkalinity	10	-
Acidity	2.0	-
Hardness	2.5	-
Suphates	0.2	-
Chlorides	3.0	-
BOD <sub>5</sub>	-	50
Phenolics(C <sub>6</sub> H <sub>5</sub> OH)	-	1.0
Oil and Grease	-	10
Bio- Assay Test	-	90% Survival of test animals
Zinc (Zn)	-	5.0
Lead (Pb)	-	0.1
Copper (Cu)	-	2.0
Nickel (Ni)	-	2.0
Chromium (Cr)	-	2.0
Total Heavy Metals	-	7.0

### 3.2.4 Metals

Treated wastewater from paint industry was collected. The paint industry wastewater contains heavy metal ions that are Zn, Pb, Cu, Ni, and Cr. Each metal dissolved in deionised water with different selected concentrations. The selected concentrations of each metal presented in Table 3.5.

**Table 3.5: Selected Concentrations of Metals**

Sl. No.	Name and symbol	Range of Concentrations (mg/l)			
		Cycles			
		I	II	III	IV
1	Zinc (Zn)	5	25	250	500
2	Lead (Pb)	0.1	0.5	5	500
3	Copper (Cu)	2	10	100	500

4	Nickel (Ni)	2	10	100	500
5	Chromium (Cr)	2.1	10.5	1.5	500

### 3.3 METHODS

The experimental methods adopted were in accordance with the standard procedures in BIS. They are briefly presented in the following sub sections.

#### 3.3.1 Test Program

The details of the different concentrations of waste water used in the experimental work are presented in Table 3.5. A standard mould used in Vicat's apparatus were cast and tested for initial and final setting time experiments and mortar cubes of 50 cm<sup>2</sup> cross sectional area were tested at different ages (3 day, 7 day and 28 day) of compressive strength for different cycles of PITE.

#### 3.3.2 Experimental Procedure

Normal consistency, initial and final setting times are determined by the Vicat's apparatus, which measures the resistance of cement paste of standard consistency to the penetration of a needle under a total load of 300g. The initial set is an arbitrary time in the setting process, which is reached when the needle is no longer able to pierce the 40mm deep pat of the cement paste to within about 5 to 7 mm from the bottom. The final setting time is reached, when the needle makes an impression on the surface of the paste but does not penetrate.

Vicat's apparatus conforming to IS 5513:1976 consists of a frame to which a movable rod having an indicator is attached which gives the penetration. The rod weights 300 g and has diameter and length of 10mm and 50 mm respectively. Vicat's mould is in the form of cylinder and it can be split into two halves. Vicat's apparatus includes three attachments – plunger for determining normal consistency, square needle for initial setting time, and needle with annular collar for final setting time. Detailed experimental procedures adopted in the investigation are given in the following sub sections.

##### 3.3.2.1 Consistency

About 400g of cement was initially mixed with 30 percent mixing waste water. The paste was filled in the mould of Vicat's apparatus and care was taken such that the cement paste was not pressed forcibly in the mould and the surface of the filled paste was smoothed and leveled. A square needle of size 1mm x 1mm attached to the plunger is then lowered gently on to the surface of the cement paste and is released quickly. The plunger pierces the cement paste and the reading on the attached scale was recorded. The experiment was performed carefully away from vibrations and other disturbances.

The test procedure was repeated by increasing the percentage of mixing water at 0.5% increment until the reading was 5 to 7 mm from the bottom of the mould. When this condition is fulfilled, the amount of water added was taken as the correct percentage of water for normal consistency. The entire test was completed within 3 to 5 minutes; if the time taken to complete the experiment exceeds 5 minutes, the sample was rejected and fresh sample was taken and the operation was repeated again. Fresh cement was taken for each repetition of the experiment. The plunger was cleaned each time the experiment is carried out.

##### 3.3.2.2 Initial and Final Setting Times

Cement paste was prepared by gauging cement with 0.85 times appropriate mixing water required to give a paste of standard consistency. The stop watch was started at the instant the mixing water was added to the cement. After half-a-minute, the paste was thoroughly mixed with fingers for one minute. The mould resting on a non porous plate was filled completely with cement paste and the surface of filled paste was leveled smooth with the top of the mould. The test was conducted at room temperature of 27±2<sup>0</sup>C at a relative humidity of 60%. The mould with the cement paste was placed in the Vicat's apparatus and the needle was lowered gently to make contact with the test block and was then quickly released. The needle thus penetrates the test block and the reading on the graduated scale of Vicat's apparatus was recorded. The procedure was repeated until the needle fails to pierce the block by about 6mm measured from the bottom of the mould. The stop button of stop watch was pushed down and the time was recorded which gives the initial setting time. The cement paste was considered finally set when upon applying the needle gently to the surface of test block, the needle makes an impression, but fails to penetrate and the time was noted which gives the final setting time. The needles were cleaned after every repetition and also care was taken such that there could not be any vibrations.

##### 3.3.2.3 Compressive Strength

Moulds for the cube specimens of 50 cm<sup>2</sup> face area are of metal not amenable to attack by cement mortar and the sides of the mould shall be sufficiently thick, to prevent spreading and warping. The moulds are rigidly constructed in such a manner as to facilitate the removal of the moulded specimen

without damage. The moulds are machine so that when assembled, the dimensions and the internal faces are accurate to the following specifications:

The height of the mould and the distance between opposite faces shall be 70.60 mm. The angle between the adjacent interior faces and top and bottom planes of the mould shall be  $90^{\circ}$ . The interior faces of the moulds are plane surfaces with a permissible variation of 0.15 mm. The base plate is of such dimensions as to support the mould during the filling without leakage.

While assembling the mould, the joints between the halves of the mould were covered with a thin film of petroleum jelly and a similar coating of petroleum jelly was applied between the contact surfaces of the bottom of the mould and its base plate in order to ensure that no water escapes during vibration. The interior faces of the mould were treated with a thin coating of mould oil.

The assembled mould was placed on the table of the vibration machine and firmly held it in position by means of a suitable clamp. A hopper of suitable size and shape was attached securely at the top of the mould to facilitate filling and this hopper was not removed until the completion of the vibration period. A mixture of cement and standard sand in the proportion 1:3 by weight was mixed dry (IS 4031 (part 6):1968). Mixing was carried out using a mechanical mixer corresponding to IS specifications. The constituents were first poured into the mixer and mixed in dry condition till uniform color was obtained. Then spiked water of the calculated amount was added to it and mixing was continued till a uniform and homogeneous paste was obtained. The quantities of cement, standard sand and mixing water for each cube are 200g, 600 g and  $(0.25 p+3)$  where P=percentage of water required to produce a paste of standard consistency (IS 269:1976). The temperature of water and that of the test room at the time when the above operations were being performed was kept at  $27 \pm 2^{\circ}\text{C}$  and the relative humidity 60%. Immediately after mixing the mortar, it was placed in the cube mould and prodded with the rod. The mortar was prodded 20 times in about 8 seconds to ensure elimination of entrained air and honey combing. The remaining quantity of mortar was placed in the hopper of the cube mould and prodded again as specified for the first layer and further compacted by vibration. The period of vibration was maintained for two minutes at the specified speed of  $12,000 \pm 400$  vibrations per minute.

At the end of the vibration the mould together with the base plate was removed from the machine and the top surface of the cube was finished smooth with a blade or a trowel. The compacted cubes in the moulds were maintained at controlled temperature of  $27 \pm 2^{\circ}\text{C}$  and at 90 percent relative humidity for 24 hrs by keeping the moulds under wet gunny bags. After 24 hrs, the cubes were removed from the moulds and immersed in the corresponding mixing water until taken out for testing, the maximum period of curing being 28 days. Storage pot is used for curing of cubes in the corresponding mixing water.

Three cubes were tested for compressive strength each time in the 40-tonne universal testing machine at 3 day, 7 day and 28 day periods. The cubes were tested on their sides without any packing between the cube and the steel plates of the testing machine. One of the plates is carried on a base and is self-adjusting and the load was steadily and uniformly applied, starting from zero at the rate of  $350 \text{ kg/cm}^2/\text{min}$ .

## 4.RESULTS AND DISCUSSIONS

### 4.1 GENERAL

The results of the present investigation are presented both in tabular and graphical forms. The interpretation of the results is based on the current knowledge available in the literature as well as on the nature of results obtained. The significance of the result is assessed with reference to the standards specified by the relevant IS Codes:

Average of initial and final setting times of three cement samples prepared from different types of mixing water under consideration were compared with those of the cement specimens prepared from deionised water. As per (IS 456:2000), if the difference in setting times is less than 30 minutes, the change is considered to be insignificant. However, if the difference is more than 30 minutes, then the change is considered to be significant. The limits for significance criteria in setting times of all these samples under consideration are within the range of standards specified in IS 8112:1989. This IS Code prescribed that initial setting time should not be less than 30 minutes and final setting time should not be more than 600 minutes.

An average compressive strength of at least three test specimens are compared with that of three similar reference specimens. As per (IS 456:2000), if the difference in the strength is less than 10 percent, it is considered to be insignificant and if greater than 10 percent, then the change is considered to be significant.

### 4.2 PAINT INDUSTRY TREATED EFFLUENT (PITE)

The characteristics of the deionised water tap water and treated effluent of paint industry used in this experimental study. The impurities present in PITE are different concentrations and each one react differently with the constituents of the cement. Not all impurities will have adverse effects on the properties of the cement. Some react in such a way that the net result may be harmless or may even improve the concrete properties. The concentrations of the various constituents of the treated wastewater of paint industry are above the tolerable limits established by the CPCB.

#### 4.3. CONSISTANCY, INITIAL SETTING AND FINAL SETTING OF DIFFERENT CYCLES

The values of Consistency, Initial setting and Final setting for PITE of different cycles are Presented in the Table 4.3.

Table 4.3: Constistency and Setting times of Deionised water and Different cycles

Cycle	Consistency (%)	Initial Setting Time (min)	Final Setting Time(min)
Deionised water	31.0	190	310
I	31.5	190	315
II	31.5	180	285
III	32.0	160	260
IV	32.5	150	240

Comparison between Cycles and Initial and Final Setting times

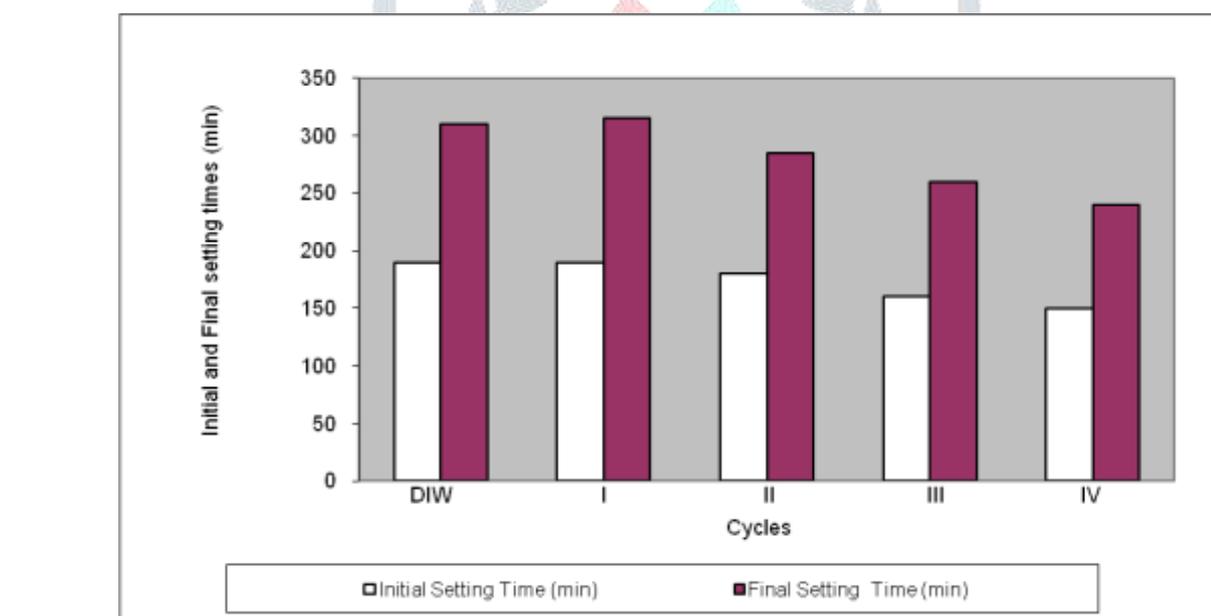


Fig. 4.3. Comparison between Cycles and Initial and Final Setting times

1. The figure 4.3 observations in Cycle-1 is made that initial setting time is equal to the Deionised water. The final setting time is retarded by 5 minutes when compared to deionised water.
2. The effect on cement is given in table 3.5 and also graphically shown in figure 4.3. From the figure 4.3 observations in Cycle-II is made that initial setting time is accelerated 10 minutes when compared to Deionised water which is insignificant. The final setting time is accelerated by 25 minutes when compared to deionised water which is insignificant.
3. The figure 4.3 observations in cycle-III is made that initial setting time is accelerated 30 minutes when compared to deionised water. The final setting time is accelerated by 50 minutes when compared to deionised water.
4. The figure 4.3 observation in cycle-IV is made that initial setting time is accelerated 40 minutes when compared to deionised water. The final setting time is accelerated by 70 minutes when compared to deionised water.

5. Finally the initial setting times are accelerated with respect to higher concentrations of metals in water.
6. Finally the final setting times are also accelerated with respect to higher concentrations of metals in water.

#### 4.4. COMPRESSIVE STRENGTH RESULTS OF DIW AND CYCLE I :

Table 4.4: Compressive strength results of DIW and Cycle I

Age of Cubes (DAYS)	COMPRESSIVE STRENGTH (N / mm <sup>2</sup> )	
	DIW	CYCLE I
3	22.6	23.2
7	36.7	32.5
28	43.4	44.0

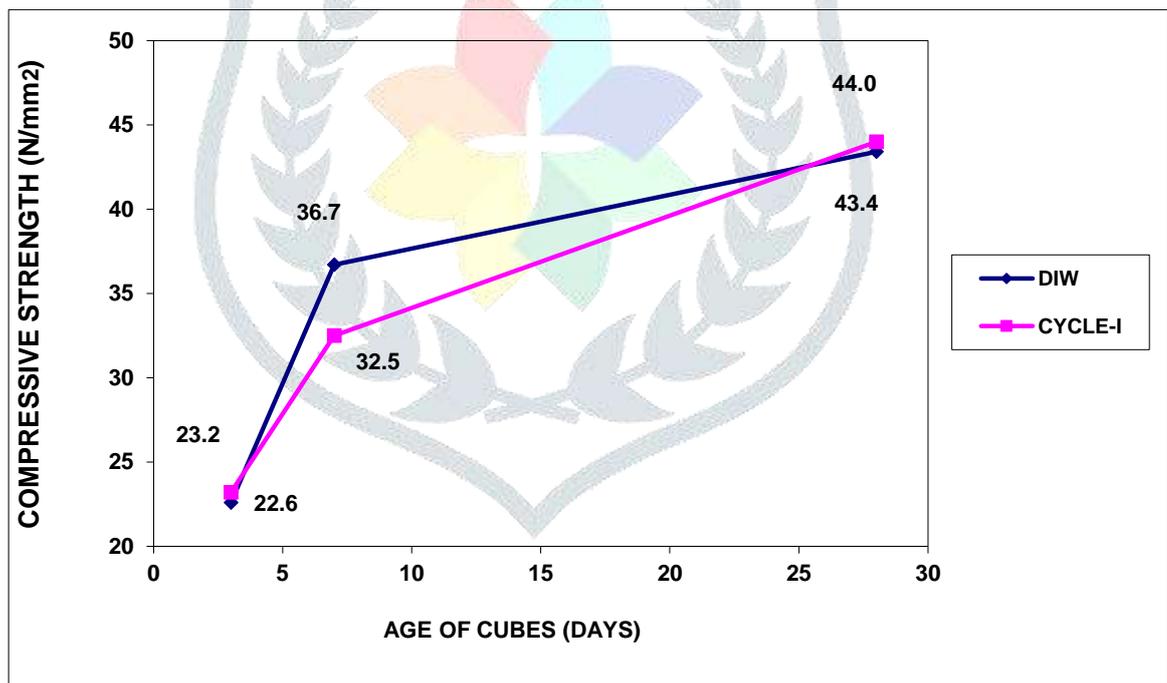


Fig 4.4. Variation of compressive strength for DIW and Cycle I

The effect on compressive strength is tabulated in table 4.4 and also graphically shown in figure 4.4. Figure observations are made that compressive strength increases a little as age increases. Comparison of compressive strength obtained values of Cycle I is more or less equal to the DIW compressive strength. In this cycle we use initial metal concentrations.

## 4.5. COMPRESSIVE STRENGTH RESULTS OF DIW AND CYCLE II :

Table 4.5: Compressive strength results of DIW and Cycle II

Age of Cubes (DAYS)	COMPRESSIVE STRENGTH (N / mm <sup>2</sup> )	
	DIW	CYCLE II
3	22.6	24.0
7	36.7	34.2
28	43.4	45.2

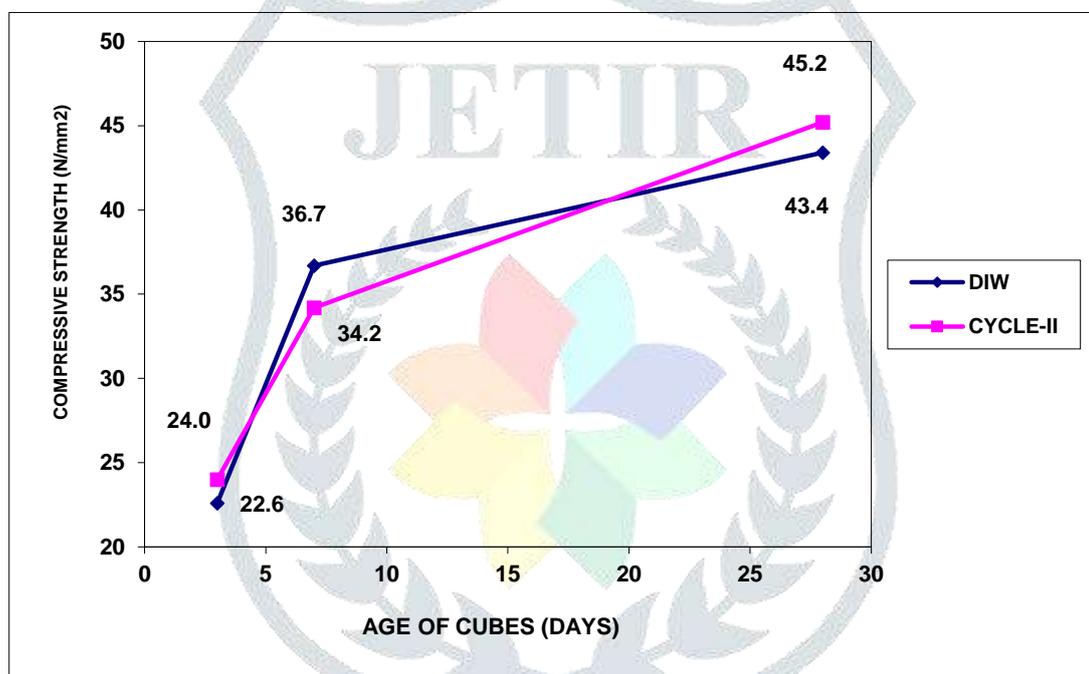


Fig 4.5. Variation of compressive strength for DIW and Cycle II

The effect on compressive strength is tabulated in table 4.5 and also graphically shown in figure 4.5. Figure observations are made that compressive strength increases a little as age increases. Comparison of compressive strength obtained values of Cycle I is more or less equal to the DIW compressive strength. Due to 5 times of initial metal concentrations.

## 4.6. COMPRESSIVE STRENGTH RESULTS OF DIW AND CYCLE III :

Table 4.6: Compressive strength results of DIW and Cycle III

Age of Cubes (DAYS)	COMPRESSIVE STRENGTH (N / mm <sup>2</sup> )	
	DIW	CYCLE III
3	22.6	24.7
7	36.7	35.2
28	43.4	46.5

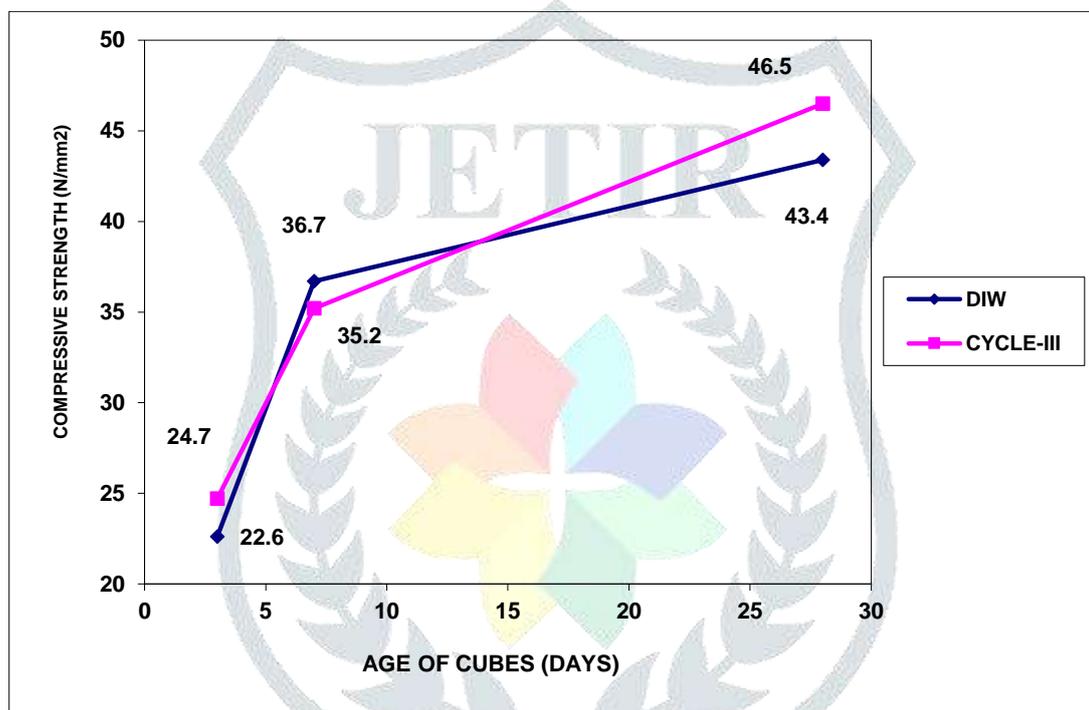


Fig 4.6. Variation of compressive strength for DIW and Cycle III

The effect on compressive strength is tabulated in table 4.6 and also graphically shown in figure 4.6. Figure observations are made that compressive strength increases a little as age increases. Comparison of compressive strength obtained values of Cycle III is more or less equal to the DIW compressive strength. Due to 50 times of initial metal concentrations.

#### 4.7. COMPRESSIVE STRENGTH RESULTS OF DIWANDCYCLE IV

Table 4.7: Compressive strength results of DIW and Cycle IV

Age of Cubes (DAYS)	COMPRESSIVE STRENGTH (N / mm <sup>2</sup> )	
	DIW	CYCLE IV
3	22.6	26.0
7	36.7	37.5
28	43.4	49.8

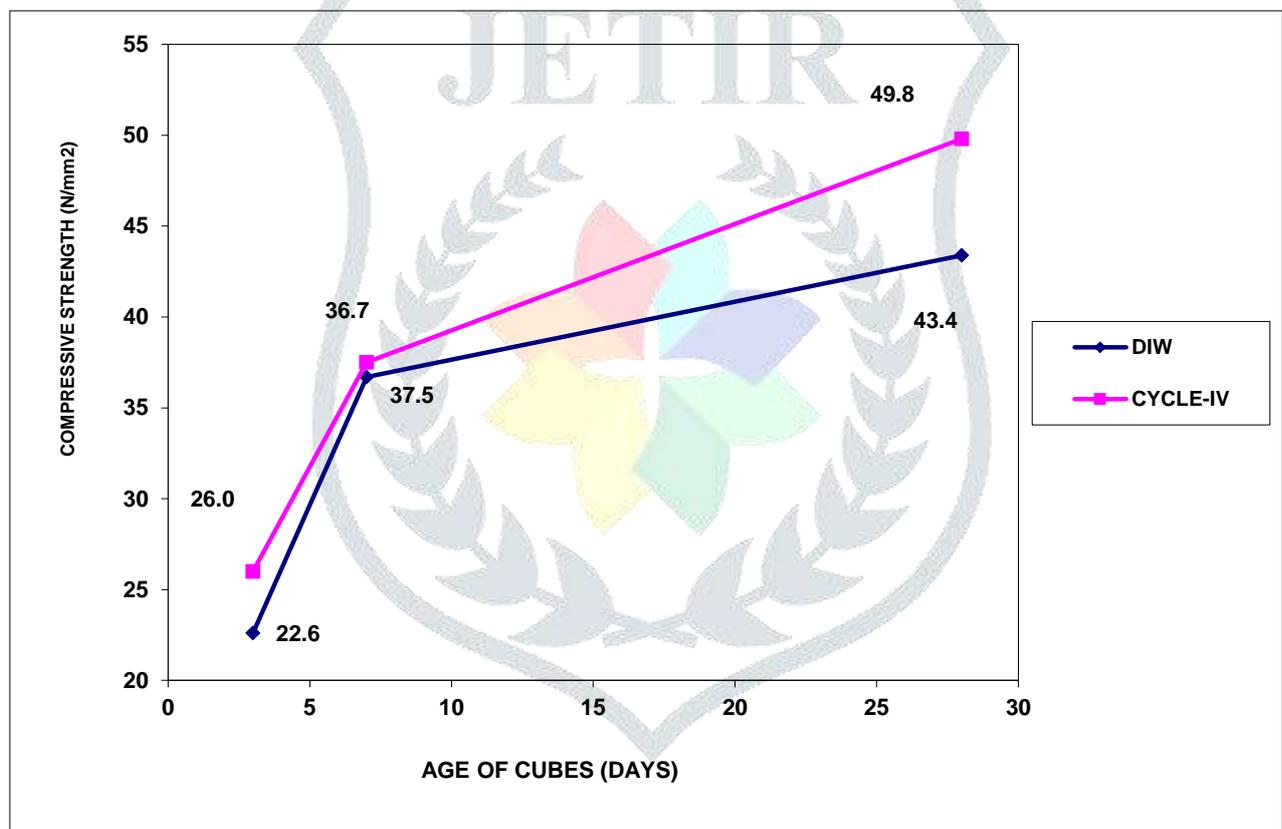


Fig 4.7. Variation of compressive strength for DIW and Cycle IV

The effect on compressive strength is tabulated in table 4.7 and also graphically shown in figure 4.7. Figure observations are made that compressive strength increases a little as age increases. Comparison of compressive strength obtained values of Cycle IV is more or less equal to the DIW compressive strength. Here we use all concentrations of 500Mg/l.

#### 4.CONCLUSIONS:

The following conclusions on the effect of mixing water on the properties of cement mortar can be drawn from the experimental study.

Density is not affected by the different types of mixing water.

1. Setting times are found to significantly retard with PITE.
2. As metal concentration increased setting times are accelerated.

3. There are no adverse effects on resulting compressive strength, when cement mortar specimens are cured in PITE.
4. Cement mortar specimens cured in there corresponding metal mixing water showed slightly compressive strength increased with concentration of metal increased.
5. Metal ions are observed that they can slow down hydration process, but finally they can positively interact with cement compounds especially at low concentration.
6. The heavy metal ions presence in cement matrix positively influence its engineering properties and their long term stability.
7. The industrial wastewater can be used as mixing water for making cement mortar without desirable concentrations removal of metals when concentration levels of non metal constituent's effect on cement mortar properties with in tolerable limits.
8. The present experimental study confirms the feasibility of using PITE in cement mortar and metal ions also are interacted friendly with cement matrix.

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