CHAPTER 5

PERFORMANCE EVALUATION OF DEVELOPED CONCRETE
5.1. INTRODUCTION

Lastly, performance of developed concrete is evaluated by three ways: environmental & chemical stress condition, diffusion modeling and TCLP. The durability of concrete refers to the extent to which the material is capable of resisting deterioration caused by exposure to service conditions while maintaining its desired engineering properties [1.29, 5.1]. Different concretes require different degrees of durability depending on the exposure to the environment. Concrete ingredients, their proportion, interactions between them, placing, curing practices, and the service environment determine the ultimate durability and life of the concrete. No standards are currently established to determine whether stabilized material had passed durability test. Stegemann et al. suggested 30% weight loss is acceptable [1.88]. This is one of the important test to levy long term risk assessment for the waste reuse. It is necessary to verify whether the pollution release from developed matrix is compatible with the specified environmental conditions [1.66, 2.21].

The Government of India has promulgated the Hazardous Waste (Management & Handling) Rules [HW (M&H)] in 1989 through the Ministry of Environment and Forests (MoEF) under the aegis of Environment (Protection) Act [E(P) Act], 1986. Under the HW (M&H) Rules, the hazardous wastes are divided into 18 categories. Moreover, the role and responsibilities of the waste generator, state/central pollution controls boards and state Government is clearly defined. In order to encourage the effective implementation
of these rules, the MoEF has further amended the Guidelines for HW (M & H) Rules in 1991 and 2006 [1.1] giving the technical details of the principles of HWM covered under the HW (M&H) Rules, 1989 [1.89]. In order to determine toxicity, the USEPA has established the Toxicity Characteristic Leaching Procedure (TCLP) designated as SWLT Method, a procedure intended to produce a leachate comparable to what would be leached by the material in the environment.

5.2 OBJECTIVES

The objective of the chapter was to study the factors affecting on the matrix stability of Developed concrete in terms of durability and leachability index.

- To assess the effect of Environmental stress condition (long term stability) on the screened concrete samples
- Assessment of potential long term diffusion (64 days) and leachability index
- Fulfillment of regulatory requirement: TCLP test

PART A – IMPACT OF LONG TERM STABILITY AND ITS EFFECT ON LEACHING OF HEAVY METALS

5.3 LONG TERM STABILITY

The durability of concrete refers to the extent to which the material is capable of resisting deterioration caused by exposure to service conditions. Durability includes influences of mechanical damage, e.g. abrasion, thermal expansion, but is more commonly associated with chemical effects, e.g. sulfate attack, chloride induced or general corrosion of steel reinforcement, alkali-aggregate reaction, etc [1.29, 5.1]. The
durability of cement pastes is strongly influenced by: (i) internal chemistry, and (ii) its microstructure [1.53, 4.3]. The industrial by-products additives influence the development of paste microstructures.

5.3.1 Method of Sample Preparation

Sample preparation, unmolding and curing was given in chapter 2. The effect of environmental stress condition on the durability of screened concrete samples was assessed. Leachability of heavy metals were also performed after durability test on the same samples of developed concrete. Samples (durability at 7, 28 & 90 Days curing) was crushed and ground to < 125 μm. The available leaching test method was used to measure heavy metal leaching [2.19].

5.3.2 Result and Discussion

Concrete must be able to endure severe weather conditions such as freezing and thawing, wetting and drying, heating and cooling, chemicals and the like. An increase in the concrete durability will enhance concrete resistance to severe weather conditions [4.3, 5.2, 5.3]. Heating-Thawing (HT) and Freezing-Thawing (FT) are the weathering simulation studies. Samples for HT and FT were alternately wet-heated and wet-freeze as per procedure (chapter 2). In this study, 30% weight loss was used as a rejection ground after durability testing of the ratio. Wet/dry and freeze/thaw durability tests showed up to 10% weight loss after 12 cycles (Figure 5.1 (a & b)). The developed products when subjected to heating thawing process withstand all 12 cycles (Figure 5.2 (a & b)). Changing wet and dry period may influence the precipitation and redistribution of
contaminant concentration in pore water. In cold climate freezing and thawing might also affect leaching because particles can break and create new surfaces accessible to water [5.4]. The results obtained in this study, proved to extensive curing increase the durability of the treated waste. Thus at 28 & 90 days curing were determined to be the most effective in the S/S application.

The major factor that controls the durability of concrete is its strength [5.5]. The physical test results were good. As the strength increases, durability of the concrete is also increases. Weight loss from the freeze/thaw durability test ranged from 0.37 – 0.98% and heat-thaw durability test ranged from 0.28 – 0.42% after 4 cycles. The obtained values were less as compared to the 30% weight loss standard. L1 and L2 concrete samples were soiled during FT & HT durability test [5.5]. Strength of these two samples very low as compare to other samples. Modeling and statistical analysis also showed unconstructive results for these two samples.

The chemicals are mineral admixtures like micro silica, fly ash and slag for durability. Presence of fly ash in developed pure concrete (Sp, Fp & Lp) decreases the porosity due to pozzolanic activity that fills concrete’s microstructure space promoting reduction and discontinuity of capillary pores. These features contributed in pore refinement by increasing the amount of smaller pores and decreasing the amount of bigger once [5.6]. Sludge has also showed pore refinement and pozzolanic activity. Smaller size of waste and by-product fill pores, which are present in the matrix and decreases the permeability. FT was found to be more deteriorating as compared to HT (Figure 5.3).
Figure 5.1 (a): Freezing - Thawing Durability of Developed Concrete

Figure 5.1 (b): Freezing - Thawing Durability of Developed Concrete
Figure 5.2 (c) : Heating - Thawing Durability of Developed Concrete

Figure 5.2 (d) : Heating - Thawing Durability of Developed Concrete
5.3.3 Effect of Weathering Studies on Availability of Heavy Metals

Short term leaching test (NEN-7341) was performed on the samples after durability test, to assess the effect of HT and FT cycle on metal fixation. The results were compared with available leaching test which was taken before durability. Very less leaching was found after durability test. It was found metal like Fe, Cu, Zn, Ni and Cr were in the detectable limit but in the limit of hazardous waste management rules, 1986 [1.1].

Iron: Iron Leaching found less than other metals (Cu, Zn) due to presence of high iron content in FT and HT cycle. FT and HT cycle Leaching was found in the range of 355 – 550 mg/kg and 97 – 480 mg/kg. Leaching at ambient condition cured samples was in the range of 89.7 – 101.9mg/kg. FT was found to be more deteriorating than HT.

Copper: Copper leaching found more in sludge mixed samples (S1, S2, L1 & L2). Samples passed through FT cycle found less leaching from 32 – 613 mg/kg. HT samples
were in the range of 118.1 - 729.01 mg/kg. Copper leached from control samples is in the range of 65.6 - 383 mg/kg. FT cycle was more deteriorating than HT in the case of copper.

**Zinc:** Zinc Leaching was in the range of 102.3 - 387 mg/kg for samples cured at ambient temperature. Zinc was found to be 5111-403 mg/kg after HT and 5.37 - 517.63 mg/kg after FT cycles. HT was more deteriorating than FT.

**Chromium and Nickel:** Chromium was in the range of 26 -105 mg/kg for the samples cured at ambient temperature, 58 - 176 mg/kg after HT and 152 - 263 mg/kg after FT cycles. Nickel leaching for HT is between 64 - 119.8 mg/kg and 99.6 - 136 mg/kg after FT (Figure 5.4 (a, b & c)). Nickel was in the range of 64 - 119.8 mg/kg for the samples cured at ambient condition. In most of cases FT was more deteriorating than HT. Leaching at ambient condition was lower as compared to leaching after HT and FT.

**Figure 5.4 (a): Metals Leached Concentration from Developed Concrete at Ambient TEMPRATURE**
Figure 5.4 (b): Metals Leached Concentration from Developed Concrete after Heat-Thaw Cycle

Figure 5.4 (c): Metals Leached Concentration from Developed Concrete after Freeze-Thaw Cycle
5.4 LONG TERM DIFFUSION LEACHING TEST

Long term leaching test (64 days) is used as tool to estimate the release potential of constituent from waste materials over a range of possible waste management activities including during recycling or reuse. This diffusion test can be used to determine the long term leaching behaviour of solid, non-granular building materials and waste products [2.21, 5.7]. This test determines the nature and properties of the material matrix to be studied by placing a complete sample in the leaching fluid (acidified water) and replenishing the elute at specified times. The concentrations of the leached components in the successive elute fractions are measured. The pH value at which leaching takes place is determined by the material itself. These materials are characterized by a porous structure with good mechanical properties. Therefore, they are generally considered as monolithic materials exposed to the environment by surface contact. In fact, the surface involve in the mass transfer not only depend on the structure characteristics of the material, but also on the physico-chemical characteristics of the components, on the hydrodynamics and physico-chemical characteristics of the fluid phase in contact with the material (Figure 5.5) [5.8].
Figure 5.5: Different release mechanisms obtained using Dutch diffusion leaching test NEN 7345 [Reference 5.9]; cumulative releases during the diffusion leaching test (crosses); calculated releases per interval (open circles); availability of components for leaching assessed by the availability test (bold horizontal line); total elemental content of the component (horizontal line); 0.5 slope (thin line).
5.4.1 Method

The leaching procedure was based on the dutch diffusion leaching test NEN 7345. The diffusion leaching test conducted in eight successive leaching steps of specific length, giving eight leachate functions. Demineralised water acidified to pH 4 was used as lechant. The monolith leaching test (NEN 7345) [2.19, 5.10] is a tool that is suitable for most monolithic forms that maintain their physical integrity during testing. Sample Preparation and Curing method are discussed in chapter 2. Cube size used for the experiment was 5×5×5 inch sample preparation and unmolded after 24 hours. Visual of sample are presented in figure 5.6. The high density polypropylene plastic containers were used for this purpose; specified volume of acidified water (leachant) was filled in the tank. Test piece was hanged such that it was in contact with the leachate from all sides and was submerged by at least 2cm. Tank was sealed after hanging the test piece in the leachant.

After the specified time periods the leachate was drain off and fresh leachant was introduced in the tank, drying of test piece was avoided in between change over. The leachants were stored for analysis. Experimental set up is given in figure 5.7.

Figure 5.6: Pure and Developed concrete cube
5.4.2 Leaching Mechanism

Leachate fractions from the diffusion test are analyzed for the species of interest. Concentrations of species in leachate fractions are also used to calculate the effective leaching coefficient. Moreover, the leaching mechanism in the matrix was studied and can be identified from the results of the diffusion leaching test (Table 5.1). Results are usually interpreted by using log release (mg/m²) vs log of time. Vertical section sketch of monolith sample (Figure 5.8) helps in the explanation of leaching mechanism [5.11].
Table 5.1: Leaching Mechanism at Different Path

<table>
<thead>
<tr>
<th>Partial Path</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td></td>
</tr>
<tr>
<td>&lt;0.35</td>
<td>0.35-0.6 or 0.65</td>
</tr>
<tr>
<td>Start Path (1-3)</td>
<td>Surface wash off</td>
</tr>
<tr>
<td>Middle Path (3-6)</td>
<td>Depletion</td>
</tr>
<tr>
<td>End Path (5-8)</td>
<td>Depletion</td>
</tr>
<tr>
<td>Total Path (2-7)</td>
<td>Surface wash-off</td>
</tr>
</tbody>
</table>

5.4.2.1 Diffusion Model for Leaching Processes

A series of diffusion leaching was performed on the developed concrete samples cured at 28 days. Cumulative leaching (mg/m²) was calculated using eq. (5.1)

\[
M_i = 2.C_0 \left( \frac{D_i t}{\pi} \right)^{1/2}
\]

(5.1)

Where, \(e_n\) is the calculated component leached for the \(n\)th period (mg/m²), \(E_i\) is the measured leaching of component in fraction i (mg/m²) and \(t_i\), \(t_{i-1}\) is the replenishment time period of fraction i and i-1. The effective diffusion coefficient was calculated using the following equation derived from the solution to Fick's second law of diffusion for semi-infinite media. Godbee et al., [5.2] provided an analytical solution for Fickian diffusion with the simplifying assumption of zero concentration at solid liquid interface.

\[
\left[ \sum \frac{a_n}{A_0} \right] \left[ \frac{V}{S} \right] = 2 \left[ \frac{D_e}{\pi} \right]^{1/2} t_n^{1/2}
\]

(5.2)

Where, \(D_e\) is effective diffusion coefficient (m²/s), \(a_n\) is the concentration loss during the leaching period (mg), \(A_0\) is the initial amount of contaminant in the sample (mg), \(V\) is the
volume of the sample (m$^3$), S is the surface area of the sample (m$^2$), $t_n$ the duration of the $n^{th}$ leaching interval (s), and is the “mean time” of the leaching interval (s) [5.9].

From Eq.5.1, $D_e$ can be calculated from the slope of $\sum a_n/A_0$ versus $t_n^{1/2}$ according to the following relationship.

$$D_e = \frac{\pi}{4} \left[ \frac{V}{S} \right] \left[ \sqrt[4]{\frac{\sum a_n}{A_0}} \right]$$ \hspace{1cm} (5.3)

From equation 5.3, one may conclude that a cumulative release following a 0.5 slope of log release vs log of time indicates a diffusion controlled release. This kind of behavior is one of the characteristic for most cement-based materials. If the slope of a release curve is 0.5 ±0.15, it is assumed that leaching is diffusion controlled.

**Depletion** of a component occur when the cumulative release approaches the amount available for leaching within the experiment time, meaning that the assumptions of Fick’s second law no longer apply, since the component concentration within the sample has changed from the initial one. The total depletion can be avoided by increasing the sample's dimension or by lowering sample's permeability.

**Delayed release** occurs when the test sample is covered with a relatively insoluble surface layer, thereby delaying constituent release during testing. Such behavior can be expected when covering layer of glass beads is used to prevent dispersion of the compacted material.

**Surface wash-off** occurs when the sample is covered with a relatively soluble surface layer. A slope less than 0.35 at the left end of the release plot indicates rapid dissolution of the sample’s surface at the beginning phases of the leaching test [5.12, 5.13]. Diffusion controlled leaching behavior may follow surface wash off in later
experiment stages. **Wash out of mobile species** occurs when dissolution of surface material is faster than diffusion through the pores of the matrix. **Change in chemical condition** may affect the release rate of the constituent. pH change affects the solubility of elements.

### 5.4.2.2 Effective Diffusion Coefficient

Effective diffusion coefficient was calculated for the component concerned from the measured leaching per fraction $E_i^*$ using the formula:

$$D_{e,i} = \frac{\pi(E_i)^3}{(4U_{\text{Avail}}\rho)^3\left(t_i - t_{i-1}\right)^2}$$  \hspace{1cm} (5.4)

Where, $D_{e,i}$ is the effective diffusion coefficient for a component calculated from fraction $i$, $E_i$ is the measured release of component $i$ (mg/m²), $U_{\text{Avail}}$ is the amount available for leaching (mg/kg), $\rho$ is the density of the product (kg/m³), $t_i$ is the time of liquid renewal of fraction $i$ (s), $t_{i-1} = $ time of liquid renewal of fraction $i-1$(s).

### 5.4.3 Result and Discussion

Long term Diffusion leaching test was performed to investigate if the leaching behavior of element from solidified material was governed diffusion mechanism [2.21]. It is believed that immobilization takes place along a physical route mainly by encapsulation [5.12] still it is assumed that some type of chemical bonding also occurs. It was found leaching was not diffusion controlled. However, the study showed that some of the components could be considerably demobilized by concrete. Concentrations of some
metals like Ni and Mn were below or not quite above the determination and were considered completely stabilized.

5.4.3.1 pH and Electrical Conductivity (EC)

Table 5.2 presents the pH and conductivity of leachate over 64 days of leaching period for samples. It was also dependent on the quantity of cement present in the matrix. Conductivity increases with the increase in the waste content in the mix design and higher for the extractions with longer contact period. pH of samples was in range 9.1–7.7 whereas electrical conductivity was 12.7 – 9.2. pH of all the extractions were comparable to that of reference, highest pH was recorded for the last extraction for reference and waste/binder ratio 0.5 – 4.1. This indicates that the alkalinity release was dependent to some extent on the contact time, as last extraction was the longest contact period [5.12]. High alkalinity was released during this period. In general, pH decreases with increase in waste quantity and decrease in binder content.

Table 5.2: pH and EC of The Leachates Over 64 Days Diffusion Test

<table>
<thead>
<tr>
<th>Samples</th>
<th>pH</th>
<th>EC (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp</td>
<td>8.3</td>
<td>9.5</td>
</tr>
<tr>
<td>Sp</td>
<td>9</td>
<td>10.9</td>
</tr>
<tr>
<td>Fp</td>
<td>8.2</td>
<td>9.4</td>
</tr>
<tr>
<td>Lp</td>
<td>8.5</td>
<td>9.2</td>
</tr>
<tr>
<td>S1</td>
<td>8.8</td>
<td>11.5</td>
</tr>
<tr>
<td>F1</td>
<td>7.9</td>
<td>10.6</td>
</tr>
<tr>
<td>L1</td>
<td>9</td>
<td>9.6</td>
</tr>
<tr>
<td>S2</td>
<td>8.8</td>
<td>12.7</td>
</tr>
<tr>
<td>F2</td>
<td>7.7</td>
<td>10.7</td>
</tr>
<tr>
<td>L2</td>
<td>9.1</td>
<td>11.2</td>
</tr>
</tbody>
</table>
5.4.3.2 Diffusion Leaching Predictions Of Ions And Heavy Metals

Leaching of the components from the solid matrix (Na, K, Cl) gives information on the physical properties of the matrix (Figure 5.9). Analysis of the leaching behaviour of these elements is usually used to determine whether leaching from the solid matrix is diffusion controlled [5.10]. Calcium solubility decreases as pH increases and become negligible at pH>12. Calcium concentration in leachate is below the solubility value of Ca(OH)$_2$ (portlandite) for the respective leachate, the release process is not limited by the solubility [2.22]. The leaching of calcium is generally higher than of other alkaline element. Cation release is necessarily accompanied by anions (ionic balance). For example, Cl release is close to the cation release. After the portlandite depletion CSH control the calcium solubility. Sulphate leaching was found low because of large size and low mobility of ions [5.6].

![Figure 5.9: Cumulative Leaching Of Ions From Developed Concrete](image-url)
Result shows that chemical processes occurring during water solidification decrease the availability of nickel, lead and manganese. Diffusion was obtained in the start path and middle path of all concrete samples. Iron release decreased with increase in waste/binder ratio. Cumulative leaching was low as compared to estimated leaching. Leaching mechanism of Fe, Zn, and Cu has given in figure 5.10, 5.11 & 5.12. The leaching mechanism was showed low leaching of copper and zinc as compared to iron.

**Iron**: Figure 5.10 presents diffusion leaching pattern of Iron. Fluctuations were observed in the iron leaching over 64 days. The results of concrete sample indicate that availability of iron increases with increase in waste/binder ratio (Table 3.8 & Figure 3.3). The leachability percentage was higher in cement and fly ash in S/S (2.9-3.9 mg/m²) compared to the sludge (3 – 4.3 mg/m²). Sample S1 was shown the higher and Lp minimum iron diffusion leaching than other samples. Cumulative release was in the range of 1658.1-7931.1 mg/kg for entire concrete samples.

![Figure 5.10: Cumulative Iron Leaching From Concrete Samples Over 64 Days For 28 Days Of Curing](image-url)
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![Figure 5.10: Cumulative Iron Leaching From Concrete Samples Over 64 Days For 28 Days Of Curing](image-url)
**Zinc:** Zinc leaching was less than iron metal. The less Zn leaching was found for sample Sp (0.5-1 mg/m²). The leaching of waste containing samples were between 1.1 - 1.7 mg/m² (Figure 5.11). Cumulative release was in the range of 12.8-150.2 mg/kg for entire concrete samples. Diffusion leaching from concrete samples was below 1.8 mg/m².

**Copper:** Figure 5.12 presents diffusion leaching of copper from concrete samples. Cumulative release was in the range of 24.5-104.8 mg/kg for entire concrete ratio. Diffusion was observed below 1.9 mg/m². Concrete sample Sp was shown lowest diffusion leaching. Sludge contained concrete samples diffusion was near about 0.4 -1.6 mg/m².

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**Figure 5.11: Cumulative Zinc Leaching From Concrete Samples Over 64 Days For 28 Days Of Curing**
Chromium, Nickel and Manganese were completely stabilized in concrete matrix and was not found during diffusion leaching test. The reason for the stabilization of these metals may be due to low concentration in raw sludge. Chromium has respeciated as silicate. Manganese has expected to precipitated as Mn(OH)$_2$ at pH 8-13 in the matrix.

5.4.3.3 Leachability Index

To evaluate the relative mobility of the different contaminants on a uniform scale, the leachability indices for the different S/S samples were calculated. The results are given in figure 5.13. The effective diffusion coefficient also called as Leachability Index of all points within the (partial) path is expressed in the negative logarithm:

$$pD_{el} = -\log D_{el}$$

(3)

The value of $pD_e$ indicates the rate of leaching. The value of the leachability index ($pD_e$) indicates the rate of leaching of heavy metals. The minimum value of leachability index
indicates the maximum rate of leaching of the metal. The higher the leachability index value the lower the speed of leaching of the component concerned with constant availability, this determines the concentration gradient which is the driving force for diffusion.

\[ p_{D_e} > 12.5 \]: Component with low mobility

\[ 11.0 < p_{D_e} < 12.5 \]: Component with average mobility

\[ p_{D_e} < 11.0 \]: Component with high mobility

A \( p_{D_e} \) value of less than 9.5 has no physical significance as the material was studied has no further internal porosity.

The leaching rate characterizes the resistance against leaching of the element confined within the concrete matrix, in such a way that the higher its value, the more strength this element opposes leaching \([5.5, 5.6]\). When the value of this parameter is more than 6, the matrix becomes efficient for confining the element, leaching rate values higher than 10 m\(^2\)/sec have been obtained, which proves that the matrix is efficient as metal solidification system. The order of fixation of metals on the basis of their leachability index is Fe>Zn>Cu>Cr>Ni>Mn.
Figure 5.13: Leachability Indexing of Heavy Metals
<table>
<thead>
<tr>
<th>Sample</th>
<th>C L mg/m²</th>
<th>Start</th>
<th>Middle</th>
<th>End</th>
<th>Total</th>
<th>Dₑ m²/sec</th>
<th>LI</th>
<th>Mobility</th>
<th>EL mg/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp</td>
<td>3917.806</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>1.3E-12</td>
<td>43.88</td>
<td>Average</td>
<td>166.608</td>
</tr>
<tr>
<td>Sp</td>
<td>4306.797</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>2.0E-11</td>
<td>50.41</td>
<td>High</td>
<td>187.556</td>
</tr>
<tr>
<td>Fp</td>
<td>5301.44</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>56.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lp</td>
<td>5298.484</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>51.18</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>S1</td>
<td>10531.34</td>
<td>SW</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>1.4E-12</td>
<td>53.2</td>
<td>Average</td>
<td>472.47</td>
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<tr>
<td>S2</td>
<td>6030.182</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Diffusion</td>
<td>SW</td>
<td>1.09E-11</td>
<td>45.83</td>
<td>High</td>
<td>252.077</td>
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<tr>
<td>F1</td>
<td>9518.976</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Diffusion</td>
<td>SW</td>
<td>1.8E-11</td>
<td>76.05</td>
<td>High</td>
<td>407.45</td>
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<tr>
<td>F2</td>
<td>6572.801</td>
<td>SW</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>77.9</td>
<td></td>
<td></td>
<td>278.36</td>
</tr>
</tbody>
</table>

SW= Surface Washoff, Dₑ= Diffusion coefficient, CL= Cumulative Leaching, EI= Estimated Leaching, LI= Leachability Index
Table 5.4: Leaching Mechanism Of Zinc In Developed Concrete

<table>
<thead>
<tr>
<th>Sample</th>
<th>C L mg/m²</th>
<th>Start</th>
<th>Middle</th>
<th>End</th>
<th>Total</th>
<th>Dₑ m²/sec</th>
<th>LI</th>
<th>Mobility</th>
<th>EL mg/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp</td>
<td>89.9404</td>
<td>Dissolution</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td></td>
<td>9.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sp</td>
<td>71.61616</td>
<td>Dissolution</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td></td>
<td>7.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fp</td>
<td>90.18592</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>4.18E⁻¹⁶</td>
<td>8.99</td>
<td>Low</td>
<td>3.99</td>
</tr>
<tr>
<td>Lp</td>
<td>97.62852</td>
<td>SW</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>7.39E⁻¹⁵</td>
<td>16.29</td>
<td>Low</td>
<td>6.879</td>
</tr>
<tr>
<td>S1</td>
<td>114.4818</td>
<td>Dissolution</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>SW</td>
<td>6.76E⁻¹⁵</td>
<td>11.84</td>
<td>Low</td>
<td>3.2697</td>
</tr>
<tr>
<td>S2</td>
<td>81.46556</td>
<td>Dissolution</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td></td>
<td>8.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>95.4646</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td></td>
<td>9.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>122.0459</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td></td>
<td>13.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SW= Surface Washoff, Dₑ= Diffusion coefficient, CL= Cumulative Leaching, EI= Estimated Leaching, LI= Leachability Index
### Table 5.5: Leaching Mechanism Of Copper In Developed Concrete

<table>
<thead>
<tr>
<th>Sample</th>
<th>CL mg/m²</th>
<th>Start</th>
<th>Middle</th>
<th>End</th>
<th>Total</th>
<th>De m²/sec</th>
<th>LI</th>
<th>Mobility</th>
<th>EL mg/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp</td>
<td>75.08468</td>
<td>Dissolution</td>
<td>Depletion</td>
<td>Depletion</td>
<td>Diffusion</td>
<td>3.43E⁻¹⁷</td>
<td>8.35</td>
<td>Low</td>
<td>3.3067</td>
</tr>
<tr>
<td>Sp</td>
<td>65.05312</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>7.569</td>
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<td>Low</td>
<td>2.7323</td>
</tr>
<tr>
<td>Fp</td>
<td>71.1414</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>1.26E⁻¹⁶</td>
<td>8.04</td>
<td>Low</td>
<td>2.7323</td>
</tr>
<tr>
<td>S1</td>
<td>164.8922</td>
<td>SW</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>15.48</td>
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<td></td>
</tr>
<tr>
<td>S2</td>
<td>97.10052</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Diffusion</td>
<td>SW</td>
<td>11.34</td>
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<td></td>
</tr>
<tr>
<td>F1</td>
<td>157.4047</td>
<td>Diffusion</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>4.16E⁻¹⁷</td>
<td>17.35</td>
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<tr>
<td>F2</td>
<td>116.0975</td>
<td>SW</td>
<td>Depletion</td>
<td>Depletion</td>
<td>SW</td>
<td>12.46</td>
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<td></td>
</tr>
</tbody>
</table>

SW= Surface Washoff, De= Diffusion coefficient, CL= Cumulative Leaching, EL= Estimated Leaching, LI= Leachability Index
PART C - REGULATORY REQUIREMENT

5.5 TOXICITY CHARACTERISTIC LEACHING PROCEDURE TEST (TCLP)

Solidification/Stabilization is a common practice for the treatment of waste containing heavy metal before they can be disposed of in a secure landfill or reuse. In order to evaluate the stability of the solidified waste for utilization, the toxicity characteristics leaching procedure (TCLP) method was used. The USEPA (1986) defines toxicity characteristic limits based on metal concentration measured in the TCLP leachates [appendix I]. Central pollution control boards (CPCB, 2006) has designed the TCLP method to study the leachability of solidified waste with water. The TCLP test is the most widely accepted leaching procedure and is capable of ensuring both inorganic and heavy metals. It is the most important test to evaluate contaminant mobility [5.15].

5.5.1 Method of Sample Preparation

Toxic Characteristic Leaching Procedure (TCLP) was performed on the treated and untreated waste. The leachates (before and after treatment) were analyzed for heavy metals. Samples were molded in 10×10×10 inch cube size and cured for 90 days. Curing method has given in chapter 3. TCLP testing was performed on duplicate samples and average values were used in calculation. During TCLP the solid was pulverized and mixed with water. The suspension was then tumbled for 18 hours and followed by, separation of the extract solution from the solid was achieved by filtration. Leachates were analysed through AAS-6300.
5.5.3 Result and Discussion

Different compositions of fly ash and hazardous waste were tested for its leaching behaviour. From the experimental result it was seen that up to Lp combination, which can be successfully stabilized accomplishing minimum leaching of heavy metal below TCLP limit with maximum compressive strength [5.1, 5.15, 5.16]. Leaching of heavy metals has showed in figure 5.14 using TCLP test. As the curing time has increased leaching rate of heavy metal from the developed concrete decrease. After treatment only Iron, Copper and Zinc metal was found in leachate. The Mn, Ni and Pb metals was below the detection limits after treatment in leachate.

The leaching of metals from developed concrete during the TCLP test depends on the amount of initial concentration of metal ($Q_0$) and the leaching time. A hyperbolic relationship is proposed to express the metal concentration after 18 h leaching.

\[
C(t) = \frac{Q_0}{A(t) + B(t)Q_0}
\]  

(5.5)

Where, $C(t)$ = Concentration after 18 h of leaching (mg/l), $Q_0$ = Initial concentration of metal (%), $A(t)$, $B(t)$ = leaching parameter (mg/l). Eq. (5.5) can be rearranged as Eq. (5.6)

\[
\frac{Q_0}{C(t)} = A(t) + B(t) \times Q_0
\]

(5.6)

The relation between $Q_0/C$ was linear and the correlation coefficient ($R^2$) were all greater than 0.8 (Figure 5.14). The prediction made using Eq. (5.6) is compatible with experimental data. In order to treat metals (Fe, Zn, Cu) successfully to meet the TCLP limit of 10 mg/l (18 h of leaching) by developed concrete.
5.6 CONCLUSION

Following conclusions were drawn from the chapter:

**Durability**: It has been observed that use of fly ash improves the stability of developed concrete. Large amount of Sludge and fly ash containing samples (L1 and L2) has been soiled during durability test. HT was more deteriorating than FT. Leaching for ambient temperature was lower as compared to leaching after HT and FT. Iron and copper leaching found more as compared to other metals due to the presence of high content in the matrix. Heavy metal was found in the permissible limit.

**Diffusion**: The Developed concrete was were blended with multi-metal bearing electroplating sludge to determine its capacity and effectiveness to stabilize heavy metals present in the sludge against long term leaching. The concrete matrix was found to be more effective in stabilization of heavy metals. The studied metals were with very low mobility. Ni, Mn and Cr were found to be below detectable limit and were considered
completely stabilized within concrete matrix. The order of fixation of studied heavy metals was Fe>Zn>Cu>Ni>Mn>Cr.

TCLP: All tested concrete samples were effective in reducing leaching of all heavy metals. The result was proved that the developed material were within the permissible limits of hazardous waste (management & handling) rules under the aegis of Environmental (Protection) Act, 1986.

Selection of the sample is followed by the durability, diffusion and TCLP. Fly ash contained pure samples has given the result near about Cp (Cement Pure) and sludge mixed samples S₁, S₂, F₁, F₂ also screened through above mention tests. L₁, L₂ was rejected during the durability test and not recommended for the reuse.
REFERENCES


