CHAPTER 4

INFLUENCE OF PH ON THE HEAVY METALS FIXATION BEHAVIOUR AT DIFFERENT CURING DAY
4.1 INTRODUCTION

Chapter is focuses on the utilization of byproduct and hazardous solid waste (sludge) to prepare concrete with superior long-term fixation. In all developing and developed countries, large amounts of industrial waste and their byproduct accumulate every year. Hence, the world’s major concern is increasing level of land pollution largely due to the uncontrolled disposal of industrial hazardous solid waste [4.1, 4.2]. Consequently, it is desirable to give proper treatment to the waste before recycling or reuse, so that the present soluble constituents can immobilize. Utilization of these materials are increasing interest, due to the high environmental impact of the cement and concrete industries. Harmful effect of waste on the environment can be reduced by producing durable concrete by using these materials.

Presently, the use of hazardous waste with replacement of natural material is widely encouraged in construction. This is practically enables waste material to recycled and reused, while at the same time saving natural resources and environmental hazardous [4.3]. The consequence of more and more alternative materials (solid waste) are used in the world in different construction applications like: green concrete, filling material, roadbeds etc [4.3, 4.4].
4.2 OBJECTIVES

Aim of the study is to explore the extent of stabilization of heavy metals when the fixation is strong and also when leaching is strong. The pH has studied in connection to its effect on the mobility of the elements, as there is a relative tendency that matrix with high compressive strength has fixed efficiently. Chapter is divided into two parts.

The chapter further elucidated:

➢ Performance evaluation of developed concrete under different pH conditions
➢ Assessment of potential leaching/fixation behavior of developed concrete through geochemical modeling and statistical analysis prediction

PART A - PREDICTION OF HEAVY METALS FIXATION THROUGH SHORT TERM LEACHING AT VARIOUS pH AND CURING DAY

It is widely accepted that cement and pozzolan based concrete can be use for metal fixation through S/S (solidification/stabilization) process. The fixation of heavy metals from fly ash and sludge has been subjected to extensive investigation on different pHs in the past [4.2, 4.5]. Portland cement along with the different combination with fly ash and waste can restrict the mobility of heavy metals due to high pH and capability of cement to precipitate the metals in insoluble form. Solidification/stabilization by portland cement is one of the most popular techniques (Best Demonstrable Available Technique). This stabilization process relies on the formation of CSH, ettringite hydrate \((\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O})\) and mono-sulphate \((\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O})\) in the matrix. Due to the hydration of Portland cement and fly ash, heavy metals chemically fixed in the lattice
of product and physically encapsulated in the matrix [4.6, 4.7]. Leaching of heavy metal was considered as a pH dependent and corresponding metal hydroxide solubility control process [4.5]. Cheng and cocke were proposed heavy metal to be either adsorbed into the CSH matrix of cement or precipitated as metal silicates/hydroxides [4.8, 4.9].

4.3 PHYSICO-CHEMICAL CHARACTERIZATION OF WASTE

The physico-chemical properties of sludge have given in table 3.3. There was very low moisture content in sludge hence no pre treatment was required. Raw water was added for the preparation of concrete mix. Water holding capacity of sludge was 32%. It shows that the water absorption potential of the waste is high. Metal processing operation of the industry makes heavy metals bearing waste. Waste contains copper, chromium, lead, zinc, iron, manganese, and nickel [4.10].

4.4 DEVELOPMENT OF S/S CONCRETE BY USING FLY ASH AND WASTE

Table 4.1 presents the percentage composition of the developed concrete. An adequate amount of water was added to maintain the proper workability of mixture as recommended by ASTM C230-90 [1.21]. Experiments of various sludge amounts were done by different mass percentage of cement and fly ash (Table 4.1). Triplicate solidified samples were tested for both compressive strength and leachability of developed concrete. Reference samples (Pure M15) were prepared for parallel test. All samples were cured for 7, 28 and 90 days to simulate the worst condition of actual field practice [2.10].
Table 4.1: Percentage Composition Of Fly Ash Concrete Used For S/S Of Sludge

<table>
<thead>
<tr>
<th>Composition</th>
<th>Reference Mass %</th>
<th>Mass % (I)</th>
<th>Mass % (II)</th>
<th>Mass % (III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>14.28</td>
<td>9.52</td>
<td>7.143</td>
<td>4.76</td>
</tr>
<tr>
<td>Fly ash</td>
<td>-</td>
<td>4.76</td>
<td>7.143</td>
<td>9.52</td>
</tr>
<tr>
<td>Sand</td>
<td>28.5</td>
<td>28.5</td>
<td>28.5</td>
<td>28.5</td>
</tr>
<tr>
<td>Coarse Aggregate</td>
<td>57.14</td>
<td>57.14</td>
<td>57.14</td>
<td>57.14</td>
</tr>
<tr>
<td>L/S Ratio</td>
<td>0.088</td>
<td>0.09</td>
<td>0.093</td>
<td>0.092</td>
</tr>
<tr>
<td>Water/Cement Ratio</td>
<td>0.62</td>
<td>0.61</td>
<td>0.64</td>
<td>0.64</td>
</tr>
</tbody>
</table>

4.5 LEACHING TEST

The surfaces involved in the mass transfer not only depend on the structural characteristics of the material, but also on the physicochemical characteristics of the components and on the hydrodynamics and physicochemical characteristics of the fluid phase in contact with the material. Generally, the solid/liquid transfer is known as leaching process [4.6, 4.11].

The leaching test involves testing the material in the worst conditions to simulate the effects of handling and other environmental conditions. The solidified/stabilized product was ground to <125μm. The rapid attainment of equilibrium was achieved by agitation, which prevented stratification. To identify the optimum ratio, the leaching tests were conducted after 7, 28 and 90 days of curing. Owing to dilution by the binders, the availability data for raw and treated sludge cannot be compared. The leaching data were normalized to the dry waste concentration. During leaching test pH of the solutions were maintained by the acid (HNO₃) or alkali (NaOH) addition. In this leaching test author used the formula of available leaching test (NEN 7341) for calculation [2.19].
Table 4.2 shows the total and available metal contents in the raw sludge, cement, fly ash of treated a S/S sample after 7, 28 and 90 days of curing. The leaching characteristics of the treated waste are expected to reduce because of the reduced surface area exposed to the environment. The isolation of the waste from the environment due to the formation of the low permeable cement matrix [4.11, 4.12, 4.13]. Author analysed the leaching behaviour of different samples at the same pH at first 3 hour and next 18 hours. The pH of the samples was maintained for 21 hours leaching path.

Table 4.2: Total and available metal content present in raw sludge, cement, fly ash

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Raw Sludge (mg/kg)</th>
<th>Cement (OPC) (mg/kg)</th>
<th>Fly ash (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Metal Content</td>
<td>Availability Metal Content</td>
<td>Total Metal Content</td>
</tr>
<tr>
<td>Fe</td>
<td>36221.22</td>
<td>23608.94</td>
<td>3368.33</td>
</tr>
<tr>
<td>Zn</td>
<td>10615.25</td>
<td>8680.32</td>
<td>615.0</td>
</tr>
<tr>
<td>Cu</td>
<td>9615.26</td>
<td>5655.24</td>
<td>67.92</td>
</tr>
<tr>
<td>Ni</td>
<td>2015.71</td>
<td>1750.30</td>
<td>89.47</td>
</tr>
<tr>
<td>Cr</td>
<td>1966.3</td>
<td>1648.09</td>
<td>700.0</td>
</tr>
<tr>
<td>Mn</td>
<td>210.58</td>
<td>95.10</td>
<td>42.21</td>
</tr>
<tr>
<td>Pb</td>
<td>73.50</td>
<td>26.1</td>
<td>24.56</td>
</tr>
</tbody>
</table>

4.6 RESULT AND DISCUSSION
Solidification/stabilization method is easy to operate with good efficiency to immobilize heavy metals. The probable speciations of heavy metals in the concrete matrix are in the form of metal hydroxides, nitrates and silicates. Literature has revealed that heavy metals bound themselves strongly with hydrated products and therefore permanently
immobilized [4.7, 4.9, 4.14]. Fly ash is acting as a reducing agent and quickly immobilized at high pH, due to the precipitation of insoluble hydroxides.

Samples were analyzed in extreme chemical environment and observed its effect on the stabilization of metals at different pH & curing days.

### 4.6.1 pH and Electrical Conductivity

Table 4.3 represents the electrical conductivity variations of leachates after leaching test for samples cured at 7, 28 and 90 days. The chemical factors influences leaching process and leachate concentrations at various pH. pH was fixed for each leaching test it affected the conductivity of the sample. pH and conductivity are indirectly correlated. Conductivity indicates the presence of charged species.

**Table 4.3: Electrical Conductivity At Different Days Of Curing**

<table>
<thead>
<tr>
<th>Samples</th>
<th>2pH</th>
<th>6pH</th>
<th>10pH</th>
<th>14pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7</td>
<td>28</td>
<td>90</td>
<td>7</td>
</tr>
<tr>
<td>C_p</td>
<td>8.1</td>
<td>9.1</td>
<td>7.4</td>
<td>2.3</td>
</tr>
<tr>
<td>S_p</td>
<td>10</td>
<td>10.9</td>
<td>7.5</td>
<td>2.1</td>
</tr>
<tr>
<td>F_p</td>
<td>8.6</td>
<td>9.1</td>
<td>8.3</td>
<td>1.9</td>
</tr>
<tr>
<td>L_p</td>
<td>8.9</td>
<td>9.2</td>
<td>8.1</td>
<td>1.4</td>
</tr>
<tr>
<td>S_1</td>
<td>8.9</td>
<td>11.5</td>
<td>8</td>
<td>1.7</td>
</tr>
<tr>
<td>F_1</td>
<td>7.9</td>
<td>10.6</td>
<td>6.7</td>
<td>1.7</td>
</tr>
<tr>
<td>L_1</td>
<td>9</td>
<td>9.6</td>
<td>7.5</td>
<td>1.4</td>
</tr>
<tr>
<td>S_2</td>
<td>8.8</td>
<td>12.7</td>
<td>6.7</td>
<td>1.8</td>
</tr>
<tr>
<td>F_2</td>
<td>7.7</td>
<td>10.7</td>
<td>6.5</td>
<td>1.7</td>
</tr>
<tr>
<td>L_2</td>
<td>9.1</td>
<td>9.2</td>
<td>7.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Lowest pH shows high conductivity. With the increase in the pH the conductivity decreases (Table 4.3). pH 10 showed minimum conductivity and as the pH increase conductivity is also found increases with increase in curing days. Cement and fly ash (pozzolana based by-product) are alkaline binders which incorporates the heavy metals in a high pH matrix. Significant portion of the heavy metal ions are precipitated in their least soluble forms within high alkaline pH condition (7–11) [4.15].

4.6.2 Anions and Cations
Ca, Na, K, Cl were treated as static components, leaching of such species which do not react with the solid matrix. These elements are expected to be weakly bound to the solids matrix. Anion and cation concentrations in pure raw material are shown in table 4.4. Sodium concentration increases with the increase in the waste and by-product from the concrete solidified surface. Maximum quantity of sodium was stabilized in the pH range 2-10 at all days of curing. 28 and 90 days cured concrete sample was showed sodium leaching due to addition of NaOH.

Table 4.4: Anion And Cation Concentration In Cement, Fly Ash And Sand

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameter</th>
<th>Unit</th>
<th>Cement</th>
<th>Fly ash</th>
<th>Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Calcium (Ca(^+))</td>
<td>mg/kg</td>
<td>63.4</td>
<td>2.75</td>
<td>BDL</td>
</tr>
<tr>
<td>2.</td>
<td>Chloride (Cl(^-))</td>
<td>mg/kg</td>
<td>9497</td>
<td>3627</td>
<td>11996</td>
</tr>
<tr>
<td>3.</td>
<td>Sodium (Na(^+))</td>
<td>mg/kg</td>
<td>BDL</td>
<td>882</td>
<td>938</td>
</tr>
<tr>
<td>4.</td>
<td>Potassium (K(^+))</td>
<td>mg/kg</td>
<td>1571</td>
<td>317</td>
<td>133</td>
</tr>
<tr>
<td>5.</td>
<td>Sulphate (SO(_2)^{4-}))</td>
<td>mg/kg</td>
<td>1430</td>
<td>1870</td>
<td>340</td>
</tr>
</tbody>
</table>

Calcium is act as a binder constituent. Its leaching was found high from the reference matrix. The availability of calcium decreases with the increase in the waste content. It also originated from dissolution of gypsum and hydration of cement clinker.
phases. Ca$^{2+}$, SO$_4^{2-}$ and Cl$^-$ leaching was low in samples with low sludge content, and increasing with increase in waste/binder ratio. When sodium sulfate reacts with pure minerals, crystals of gypsum are quickly formed from tricalcium silicate, but with dicalcium silicate the reaction proceeds slowly. Leached concentration of sulfate is explained with the help of figure 4.1. Sulfate leaching was not affected by the curing days. The addition of NaOH (to maintain the alkalinity of leachate) increases the mobility of sodium. pH was affected leaching of sulfate from concrete samples. Leaching pattern for anions and cations was much similar for 7, 28 and 90 days of curing.

Table 4.5 represents the cumulative leaching of cations at different curing ages. At 90 days, cured sample shows higher leaching of sodium. Sodium leaching is higher in Sp, Fp and Lp samples.

Potassium release was dependents on the concrete composition. It is also treated as static material and provides the information about the leaching mechanism in the matrix. Potassium content was high for high cement content matrix and decreases with the increase of sludge content. The cumulative potassium was released in the assortment of 855.9 – 3629.7 mg/kg from concrete samples (C$_p$ - L$_2$). Potassium leaching was not affected with the pH and curing days (7, 28 & 90) (Table 4.6). Chloride was found BDL at pH 2.
Figure 4.1: Sulfate Concentration Leached From Samples

Table 4.5: Cumulative Leaching Of Cation At Different Curing Age

<table>
<thead>
<tr>
<th>Samples</th>
<th>Na (mg/kg)</th>
<th>K (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Days of Curing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>28</td>
</tr>
<tr>
<td>Cp</td>
<td>4449.3</td>
<td>2763.3</td>
</tr>
<tr>
<td>Sp</td>
<td>4259.2</td>
<td>4223.1</td>
</tr>
<tr>
<td>Fp</td>
<td>3708.6</td>
<td>4122.9</td>
</tr>
<tr>
<td>Lp</td>
<td>3620.2</td>
<td>4275.6</td>
</tr>
<tr>
<td>S1</td>
<td>4083.6</td>
<td>3702.3</td>
</tr>
<tr>
<td>F1</td>
<td>3970.6</td>
<td>4054.9</td>
</tr>
<tr>
<td>L1</td>
<td>5052</td>
<td>3888.2</td>
</tr>
<tr>
<td>S2</td>
<td>2918.1</td>
<td>2843.7</td>
</tr>
<tr>
<td>F2</td>
<td>3751.7</td>
<td>2493.7</td>
</tr>
<tr>
<td>L2</td>
<td>3791.5</td>
<td>2359.4</td>
</tr>
</tbody>
</table>
Table 4.6: Cumulative Chloride Concentration At Different pH And Curing Days

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chloride Leaching (mg/kg)</th>
<th></th>
<th>6 pH</th>
<th>10 pH</th>
<th>14 pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Days of Curing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>28</td>
<td>90</td>
<td>7</td>
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<tr>
<td>Cp</td>
<td></td>
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<td>999</td>
<td>8497</td>
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<tr>
<td>Sp</td>
<td></td>
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<tr>
<td>S2</td>
<td></td>
<td>499</td>
<td>499</td>
<td>9996</td>
<td>1999</td>
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<td>9497</td>
<td>999</td>
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<td></td>
<td>499</td>
<td>999</td>
<td>11996</td>
<td>999</td>
</tr>
</tbody>
</table>

Leaching of chloride is increases with the increase in sludge content in the matrix. Chloride leaching is very high for developed concrete at alkaline pH (Table 4.6). Table 4.5 represents the actual concentrations of raw material. Chromium leaching was very low in samples cured at 7 and 28 days. Concrete sample which was cured for 90 days shows maximum chloride leaching (Table 4.6). The release of sodium, sulfate, chloride and potassium increases as the waste and fly ash content increase in the matrix.

4.6.3 Fixation of Heavy Metals

The leaching test has performed in two ways: (i) to assess the pH which influences the species solubility (Figure 4.2) (ii) and impact of curing days [4.16]. The metals have precipitated with lime and like sulfide to produce metal hydroxide. Sulfide and other
compound have low solubility and precipitated at pH 7 – 10 [4.6]. During cement hydration, the surface of cement particles will be negatively charged and therefore able to absorb metal cations. The most readily available cation in solution is Ca$^{2+}$, and these are believed to coat the silicate surfaces forming a high charge density Ca$^{2+}$ layer. Anionic species in solution such as Pb(OH)$_3^-$, SO$_4^{2-}$, NO$_3^-$ and OH$^-$ also compete for adsorption sites to forming a further layer. Solubility curve for various metal hydroxides is shown in figure 4.2.

To illustrate the effect of pH, experiments were carried out the fixation of heavy metals using acid (HNO$_3$) or alkali (NaOH) solution at pH 2 – 14. During the leaching test, the pH was maintained at 2 till extraction leachate. The metal hydroxides are supposed to be leached out completely at pH 2. In a similar way other pH like 6, 10, and 14 also analysed. AAS-6300 analysis indicates all the heavy metals were leached out at pH 2 – 6 (Figure 4.3, 4.4 (a, b, c, d, e)). While the pH increases from 6 – 10 the fixation of heavy metals increases significantly [4.7, 4.16]. The hydroxides of heavy metals exhibit minimum solubility in pH 8 – 10. The solubility of hydroxide at pH 12 indicates there is chemical entrapment of heavy metals in hydrated cement phase where they are strongly immobilized [4.17].

In the case of Zn, the zinc hydroxy anions (Zn(OH)$_3$ and Zn(OH)$_4^{2-}$) were reported to be present between pH 12 and 13. These are transformed into CaZn$_2$(OH)$_6$.H$_2$O, which completely covers the cement grain. The zinc hydroxide sludge contains crystalline zinc nitrate hydroxide hydrate [Zn$_5$(NO$_3$)$_2$(OH)$_8$2H$_2$O], ZnO and NaNO$_3$. The Fe hydroxide sludge was predominantly crystalline Fe(OH)$_2$. The major
phase was Portlandite [Ca(OH)$_2$] in the concrete system which was hydrated for 28 days [3.9, 3.17, 4.18].

The rate of fixation increases with time and the total amount of metal fixed is also increase with decrease in the sludge & fly ash/cement ratio. Total concentration and available fraction of heavy metals fixed in concrete at 7, 28 and 90 days of curing are presented in figure 4.3, 4.4, 4.5, 4.6 (a, b, c, d & e). All concrete samples were initially high alkaline and this alkalinity was neutralised by acidic influences. It is gradually causes the dissolution of the cement hydrated products which composed the matrix and as

Figure 4.2: Theoretical Solubilities of Metal Hydroxide
well as metal contaminants. Thus, measurement of dissolved contaminant concentrations and pH as a function of acid can help to characterise chemical immobilization. Ni, Cr, Mn and Pb concentration were low in the waste as compared to other heavy metals. These metals were stabilized when they are encapsulated in the concrete matrix [4.15, 4.19].

4.6.4 Effect of pH on Metal Fixation

4.6.4.1 pH 2

Fixation at pH 2 with 7, 28 and 90 days of curing given in the figure 4.5 (a,b,c,d,e). Zn at 90 days and Cu at 28 days of curing showed fewer fixations then other metals. Minimum fixation was observed at pH 2 and all metal hydroxides and silicates were leached out at 2 pH. Fe, Zn, Cr, Cu and Ni were present in the sludge and the species of these metals have stabilized in the concrete matrix.

![Fixed Zn Metal Concentration (mg/kg)](image)

**Figure 4.3 (a): Zn Metal Fixation on pH 2 at 7, 28 & 90 Days of Curing**
Figure 4.3 (b): Fe Metal Fixation on pH 2 at 7, 28 & 90 Days of Curing

Figure 4.3 (c): Cr Metal Fixation on pH 2 at 7, 28 & 90 Days of Curing
Figure 4.3 (b): Fe Metal Fixation on pH 2 at 7, 28 & 90 Days of Curing

Figure 4.3 (c): Cr Metal Fixation on pH 2 at 7, 28 & 90 Days of Curing
Figure 4.3 (d): Cu Metal Fixation on pH 2 at 7, 28 & 90 Days of curing

Figure 4.3 (e): Ni Metal Fixation on pH 2 at 7, 28 & 90 Days of Curing
4.6.4.2 pH 6

At pH 6 found more stabilization of Heavy metals. To maintain the pH of solution less acid quantity was required because of the alkaline nature of the raw mix of concrete. The metal hydroxides exhibit maximum fixation after the pH 6. Below this pH, solubility increases rapidly and as the pH increases up to 8 solubility will decreases.

Ni stabilization was not affected with the curing days. Cu and Ni metals were completely fixed in pure & cement/fly ash samples like; Cp, Sp, Fp & Lp (Figure 1, 2(e)). Metals show maximum fixation with given curing days; Cu at 7 & 28 days, Cr at 7 & 90 days, Zn at 7 & 90 days, Fe at 28 & 90 days (Figure 4.4(a, b, c, d, e)).

![Fixed Zn Metal Concentration (mg/kg)](image_url)

**Figure 4.4 (a): Zn Metal Fixation on pH 6 at 7, 28 & 90 Days of Curing**
Figure 4.4 (b): Fe Metal Fixation on pH 6 at 7, 28 & 90 Days of Curing

Figure 4.4 (c): Cr Metal Fixation on pH 6 at 7, 28 & 90 Days of Curing
Figure 4.4 (d): Cu Metal Fixation on pH 6 at 7, 28 & 90 Days of Curing

Figure 4.4 (e): Ni Metal Fixation on pH 6 at 7, 28 & 90 Days of Curing
4.6.4.3 pH 10

Fe solubilization is strongly dependent on pH [4.16] (Figure 4.5 (a,b,c,d)). Cu and Ni completely stabilized in all samples while Fe fixation is found maximum in the pH range from 8 – 10 (Figure 4.5 (b)). The possible species of heavy metals in the concrete matrix were in the form of metal hydroxides, nitrates and silicates though hydration of cement and reveals highest fixation after the pH 6 [4.15].

![Figure 4.5 (a): Zn Metal Fixation on pH 10 at 7, 28 & 90 Days of Curing](image-url)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cp</th>
<th>Sp</th>
<th>Fp</th>
<th>Lp</th>
<th>S1</th>
<th>F1</th>
<th>L1</th>
<th>S2</th>
<th>F2</th>
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Figure 4.5 (a): Zn Metal Fixation on pH 10 at 7, 28 & 90 Days of Curing
Figure 4.5 (b): Fe Metal Fixation on pH 10 at 7, 28 & 90 Days of Curing

Figure 4.5 (c): Cr Metal Fixation on pH 10 at 7, 28 & 90 Days of Curing
4.6.4.4 pH 14

Most of the metals were stabilized at pH 14. Some amount of Zn and Fe are leached at this pH because the solubility of these metals was more in alkaline media (Figure 4.6 (a,b,c)). The optimum pH is different for each metal often, for different valence state of a single metal. It may also vary for a specific metal ion with the presence of other species in solution with aging of the hydroxide. In the high alkaline pH, the metal may start to resolubilize. Most metal sulfides are less soluble than the hydroxides at alkaline pH [4.6]. Fixation at pH 14 presented in the figure 4 (a,b,c). 7 & 90 curing days gives best results of metal fixation in all samples.
Figure 4.6 (a): Zn Metal Fixation on pH 14 at 7, 28 & 90 Days of Curing

Figure 4.6 (b): Fe Metal Fixation on pH 14 at 7, 28 & 90 Days of Curing
Results indicate that 70% - 90% of metals (Fe, Zn & Cr) were retained in the concrete matrix. Wherever, Pb, Mn, Cu & Ni metals were completely fixed in the matrix. This fixation is probably due to the respeciation of metals in the form of non-stoichiometric silicates in the concrete matrix. Fixation of Cr with 7 days curing found more suitable among all the pH. The fixation of Heavy metals in the pH ranges from 2 – 14 is in order of Pb<Ni<Cr<Cu<Zn<Fe. The fixation trend has found to be influence by the manner in which the metals were incorporated into the concrete matrix. The partial replacement of sludge has less effect on the leaching behaviour of the concrete [4.20]. Solidification/stabilization is cost effective and easy to operate method with good efficiency to trap and immobilize heavy metals. The probable speciation of heavy metals in the cement matrix is in the form of metal hydroxides, nitrates and silicates. The metal
hydroxides exhibit minimum solubility after the pH 6. Below this pH, solubility increases rapidly [1.39, 1.65].

Theoretically, environment with pH lower than 12.5 may be predicted to be aggressive because a reduction of the alkalinity of the fluid would, eventually, lead to destabilization of the cementitious products of hydration. However, the rate of fixation in concrete is a function of the pH of the aggressive fluid and the permeability of concrete. When the permeability of the concrete is low and the pH of the aggressive water is above 6, the rate of heavy metal leaching is considerably low. Maximum leaching observed at pH 2, all metal hydroxide and silicate are leached out (Figure 4.3 (a, b, c, d, e)). Fixation of metals at different pHs are shown in the figure 4.3, 4.4, 4.5, 4.6; (a,b,c). It was observed that leaching at 28 days curing was high as compared to 7, 90 days curing for entire W/B (Waste/Binder) ratio [1.80].

Developed concrete could be considered is not harmful for the environment in terms of the leaching of heavy metals. The partial replacement of sludge has less effect on the leaching behaviour of the concrete.

4.7 FACTOR AFFECTING ON FIXATION OF HEAVY METALS IN DEVELOPED CONCRETE

4.7.1 Curing Days

Fixation of heavy metals is influence by curing days. Curing of the concrete is a very important process. After unmolding of concrete it should be prevented from the drying. Concrete samples were dip into the water for (15 – 30 minutes) twice in a day, which does not allow the concrete samples to dry. Enough moisture leads to promotes hydration
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and chemical reaction in concrete. Since the rate of hydration is influenced by cement composition and fineness. The curing period should be prolonged for concrete made with cements of slow chemical reactions. Therefore, Concrete samples were cured for longer duration of 90 days. Anhydrous cement compound mixed with water and react with each other to form hydrated compound of very low solubility. Cement compound dissolve to produce a super saturated solution from which different hydrated products get precipitated with strong bonding with heavy metals. Hydration process is not an instantaneous one. The reaction is faster in early period. Complete hydration can be obtained under a period of one year.

As the curing period increases the fixation of metals from concrete also increases and it becomes constant between 28 and 90 day of cured samples. At the end of 90 days of curing, the concentration of all metals were found to be well below the USEPA’s leaching limit required to secure landfill [2.13, 4.15, 4.21]. Fixation of the metals at different curing days are shown in the figure 4.5, 4.6, 4.7, 4.8: (a,b,c,d,e).

### 4.7.2 Waste/Binder Ratio

Effectiveness of the treatment was assessed by the mechanical test. Strength of the cementitious material is depends upon the three factors waste/binder ratio, water/solid ratio and compaction. Strengthen material helps in the immobilization of metals. Heavy metals are trapped in compacted material matrix due to less air pore volume and waste/binder ratio (Figure 3.3).
4.7.3 Water/Solid Ratio

Water/solid ratio is also an important factor which affects the fixation of metals. The requirement of water quantity is found higher in the developed concrete due to high water holding capacity of sludge. Water/cement and waste/binder ratio is higher than the water/solid ratio. The water solid ratio is in the range of 0.12 – 0.088 (Figure 3.3).

4.8 MICROSTRUCTURE OBSERVATIONS

Figure 4.8 represents the micrograph of pure sludge. SEM micrographs of surface of the concrete samples cured for 28 days are shown in figures 4.9 (a-j). A compared to pure concrete (Figure 4.9 (a)), when cement is substituted with fly ash, the resulting material shows the pozzolanic structures in micrograph (Figure 4.9 (b, e & h)). It is clear that the development of microstructure was delayed due the pozzolanic contribution of fly ash in the matrix, which resulted in the formation of clusters of hydrated products and other compound like CSH, portlandite, ettringite, metal complex etc. However, as waste was introduced in the matrix (Figure. 4.9 (c, d, f, g, i & j)), the morphology of the concrete was changed significantly indicating the formation of a denser structure as compared to pure and fly ash contained concrete. The morphology of the sludge mixed concrete appears good (Figure. 4.9 (d, g, & j)) because the cluster phase of hydration products were bigger and more in the presence of fly ash in it [3.15]. The amount of unhydrated C₃S decreased with increasing of time, as expected. The phases identified were: CSH gel, portlandite, ettringite Al₂O₃ etc. Bothe and Brown [3.16] pointed out that the hydration product, ettringite, was formed with high amount [3.10, 3.13]. Due to the formation of hydrogenate phases most of the heavy metal trapped in concrete. Ettringite is a hydrated
calcium aluminum sulfate hydroxide \((\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O})\). It is a mineral that rarely occurs in nature but is an important hydration product of Portland cement, formed from the reaction of calcium aluminate with calcium sulfate, affecting short term strength development \([4.22]\) and long term stability \((\text{Figure 4.7})\) \([4.23,4.24]\). The micrograph spectra showed the presence of large quantity of CSH that would be indicative of a pozzolanic reaction. The CSH gel phase is thought to be highly reactive and is most probably produced by copolymerization of individual calcium and silica species \([3.14]\). Ettringite is an important secondary hydration product which was commonly found in concrete.

![Figure 4.7: Crystal Structure Of Ettringite](Calcium, Oxygen, Aluminum, Sulfate Tetrahedral and hydrogen)

Most of the particles appeared to have lost their spherical morphology and had convert into gel which, in effect, was featureless mass devoid of any geometrical configuration \((\text{Figure 4.9 (a-j)})\). This represents the silica gel formation. Transformation of large pores into finer ones as a result of the pozzolanic reaction is said to play an important role in strength enhancement. Noteworthy microstructure features in this concrete included the development of strong bonding between paste and aggregate from very early age, the absence of oriented CH crystal at the interface, tubular CH crystal in
the paste and highly reactive amount of ettringite formation. Silicious gel particles with cement solution leads to the adsorption of OH-, Ca$^{2+}$ and alkalis on the silica. Ca$^{2+}$ is adsorbed much more strongly, whereas OH$^{-}$ adsorption initiates the dissolution process. Beyond 28 days consolidation of CSH structure results in the stabilization of CSH into different morphological type. The absence of CH in the transition zone and its replacement by CSH also help improve paste aggregate bonding. This type of bonding is far superior to the conventional one from the strength standpoint.

EDAX analysis has been performed to determine the composition of the developed matrix. Ca, O, Si, Al, Mg, K, Fe and Na have been detected in combinations of develop concrete. Ca content is higher in Cp and Sp (Figure 4.9 (a & b)). Fe metal is increases with increases in amount of sludge content (Figure 4.9 (c, f & i)). Excepting L$_2$ sample, all sample showed high amount of silica (Figure 4.9 (j)). From the result of EDAX analysis it is conformed that the developed concrete content high amount of silica, calcium, aluminum percentage. The interfacial area between the aggregate and aluminosilicate gel matrix is almost nonexistent which could mean that the adherence of the cementitious material with the aggregate is good.

Figure 4.8: Micrograph of pure sludge
Figure 4.9 (a): EDAX & Micrograph of Cₐ

Figure 4.9 (b): EDAX & Micrograph of Sₚ

Figure 4.9 (c): EDAX & Micrograph of S₁
Figure 4.9 (d): EDAX & Micrograph of $S_2$

Figure 4.9 (e): EDAX & Micrograph of $F_p$

Figure 4.9 (f): EDAX & Micrograph of $F_i$
Figure 4.9 (g): EDAX & Micrograph of F

Figure 4.9 (h): EDAX & Micrograph of Lp

Figure 4.9 (i): EDAX & Micrograph of L₁
4.9 CONCLUSIONS

It is concluded that to evaluate a particular concrete formulation before predicting its performance in acid environment. At least under certain circumstances the addition of fly ash can improve the acid resistance of concrete. The UCS and leaching of metals indicate that cement solidification/stabilization is effective for heavy metals bearing waste. The heavy metals bearing waste was stabilized by using OPC in a waste/binder ratio of 0.5–4.0. Fixation of metals increases with increase in the pH up to 8. Fixed pH for each leaching test affected the conductivity of the sample. Lowest pH shows high conductivity and its decreases with pH. Leaching pattern for anions and cations was similar for 7, 28 and 90 days of curing and fixed at 6 -10 pH. The leaching behaviour of heavy metal is indeed known to be pH dependent. Fixation of metals increased with increase in the pH up to 8, after that solubility increased. 28 and 90 days of curing are sufficient for the fixation of heavy metals present in the waste. Another finding of these experiments is that, the risk of contamination due to release of heavy metals from concrete on-site appears low. Fe fixation is found minimum rather than other metals due high content in
raw material. Ni, Mn and Pb were found in very least amount, they were completely fixed easily in the developed matrix. It is clear from the SEM micrographs of concrete samples cured for 28 days that the development of microstructure was improved due the pozzolanic contribution, which resulted in the formation of clusters of hydrated products and other compound like CSH, portlandite, ettringite, metal complex etc. Ettringite & CSH are important hydration product commonly found in concrete. Due to the formation of hydrogenate phases most of the heavy metal trapped in concrete. Excepting L2 sample, all sample shows high amount of crystalline structure. It is conformed by EDAX analysis that the developed concrete content high amount of silica, calcium, aluminum percentage.

PART B - GEOCHEMICAL MODELING AND STATISTICAL ANALYSIS OF DEVELOPED CONCRETE

4.10 GEOCHEMICAL MODELING

Heavy metals leaching process of hazardous waste and by-product have been found to be controlled by pH condition, when these materials are used in construction. They will be exposed to leaching by percolating through rainwater. In many circumstances, the pH in the leaching processes is also controlled by reaction of waste. The environment was affected by the release of toxic elements from the matrix at certain pH [4.25].

The acid base chemistry of the system was depend on the by dissolved acidic or alkaline substances, pH value, acid neutralising capacity (ANC) or base neutralising capacity (BNC) as well as buffer intensity of the system. The neutralizing capacity at different pH levels were considered to be one of the most important acid/base properties of the waste. The hazardous waste was heterogeneous in nature. Modeling provides a
way to an insight into a part of the neutralizing processes for this complex system. In addition, geochemical speciation modeling is useful insights into leaching behavior, as it provides information on possible solubility controlling mineral phases [4.25-4.27], although the above framework provides the specific basis for evaluation of inorganic and heavy metal constituents in the waste. Most of the heavy metals were fixed in the matrix of cement binder has been reported [4.28-4.33].

4.10.1 Methodology of Geochemical Modeling

The modeling has been performed by using a geochemical model (MINTEQ Version 3.2) developed by U.S. EPA [4.34] that calculates values on the basis of chemical equilibriums. A program has created that changed the input file of MINTEQ, based on the change of the variables. Consequently, MINTEQ has run and the essential concentration values have collected from the results file. These data have served as a basis for graph of metal concentration present in the developed concrete (Figure 4.10).

![Image](image_url)

Figure 4.10 Virtual Plan of Experimental and Geochemical Modeling
4.10.2 Result and Discussion

Previously MINTEQ model has been used by many researchers to evaluate the mobility of heavy metals in waste and other materials. Modeling of the matrix can play a significant role in prediction of long-term release of heavy metal species, which was pH dependent [4.35]. The conversion of calcium hydroxide to calcium carbonate has been found to reduce leachate pH towards 8 for Portland cement based matrices [4.36, 4.37]. Metals are efficiently stabilized when the pH is raised above 6 – 11 for all developed concrete samples (Figure 4.13 (a-o)). While the heavy metal solubility tends has increased dramatically at > 6 and < 11 pH. Graphical representation of heavy metal formed with different curing days (7, 28 and 90 days), which are given in figure 4.11 (a, b, c, d, e, f, g, h, i, j, k, l, m, n, o). Zinc has effective stabilized by adjusting the pH between 6 – 10 on 7 and 90 days of curing period (Figure 4.11 (a, b, c)). Zinc metal gives inconsistent result for 28 days cured samples at alkaline pH. Maximum stabilization of Iron has been found at 6 pH with less effect of curing days (Figure 4.11 (d-f)). Heavy metals that exhibit this kind of behaviour with increased solubility at both high and low pH values are often referred to as amphoteric in nature. Chromium concentration has been decreased after pH 6. Curing age was not significantly affected chromium leaching (Figure 4.11 (j-i)). Copper and iron are in the high amount in the waste, which leached more than other metals. Cu metal is below detectable limit in Cp & Sp at 7 days curing (Figure 4.11 (g)). Curing of 7 days is better for copper stabilization. Ni metal is below detectable limit in Cp, Sp, Fp & Lp (Figure 4.11 (m-o)).

On the basis of above discussion pH leaching test reveal information on heavy metal speciation behaviour and its solubility [4.38]. The pH control and chemical
speciation are the main factors governing the solubility of inorganic components in stabilized matrix [4.15]. The formation of insoluble metal hydroxides, metal silicates and metal sulfides are important chemical specification reactions. Entrainment and acidic aggression of leachant continuously deplete the alkaline material contained in concrete system. The speciation of heavy metals is very important to describe the form of the metal available for any subsequent stabilization mechanisms and is strongly dependent upon the pH of the solution [4.37, 4.39]. The hydroxide is more likely to combine with the cation. Therefore, the cations are more likely to react with the silicate at pH 8 than 10. The cations are more likely to react with hydroxide at pH 10 than 8. This observation tends to confirm that the metal ions are chemically bound within two different environments at these pH levels [4.30, 4.32, 4.40, 4.41]. The model was run with different combinations in order to determine the effect of pH alterations [2.4].

Figure 4.11 (a): Leached Concentration of Zn

![Graph showing Zn Metal Concentration (mg/kg) vs pH for 7 Days curing](image-url)
Figure 4.11 (b): Leached Concentration of Zn

Figure 4.11 (c): Leached Concentration of Zn
Figure 4.11 (d): Leached Concentration of Fe

Figure 4.11 (e): Leached Concentration of Fe
Figure 4.11 (f): Leached Concentration of Fe

Figure 4.11 (g): Leached Concentration of Cu
Figure 4.11 (h): Leached Concentration of Cu

Figure 4.11 (i): Leached Concentration of Cu
Figure 4.11 (j): Leached Concentration of Cr

Figure 4.11 (k): Leached Concentration of Cr
Figure 4.11 (I): Leached Concentration of Ni

Figure 4.11 (m): Leached Concentration of Ni
4.11 STATISTICAL ANALYSIS

Statistical interpretation plays an important role in the prediction of results and correlation between parameters. The precision parameters of the method were determined and the variance of the entire data set was apportioned among the sources of variation. The systematic differences between participating laboratories and heterogeneity of the samples were identified as major source of variability of results [4.35, 4.42, 4.43].

This statistical analysis was determined by two ways:

- Univariant analysis
- Multivariate analysis
4.11.1 Univariant analysis

Univariant statistical analysis is appropriate technique to find out the correlation between two parameters. This regression analysis can be used any type of relationship. Degree of relationship between two variables is presented by the means of correlation coefficient \( R^2 \) [4.35, 4.42, 4.43]. The statistical analysis is obtained by the regression analysis method (equation 4.1, 4.2 & 4.3) [4.44].

\[
R = \frac{CoV(X,Y)}{SD(X) \times SD(Y)} \quad (4.1)
\]

\[
= \frac{\sum (X_i - \bar{X})(Y_i - \bar{Y})/(N-1)}{SD(X) \times SD(Y)} \quad (4.2)
\]

\[
SD(X) = \sqrt{\frac{\sum (X_i - \bar{X})^2}{N-1}} \quad (4.3)
\]

Where, \((X_i, Y_i)\) = Observation for pair of parameters, \(N\) = Number of observations,

\(\bar{X}\) = Mean of \(X\), \(\bar{Y}\) = mean of \(Y\)

The square of correlation coefficient is termed as coefficient of determination. A coefficient of determination of 0.9 implies that approximately 90% of the variance, if at any pH or any sample showed value less than 6, that pH or sample can be omitted. The value of \(R^2\) is increases with the stabilization of metals. The highest value of the \(R^2\) is 1, which represents highest correlation between parameters. The numerical value of the correlation coefficient between two variables is grater this exhibits highest correlation and a linear relationship is given by the straight line equation (4.4).

\[
Y = mX + C \quad (4.4)
\]

Where, \(m\) = Slope of regression line, \(C\) = Intercept with Y axis

For the calculation of \(R^2\) the value \(m\) and \(C\) is given by equation 5 & 6.
\[
m = \frac{n \times \sum (XY) - \sum X \times \sum Y}{n \times \sum (X \times \bar{X})^2}
\]  

(4.5)

\[
C = \bar{Y} - m\bar{X}
\]  

(4.6)

Where, \( \bar{X} = \frac{\sum X}{n} \) and \( \bar{Y} = \frac{\sum Y}{n} \)

Following parameters have been selected for the correlation analysis (i) pH (ii) leaching of the metals (iii) curing days. Correlation in above mentioned parameters has been investigated separately for each metal (Zn, Fe, Cu, Cr & Ni). Parameters have statistically significant correlation with metals. The visual evaluation of the relationship between parameters has carried out by plotting the data for individual and clubbed data of samples at different curing days table 4.7, 4.8, 4.9 (a & b).

4.11.2 Multivariate Analysis

Multivariate analysis is use to perform factor analysis through Minitab -15 software [2.23, 2.24, 4.44].

4.11.2.1 Factor or principal component Analysis

Factor analysis is use to summarize the data covariance structure into a smaller number of dimensions. The emphasis in factor analysis is to describe the covariance among variables in terms of a few underlaying unobservable random quantities or factors.

Curing days (7, 28, 90) were measured on different characteristics like different combinations of concrete (Cp, Sp, Fp, Lp, S1, S2, F1, F2, L1, L2) pH, EC, Heavy metals (Fe, Cu, Zn, Cr, Ni) anions (Cl, SO4) and cation (Na, K) leaching.
Variance is variability in the data explained by each factor. Variance is equals to the eigenvalue of the correlation matrix of the factor in the unrotated solution. % var is the proportion of the variability in the data explained by the each factor. Loading represent how much a factor explain a variable. High loading (positive or negative) indicate that the factor strongly influences the variable. Low loading (positive or negative) indicate that the factor has weak influence on the variable. Communality (h²) is 1, which indicates better the variable is explained by the factors. It shows how much the each variable is account for by the under laying factors taken together (eq. 4.7).

$$h^2_{\text{for the } i^{th} \text{ variable}} = \frac{(i^{th} \text{ factor})^2}{\text{Loading of factor A}} + \frac{(i^{th} \text{ factor})^2}{\text{Loading of factor B}} + \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4.7)$$

Rotation: Factor rotation simplifies the loading structure, allow to more easily interpret the factor loadings. There are four methods to orthogonally rotate the initial factor loadings:

Equimax - maximizes variance of squared loadings within both variables and factors.

Varimax - maximizes variance of squared loadings within factors (i.e. simplifies the columns of the loading matrix); the most widely used rotation method.

Quartimax - maximizes variance of squared loadings within variables (i.e. simplifies the rows of the loading matrix).

Orthomax - rotation that comprises the above three depending on the value of the parameter gamma (0-1).

Varimax rotation is used for the factor analysis because this method attempts to make the loadings either large or small to ease interpretation. The percent of the total variability explained by the factors does not change with rotation and the communalities remain the
same. But after rotation, the factors are more evenly balanced in the percent of variability.

4.11.3 Result and Discussion

Average correlation of metals were observed for pH 10 and 14 (Figure 4.12, 4.13, 4.14, 4.15, 4.16 (a,b,c)). X axis represent samples code where 1 is stand for Cp, 2=Sp, 3=Fp, 4=Lp, 5=S1, 6=S2, 7=F1, 8=F2, 9=L1, 10=L2 and Y axis shows log of release (Figure 4.13 – 4.16 (a,b,c)).

Analysis result shows there is a significant correlation between parameters. All samples showed the highest correlation with pH 2. The highly correlated metals are Fe & Zn at different curing days. Nickel metal, anion and cation species showed lowest correlation.

Different curing days is highly correlated with metals leaching. pH 2 & 10 appears to be highly correlated with leaching concentration of metals. These are pH show maximum leaching of metals. Correlation coefficient has increased in order of Zn>Fe>Cu>Cr>Ni. Each metal has its own reacting behavior, which varies with days of curing, pH and mixed composition of sample.
Figure 4.12: Correlation Coefficient For pH & EC at 7, 28 & 90 Days Of Curing (2-14 pH)
Figure 4.13: Correlation Coefficient For Leached Metal at 7, 28 & 90 Days Of Curing And 2 pH
Figure 4.14: Correlation Coefficient For Leached Metal at 7, 28 & 90 Days Of Curing And 6 pH
Figure 4.15: Correlation Coefficient For Leached Metal at 7, 28 & 90 Days Of Curing And 10 pH
Figure 4.16: Correlation Coefficient For Leached Metal at 7, 28 & 90 Days Of Curing And 14 pH
There is a perfect linear relationship between samples and 7 days of curing. Fe, Zn, Cu, Cr and Ni leaching show high coefficient value at 7 and 28 days of curing (Figure 4.13 (a, b). Leaching of Ni does not appear to be related to observe curing days. Samples are released high concentration of metals in leachate at 2 & 4 pH after stabilization, compared with pH 12 & 14. Correlation coefficient value is high for each sample at acidic pH and low at pH 6-10 [2.4, 4.28, 4.31, 4.33].

Scree or eigenvalue plot is the graph of the factor versus the corresponding eigenvalues. Eigenvalue measured the amount of variance in the variable samples accounted by each factor. Principal component are shorted decreasing order of variance. First two components show the much more of the variance in the data. If the factor has allow eigenvalue than it is contributing little to the explanation of variance in the variable.

Score plot graphs generated between the second factor scores versus the first factor scores. The plot of the factors provides checks on the assumption of normality and reveals outliers. The first two components account for most of the variance in the data, the score plot is used to assess the data structure and detect clusters, outliers, and trends.

Biplot overlays the score and loading plots. The loading provides information about the loadings of the first two factors. Use the biplot to assess the data structure and loadings on one graph. The second principal component scores are plotted versus the first principal component scores.
4.11.3.1 Factor Analysis on 7 Days Cured Samples

First five factor accounts highest variability in data. Remaining factor shows small portion of the variability in data and 9-11 are likely unimportant (Figure 4.17 (a)). The data appear normal no outliers are apparent (Figure 4.17 (b)). Data follow a normal distribution and the points are randomly distributed around zero. Large positive loading is observed for Fe and Cu metal (Figure 4.17 (c)). Principal component and communality are given in table 4.7.

Figure 4.17 (a): Scree Plot at 7 Days Curing
4.11.3.1 Factor Analysis on 7 Days Cured Samples
First five factor accounts highest variability in data. Remaining factor shows small portion of the variability in data and 9-11 are likely unimportant (Figure 4.17 (a)). The data appear normal no outliers are apparent (Figure 4.17 (b)). Data follow a normal distribution and the points are randomly distributed around zero. Large positive loading is observed for Fe and Cu metal (Figure 4.17 (c)). Principal component and communality are given in table 4.7.

Figure 4.17 (a): Scree Plot at 7 Days Curing
Figure 4.17 (b): Score Plot at 7 Days Curing

Figure 4.17 (c): Biplot at 7 Days Curing
Table 4.7: Principal Component Factor Analysis of the Covariance Matrix for 7 Days Cured Samples

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<tr>
<th></th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
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<th>F6</th>
<th>F7</th>
<th>F8</th>
<th>F9</th>
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<td>Variance</td>
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<td>162.92</td>
<td>107.88</td>
<td>14.11</td>
<td>12.43</td>
<td>5.66</td>
<td>2.06</td>
<td>0.82</td>
<td>0.26</td>
<td>0.13</td>
<td>1086.00</td>
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<td>% Var</td>
<td>0.718</td>
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<td>0.099</td>
<td>0.013</td>
<td>0.011</td>
<td>0.005</td>
<td>0.002</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
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Rotated Factor Loadings and Communalities (Varimax Rotation)

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<tr>
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<th>F1</th>
<th>F2</th>
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<th>F7</th>
<th>F8</th>
<th>F9</th>
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<tr>
<td>Variance</td>
<td>487.74</td>
<td>161.85</td>
<td>87.58</td>
<td>76.82</td>
<td>76.08</td>
<td>70.20</td>
<td>69.97</td>
<td>29.73</td>
<td>24.23</td>
<td>1.80</td>
<td>1086.00</td>
</tr>
<tr>
<td>% Var</td>
<td>0.449</td>
<td>0.149</td>
<td>0.081</td>
<td>0.071</td>
<td>0.070</td>
<td>0.065</td>
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<td>0.022</td>
<td>0.002</td>
<td>1.000</td>
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F = Factor, C = Communality
4.11.3.2 Factor Analysis on 28 Days Cured Samples

First six factor accounts highest variability in data. Remaining factor shows small variability in data and are likely unimportant (Figure 4.18 (a)). The data is found in clusters there are groupings of points and not randomly distributed near zero (Figure 4.18 (b)). Large positive loading is observed for Na and Cu metal (Figure 4.18 (c)). Principal component factor analysis of the covariance matrix are given in table 4.8.

Figure 4.18 (a): Scree Plot at 28 Days Curing
4.11.3.2 Factor Analysis on 28 Days Cured Samples

First six factor accounts highest variability in data. Remaining factor shows small variability in data and are likely unimportant (Figure 4.18 (a)). The data is found in clusters there are groupings of points and not randomly distributed near zero (Figure 4.18 (b)). Large positive loading is observed for Na and Cu metal (Figure 4.18 (c)). Principal component factor analysis of the covariance matrix are given in table 4.8.

Figure 4.18 (a): Scree Plot at 28 Days Curing
Figure 4.18 (b): Score Plot at 28 Days Curing

Figure 4.18 (c): Biplot at 28 Days Curing
Table 4.8: Principal Component Factor Analysis of the Covariance Matrix for 28 Days Cured Samples

### Unrotated Factor Loadings and Communalities

<table>
<thead>
<tr>
<th></th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
<th>F6</th>
<th>F7</th>
<th>F8</th>
<th>F9</th>
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<tbody>
<tr>
<td>Variance</td>
<td>1602.8</td>
<td>670.6</td>
<td>103.9</td>
<td>30.4</td>
<td>17.7</td>
<td>13.7</td>
<td>6.0</td>
<td>0.7</td>
<td>0.4</td>
<td>0.1</td>
<td>2446.2</td>
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<tr>
<td>% Var</td>
<td>0.655</td>
<td>0.274</td>
<td>0.042</td>
<td>0.012</td>
<td>0.007</td>
<td>0.006</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
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</tr>
</tbody>
</table>

### Rotated Factor Loadings and Communalities (Varimax Rotation)

<table>
<thead>
<tr>
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<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
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<th>F8</th>
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<th>F10</th>
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</thead>
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<tr>
<td>Variance</td>
<td>1057.1</td>
<td>725.3</td>
<td>207.3</td>
<td>166.0</td>
<td>84.6</td>
<td>72.3</td>
<td>54.2</td>
<td>48.2</td>
<td>29.9</td>
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<td>2446.2</td>
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<tr>
<td>% Var</td>
<td>0.432</td>
<td>0.297</td>
<td>0.085</td>
<td>0.068</td>
<td>0.035</td>
<td>0.030</td>
<td>0.022</td>
<td>0.020</td>
<td>0.012</td>
<td>0.000</td>
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F = Factor, C = Communality
4.11.3.3 Factor Analysis on 90 Days Cured Samples

First five factor accounts highest variability in data. 6-11 factor shows small variability in data and are likely unimportant (Figure 4.15 (a)). No outliers are apparent and points are randomly distributed near zero (Figure 4.15 (b)). Large positive loading is observed for Na and Cu metal (Figure 4.15 (c)). Principal Component Factor Analysis of the Covariance Matrix of 90 days cured samples are given in table 4.9.

Figure 4.19 (a): Scree Plot at 90 Days Curing
4.11.3.3 Factor Analysis on 90 Days Cured Samples

First five factor accounts highest variability in data. 6-11 factor shows small variability in data and are likely unimportant (Figure 4.15 (a)). No outliers are apparent and points are randomly distributed near zero (Figure 4.15 (b)). Large positive loading is observed for Na and Cu metal (Figure 4.15 (c)). Principal Component Factor Analysis of the Covariance Matrix of 90 days cured samples are given in table 4.9.

Figure 4.19 (a): Scree Plot at 90 Days Curing
Figure 4.19 (b): Score Plot at 90 Days Curing

Figure 4.19 (c): Biplot at 90 Days Curing
Table 4.9: Principal Component Factor Analysis of the Covariance Matrix for 90 Days Cured Samples

<table>
<thead>
<tr>
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<tr>
<td>Variance</td>
<td>2046.4</td>
<td>860.6</td>
<td>98.8</td>
<td>92.3</td>
<td>20.1</td>
<td>14.7</td>
<td>9.4</td>
<td>5.1</td>
<td>0.8</td>
<td>0.2</td>
<td>3148.4</td>
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<tr>
<td>% Var</td>
<td>0.650</td>
<td>0.273</td>
<td>0.031</td>
<td>0.029</td>
<td>0.006</td>
<td>0.005</td>
<td>0.003</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Rotated Factor Loadings and Communalities (Varimax Rotation)

<table>
<thead>
<tr>
<th></th>
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<th>F2</th>
<th>F3</th>
<th>F4</th>
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<th>F8</th>
<th>F9</th>
<th>F10</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variance</td>
<td>1070.0</td>
<td>1011.0</td>
<td>394.0</td>
<td>170.7</td>
<td>122.9</td>
<td>109.1</td>
<td>94.9</td>
<td>84.2</td>
<td>54.5</td>
<td>37.1</td>
<td>3148.4</td>
</tr>
<tr>
<td>% Var</td>
<td>0.340</td>
<td>0.321</td>
<td>0.125</td>
<td>0.054</td>
<td>0.039</td>
<td>0.035</td>
<td>0.030</td>
<td>0.027</td>
<td>0.017</td>
<td>0.012</td>
<td>1.000</td>
</tr>
</tbody>
</table>

F = Factor, C = Communality
4.12 CONCLUSIONS

MINTEQ model has been used to predict quantitative stabilization of heavy metals in matrix. The computed results showed that increasing addition of alkaline binder is more effective to improve the stability of heavy metals in the matrix. Alkaline pH values can also increase the solubility of heavy metals like acidic pH for some metals. Already, the concentration levels encountered in leachate for a variety of constituents are relatively low and would not require further treatment. This indicates that in spite of an apparently very heterogeneous mix of materials, leaching is governed by well defined solubility controls for many constituents. The key aspect is to identify, which waste streams or external stresses can affect this balance in such a way that control is lost. Curing days referred for these type of samples are 28 and 90 days. Some heavy metals stabilization is not affected by the days of curing. pH range from 6 – 10 is more acceptable to developed concrete.

The results showed that acidic pH have correlation in the range of 0.272–0.988. This indicates the efficiency of the coefficient after addition of fly ash and waste matrix. A reduced leaching of metals after stabilization was observed by univariant analysis, whereas the leaching of metals in samples from correlation coefficient decreases significantly after stabilization. Each metal showed different correlation coefficient at different pH and days of curing. Correlation coefficient is higher for pH 2 due to maximum leaching of heavy metals. But 90 days cured samples shows lowest correlation coefficient and gives best results.

First five factor accounts highest variability in data for 7, 28 and 90 days of curing. The data appear normal for 7, 90 days and cluster structure has found on 28 days cured
samples. The large positive loading has been observed for Cp, Sp, Fp, Lp, F1, L1, L2 factors, while samples S1, S2, F1, and F2 find most suitable for further analysis. The data appear normal; no outliers have been apparent. High positive loading was observed for Fe, Na, and Cu for 7, 28, and 90 days of curing, respectively. The scree plot, score plot, and biplot show the highest correlation for 7 days cured samples. Communality is 1 for all days of curing and parameters.
samples. The large positive loading has observed for Cp, Sp, Fp, Lp, F1, L1, L2 factors, while samples S1, S2, F1 and F2 find most suitable for further analysis. The data appear normal no outliers have apparent. High positive loading was observed for Fe, Na and Cu for 7, 28, 90 days of curing respectively. The scree plot, score plot and biplot show the highest correlation for 7 days cured samples. Communality is 1 for all days of curing and parameters.
REFERENCES


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