Immobilization of heavy metals from steel plating industry sludge using cement as binder at different pH

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Abstract: Solidification and stabilization of hazardous sludge from steel plating industry containing Fe, Ni, Cr, Zn, Cu and Mn using cement can restrict the mobility of heavy metals due to high pH and capability of cement to precipitate the metals in insoluble form. Many leaching tests are available to evaluate the leaching characteristic of solidified matrix. Leaching of heavy metals from solidified matrix using Toxicity Characteristic Leaching Procedure (TCLP) at different pH are studied in the present paper. Different combination of cement and sludge has been used to study the leaching behavior of heavy metals from solidified matrix at different pH. Upto 80% sludge can be stabilized using cement as a binder. Compressive strength of solidified matrix required for secure landfill is also studied. Compressive strength decreases with the increase in the sludge ratio. Though TCLP study shows higher leaching concentrations of heavy metals, leaching of all metals using both tests are well below USEPA's limit for maximum sludge ratio upto 80% used with respect to cement. The broad objective of the S/S process is to contain waste contaminant and prevent or minimize the release of the contaminant into the environment.

Keywords: Solidification and Stabilization; Toxicity Characteristic Leaching Procedure (TCLP); Compressive strength.

INTRODUCTION

Steel processing unit generates hazardous iron oxide ash along with chromium, nickel, copper, zinc and manganese as a major constituent. Disposal of such waste containing high content of heavy metals could cause serious environmental and ecological problems. (Federal Register, 1990) It is therefore desirable to give proper treatment to the waste before disposal, so that the soluble constituent present can restricted to mobilization. Stabilization/solidification (S/S) is one of the major methods in treating hazardous wastes prior to land disposal (Weitzman, 1990). It involves adding one or more solidifying reagents to a waste and turning it into a monolithic solid with some structural integrity. The mechanism of S/S is believed to be through chemical stabilization and physical encapsulation (Halim et al., 2004). The leaching of hazardous components from S/S treated wastes is hence reduced and the final product may be easier to handle and transport than the original waste (LaGrega, et al., 1994, Chaudhary, 2004). Portland cement along with the different combination can restrict the mobility of heavy metals due to high pH and capability of cement to precipitate the metals in insoluble form. Among various binders, Portland cement is one of the most regular binders used for S/S matrix. This stabilization process relies on the formation of calcium silicate hydrate (CaO·SiO₂·nH₂O, briefly as C–S–H), ettringite hydrate (3CaO·Al₂O₃·3CaSO₄·32H₂O, abbreviated as AFT) and monosulphate (3CaO·Al₂O₃·CaSO₄·12H₂O, abbreviated as AFm) in the matrix, due to the hydration reaction of Portland cement, and thus the heavy metals both chemically fixed in the lattice of hydration production and physically encapsulated in the matrix. (Jones, 1990, Fu et al., 2003, Mollah, et al., 2000).
MATERIALS AND METHODS
Hazardous solid waste was collected from Unison Metal Ltd, Manufactures and Resources of Stainless Steel hot/cold Patta, Ahmedabad, India. All chemicals used were of analytical grade (AR). Zinc Nitrate, Ferrous sulfate, Nickel nitrate, chromium nitrate, lead nitrate, copper nitrate, NaOH, and HNO₃ were purchased from Merck (India) Ltd. Cement used for casting cubes was 53 grades Ordinary Portland Cement manufactured by M/s Ambuja Cement Pvt Ltd. Casting of six cubes at a time of size 25.4mm X 25.4mm X 25.4mm (1in X 1in X 1 in) were carried out using a mold made of acrylic specially designed at CESE, IIT Bombay, workshop. Size of cube was according to ASTM STP 897 (Lin et al., 2004,).

RESULT AND DISCUSSION
Microwave Digestion of Hazardous Sludge Cement
Heavy metals concentration present in cement and black sludge was analyzed using microwave digestion method. Aqua regia was used to extract heavy metals. Temperature program for microwave digestion is shown in table 1.

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Temp (°C)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>5</td>
</tr>
</tbody>
</table>

Extract was filtered and makeup with deionized water to 100 ml. AAS (Model GBC 908, Make: Australia and ICP (Ultima 2000, Horriba Jyobin, Make France) were used for analyzing metal concentration in the extract.

Physical Characteristics
The physical characteristics of the hazardous solid is given in table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry density (g/cm³)</td>
<td>1.25</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.98</td>
</tr>
<tr>
<td>Specific gravity (%)</td>
<td>1.65</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>24</td>
</tr>
<tr>
<td>Water holding capacity (%)</td>
<td>21</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>9.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
<tr>
<td>Conductivity (mS)</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Heavy Metal Content
Concentration of various heavy metals initially present in the hazardous solid waste as obtained from the industry and their respective total leachable content (as per microwave digestion method) are shown in table 3. Concentration of the metals in the leachate of cube having optimum cement, solid waste combination after 112 days curing are also shown.
Table 3. Concentration of metals and other ions extracted using aqua regia

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>Heavy metal</th>
<th>Conc. (mg/Kg) (Total Metal)</th>
<th>Conc. (mg/Kg) (TCLP Extract)</th>
<th>Conc of metals in leachate after curing of 112 days for optimum combination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe</td>
<td>106,000</td>
<td>1276</td>
<td>190.0</td>
</tr>
<tr>
<td>2</td>
<td>Cr</td>
<td>9640</td>
<td>26</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>Ni</td>
<td>565</td>
<td>156</td>
<td>28.0</td>
</tr>
<tr>
<td>4</td>
<td>Cu</td>
<td>1220</td>
<td>542</td>
<td>75.0</td>
</tr>
<tr>
<td>5</td>
<td>Mn</td>
<td>17500</td>
<td>679</td>
<td>48.0</td>
</tr>
<tr>
<td>6</td>
<td>Zn</td>
<td>480</td>
<td>310</td>
<td>95.0</td>
</tr>
</tbody>
</table>

Compressive Strength Study

Compressive strength for all the combinations was found to be well above the required strength for landfill. Presence of iron seems to govern the strength to the solidified matrix (Tashiro, 1977, Minocha et al., 2003). Compressive strength of the solidified matrix for the combination of 20:80 cement to hazardous solid waste is shown in figure 1.

Figure 1. Compressive strength of 20:80 cement to hazardous waste combination

Optimum Combination Based on Leaching Study

Different ratios of cement and hazardous solid waste were tested for its leaching behaviour and compressive strength (detailed results not shown). From the experimental results it was seen that up to 20:80 combination of cement and hazardous solid waste can be successfully stabilized accomplishing minimum leaching of heavy metals below USEPA’s limit with maximum compressive strength required for secure landfill.

It was found that, the leaching of iron, manganese and copper for all combinations below 20:80 cement to waste ratio was maximum for the 3 day curing sample. As the curing time was increased the leaching rate of heavy metals from the solidified matrix reduces (Shively, et al., 1986, Chaudhary, 2004). Depending on the leaching study, and compressive strength, optimum combination found was 20:80 cement to solid waste. Leaching of heavy metal using TCLP test is shown in the figure 2 (a).

Effect of pH for Optimum Combination

Observing the TCLP leaching results for various combination, 20:80 cement and solid waste ratio was found to be most optimum combination required for solidification and stabilization of hazardous solid waste. Optimum combination of cement and solid waste (20:80 ratio) was further tested for the effect of different pH on the leaching of heavy metals. After curing the sample from 3 days to 112 days the TCLP test with different leachate pH was carried out Variations in leaching are shown in figure 2 (a-d).
Figure 2(a). Effect of pH 2.88 on the 20:80 cement and solid waste ratio

Figure 2(b). Effect of pH 4 on the 20:80 cement and solid waste ratio

Figure 2(c). Effect of pH 6 on the 20:80 cement and solid waste ratio

Figure 2(d). Effect of pH 8 on the 20:80 cement and solid waste ratio

Figure 2. TCLP test for 20:80 cement to solid waste combination with varying pH of extract, viz (a) pH 2.88 (b) pH 4.0 (c) pH 6.0 (d) pH 8.0

Maximum leaching of all six metals was observed when TCLP extract having pH 2.88 was used. Leaching of metals from the solidified matrix cured of 3 days was found to be high (Diet, et al., 1998). As the curing period increases the leaching rate of metals from the solid cube decreases and it becomes constant between 56 and 112 day of curing of solid cube. At the end of 112 days of curing, the concentration of all metals were found to be well below the USEPA's leaching limit required for secure landfill. When alkaline extract with pH 8 was used for leaching of metals from solid cube, leaching of manganese and zinc was more as compared to the leaching concentration of both metal ions using extract with pH 6.

Surface Analysis of Solidified Cube Using (SEM)

SEM analysis of the solid sample containing 80 percentage solid waste and 20 percentage cement was done. SEM images are as shown in figure 3.

Figure 3 SEM image of solid matrix (optimum combination) magnified at (a) 160x and (b) 1100x
CONCLUSIONS

1. Solidification and stabilization is cost effective and easy to operate method with good efficiency to trap and immobilize heavy metals.

2. 20:80 ratio of cement and solid waste showed minimum leaching of all heavy metals well below the USEPA's limit after 112 days of curing using TCLP analysis. Iron showed leaching of 190 mg/kg along with leaching of 95 mg/kg of Zinc, 48 mg/kg of manganese, 75mg/kg of copper, 4.5 mg/kg of total chromium and 28 mg/kg of nickel.

3. Leaching of metals (manganese and zinc) decreases with increase in the pH of TCLP extract up to pH 6, after that it increases with increase in the pH.

REFERENCES


