Abstract

Objectives: Heavy metal contaminated land is increasingly becoming an important environmental, health, economic, and planning issue in the World. The unplanned disposal of heavy metal containing wastes, has resulted in a multi fold increase in environmental issues. Around 2.2 Lakhs tons of Chromium Ore Processing Residue (COPR) is left untreated at Ranipet SIPCOT Industrial complex. Solidification technique is proposed for the safe disposal of COPR in this study.

Methods/Analysis: Solidification process curtails migration of contaminants from the Cr(VI) bearing waste and reduces the toxicity of Cr(VI). In the present study ceramic composite are used as binding material. Mixture of COPR and ceramic composite in different ratios are verified at 1000 & 1200 °C. The resultant composite has more strength and are bound like solid matrix, thereby avoid leaching of metal ions trapped in the middle. Findings: It is observed that more than 98% fixation is possible at specific composition. Leaching ability at 1200 °C is very low than it observed for 1000 °C. Compressibility strength also depends upon the temperature. Composition of the composite influences compressibility test. Novelty/Improvement: The vitrified composite of COPR and ceramic at 1200°C has acceptable non leachable character with porcelain tiles of appearance. It may be used in construction activity.

Keywords: Ceramic Solidification, Chromium(VI), Chromium Ore Processing Residue, Leaching ability

1. Introduction

The inappropriate disposal and accidental release of hazardous and toxic substances into environment from industrial activities have created adverse environmental1,2 and public health problems all over the world. Heavy metals are really hazardous constituents. Chemical and thermal treatments may convert them into their salts which in turn give back metal by the environmental reactions. It is therefore essential to convert metal into most insoluble form to prevent their re-entry into the environment. Presence of certain metals in the environment are hazardous in one way or other to humans and/or to other forms of life in the form of acute or chronic toxicity3 or the metal may act in subtler ways, causing cancer and other secondary effect diseases or damage to foetus.

The defunct industry M/s. Tamil Nadu Chromates and Chemicals Limited, located in Plot No.25, SIPCOT Industrial Estate, Ranipet, Vellore District, Tamilnadu, India has dumped about 2,20,000 Tons of residue/waste [Chromite Ore Processing Residue (COPR)] generated from its process within the premises in a haphazard manner. The Cr(VI) salts are very soluble in water and pose health hazard to humans since it is carcinogenic. This poses severe environmental threat to the ground water (Figure 1) and environment and need war footing remedial action since 2001.

2. Materials and Methods

2.1 Estimation of Chromium in COPR Sample

COPR sample is analyzed by IVC Labs, Perungudi, Chennai-96 for the Cr content using Shimadzu AA7000 Atomic Absorption Spectrophotometer.
2.2 Concept of Solidification / Stabilization

Solidification and Stabilization (S/S) is a process that involves mixing of binding materials/additives with waste to minimize the rate of contaminants migration from the waste and to reduce the toxicity of waste\textsuperscript{4-9}. The contaminants are fully or partially bound by addition of binders. The basic approach of this solidification / stabilization technology is to reduce the mobility of toxic constituents from waste and safe transportation and disposal of the waste. Ceramic products have more strength and are bound like solid matrix and avoid leaching of metal ions trapped in the middle\textsuperscript{10,11}.

The waste (COPR sample) was first dried, powdered and then mixed with Ceramic raw materials viz. Clay (China clay), Feldspar powder and Quartz powder (Figure 2) in different proportions (Vide Tables 1 and 2) and blocks of sizes 5 cm × 5 cm × 2.5 cm were moulded, dried and vitrified at two different temperatures 1000°C (Figure 3) and 1200°C [Figure 4] in muffle furnace with a temperature increase of 150°C raise for every one hour period and cooling after maintaining at 1000°C and 1200°C for two hours. The resulted Blocks were tested for

a. Compressive strength of the Blocks
b. Leachability by Toxicity Characteristic Leaching Procedure (TCLP) test.

TCLP test simulates leaching of toxic chemicals when the waste is land disposed\textsuperscript{12-14}.

2.3 Analytical Procedure

Composite containing ceramic and COPR samples are crushed and passed through a 9.5 mm screen. Then leaching solution (5.7 ml glacial acetic acid diluted to 1 lit with double distilled water) is added to the composite sample in a Zero Head space Extractor (ZHE) at a Liquid: Solid ratio 2:38 in a Zero Head space Extractor (ZHE) at a Liquid: Solid ratio 2:38.

Figure 1. View of contaminated water from waste dump site of M/s. Tamil Nadu Chromates and Chemicals Limited, Ranipet.

Figure 2. Various materials used in the project study along with blocks made.

Table 1. Compressive strength of Blocks made from COPR and ceramic

| Sl No | Proportion | Compressive strength in Kg/Cm\textsuperscript{2} after firing |
|-------|------------|------------------------------------------------------------|
|       |            | 1000\textdegree C | 1200\textdegree C |
| 1     | 20:80      | 4.3               | 6.7              |
| 2     | 30:70      | 5.6               | 4.7              |
| 3     | 50:50      | 7.3               | Shape deformed   |
| 4     | 70:30      | Blocks damaged during drying                               |

Table 2. Encapsulation efficiency of ceramic

| Sl No | Proportion | Encapsulation efficiency |
|-------|------------|--------------------------|
|       |            | 1000\textdegree C | 1200\textdegree C |
| 1     | 20:80      | 65                       | 98.9             |
| 2     | 30:70      | 67                       | 97.8             |
| 3     | 50:50      | 68                       | Shape deformed   |
| 4     | 70:30      | Blocks damaged during drying                               |

Figure 3. COPR sample: Ceramic material combinations vitrified at 1200\textdegree C.
ratio of 20:1. Leaching solution (500 ml) with composite material (25 gr) has been used. The sample is agitated in rotary shaker at 30 rpm for 18 hours. The leached solution is filtered and analyzed for quantity of chromium present by Atomic Absorption Spectrophotometer.

### 2.4 Fixing Efficiency Calculation of Ceramic for 20:80 Composite

Concentration of Cr in the COPR sample = 9873 mg/Kg

Weight of one composite Block (5 cm × 5 cm × 2.5 cm) = 200 gr

COPR added in one Block = 40 g

Total quantity of Chromium in one Block = 0.040 × 9873 = 394.92 mg

Chromium leached out in TCLP test = 1.093 mg/l

Volume of leaching solution = 500 ml

Amount of solidified material taken for TCLP test = 25 gr

Total weight of one Block = 200 g

⇒ Chromium leached out in the TCLP test = \( \frac{1.093 \times 500}{1000} \times \frac{200}{25} = 4.372 \) mg

Efficiency of Chromium fixing by ceramic = \( \frac{[\text{Total quantity of Chromium in one Block}] - [\text{Chromium leachout from one Block}]}{\text{Total quantity of Chromium in one Block}} \times 100 \)

= \( \frac{394.92 \times 4.372}{394} \times 92 \times 100 \)

= 98.9%

### 3. Summary and Conclusion

The following conclusion is made based on this study.

1. The optimum proportion (by % weight) for COPR sample: ceramic compound mix is 20:80 with a compressive strength of 6.7 Kg/Cm² and TCLP test result is 1.093 mg/l after vitrified at 1200°C.

2. Vitrified composite of COPR and ceramic at 1200°C has porcelain tiles appearance. It may be used in construction activity.

3. The scope for further study is
   (i) The vitrified composite of COPR and ceramic at 1200°C has good non leachable character (Figure 5); hence further study on the composition of the same is in progress.
   (ii) The other factors affecting solidification like particle size, shape, mixing, specific gravity and humidity studies are in progress.
   (iii) Further studies to identify factors that increase the strength with less cost effective methods are in progress.
   (iv) Study could be extended to adopt the suitability of solidification process for other heavy metals.
   (v) The vitrified composite of COPR and ceramic at 1200°C has more air-holes which may be the cause for low strength, hence further study in this line is in progress.

### 4. Limits and Standards

1. The minimum strength required for solidified Blocks is 3.51 kg/cm² for land disposal as per USEPA
2. The Drinking Water standard for Chromium as per IS 10500:1991 is 0.05 mg/l.
3. TCLP standard for chromium is 5.0 mg/l prescribed by USEPA. (EPA HW D007)
5. References

1. Sathyaselvabala V, Panneerselvam P, Arulmozhi K, Thiruvengadaravi V, Thinakaran N, Sivanesan S. A study on expulsion of Cadmium (II) and Chromium (III) from electroplating effluent. Indian Journal of Science and Technology. 2009 Nov; 2(11):1–5. DOI: 10.17485/ijst/2009/v2i11/29531.

2. Subrahmanyan PVR. Hazardous waste scenario in India. International Association of Emergency Managers. 1991; 18:49–58.

3. Conner JR. Chemical fixation and Solidification of Hazardous wastes. Van Nostrand Reinhold, New York; 1990. p. 692.

4. Sudhakar DM. Studies on solidification/fixation of heavy metals in metal bearing hazardous wastes. A Thesis of Master of Technology in Civil Engineering, Indian Institute of Technology, Madras; 1995.

5. Annual Book of ASTM standards, Section 4, Construction, Concrete & Aggregate; 1995.

6. Cook DJ, Pama RP, Paul BK. Rice husk ash-lime, cement mixes for use in masonry units. Building & Environment. 1997; 12(4):281–88.

7. Heimann RB, Conrad D, Florence LZ, Neuwirth M, Ivey DG, Mikula RJ, Lam WW. Leaching of simulated heavy metal waste stabilized/solidified in different cement matrices. Journal of Hazardous Materials. 1992 Jun; 31(1):39–57.

8. Means JL, Smith LA, Nehring KM, Brauning SE, Gavaskar AR, Sass BM, Wiibs C C, Mashni CI. The application of solidification/stabilization to waste materials, Lewis Publications; 1995.

9. Johannesmeyer H, Gosh MM. Fixation of heavy metals in electroplating wastes. AICHE Symposium series. 81(243):119–25.

10. Ceramic Materials [Internet]. [Cited 2010 Sep 28]. Available from: www.intechopen.com.

11. Metal, ceramic and polymeric composites for various uses [Internet]. [Cited 2011 Jul 20]. Available from: www.intechopen.com.

12. Viji V. Studies on solidification of chrome metal bearing hazardous waste. A thesis of Master of engineering in Environmental Engineering, Anna University, Chennai; 1998.

13. Geetha G. Hazardous waste management. International Association of Emergency Managers. 1995; 22:161–64.

14. Jeyasingh J, Somasundaram V, Philip L, Bhallamudi SM. Pilot scale studies on the remediation of chromium contaminated aquifer using bio-barrier and reactive zone technologies. Department of Civil Engineering, Indian Institute of Technology Madras. Chemical Engineering Journal. 2011 Feb 15; 167(1):206–14.