

Notes

Immobilization of toxic metals of industrial waste via low temperature vitrification

I B Singh* & K Chaturvedi

CSIR-Advanced Materials and Processes Research Institute,
Bhopal 462 064 (M.P.), India

E-mail: ibsingh58@yahoo.com

Received 14 March 2014; accepted 23 May 2014

Wastes generated from metal finishing and galvanizing processes, have been vitrified at 800-950°C after heating of waste, clay and sodium carbonate in their different proportions. Observed results indicate that a composition containing 1:1:2 ratio of waste, sodium carbonate and clay attains a clear vitrification at 950°C. TCLP analysis of the leachates obtained from the vitrified masses of different wastes indicates the leachability of Cr, Cu, Zn and Pb becomes far below from their threshold values. Decrease of waste content and increase of sodium carbonate in the mixture has shown a further decrease of vitrification temperature. However, compressive strength of the vitrified mass is found to reduce considerably with the increase of sodium carbonate content in the vitrifying compositions.

Keywords: Hazardous waste, Leachability, TCLP, Toxic metals, Vitrification

Fast industrialization has resulted in generation of a large amount of toxic metals like Cr, Pb, Cu, Zn, etc bearing hazardous waste from the metal finishing, electroplating and galvanizing processes. Disposal of such types of waste in the soil causes contamination of ground and surface water. Because physical and chemical changes due to weathering or other effects start the release of contaminants from the waste that percolate in to the water. To control leaching of toxic elements from waste, thermal treatment is known to decrease the mobility of the toxic metals with the increase of thermal treatment temperature¹⁻⁵. Thermal treatment approaches like vitrification, sintering, bricks firing, etc are being employed for stabilization and solidification of the wastes. Among them, vitrification is considered to be promising one as contaminants get imbedded/immobilized in to the glassy structure of the vitrified mass that reduces the susceptibility of their release in the environment.

Kox and Vlist⁶ have carried out vitrification at >1650°C in year 1980 itself for the treatment of metals bearing hydroxide of the plating waste. Later on, a number of studies have been carried for the

thermal treatment of industrial metals bearing hazardous wastes *via* vitrification process. Thermal treatment of electroplating sludge containing Cr with/without bottom ash via vitrification at ~1300°C, has been found to retain more than 98% Cr of the waste in the vitrified slag⁷. Heavy metals like Cr, Ni, Cu, Zn, Pb of galvanic waste have been immobilised using soda-lime-borosilicate glass *via* vitrification at ~1300°C⁸. In vitrification of stainless dust with silica-clay mixture at 1100°C, it was observed that hazardous components of the waste get entrapped into the amorphous silica-alumina-clay vitrified matrix⁹. Addition of silica/clay/alumina plays a major role in making of amorphous matrix after vitrification. Silica (SiO₂) addition is beneficial on the immobilization of hazardous metals and the encapsulation of a glass network during the vitrification process^{10,11}. Invention related to treatment of radioactive and/or hazardous waste by making silicate-based glass after heating at 1150°C has revealed entrapping of toxic elements of the waste in to the glassy structure¹². Another invention describes the treatment of contaminated soil containing stainless steel dust via vitrification at 1450°C¹³. However, involvement of a higher thermal energy for attaining vitrification at high temperature (~1400°C), makes this process very expensive. In addition, some of the components of the waste get vaporized at this range of temperature, create secondary pollution problem in the environment. This is another major disadvantages of vitrification at high temperature. To reduce cost and minimize formation of toxic vapours, attainment of vitrification at lower temperature (<1000°C) could be a viable thermal treatment technology for the immobilization of toxic metals of industrial hazardous wastes. In view this, present investigation was aimed to develop low temperature eutectic composition containing waste, clay/fly ash and sodium carbonate (Na₂CO₃) in their different proportions to obtain vitrification at <1000°C. Determination of leachability of different metals of the waste from the vitrified masses, was another objective of the study to examine the extent of the immobilization of the toxic metals of the waste in the vitrified matrix.

Experimental Section

Collection of industrial wastes

All the three types of waste namely, metal finishing waste (designated as MF waste), zinc galvanizing (designated as GI waste) and chromium plating (designated as Cr-GI waste) were collected from different industries. The collected wastes were dried at 110°C till a complete removal of moisture. The clay used in the making of vitrified mass were collected locally while fly ash was collected from thermal power plant. Quantitative analysis of the clay, fly ash and wastes was performed using atomic absorption spectrophotometer (GBC Australia make, model 902).

Thermal treatment methodology

Dried wastes were grinded (50-100 µm in size) and mixed homogeneously with clay/fly ash and Na₂CO₃ in their different ratios. The homogenized mixture was kept in the alumina crucible (one inch diameter and depth). Mixture was compacted properly in the crucible before keeping it in furnace for heating. After heating at different temperature 800 to 950°C, the molten mixture containing alumina crucible was taken out from the furnace and allowed to solidify at room temperature.

TCLP test

Toxicity characteristic leachability procedure (TCLP) was employed in the determination of the leachability of toxic elements present in the waste as well as in the vitrified masses. After grinding of wastes and vitrified mass, 25 g of grinded powder (size ~ 0.9 mm) was mixed in extraction liquid of acetic acid and sodium hydroxide of pH 4.93 as per US EPA standard. The details of procedure employed in the TCLP test is given elsewhere^{4,5,14,15}. Hexavalent chromium [Cr (VI)] of the TCLP leachates was determined by diphenyl carbohydrazide method^{15,16} utilizing microprocessor based spectrophotometer (Hach DR-2000, USA). Different metals present in the leachates, were analyzed by AAS.

Microstructural and compressive tests

Microstructural study of the vitrified mass was performed by Scanning Electron Microscopy (SEM) using Jeol, Japan make JSM 5600 SEM model. While compressive strength of the vitrified mass was measured as per Indian Standard (IS 3495) using instron machine.

Results and Discussion

The physical appearance of the MF waste was in dark brown colour while Cr-GI and GI waste were in light greenish and in yellow colour, respectively. The bulk density of MF waste was measured as 1.12 g/cc while the bulk density of Cr-GI and GI waste were found as 0.70 and 0.80 g/cc respectively. The moisture present in the waste was measured as 27, 17 and 16% respectively for MF, Cr-GI and GI waste. The elemental analysis of the wastes carried out by AAS, is presented in Table 1. Analysis data indicates that Cr present in a significant amount (~37000 mg/kg) in Cr-GI waste while it contains in small amount (320 mg/kg) in MF waste. Cr was found in traces only in the GI waste. Pb was analyzed in a noticeable level in MF (150 mg/kg) and GI (615 mg/kg) waste. Zn was measured in a substantial amount (> 100000 mg/kg) in Cr-GI and GI wastes but comparatively less in MF waste (~20000 mg/kg). In all the three wastes, Mn was analyzed in somewhat lower concentration (~3000 mg/kg). A very small presence of heavy metal like Ni and Co was determined in the MF waste. Cu was also analyzed in a noticeable level in MF waste. Present analysis results indicate that all the three wastes are hazardous in nature as they contain a significant concentration of toxic metals like Cr, Cu, Zn, Pb, etc.

The composition of the local clay used in the present study, was analysed as 5.82% Fe₂O₃, 18.33% Al₂O₃ and 63.38% SiO₂ as major constituents, CaO and MgO as minor constituent (< 2 %) and Na₂O, K₂O etc as micro constituents (< 1%). The composition of the fly ash used in the vitrification, was determined as 5.6% Fe₂O₃, 24% Al₂O₃, 58.2% SiO₂ as major constituent and oxides of Ca, Mg, Na, K as minor constituents (< 2%). Presence of a considerable amount of silica quite useful in the making of low eutectic glassy structure of the vitrified mass while presence of alumina is

Table 1 — Presence of different heavy metals in metal finishing, plating and galvanizing waste analyzed by AAS

| Metals | MF waste mg/kg | Cr-GI waste mg/kg | GI waste mg/kg |
|--------|-------------------|----------------------|-------------------|
| Fe | 159000 | 7800 | 226000 |
| Pb | 1500 | Traces | 6100 |
| Cr | 3200 | 36700 | Nil |
| Cu | 4500 | 2100 | nil |
| Zn | 26000 | 106000 | 138000 |
| Ni | 4500 | Nil | Nil |
| Co | 600 | Nil | Nil |
| Cd | Nil | Nil | Nil |
| Mn | 3100 | 3000 | 4100 |

likely to increase the strength of the vitrified mass. At the same time, a very high melting temperature of alumina ($>1800^{\circ}\text{C}$) may likely to increase the eutectic temperature of the mixture to be vitrified.

A number of compositions containing different ratio of waste, clay, fly ash, Na_2CO_3 were heated for two hours in $800\text{--}950^{\circ}\text{C}$ of temperature range. Table 2 shows the different compositions of waste, clay, fly ash, and Na_2CO_3 were used in present vitrification study. A composition containing 50% each of waste and clay was heated up to 950°C . However, the heated mixture did not melt. Another composition containing 50% waste and balanced fly ash also did not show vitrification. Next composition comprising 25% waste, 25% fly ash, 25% Na_2CO_3 and balanced clay showed the presence of slightly viscous mixture. Since the melting temperature of Na_2CO_3 is low ($\sim 850^{\circ}\text{C}$), it melted alone. Therefore remaining constituents were intact. However, composition containing 25% waste, 25% Na_2CO_3 and balanced clay showed occurrence of a clear vitrification at 950°C . In fact MF waste containing composition shown vitrification even at 920°C itself. Above observations indicated that presence of fly ash in the mixture is not beneficial for reducing of eutectic temperature. Reduction of waste content and increase of Na_2CO_3 content in the mixture has shown the occurrence of vitrification at further lower temperature. A composition containing 15% waste, 35% Na_2CO_3 and balanced clay has shown vitrification 850°C . Even MF containing waste composition has shown vitrification at 820°C itself. Visual observation of the vitrified masses has indicated the occurrence of a better compactness of MF bearing vitrified masses.

The compressive strength of the vitrified masses of different compositions and temperature are compared in Fig 1. The compressive strength of MF containing vitrified mass occurs maximum 390 kg/cm at 950°C which reduces substantially to 235 kg/cm at 850°C .

An increase of Na_2CO_3 content and decrease of the waste content in the mixture is appeared the main reason for the decrease of compressive strength. Similar trend of compressive strength measurements was found for Cr-GI and GI bearing vitrified masses. If compare the compressive strength measurements, it can be noticed that compressive strength of the Cr-GI waste containing vitrified mass reduces marginally as compared to MF containing vitrified mass of the same composition. The compressive strength of GI containing vitrified mass occurs even lower than Cr-GI wastes bearing vitrified mass. Presence of a number of heavy metals in the MF waste seems to make more cohesive structure of the solidified mass. This increases the compressive strength of the vitrified mass.

SEM photomicrographs of the MF, Cr-GI and GI waste containing vitrified mass in their 1:1:2 ratio (25% waste, 25% Na_2CO_3 and balanced clay) heated at 950°C , are given in Fig. 2(a, b and c), respectively. Microstructure of MF containing waste as shown in Fig. 2a demonstrates the presence of a glassy structure

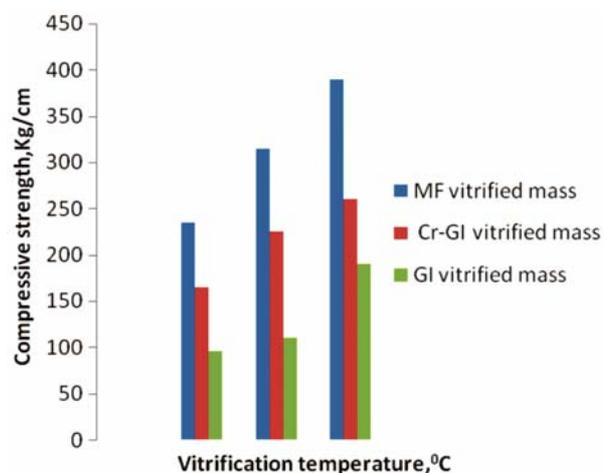


Fig. 1 — Compressive strength of MF, GI and Cr-GI waste bearing vitrified masses obtained after heating 15% waste + 35% Na_2CO_3 + 50% clay at 850°C , 20% waste + 30% Na_2CO_3 + 50% clay at 950°C and 25% waste + 25% Na_2CO_3 + 50% clay at 950°C

Table 2 — Different compositions of waste, Na_2CO_3 , flyash and clay used in vitrification study

| Vitrification composition (%) | Heating temperature ($^{\circ}\text{C}$) | Visual observation |
|---|--|---------------------|
| 50% waste + 50% clay | 950 | No vitrification |
| 50% waste + 50% flyash | 950 | No vitrification |
| 25% waste + 25% Na_2CO_3 | 950 | No vitrification |
| 25% flyash + 25% clay | | |
| 25% waste + 25% Na_2CO_3 + 50% clay | 950 | Clear vitrification |
| 20% waste + 30% Na_2CO_3 + 50% clay | 900 | Clear vitrification |
| 15% waste + 35% Na_2CO_3 + 50% clay | 850 | Clear vitrification |

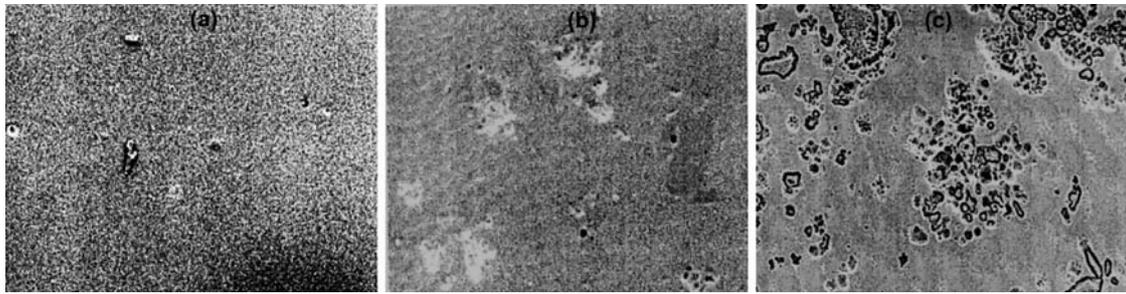


Fig. 2 — SEM photomicrographs of MF (a), Cr-GI (b) and GI (c) waste bearing vitrified mass at same magnification ($\times 200$)

of the vitrified mass. The presence of silica, alumina, iron oxides and other micro constituents of the clay, waste alongwith, sodium carbonates make a low eutectic composition that melt completely at 950°C . The metallic constituents of the waste which generally present in their oxide forms, get imbedded in the glassy structure. In case of Cr-GI and GI containing vitrified masses, some of heterogeneities can be seen in their microstructures (Fig. 2b and c). Presence of such heterogeneities in GI containing vitrified mass appears more. This is main reason for the occurrence of lower compressive strength of GI waste containing vitrified mass.

Leachates collected through TCLP test from the waste and the vitrified masses containing 25% waste, 25% Na_2CO_3 and balanced clay heated at 950°C , were analysed by AAS. Figures 3, 4 and 5 demonstrate a comparative concentration of Cu, Cr, Zn, Pb obtained from the waste and leachates of their vitrified masses. TCLP results of the leachates of the metal finishing waste indicate more than 3 mg/L Cu, 2 mg/L Pb and 41 mg/L Zn whose concentration reduces considerably as < 0.2 mg/L Cu and Pb and around 6 mg/L Zn in the leachate of their vitrified mass (Fig. 3). The leachate of the Cr-GI waste shows the presence of total Cr as 45 mg/L, 2.6 mg/L Cr (VI) as 2.6 mg/L and Zn as 96 mg/L (Fig. 4). After vitrification the concentration of these metals become quite low as 3.8 mg/L Cr, 0.2 mg/L Cr(VI) and 13 mg/L Zn were analysed in the leachate of the vitrified mass. In GI waste the leachability of Zn and Pb was found as 160 mg/L and 2.7 mg/L, respectively which reduces to 18 mg/L as Zn and 0.3 mg/L as Pb in the leachate of their vitrified mass (Fig. 5). The leachability of the other metals present in the vitrified masses like Mn, Ni, Co etc was found < 0.1 mg/L. Present TCLP test results indicate the leachability of above metal becomes far below from their threshold

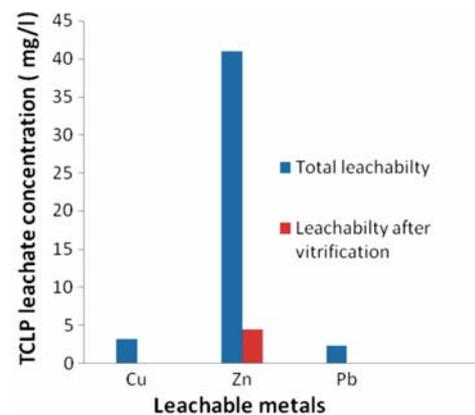


Fig. 3 — TCLP analysis of Cu, Pb and Zn of the MF waste bearing vitrified mass

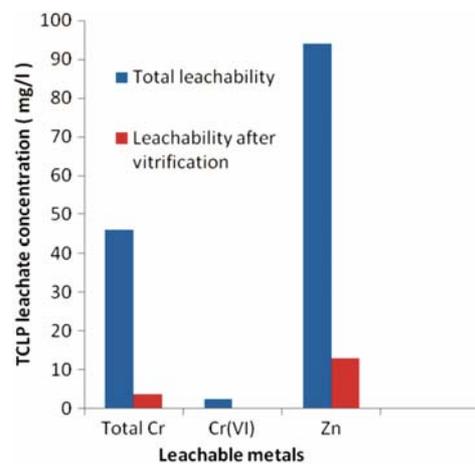


Fig. 4 — TCLP analysis of, Cr(VI) and Zn of the Cr-GI waste bearing vitrified mass

values $\{(15 \text{ mg/L Cu}, 25 \text{ mg/L Zn}, 5 \text{ mg/L Pb}, 5 \text{ mg/L Cr}$ and $0.5 \text{ mg/L Cr(VI)}\}$ as determined by US EPA for hazardous waste¹⁴.

Based on the leachability and compressive strength measurements of the vitrified masses, it can be concluded that low temperature vitrification is quite

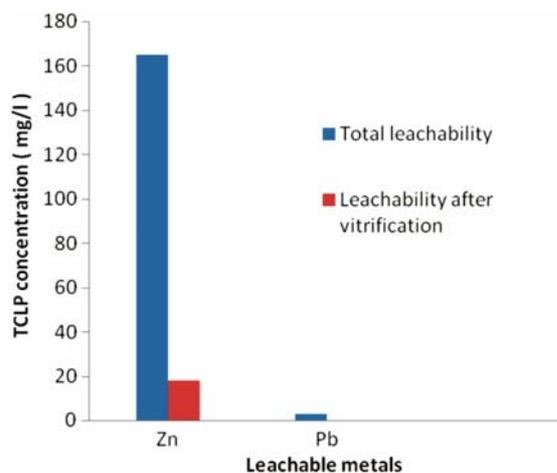


Fig. 5—TCLP analysis of Zn and Pb of MF waste bearing vitrified mass

effective in the controlling of mobility of the toxic metals of metal finishing, chromium plating and galvanising wastes. Present vitrification approach could be considered a less energy consuming thermal treatment technology for the stabilization and solidification the such types of hazardous waste. However, further study is necessary to make vitrification in larger sample size and evaluate their stability in different weathering conditions in order to utilize vitrified mass as concrete aggregates in building materials.

Conclusion

- i) Present investigation indicates the vitrification of metal finishing, chromium plating and galvanising wastes can be achieved at 950°C by taking a mixture containing waste, Na_2CO_3 , and clay in their 1:1:2 ratio.
- ii) TCLP analysis of the leachate obtained from the vitrified mass indicates the leachability of the toxic metal like Cr, Cu, Zn, Pb occurs far below from their threshold values as determined by US EPA.
- iii) Increase of Na_2CO_3 content decreases the melting temperature of the mixture further low but increases the ductility of the vitrified mass.

- iv) Metal finishing waste containing vitrified mass shows better compressive strength than chromium plating and zinc galvanising waste containing vitrified masses.
- v) Microstructural studies of the vitrified mass reveals that metal content of the waste get imbedded in to the glassy structure of the vitrified mass.

Acknowledgements

Authors are thankful to the Director, Advanced Materials and Processes Research Institute, Bhopal for providing of laboratory facilities for this study. The financial support provided by the Ministry of Environment & Forest, New Delhi for carrying this work, is also acknowledged.

References

- 1 Winter R M, Mallepalli R R & Hellem K P, *Comb Sci Technol*, 101 (1994) 45.
- 2 Wei Y L, Yang Y W & Lee C N, *Environ Sci Technol*, 35 (2001) 416.
- 3 Sorensen A M, Koch C B, Stackpoole M M, Benniamin M M & Chritensen T N, *Environ Sci Technol*, 34 (2001) 4620.
- 4 Singh I B, Chaturvedi K, Morchhale R K & Yegneswaran A H, *J Hazard Mat*, 141 (2007) 215.
- 5 Singh I B, Chaturvedi K & Yegneswaran A H, *Environ Technol*, 28 (2007) 713.
- 6 Kox W M A & Vlist E V D, *Conservation and Recycling*, 4(1981) 29.
- 7 Li C T, Lee W J, Huang K L, Fu S F & Lai Y C, *Environ Sci Technol*, 41 (2007) 2950.
- 8 Castanho S M, Guitian F, Sobrados I, Silva A C, Montero I, Cubillo A E, Sanz J & Moya J S, *Am Cer Soc*, 91 (2008) 1300.
- 9 Tang M T, Peng J, Peng B, Yu D & Tang C B, *Trans. Nonfer Met Soc*, 18 (2008) 202.
- 10 Kuo Y M, Lin T C & Tsai P J, *Air & Waste Manage Assoc*, 53 (2003) 1412.
- 11 Kuo Y M, Wang J W & Tsai C H, *J Air & Waste Manage Assoc*, 57 (2007) 820.
- 12 Anatoly C & Arthur G, *US Patent* No 8115044 (2012).
- 13 Battleson D M, Cashell P V, Filius K D, Flannery P A, Kujawa S T, Rademacher E L & Whitworth C G, *US Patent* No 5877394 (1999).
- 14 Federal Register, U S EPA, 1998, *Toxicity Characteristics Leaching Procedure (TCLP)*, 40 CFR, Vol 51 No 256, Appendix 2, Part 268: 40643; 1998.
- 15 Singh I B & Singh D R, *Environ Technol*, 24 (2003) 1041.
- 16 *Standard Methods of Examination of Water and Wastewater*, 18th edn, (American Public Health Association, Washington DC) 1992 pp. 3.5-5.2.