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Mining Industry Waste Remediated for Recycle by Vitrification: A Case History

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The Global Materials Cycle

Raw materials taken from the earth to produce a wide variety of products and processes must be disposed of safely back into the earth once declared a waste (Figure 1). The only other option is remediation for recycle into new products or new end uses. Technologies have been developed by the US Department of Energy's (DOE) Westinghouse Savannah River Technology Center (SRTC) to convert a wide variety of hazardous (and/or radioactive) wastes to a solid stabilized glass via the process of vitrification. This vitrification technology can render hazardous wastes to be non-hazardous and/or convert non-hazardous sludges, asbestos, etc. into recyclable products or reusable raw materials.

Vitrification

- Vitrification atomistically bonds any hazardous or radioactive species in a solid glassy matrix providing for recycle of the end product under certain conditions
- The final waste form or product is, therefore, very durable and environmentally stable over long time duration.
- Vitrification processes are flexible enough to handle process chemistry variations and can accommodate dry or wet waste/recycle materials.
- The U.S. EPA has declared vitrification the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste and produced a Handbook of Vitrification Technologies for Treatment of Hazardous and Radioactive Waste.
- Vitrification produces large volume reductions, e.g., up to 97%

- Vitrification can use cheap sources of glass forming agents, e.g., sand, soil, mill tailings, crushed reagent bottles, beer bottles, broken window glass, etc.
- Vitrification produces large reductions in volume.
- Compact and/or transportable melter (capable of vitrifying about 1.8 tons/day of wet feed or 3.5 tons/day of dry feed) technology minimizes costs.
- Vitrification is cost effective on a life-cycle basis compared to other stabilization technologies.

The Regulations

Wastes that Fail the U.S. Environmental Protection Agency (EPA) Characteristically Hazardous Leaching Procedure (TCLP) for any of the inorganic species listed in Table I (Column A) are considered characteristically hazardous. Prior to May 28, 1998 characteristically hazardous wastes could be treated so that they would meet the TCLP leachate levels given in Column A. The U.S. EPA promulgated a regulation on May 28, 1998 that characteristically hazardous wastes must be treated to the Universal Treatment Standards (UTS) shown in Table I (Column B).

The Problem

A U.S. Mining company had a waste water treatment sludge which failed TCLP for Cd. It was, therefore, characteristically hazardous for Cd. The waste water facility treated 3000 tons of wet sludge waste per year. The current remediation being used was to mix the sludge with cement. The cured sludge-cement mixture passed TCLP at the levels given in Table I Column A. The sludge-cement remediation was problematic for the following reasons:

- the porosity of cement might cause the cured cement to fail TCLP at the newly promulgated and more stringent UTS limits
- the cement could not be recycled and was a long term liability
- the cement created large volumes (6000 tons on a weight basis or 5.44×10^6 liters on a volume basis) of cement/year

Table I. Environmental Protection Agency Concentration Limits for Inorganic Constituents of Hazardous Wastes

	Column A Characteristically Hazardous Limits (TCLP; mg/L)	Column B Final Universal Treatment Standard Limits (TCLP; mg/L)
Ag	5.0	0.14
As	5.0	5.0
Ba	100.0	21
Be	-	1.22

Cd	1.0	0.11
Cr	5.0	0.60
Pb	5.0	0.75
Hg	0.2	0.025
Ni	-	11
Sb	-	1.15
Se	1.0	5.7
Tl	-	0.20
V**	-	1.6
Zn**	-	4.3

** not underlying hazardous constituents

Se must be treated to the characteristic limit (1.0 mg/L) to be non-hazardous, although it may be land disposed as a hazardous waste if <5.7 mg/L TCLP

The Solution

The raw waste was analyzed after drying at a variety of temperatures. It was determined that the waste contained 86.7 wt% H_2O, an additional ~1.5 wt% OH^- from hydroxide minerals present, plus small amounts of carbonate species, e.g. $CaCO_3$ (calcite).

Whole element chemistry indicated that the waste not only contained Cd (0.11 wt%) but also contained >20 wt% Zn.

The combined analyses indicated that upon vitrification at >=1150°C there would be a Loss-On-Ignition (LOI) or vaporization to the off-gas system during vitrfication that will be composed of the following species:

- 86.7 wt% H_2O as steam

- ~1.5 wt% OH^- as steam
- ~1.3 wt% CO_2
- all of the NO_2 and NO_3 (~0.5 wt%)
- 1/2 to all of the ~5.0 wt% SO_4 present depending on the melt
- none to all of the Cl (0.75 wt%) and F (0.33 wt%) depending on the melt temperature

At these low levels none of the acid gases that could be produced (dilute HCl, HF, or H2SO4 in steam) were considered troublesome to the melter off-gas.

Mill tailings provided by the mining company were analyzed in the same fashion to examine their usage as glass forming additives. The mill tailings were determined to contain ~73-75 wt% SiO_2, ~9 wt% Al_2O_3, ~4-5 wt% K_2O which are all excellent glass forming oxides. However, the mill tailings contained $CaSO_4$*$2H_2O$ (gypsum) which would add considerable SO4 to the melter feed and produce acid gas (dilute H2SO4) which would cause a secondary waste to be generated. It was advised to find a mill tailings that contained less gypsum as a glass former.

The waste was made into three different types of glass:

- Soda-Lime-Silica (SLS) glass (1150-1350°C)
- Borosilicate glass (1150°C)
- Basalt glass (1300-1500°C)

at waste loadings of 35-50 wt% on a dry sludge basis with and without the mill tailings. The lower melting, ~1150°C, glasses were recommended since low melting temperature glasses are preferred to minimize volatilization of hazardous constituents.

Large volume reductions (87-93%) were achievable due to a combination of the following:

- vaporization of water (~86.7 wt% for the sludge)
- densification from a sludge of ~1 g/cc to a glass of ~2.7 g/cc
- volatilization of OH^-, NO_x, CO_2 , SO_4 from hydroxide, nitrate, carbonate, and sulfate species present in the sludge

The glass creates small volumes (897 tons on a weight basis or 0.3×10^6 liters on a volume basis) which is a *94% volume reduction for glass compared to alternative stabilization in cement.*

Recycle Markets

The use of treated materials containing hazardous metals has been previously considered by the EPA for residues remaining from High Temperature Metal Recovery (HTMR) operations.[1] In this proposal dealing with the use of residues from HTMR, the EPA proposed that such wastes would not be subject to hazardous waste disposal regulations - if they meet 3 conditions:

1. they are used to produce products (re-cycled),
2. the hazardous waste must undergo a chemical reaction in the course of becoming products - so as to be inseparable by physical means, and
3. the waste derived products must meet the treatment standards under the LDR program for every prohibited hazardous waste that they contain.

These treated materials could be used for recycling as 1) covered sub-base materials (e.g., in construction of paved roads, parking lots, and driveways), 2) additive ingredients in cement or concrete/asphalt mixtures, 3) top grade or surfacing materials, e.g., in construction of roads, parking lots, and driveways (glassphalt or glasscrete), and as anti-skid/de-icing materials. Note; the current regulations for the HTMR residues specify that the wastes are NOT hazardous wastes, if they meet the exclusion requirements - but they MUST be disposed to Sub-Title D landfills (i.e., at this time the proposed reuse (59 FR 67256, 12/29/94) for the HTMR residues has not been adopted). Therefore, if vitrified the treated mining wastes meet the two restrictions above (inseparable and LDR standards) and the mining waste glass should be allowed into the recycle market.

References

1. Organic species are also listed by EPA in regulation 40CFR268.40) but organic species are volatilized at the high temperatures used in vitrification and are, therefore, not discussed further.
2. Federal Register, V.63,#100,p.28748-9.
3. Standards for the Management and Use of Slag Residues Derived From HTMR Treatment of K061, K062, and F006 Wastes. 59 FR 67256, December 29, 1994.
4. Uses for glassphalt (crushed glass is added to asphalt to improve its rigidity) can be found on the WWW and include air-port runways, highways in Virginia, New York City, and Los Angeles most notable of which is Hollywood Blvd (glassphalt gives it sparkle).