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VITRIFICATION OF NORM WASTES

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Vitrification of NORM Wastes

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Abstract

Vitrification of wastes is a relatively new application of one of man's oldest manufacturing processes. During the past 25 years it has been developed and accepted internationally for immobilizing the most highly radioactive wastes from spent nuclear fuel. By the year 2005, there will be nine operating high-level radioactive vitrification plants. Many of the technical "lessons learned" from this international program can be applied to much less hazardous materials such as naturally occurring radioactive material (NORM).

One NORM soil sample was characterized and several glasses were made and leach tested. Compared to the original soil, vitrification provided a 67% volume reduction in the sample. The chemical durability of these NORM glasses was comparable to container glass and was superior to Columbia River basalt rock. Based upon the durability of some natural basalt glasses, the longevity of NORM glasses should remain unaltered in normal environmental conditions for millions of years. Vitrification of the NORM sample will reduce the radon emanation to less than 0.1 % of standard construction materials such as brick and concrete. Technically, the vitrified NORM soil can be transformed into useful, salable products which could significantly reduce the processing costs. For example, if road barriers could be fabricated and sold from the NORM soils, they could generate about \$100 per ton of glass product.

With the deployment of low capital and operating cost systems, vitrification should become a broadly applied process for treating a large variety of wastes. In many situations, the wastes can be transformed into marketable products. This paper will present a general description of waste vitrification, summarize some of its key advantages, provide some test data for a small sample of one NORM, and suggest how this process may be applied to NORM.

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Introduction

Vitrification, or glass making, is one of man's oldest industries, dating back nearly 5,000 years (1). Early glasses were not very chemically durable because of the limited technology available then. However, glass artifacts that are nearly 3,500 years old are currently being displayed in museums around the world. Glass was attractive to early man because of its appearance; transparent glasses were like solid water that could be formed into interesting shapes. Their lustrous, shiny surfaces and colors were aesthetically pleasing. At that time, glass was considered to be as valuable as most precious gems.

Vitrification of wastes is a relatively new industry, dating back less than 45 years. This industry has drawn upon past scientific and technical experience. The objective of early waste vitrification was to transform a slurry or sludge containing radioactivity into a solid, chemically durable material. The first radioactive waste vitrification plant started operation in the mid-1980's (2) (3), and by the end of the century about nine plants will be processing the most highly radioactive wastes. The merits of vitrification have currently been limited to the most expensive waste streams, such as high-level radioactive wastes. The application of vitrification to other waste streams is in its infancy, but it is believed that it will become a dominant waste management technology in 10 to 15 years.

Waste vitrification is a thermal process that may involve drying, pyrolysis, decomposition of inorganic salts, and the oxidation of metals and carbon; it always involves the melting of oxides. If allowed to reside in the molten pool for sufficient time, this molten oxide material homogenizes and makes a nearly uniform liquid. This liquid can then be cast and, if cooled quickly enough, result in an amorphous solid or glass. Alternatively, through heat treatment, the liquid oxides can be slow-cooled to create different crystalline materials with the potential for a glassy phase—either as a matrix or as an interstitial amorphous phase. Most commercial glasses, flatware, containers and other glass products sold today are transparent; also, they have few enclosed gas bubbles or seeds and few undissolved oxides or stones. Many precautions are required to achieve these results. Minor additions of various metal ions can alter the color, transparency, and other important material properties. Glasses made from wastes are typically black and opaque due to oxides of iron and other transition metals that are common in nature. A typical glass contains silica as its major constituent. Although other specialized glasses can be made with other materials and techniques, the most common and well-understood is one founded upon silica, the most abundant oxide on earth.

Silicate glasses are important environmentally because a broad spectrum of waste materials can and have been incorporated into

chemically durable silicate glasses. Studies show that naturally occurring basalt glasses have a very low corrosion rate. Depending upon the glass's environment, the alteration or corrosion rate can vary from 0.1 millimeters per million years in arid climates to 10 millimeters per million years in water-saturated environments at average temperatures below 10 degrees centigrade (4). Thus, incorporation of heavy metals or radioactive elements within a silicate glass casting would safely retain these materials for very long periods.

Process Description

Hazardous slurries, solutions, contaminated soils, or miscellaneous solids are fed into the melter using existing technologies. These materials can be either combustible or non-combustible. After entering the high-temperature cavity, the feed material is heated. It first dries, then pyrolyzes if it has organic content. If residual char exists after pyrolysis, oxygen in the air oxidizes the residual carbon. When oxidized, the oxides settle toward the molten glass surface, are heated, and eventually melt into the molten pool. This is shown generally in Figure 1.

The heart of the process is the melter, a refractory-lined cavity with submerged electrodes. After preheating of the cavity and the initial charge, the melt becomes electrically conductive. With an alternating current placed between pairs of electrodes, the molten glass is self-heated. Molten glass temperature is typically limited only by the extent of corrosion resistance and refractoriness in the lining and the electrodes. Temperatures up to 3000°F are sustainable for hazardous waste processing. At these temperatures, almost any material can be melted or dissolved. Small additions of chemicals may be needed to achieve suitable product durability or processability. Local soils, recycled bottle glass, slag and many other sources can be used as these additives.

A large melter of this type typically has a mean residence time of over 24 hours. Since these melters behave like a well-mixed tank, large variations in the waste feed can be accommodated without dramatically influencing the discharged glass composition. Thus, melters of this type serve to homogenize a heterogeneous waste feed into a time-average of the waste fed. With a suitable off-gas system, the same melter can process many different types of waste and provide a universal "one stop" processing capability.

Vitrification process rates depend on several properties of the waste, such as water content, chemical composition, inherent energy content, and particle size. To achieve the desired process capacity, the surface area of the molten pool is adjusted. For solutions and concentrated slurries, with no

As shown in Figure 2, the alteration or corrosion rate for these basalt glasses is measured in thousandths of an inch per **million years!** The Columbia River basalt glass has been exposed to mostly an arid climate during the past 12 to 14 million years. The British Columbia and Icelandic basalts were immersed in fresh lake water or under the ocean. Here the corrosion rate is, as expected, higher. However, the corrosion rate of about 0.1" per million years is still very low. These data are valuable for the application of vitrification of wastes. If we make glasses from wastes that have a composition sufficiently similar to these basalt glasses, these natural data provide the confidence that it will endure similar environments with similar results. Thus, for many glasses from waste, nature has completed million year experiments that show it is extremely durable.

To provide perspective on the durability of glass, it is compared to the evolution and duration of man-kind in Figure 3. Note that the duration of civilization as represented by the span of written history (~6,000 years) is but a fine line compared to the endurance of natural glasses.

Another important characteristic of the waste nitrification process is its practical versatility. The same system can process a diversity of wastes which can be transformed into chemically stable products. To provide a perspective for the different applications of the process, the following listing identifies waste streams for which we have completed treatability experiments. All have been transformed into chemically durable glasses.

NON-HAZARDOUS WASTES

Municipal Solid Waste Incinerator
Ash
Medical Wastes
Hog Fuel Fly and Bottom Ash
Hog Fuel Pyrolysis and Ash
Vitrification
Non-Recyclable MSW Residues
Mass Burn MSW
Combustible and Non-Combustible
Construction Debris Solid Wastes
Cardboard Recycling Wastes
10 To 15 Wt% Solids Sewage
Sludges

HAZARDOUS WASTES

Foundry Sands

Aluminum Spent Pot Liners
Plating Sludges (FeSO₄)
Weapons Components
Declassification and
Demilitarization
Electric Arc Furnace Dust
Pesticide Contaminated Soils
Paper Recycling De-Inking Sludges
Chemical Weapons And Related
Wastes
Electronic Circuits, Old Computers,
Terminals and CRT's
K-Waste Sludges
Hazardous Organic Solutions

RADIOACTIVE

High-Level Radioactive Slurries

Fernald Contaminated Sludges And
 Soils (OU #1)
 Radium-Enriched, High Radon
 Emanating Soils (Fernald OU #4)
 Low-Level Reactor Wastes (Organic
 Resins, Dry Active Wastes and
 Sludges)
 Weldon Spring Uranium Sludges
 and Contaminated Soils
 Mixed Radioactive and Hazardous
 Wastes
 Plutonium Warhead "Denaturing"
 Hanford Low Level Salt Cake
 Vitrification (~NaNO₃)

For some situations, the volume reduction achieved during processing of the waste is important. Typical values for some tested materials are shown graphically in Figure 4. The bar chart shows the volume percent of the final glass compared to the original volume.

Vitrification Test Data for a NORM Sample

A NORM sample was obtained and characterized using our standard characterization procedures. From these procedures, we were able to characterize the sample as follows:

Fraction lost on drying	0.146
Fraction of dry sample as "sea shells"	0.309
Fraction of dry sample as soil & NORM	0.693
Fraction of dry soil & NORM as organics	0.118
Fraction lost during firing (held at 1200 C)	0.028
Total mass lost	0.354
Approximate volume reduction	0.677

Next, the chemical composition of the dried, oxidized soil was determined. Based upon the chemical composition of the soil, several chemical additions were completed to see how the TCLP leaching characteristics would vary. These glasses were melted at 1500°C. The chemical composition of these glasses are presented in Table 1. Samples of these glasses were taken and a modified TCLP test were completed for these glasses. The results of these leach tests for the corresponding glasses is presented in the Table 2. The relevance of these results can be better understood by comparing the mass fraction

silica losses from these samples to other common materials we have tested. These results are presented in Figure 5. This figure shows that the NORM glass samples are very chemically durable. They are comparable to clear container and Pyrex glasses and are far superior to basalt rock.

Vitrification of NORM materials also provides the significant benefit of nearly eliminating radon and daughter product emissions from the material. After vitrification, radon emanation becomes less than many common construction materials. This fact is shown in Table 3 and is discussed in greater detail by Merrill and Janke (5). Since the K-65 material has a radium content that is over 2,000 times higher, the emanation should be proportionately less. This characteristic is retained as long as the glass is unaltered. Since the glass is very chemically durable, radon retention should be maintained for millions of years for normal environmental conditions.

Table 3
Comparison of Radon Emanation and Radium Content of Different materials

Material	Radium Concentration (pCi/g)	Rn Emanation Rate (pCi/m ² /s)
Concrete	0.3 - 2.2	0.02 - 0.22
Alum Shale Concrete	10 - 70	0.4 - 1.5
Brick	0.5 - 5	0.02 - 0.04
Vitrified K-65 Material	$2 \times 10^5 - 3 \times 10^5$	0.01 - 0.06
NORM soil	~100**	~4**
Vitrified NORM soil	~100**	~0.00001**
Regulatory limit		20

** Values not measured but extrapolated from existing data

Since vitrification of NORM waste transforms the material into a chemically durable solid with essentially no radioactive characteristics, there is technical potential of using the discharged material for useful purposes. Sale of products could represent a significant reduction in the processing cost of the NORM soil. For example, if road barriers could be manufactured and sold, the income from this product would be about \$100 per ton. Some examples of other potential products from NORM waste material are illustrated in Figure 1.

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Figure 1 Schematic of the Terra-Vit Waste Vitrification Process

Figure 2. Alteration or corrosion rate for natural basalt glasses under differing environmental conditions

Comparison of Glass Endurance to Human History

Figure 3. Comparison of glasses endurance to human history

Volume % of Original

Figure 4 Volume % of vitrified product compared to the original

**Weight Fraction Silica Lost
From Various Samples
In TCLP Test**

Figure 5. Comparison of different material's weight fraction silica lost in TCLP test

Table 1
Chemical Composition of an Oxidized NORM Soil and NORM Glasses.
Listed in Weight Percent

Oxide	Oxidized NORM soil	KFW1	KFW2	KFW3	KFW4	RAM1	RAM2	CCC1
SiO ₂	55.24	49.30	53.24	50.21	46.21	52.60	43.36	51.62
B ₂ O ₃							17.57	
BaO	20.26	18.08	18.29	18.41	16.95	19.29	15.90	18.93
Al ₂ O ₃	7.73	13.15	6.98	7.03	14.43	7.36	6.07	13.77
CaO	5.95	5.31	5.37	5.41	4.98	5.67	4.67	5.56
Fe ₂ O ₃	5.36	4.79	4.84	4.88	4.49	5.11	4.21	5.01
Na ₂ O		4.49	6.35			4.77	3.93	
K ₂ O	1.18	1.05	1.06	1.07	0.99	1.12	0.93	1.10
PbO	1.07	0.96	0.97	0.97	0.90	1.02	0.84	1.00
MgO	0.89	0.80	0.80	0.81	0.75	0.85	0.70	0.83
ZnO	0.69	0.62	0.63	0.63	0.58	0.66	0.54	0.65
SrO	0.57	0.51	0.52	0.52	0.48	0.55	0.45	0.54
TiO ₂	0.44	0.39	0.40	0.40	0.37	0.42	0.35	0.41
P ₂ O ₅	0.26	0.23	0.23	9.34	8.59	0.24	0.20	0.24
MnO	0.13	0.11	0.11	0.11	0.11	0.12	0.10	0.12
Nd ₂ O ₃	0.06	0.05	0.05	0.05	0.05	0.05	0.04	0.05
ZrO ₂	0.05	0.05	0.05	0.05	0.04	0.05	0.04	0.05
CuO	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.03

Table 2
TCLP Leachate Results for NORM Glass Compositions of Table 1 .

Listed in ppm.

Element	Oxidized NORM soil	KFW1	KFW2	KFW3	KFW4	RAM1	RAM2	CCC1
Si		0.75	0.43	0.47	0.76	0.56	0.47	0.56
B		0.13					0.41	
Ba		1.23	1.29	1.19	5.34	2.96	1.76	1.20
Al		0.32		0.18				0.33
Ca		0.65	0.37	1.70	4.74	1.07	0.70	0.55
Fe		5.33	9.13	2.49	3.78	11.18	7.99	8.79
Na		3.30	14.93		0.82			
K						1.79		
Mg		0.09		0.10	0.31	0.14	0.10	0.10
Zn		0.01	0.01	0.02	0.07	0.08	0.04	0.02
Sr		0.04	0.04	0.07	0.32	0.09	0.05	0.04
P				0.65	2.86			
Mn		0.05	0.05	0.03	0.06	0.07	0.05	0.06
Nd		0.01				0.04	0.03	0.01
Cu		0.10	0.04					0.04

Glass Products from Waste

DATE

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