DEPLOYMENT OF POROUS CRYSTALLINE MATRIX (GUBKA) FOR STABILIZING RADIOACTIVE STANDARD SOLUTIONS AT FERNALD

D.A.Knecht, T. J. Tranter, J. Macheret
Idaho National Engineering and Environmental Laboratory, P. O. Box 1625, Idaho Falls, ID 83415

A. Meyer, D. Yesso, T. Daniels,

Fluor Fernald, P.O. Box 538704, Cincinnati, OH 45253

A. S. Aloy, N. V.Sapozhnikova,

V. G. Khlopin Radium Institute (KRI), 28 2-nd Murinskiy Ave., St. Petersburg, 194021, Russia

A. G. Anshits, O. M. Sharonova,
Institute Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences (ICCT SB RAS), 42 K. Marx St., Krasnoyarsk 660049, Russia

A. A. Tretyakov,
Federal State Unitary Enterprise "Mining and Chemical Combine" (FSUE MCC), 53 Lenin St., Zheleznogorsk, Krasnoyarsk Region, 662990, Russia

ABSTRACT

Radioactive solutions requiring stabilization exist in various compositions throughout the DOE complex. Future cleanup could generate additional actinide residue solutions requiring stabilization at facilities where processing capabilities have been dismantled. Radiological laboratory standard solutions (liquid technical standards) have recently been identified at the Fernald site, which require stabilization and disposal before the laboratory facilities at Fernald can be decommissioned. The Fernald solutions consist of approximately 25 liters of acidic solutions containing isotopes of Cs, Ba, Ra, Eu, U, Am, Po, Ru, Sr, Th, Pb, Pu, and Np and in some cases small quantities of added salts. After stabilization and waste acceptance approval, the resulting waste forms will be disposed at the Nevada Test Site. This paper describes the technology and progress in using the Russian "Gubka" technology to stabilize the Fernald liquid technical standards for disposal by September 2002 to meet the facility D&D schedule.

INTRODUCTION

Fernald Radioactive Standard Solutions Description

Radioactive solutions requiring stabilization exist in various compositions throughout the DOE complex. Future cleanup could generate additional actinide residue solutions requiring stabilization at facilities where processing capabilities have been dismantled. Radiological laboratory standard solutions (liquid technical standards) have recently been identified at the Fernald site, which require stabilization and disposal before the laboratory facilities at Fernald can be decommissioned. The radioactive isotopes contained in these liquid technical standard solutions consist of **Ba-Cs:** Barium (Ba) and Cesium (Cs) (~11.8 Liters), **Am-Sr:** Americium (Am), Strontium (Sr), Ruthenium (Ru), Polonium (Po), Radium (Ra), Thorium (Th), Lead (Pb)(~ 6.5 Liters) and **Pu-Np:** Plutonium (Pu) and Neptunium (Np)(~ 6.2 Liters). These standard solutions are contained in 98 containers of small volume in an acidic matrix (pH<2). Figure 1-1 shows a close-up of some of the solutions in storage, and Figure 1-2 shows the 1-liter **Ba-Cs** solution that was used in the first Fernald Test. Because there is no usefulness for these standards, the laboratory has declared these to be waste.

Fig. 1. Radioanlytical standard solutions at Fernald shown in cabinet (1-1) and (1-2) as used for first Fernald test.

Regulatory Considerations and Selection of Treatment

The Resource Conservation and Recovery Act (RCRA) is the U.S. federal law regulating hazardous wastes. RCRA has been implemented through the Code of Federal Regulations (40 CFR). The state of Ohio is authorized to enforce RCRA through its Hazardous Waste Rules contained in the Ohio Administrative Code. RCRA requires the management of hazardous wastes from cradle to grave. RCRA defines what types of materials are hazardous wastes or what characteristics make a material hazardous waste (ignitable, corrosive, reactive, toxic). RCRA defines a corrosive waste as ≤pH 2.0 or ≥pH 12.0. These laboratory standard solutions were acidic solutions and were considered hazardous waste under RCRA.

Treatment of U. S. hazardous waste generally must be performed in a facility with interim RCRA permit status or a full RCRA permit for such treatment. The Fernald laboratory facility in which the Gubka technology was to be used to treat the standard solutions is not RCRA permitted for this kind of activity. While the standards could also be treated under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), extensive preparation and review/approval of a work plan would be required.

However, RCRA also provides for exemptions to the permit requirements for some hazardous waste. One exemption is for treatment that is part of a limited treatability study being conducted to determine if the treatment process is appropriate for the wastes. Under the exemption, the facility must notify the appropriate regulatory agency at least 45 days before conducting the treatability study. For the acidic radioactive waste laboratory standard solutions, this treatability study notice was given to the state regulatory agency 45 days prior to conducting a treatability study with the Gubka blocks. A recordkeeping requirement of the treatability process involves recording dates over which a batch was treated, listing the standards involved in each batch (to include concentration, molarity of acid, volume, the isotope, etc.), and the dates of disposition/shipment.

Before the treatability study was started, neutralization to a pH >2.0 was used to render approximately 1 liter of the **Ba-Cs** solutions non-corrosive under the RCRA definition of hazardous wastes. This solution could be treated with Gubka without formal notification of the regulatory agency. Following treatment, these dry Gubka blocks were not considered to be corrosive or regulated as hazardous waste. Since this neutralize solution was successfully stabilized using the Gubka technology, treatment of the remaining acidic solutions under a RCRA treatability study exemption was selected and started after the 45-day notification was complete.

Based on the current waste disposal options at Fernald, the dried Gubka blocks were evaluated under the Nevada Test Site (NTS) shallow land burial disposal criteria used for other similar low-level wastes. The Gubka blocks alone before application to waste treatment were tested under the RCRA toxic characteristic leach procedure (TCLP) to determine that no RCRA hazardous material is added to the waste disposal from the Gubka. The test results demonstrated that all RCRA hazardous elements are not released at the regulatory and more stringent UTS limits. Since the waste form was not hazardous and physically and chemically stable with no free liquids or particulates, the matrix was accepted by NTS under the existing NTS profile for Fernald LLW. The bagged Gubka blocks containing the residues of the liquid technical standards were accepted as packaged with other LLW in the General Trash category with no additional packaging requirements for shipment and disposal at the NTS.

GUBKA TECHNOLOGY DESCRIPTION

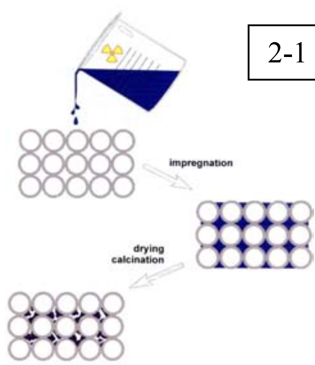
Gubka Material Description and Previous Application

The "Gubka" process uses a new open-cell porous material (Gubka, or "sponge" in Russian), developed by the Russian Institute of Chemistry and Chemical Technology. The Gubka is manufactured from hollow glass crystalline microspheres (cenospheres) recovered from fly ash and having a high, uniform, open-cell porosity. The Gubka matrix is formed from 100-500 micron cenospheres and has been tested in a number of applications, including high-temperature catalysis [1], high temperature filtration, and adsorption of problematic solution components. In producing the Gubka, the cenospheres are separated into fractions based on grain size, density, magnetic properties, and whether or not they were perforated. Selected fractions are molded and agglomerated by sintering at high temperatures with or without a binder. Depending on the cenosphere fractions selected, sintering conditions, and additional treatments, Gubka is formed with an open-cell porosity ranging from 40-90 %. The porous material has a bulk density of 0.3-0.6 g/cm^3, and two types of porous openings: 0.1-30 micrometer flow-through pores in the cenosphere walls and 20-100 micrometer interglobular pores between the cenospheres. [2, 3] Preliminary studies demonstrated the feasibility of using Gubka to stabilize rare earth elements, actinide surrogates as well as long-lived radionuclides such as technicium-99, zirconium-95 and neptunium. Solution components, including plutonium, americium, neptunium and other radionuclides, are adsorbed from the waste solution at ambient to moderate, below boiling temperatures. Repeated saturation-drying-calcining cycles were performed to achieve the final loading. The Gubka material is chemical stable in concentrated nitric, hydrochloric, phosphoric, and sulfuric acid at elevated temperatures [4].

Gubka has also been used to sorb and stabilize surrogate U.S. DOE Savannah River Site Am/Cm residue solutions, which contained lanthanide mixtures in nitric acid and tracer americium–241. These tests resulted in maximum loading up to about 45 wt.% nitrate salts after drying and 33 wt.% oxides after calcination. The rates of americium–241 recovery were measured in 6 M nitric acid at 60 ^{o}C. [1] Other solutions tested included actual and surrogate radioactive waste solutions containing 0.0001-0.7 M nitric/hydrochloric acid and 0-1.2 M sodium nitrate. Waste solid loadings of 46-55 wt.% nitrate salts or 26-37 wt.% oxides after calcination were achieved in those tests. [3] Solutions using uranium as a surrogate for plutonium were stabilized in the porous Gubka block by successive saturation and drying cycles. After calcining, fully dense glass-ceramic tablets were formed in a hot uniaxial press. [5]

Gubka Solution Stabilization Process and Application to Fernald Standards

Gubka technology can be applied in two different methods to stabilize a solution. In both methods the end result is the same, and the dried components of the solution are sorbed in the pores of the Gubka block while the water phase is evaporated. In the first method illustrated by the diagram in Figure 2-1, the porous blocks are repeatedly saturated with solutions containing the radioactive tracers and waste simulants, alternating with drying. The time for each liquid sorption on the Gubka is about 30 seconds, and the drying process is generally finished in about 1 hour at 100°C.



2-1

2-2

Fig. 2. Methods of using Gubka to stabilize solutions. 2-1 illustrates the method of successively loading and drying a solution on a Gubka block. 2-2 shows a container of solution with a Gubka block floating on the liquid surface. As the solution evaporates, the non-volatile components are sorbed in the pores of the Gubka block.

In order to minimize manpower and exposure requirements, a second method, shown in Figure 2-2, was tested. The Gubka blocks used in this demonstration were prepared at Krasnoyarsk from a pilot-plant lot (PS-171c) with unit volume of about 50 cm^3, apparent density of 0.38-0.42 g/cm^3, and total open-cell porosity of 49-54 %. Rather than successively adding and evaporating small quantities of solution on the Gubka block, a larger quantity, typically one-half liter, was placed in an open container in a fume hood and the Gubka block added to float on the surface. This method provides a simple passive approach that minimizes direct solution handling and active heating but requires longer times to complete the stabilization.

Test results show that for some radioanalytical standard solutions with low concentrations of cesium-137, evaporation rates of about 1-2 mL/hr allow 500 mL of solution to be dried on a 50 mL Gubka block in about 10-20 days. Using a cesium-137 tracer solution, about 99 % of the cesium was sorbed in the block and 1 % remained on the container wall. Figure 3 shows the stabilization of the first 1-L batch of the Cs-Ba liquid technical standard solution (shown in Figure 1-2) and resulting bagged Gubka blocks containing Cs-137.

RESULTS

This method was successfully used to stabilize the **Ba-Cs** radioanalytical standard solutions at Fernald in early 2002. The remaining **Am-Sr** and **Pu-Np** solutions are scheduled to be stabilized by September, 2002, to meet the facility D&D schedule. All stabilized waste in bagged Gubka blocks will then be packaged for shipment to the NTS LLW disposal site.

Fig. 3. Passive stabilization of first batch of Fernald cesium-137 liquid technical standard solution (3-1) and bagged Gubka blocks containing residual Cs-137 salts (3-2).

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