DEPLOYMENT OF THE GUBKA TECHNOLOGY TO STABILIZE RADIOACTIVE STANDARD SOLUTIONS AT THE FERNALD ENVIRONMENTAL MANAGEMENT PROJECT

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ABSTRACT

This paper describes the deployment of the Gubka technology to stabilize liquid technical standards at the Fernald Environmental Management Project. Gubka, an open-cell glass crystalline porous material, was developed by a joint research program of Russian Institutes at St. Petersburg, Krasnoyarsk, and Zheleznogorsk and the Idaho National Engineering and Environmental Laboratory.

Gubka technology can be applied in an active or a passive method to stabilize a solution. In both methods the result is the same, and the dried components of the solution are sorbed in the pores of the Gubka block while the liquid phase is evaporated. In this deployment Gubka blocks were passively floated in the solutions at ambient conditions. As the solutions evaporated, the non-volatile components were sorbed in the pores of the Gubka blocks.

The waste-loaded Gubka blocks have been packaged for transportation and disposal at the Nevada Test site within an existing waste category.

TECHNOLOGY DESCRIPTION
The “Gubka” (“sponge” in Russian) process uses an open-cell porous material 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, high temperature filtration, and adsorption of 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/cm³, 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.

TECHNOLOGY APPLICATION

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 liquid phase is evaporated. The diagrams in Figure 1 illustrate these two methods.

In the first method, the porous blocks are repeatedly saturated with solutions containing the radioactive materials and waste constituents, alternating with drying at an elevated temperature. 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. Figure 1-1 illustrates the method of successively loading and actively drying a solution on a Gubka block.

In the second method the Gubka block is passively floated in the solution at ambient conditions. As the solution evaporates, the non-volatile components are sorbed in the pores of the Gubka block. Figure 1-2 shows a container of solution with a Gubka block floating on the liquid surface.
Following either method, the loaded Gubka blocks could be further treated or left as generated depending on the application. Further treatments such as calcination and/or densification offer a more durable form than the original Gubka blocks.

LABORATORY TESTING

Laboratory studies were conducted in the United States at the Idaho National Engineering and Environmental Laboratory (INEEL) and in Russia at facilities in St. Petersburg, Zheleznogorsk, and Krasnoyarsk to develop this technology. These efforts demonstrated the feasibility of using Gubka to stabilize rare earth elements, actinide surrogates as well as long-lived radionuclides such as $^{99m}\text{Tc}$, $^{95}\text{Zr}$, and $^{237}\text{Np}$. Solution components, including Pu, Am, Np 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.

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 $^{241}\text{Am}$. These tests resulted in maximum loading up to about 45 wt.% nitrate salts after drying and 33 wt.% oxides after calcination. The rates of $^{241}\text{Am}$ recovery were measured in 6 $M$ nitric acid at 60°C. Recovery of the Am/Cm (surrogate) was also demonstrated by leaching those materials from the Gubka blocks in a nitric acid bath.

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. 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.
DEPLOYMENT AT FERNALD ENVIRONMENTAL MANAGEMENT PROJECT

Approximately 25 L of radiological laboratory standard solutions (liquid technical standards) were identified at the Fernald Environmental Management Project within Laboratory Building 15A that required stabilization and disposal before the laboratory facilities could be decommissioned. Because there was no identified reuse for these standards, the laboratory declared these to be available for stabilization and disposal. The radioactive isotopes contained in these liquid technical standard solutions consist of \textbf{Ba-Cs}: Ba and Cs (~11.8 L), \textbf{Am-Sr}: Am, Sr, Ru, Po, Ra, Th, Pb (~ 6.5 L) and \textbf{Pu-Np}: Pu and Np (~ 6.2 L). These standard solutions were stored in 98 small containers in an acidic matrix (pH<2). Figure 2-1 shows a close-up of some of the solutions in storage, and Figure 2-2 shows the 1-L \textbf{Ba-Cs} solution that was used in the initial phase of the Fernald deployment.

As Fernald is located in the state of Ohio, deployment of this technology required the cooperation of the Ohio Environmental Protection Agency (OEPA). The first portion of the deployment was accomplished by neutralizing 1 L of \textbf{Ba-Cs} solutions to a pH >2.0 to render it non-corrosive under the Resource Conservation and Recovery Act (RCRA) definition of hazardous wastes. This solution was treated with Gubka without the requirement of formal notification of the regulatory agency. This allowed the stabilization effort to have an earlier starting date. The second portion of the deployment was conducted under an exemption to RCRA, known as a treatability study. The Ohio EPA prior to the commencement of the treatability study required a 45-day notification period.

In order to minimize manpower and exposure requirements, and achieve cost savings, the passive method (previously shown in Figure 1-2) was used in the Fernald deployment. 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 500 mL, 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 avoids active heating but requires longer times to complete the stabilization.

Results showed that for some radioanalytical standard solutions with low concentrations of $^{137}$Cs, 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 $^{137}$Cs 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.

![Figure 3. Passive stabilization of first batch of Fernald $^{137}$Cs liquid technical standard.](image)

REGULATORY CONSIDERATIONS

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 (OAC).

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 $<\text{pH 2.0}$ or $>\text{pH 12.0}$. 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 deployed to treat the standard solutions was 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. A record keeping requirement of the treatability process involved 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 L of the Ba-Cs solution 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 authorized and started after the 45-day notification was complete. The Ohio EPA confirmed that the remainder of the deployment was considered a treatability study under OAC 3745-51-04 (F) and that no hazardous waste permit was required for this activity.

A concern was raised that the Gubka blocks may themselves introduce hazardous materials into the treatment process. To allay this concern, three representative Gubka blocks were subjected to the Toxic Characteristic Leach Procedure (TCLP). The results showed that all hazardous metals were measured below the hazardous action limits and also below the more restrictive Universal Treatment Standard (UTS). The TCLP was conducted under the established quality assurance protocol at INEEL for environmental samples.

**WASTE DISPOSAL**

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 TCLP to determine that no RCRA hazardous material was added to the waste disposal from the Gubka. The test results demonstrated that RCRA hazardous elements were 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.

COST SAVINGS

The deployment of the Gubka technology at Fernald involved the passive use of the Gubka blocks. That is, the block was simply floated in the solution. As the solution evaporated, the non-volatile components were sorbed in the pores and on the surface of the Gubka block. Laboratory technician time was greatly reduced by application of the Gubka technology.

Application of this technology was an improvement over the baseline technology of evaporating to dryness at an elevated temperature (in the same laboratory hood). The baseline technology would have required a laboratory technician be continually present when the solutions were being evaporated.

Fernald has estimated as savings of $280,000 (by savings in man hours expended) by deploying the Gubka technology to immobilize its liquid technical standards.

ISSUES AND LESSONS LEARNED

The availability of Gubka is of concern as no commercial product is available. During FY01, the Russian research facilities in Zheleznogorsk and Krasnoyarsk produced about 35 kg of Gubka in a pilot-scale run. The Gubka was formed into 2,000 blocks each of 50 mL volume. These blocks were shipped to INEEL. No cost estimate was made for these blocks as the pilot-scale production was jointly funded by the Russian facilities and the U.S. DOE.

After the deployment at Fernald and other experimental uses, it is estimated that enough Gubka remains in storage (1900 blocks or 95 L) at INEEL to immobilize perhaps another 950 L of solutions (similar in concentration to the Fernald solutions, and assuming comparable volume reductions).

The Russian facilities have estimated the cost of additional Gubka from another limited pilot-scale production to be about $10-50 per kg. As there is no reliable cost estimate available for large-scale production of Gubka, such a task has been proposed for FY03, but is yet to be funded.

During the Fernald deployment of the Gubka technology, crystallization of salts on the Gubka surface and on the surface of the beaker was observed for some chloride containing solutions (0.5g/L Cl). The onset of this “salting” occurred when approximately 750mL of the initial 1000mL of solution had evaporated (using a 300mL Gubka block). This salting reduced the uptake of more solution by the Gubka block.
This problem was simply addressed by removing the block, rinsing the block and beaker surfaces to dissolve the salt crystals and adding a new block to continue the stabilization. This has caused some time delays and has led to a lower-than-expected volume reduction. Similar salting had been observed in previous laboratory experiments. However, the concentration of salts in solution in those experiments were at least an order of magnitude greater that the concentration of the Fernald solutions. Russian researchers have recommended that a study of the phenomenon that was observed at Fernald be included in future work. However, no source of funding has been identified for additional work scope.

RESULTS

The Gubka technology has been successfully deployed to stabilize the Ba-Cs, the Am-Sr and the Pu-Np radioanalytical standard solutions at Fernald. The completion of the deployment met the facility closure schedule. All stabilized waste generated by this deployment was packaged for storage until the waste profile is completed for shipment to the NTS low-level waste disposal site. Figure 4 show Gubka blocks in sealed bags ready for shipment to NTS for disposal.

Figure 4. Bagged Gubka blocks containing residual $^{137}$Cs salts.