CALCINED HIGH-LEVEL RADIOACTIVE WASTE

OVERVIEW

High-level radioactive waste (HLW) generated at the Idaho National Laboratory (INL) was calcined, *i.e.*, converted from a liquid to granular solids. The HLW was the waste product of reprocessing spent nuclear fuel (SNF) to recover uranium-235, krypton-85, and certain fission products (Todd *et al.*, 1993). The SNF was reprocessed from 1952 to 1991 and the resulting liquid HLW was calcined from 1963 to 2000. In the calcination process, liquid waste is sprayed onto a fluidized bed of spherical particles heated to 400–600°C (750–1,100°F), which are most often composed of dolomite [$CaMg(CO_3)_2$] (Staiger and Swenson, 2011). At calcination temperatures, water and nitric acid in the waste are evaporated, metallic nitrates are decomposed to metal oxides, and the calcine is formed in layers on the fluidized bed particles (Freeby, 1975; Newby and O'Brien, 2000). Calcination reduces the waste volume more than six-fold (Newby and O'Brien, 2000) and decreases radionuclide mobility by converting HLW from a liquid to a solid state. The resulting solids are mainly metal oxides, but also contain fluorides, chlorides, phosphates, and sulfates. Calcined waste is a fine, granular material with particle diameters typically in the range 0.3–0.7 mm (0.01–0.03 in) (Staiger and Swenson, 2011), a particle size range similar to medium to coarse sand.

STORAGE AND LOCATION

Liquid HLW originally was calcined at the Waste Calcining Facility (WCF) and later, at the New Waste Calcining Facility (NWCF) located at INL. The calcined wastes currently are stored in Calcined Solids Storage Facilities (CSSFs). Each CSSF consists of three to twelve stainless steel storage bins (43 total bins) housed within a reinforced concrete vault. Seven CSSFs were constructed, but only six are used. Figure 1 is an aerial photograph showing the locations of the calcine processing and storage facilities. The WCF has been decommissioned. The WCF calcine is stored in CSSFs I, II, and III. The NWCF calcine is stored in CSSFs IV, V, and VI. CSSF VII is unused (Staiger and Swenson, 2011). Table 1

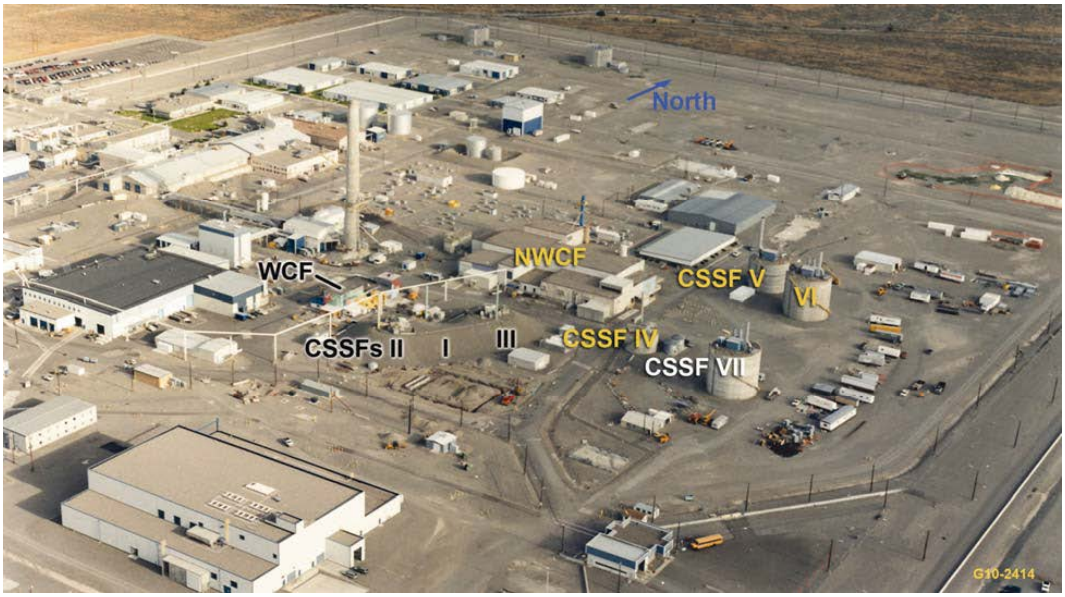

Figure 1. Aerial Photograph Showing the Waste Calcining Facility (WCF), the New Waste Calcining Facility (NWCF), and the Calcined Solids Storage Facilities (CSSFs) at the Idaho National Laboratory.

Table 1. Summary of High-Level Waste Calcination and Storage at the Idaho National Laboratory (Staiger and Swenson, 2011)

Calcined Waste Production Facility	Operating Years	Volume of Liquid HLW Processed	Volume of Calcined Waste Produced	Storage Facilities
Waste Calcining Facility	1963–1981	4,091,000 gal (15,490,000 L)	77,300 ft^3 (2,190 m^3)	CSSFs I, II, III
New Waste Calcining Facility	1982–2000	3,642,000 gal (13,790,000 L)	78,000 ft^3 (2,210 m^3)	CSSFs IV, V, VI

summarizes the calcining operations at the WCF and NWCF, as well as the calcined waste storage locations. Figure 2 is a photograph of the storage bins in CSSF III.

COMPOSITION

The composition of the calcine stored at INL varies significantly because diverse types of SNF from numerous reactors were reprocessed. The different types of SNF generated chemically different liquid HLW and, consequently, chemically different calcine. The liquid HLW and the resulting calcine often were named for the cladding on the SNF from which they were derived. For example, "aluminum waste" and "zirconium waste" were names applied to liquid HLW generated by dissolving aluminum- and zirconium-clad SNF, respectively. These names also were used to refer to the calcine, such as "aluminum calcine" or "zirconium calcine." Liquid HLW that contained relatively high concentrations of sodium (1 to 2 moles per liter) was called sodium-bearing waste (SBW). The SBWs included most of the wastes generated from equipment decontamination and support systems (*e.g.*, ion exchangers, off-gas systems, scrubbers, and laboratory analyses). SBW was not calcined by itself, but was blended with liquid HLW from SNF processing prior to calcination to prevent clumping of solids in the calciner vessel.

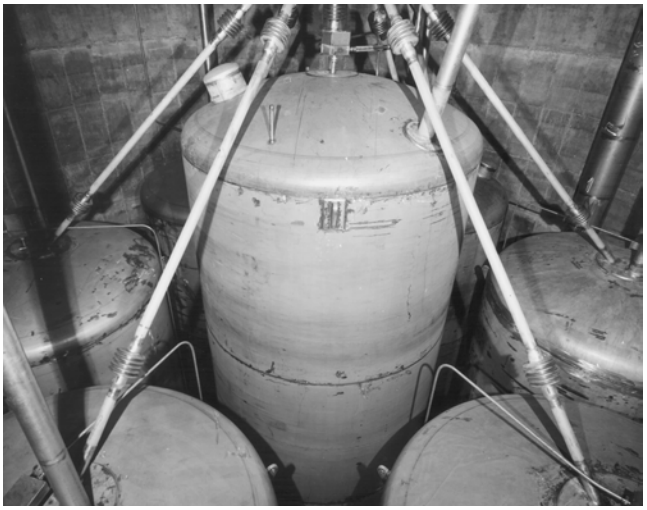

Figure 2. Storage Bins in CSSF III. The Center Bin Is Surrounded by Six Shorter Bins. From Staiger and Swenson (2011)

Figure 3 shows the typical major chemical constituents of four of the more common types of calcine: aluminum, zirconium, Fluorinel/SBW blend, and aluminum nitrate/SBW blend. Fluorinel calcine is similar to zirconium calcine, except that it contains cadmium and sulfate from the cadmium sulfate and cadmium nitrate that were used as neutron absorbers in the fuel dissolution process. Radioactive elements constitute only a small fraction (less than 1% by mass) of the calcined waste. The calcined waste also contains chromium, mercury, nickel, lead, barium, silver, arsenic, and selenium. The calcined waste stored in the CSSF bins comprises multiple layers of chemically and radiologically different calcine (Staiger and Swenson, 2011).

MASS AND RADIOACTIVITY

Approximately 4,400 m^3 (about 160,000 ft^3) of calcined waste are currently stored at INL (Staiger and Swenson, 2011). This volume is equivalent to approximately 6,140 metric tons (about 6,800 short tons) of calcine, based on an estimated average density for calcine (Dahl, 2003). The calcined waste will have

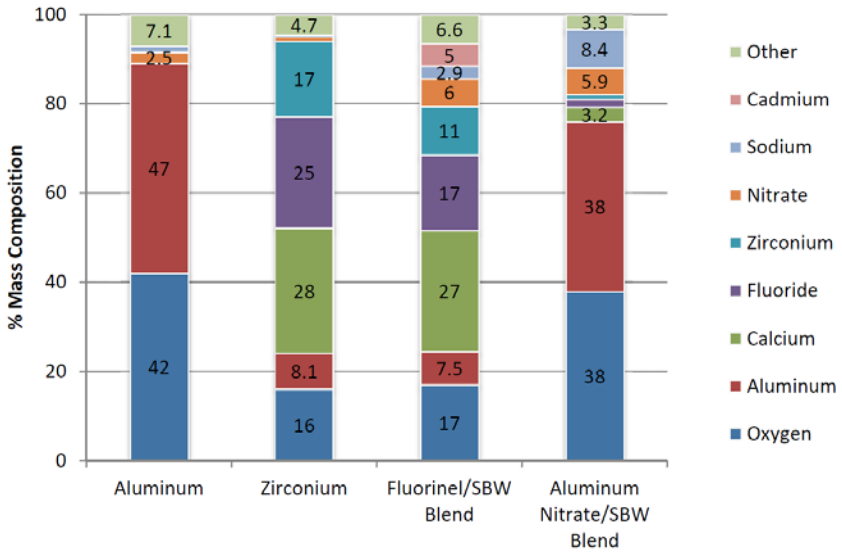

Figure 3. Chemical Compositions of Four Calcine Types
Data from Staiger and Swenson (2011)

an estimated radioactivity of 31 million curies on January 1, 2017,[1] and is the largest contributor to the total radioactivity of wastes (SNF and HLW) stored at INL. More than 99% of the radioactivity comes from relatively short-lived cesium-137 and strontium-90 and their respective daughter products, barium-137m and yttrium-90 (SNL, 2014). Radioactive decay will decrease the total radioactivity of the calcined waste by approximately 50% to about 14.8 million curies in 2048 (SNL, 2014), which is the year DOE set as its target for having a geologic repository for HLW constructed and operating (DOE, 2013).

STABILITY AND RADIONUCLIDE RELEASE IN A GEOLOGIC REPOSITORY

For interim storage, calcine is considered a safer waste form than the liquid HLW from which it was derived because radioactive material leaks are less likely when the waste is a solid. However, for the purpose of geologic disposal, calcine may be a less suitable waste form compared to others such as borosilicate HLW glass (see fact sheet on Vitrified HLW). The dissolution rate of calcine is four to six orders of magnitude greater than that of HLW glass (Stewart, 1985). Laboratory experiments have shown that calcined waste releases significant amounts of radionuclides within 100 days of exposure to water, although the waste matrix itself is slow to dissolve (Berreth, 1988).

Due to the high radionuclide release rate observed in calcine leaching experiments, an instantaneous release model is considered appropriate as a conservative representation of calcined waste degradation in a geologic repository upon breach of the calcined waste container. However, DOE is considering further processing of the calcined waste prior to disposal, which would alter its degradation rate and mechanism. In December 2009, DOE issued a Record of Decision (75 Federal Register 137) documenting the selection of hot isostatic pressing (HIP) technology to convert the granular calcine into a glass ceramic waste form. In the HIP process, calcine and ceramic-forming chemical additives would be mixed and then loaded into thin-walled canisters that would be welded shut. These canisters would then be placed in a pressure vessel that would be heated to "melt" the mixture while pressurized with argon gas. The net effect would be production of a homogeneous glass ceramic waste form that reduces the original volume

[1]Based on the value given in Carter *et al.* (2013, Table F-1), decay corrected to January 1, 2017.

by approximately 30% and generates no secondary waste stream. Glass ceramics have properties similar to HLW borosilicate glass.

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The U.S. Nuclear Waste Technical Review Board is an independent federal agency established in the 1987 amendments to the Nuclear Waste Policy Act (NWPA). The Board evaluates the technical and scientific validity of U.S. Department of Energy activities related to implementing the NWPA and provides objective expert advice on nuclear waste issues to Congress and the Secretary of Energy. The eleven Board members are nominated by the National Academy of Sciences and are appointed by the President.