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PYROCHEMICAL TREATMENT OF IDAHO CHEMICAL PROCESSING PLANT HIGH-LEVEL WASTE CALCINE

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Specific Need

The Idaho Chemical Processing Plant (ICPP), located at the Idaho National Engineering Laboratory (INEL), has reprocessed irradiated nuclear fuels for the U. S. Department of Energy (DOE) since 1951 to recover uranium, krypton-85, and isolated fission products for interim treatment and immobilization. The acidic radioactive high-level liquid waste (HLLW) is routinely stored in stainless steel tanks and then, since 1963, calcined to form a dry granular solid. The resulting high-level waste (HLW) calcine is stored in seismically hardened stainless steel bins that are housed in underground concrete vaults. About 3,500 cubic meters of radioactive HLW calcine is currently stored at the Idaho Chemical Processing Plant. Although no decision has been made on the final disposition of the calcine, development is on-going to devise a Best Demonstrated Available Technology (BDAT) treatment method to achieve compliance with Land Disposal Restriction (LDR) and minimize the volume of HLW to be sent to a federal geologic repository. The currently accepted BDAT treatment for calcine is the formation of a borosilicate glass waste form. This waste form will meet federal repository criteria, however, will result in a 60% increase in volume over the calcine. A glass-ceramic waste form is under development at ICPP and is being considered by EPA as BDAT. This waste form also meets federal repository criteria and results in a net volume decrease of 40% over the calcine.

DOE Order 5820.2A directs that all new and readily retrievable HLW be processed and disposed of in a geologic repository according to the requirements of the Nuclear Waste Policy Act, as amended. ICPP HLW is a Mixed Waste, and the disposal technology must be developed to support near-term regulatory relief on the May 1992 LDR deadline as well as meet long-term LDR compliance for storage as per 40 CFR Part 268 and the No-Migration Variance Petition being negotiated with the Environmental Protection Agency. The State of Idaho Notice-of-Noncompliance Consent Order of April, 1992, requires operation of the calciner. Storage of the resulting calcine will fall directly under Part 268, requiring further treatment using BDAT, which is under development in this program.

Overview

A research and development program has been established to determine the feasibility of treating ICPP HLW calcine using pyrochemical technology. The calcine primarily consists of inert materials that come from dissolving fuel claddings, soluble neutron poisons added to the dissolution process, and chemical additions made to enhance calcination and reduce corrosion. Several types of calcine exist from dissolution of different fuel types. Compositions of the three most abundant calcine types are shown in Table I.

Pyrochemical treatment consists of high-temperature processing for removal of inert materials and separation of actinides and fission products in a molten metal/salt environment. This conceptual process has the potential of significantly reducing the amount of HLW which would require disposal in a federal repository by up to 30 fold. A pyrochemical process can potentially separate the radioactive components from the inert with much less supplemental waste generation and therefore achieve waste minimization aims. If the non-radioactive material is separated from the radioactive and hazardous components, cost avoidance to the DOE in disposal charges at a geologic repository would be very significant. The principal incentive for partitioning actinides from the fission products and the remaining bulk waste is the cost of disposal of the long-lived radioisotopes. By reducing the volume of this waste, potentially billions of dollars can be saved in disposal costs. Furthermore, concentrating the actinide and fission products as metal alloys opens numerous new opportunities for immobilizing, packaging, and storing and/or disposing of the waste.

Table I

Calcine Compositions*

Component	Alumina (wt %)	Zirconia (wt %)	Zirconia-Sodium Blend (wt %)
Al_2O_3	83.4	14.4	14.1
B_2O_3	0.7	3.0	2.5
ZrO_2	0.7	23.4	19.0
CaF_2	--	54.3	44.4
CaO	3.5	3.9	12.8
Na_2O	3.0	--	4.5
K_2O	0.6	--	0.9
Fe_2O_3	--	0.1	0.3
SO_4	--	--	0.3
PO_4	--	--	0.2
Radionuclides	<1.	<1.	<1.
Residual Volatiles	5.5	1	3-8
Other	--	1	1

*Typical compositions, may not be additive to 100%

Traditional separation methods such as solvent extraction and ion exchange would require the calcine to be redissolved in acids, thereby generating a final liquid waste volume which would exceed that generated during fuel reprocessing. A pyrochemical process can potentially separate the radioactive components from the inert with much less supplemental waste generation and therefore achieve waste minimization aims. A potential profound cost savings in reduced numbers of HLW canisters sent to a federal repository can be realized by the DOE via the employment of a pyrochemical treatment process for ICPP calcine. Table II summarizes the results of scoping calculations concerning the relative volume of waste generated from the reprocessing of spent nuclear fuels. Glass-ceramic and glass waste forms are candidates to immobilize HLW generated by pyrochemical treatment. The waste form to be utilized would depend on feasibility, processability and durability. In either case, the anticipated HLW volume reduction is more than twice that of the current most favorable alternative. This represents potentially significant savings in HLW disposal costs.

Table II

Waste Volume Summary Per Volume of Calcine

Wasteform	Relative HLW Volume
Calcine	1.00
Calcine/Glass	1.63
Neutralization	1.28
Glass-Ceramic	0.64
Actinide Removal	0.29
Pyrochemical Treatment Glass	0.14
Pyrochemical Treatment Glass-Ceramic	0.06

Technology Description

The proposed pyrochemical process for actinide partitioning and immobilization of ICPP calcine is described as follows: Initially, calcine would be retrieved and loaded into a multi-purpose reaction vessel. These solids would then be heated to volatilize elements and compounds which would sublime prior to the melting temperature of about 1420°C for the major component, calcium fluoride. These would most likely include cesium, selenium, technetium, mercury, and cadmium. The volatile radioactive and hazardous elements and compounds would be collected from the off-gas and combined with the other hazardous and radioactive components in downstream unit operations.

If the calcine can be melted, it could be possible to convert the calcine into a molten solution, with the possible addition of small amounts of other additives, and remove Al_2O_3 and ZrO_2 by selective slagging. Preliminary tests show that a simple slagging step may not work, and further tests may identify if alternative steps are feasible.

Following the distillation of the volatile species and, if feasible, slagging removal of oxides, the calcine would be dissolved in a molten salt system and treated with an active metal reductant to reduce most of the actinides to their metallic states. Addition of a metallic solvent would then allow these metals to be contained in an alloy. The solvent metal would be needed to assimilate the reduced radionuclides and make a physical separation from the salt, since the volume of the radionuclides is rather small. The molten salt system containing the other inerts would then become a low-level waste as essentially all of the actinides would be contained in the alloy phase.

The alternative pyrochemical process to be investigated for separating the actinides and fission products from calcine is a halide volatility process. Calcine would be reacted with a chlorinating agent such as a carbon/chlorine gas mixture to give a halogenated product. This product would then be heated above the boiling or sublimation point of the halogenated calcine, and a separation would be made by condensing the off-gas in a series of condensers. Once this first separation is made, further separations would be completed on the condensed salt mixtures to reduce the high-level waste volume.

The goal of this program would be to render this salt and oxide mixture a non-radioactive, non-hazardous waste which would not be subject to radioactive and RCRA regulations. If it could not be rendered non-radioactive and non-hazardous, the salt and oxide mixture would be combined with stabilizing materials such as glass or cement and disposed of as a low-level waste.

Once the actinides are removed as an alloy, they can be potentially separated by a number of demonstrated pyrochemical processes such as salt-transport, electrorefining, distillation, and electrowinning. All of these processes have been demonstrated in LMFBR fuel reprocessing and plutonium processing development. It appears that the desired separation closely resembles the Argonne National Laboratory IFR process to purify actinides by electrotransport through a molten salt which leaves the impurities (fission products) in the alloy metal.

Depending on operating temperatures, cadmium, from the initial distillation step or from the alloy, would become an important component. A cadmium pool, containing the actinides and fission products in solution, would be placed in contact with a molten salt and made anodic. Electrotransport would then occur as a (negative) current that enters the electrolyte (salt) at the cathode and leaves at the anode (metal). Electric current is carried through the electrolyte by motion of ions and through the electrodes by motion of electrons or equivalent charge carriers. A net flow of metal leaves the anode and is collected in the cathode; the amount of metal corresponds to the magnitude and duration of the electronic current in the electrodes and of the ionic current in the electrolyte. The actinide elements will be transported to the cathode by careful control of the operating parameters. The cadmium can be distilled from the actinides and returned to the fission product portion when the reaction is complete. The salt electrolyte would be recycled. It may be possible to keep cadmium in the system to act as the carrier metal by careful adjustment of the process parameters. This would further minimize waste volumes by eliminating the need to add a solvent metal to the mixture.

At this point both fractions, the actinides and the fission products, would require stabilization and packaging for disposal. Incorporation into a glass or glass-ceramic matrix are the most probable immobilization forms. The actinides could be stored as oxides for later use in various DOE programs if desired.

Regulatory Requirements

Major regulatory drivers for this program include the following: 40 CFR Part 268 (Land Disposal Restrictions), 40 CFR Part 268.5 Case-by-Case Extension, State of Idaho NON Consent Order of April 1992, DOE Waste Reduction Policy Statement, 40 CFR Part 265.75 (Waste Minimization), Pollution Prevention Act of 1990, DOE 5820.2A. The Nuclear Waste Policy Act requires that EPA 40 CFR Part 191 and NRC 10 CFR Part 60 apply to ICPP HLW forms. NEPA requires evaluation of all alternatives prior to a Record of Decision (ROD)

The ICPP HLW Calcine Disposal Program is an integral part of the DOE LDR Case-by Case Extension Application for Radioactive Mixed Waste (September 1991). 40 CFR Part 268.5 requires, as stated in the Case-by-Case application, a "binding contractual commitment" to provide alternative treatment, recovery, or disposal capacity, specifically in this case to develop the glass-ceramic as a final waste form. The Idaho Waste Immobilization Facility (IWIF) is listed as being available to begin processing glass-ceramic logs in 2014 in the application.

The disposal of ICPP HLW must meet the licensing requirements of NRC and EPA standards in 40 CFR 191 for the radioactive constituents and in 40 CFR 268.50 for the hazardous constituents. The NRC requirements are given in 10 CFR 60 for repository disposal of HLW and include allowable radionuclide release limits as well as other assurance requirements. A procedure for waste qualification has been established by DOE-EM and DOE-RW with input from the NRC in order to assure NRC at the time of repository licensing that the HLW forms will meet the licensing requirements of the repository. Permitting requirements must be met for the construction of the a Multifunction Pilot Plant Facility and the full-scale IWIF. The EIS for the IWIF will include a Record of Decision to select the technology for full-scale implementation.

DOE Order 5820.2A requires that "new and readily retrievable waste be processed and ... disposed of in a geologic repository according to the requirements of the Nuclear Waste Policy Act ... ." The EM HLW Program goal described in the Five Year Plan is the "successful development, demonstration, and deployment of treatment technologies to produce acceptable waste forms for disposal of HLW." The recent report of the Ahearne Advisory Committee on Nuclear Facility Safety recommended converting DOE HLW to a form suitable for disposal. The DOE "Waste Reduction Policy Statement" issued by several Assistant Secretaries, as well as regulations 40 CFR Part 264.75 (h) and (i) and the Pollution Prevention Act of 1990 also drives waste volume reduction through waste minimization and waste treatment.

Accomplishments and Future Plans

A detailed survey of applicable and related literature was performed. A data base of thermodynamic and process data was compiled, and chemical systems still requiring data were defined. Safety documentation and experimental run plans were prepared for initial testing. Procurement and installation of small-scale experimental equipment was initiated. Preliminary flowsheet modelling was performed to determine feasibility of a slagging step to remove inerts, and results indicated this process may not feasible as planned. Experimental melting of calcine is still being considered a possible option as part of Phase II. A preliminary halide volatility flowsheet considered feasible for treatment of alumina calcine was issued.

Bench-scale and pilot-plant mock-up tests are required for the unit operations in the processing steps for delivering, pretreating calcine and additives, for the pyrochemical treatment step, and for the treatment of the product and waste streams after the pyrochemical step. The results of the tests will determine the feasibility of processing steps and various pieces of equipment and design information for further larger-scale tests as needed, including Integrated Pilot Plant tests. Additional tests will be run at other laboratories to evaluate selected technologies and flowsheet conditions. Equipment tests for selected waste treatment options such as glass or metal waste form fabrication will be started in FY 1994.

Pyrochemical treatment tests will include measurements and analyses of off-gas from simulated calcine at the expected treatment temperature range. Preliminary volatilization tests have indicated that up to 75% of the cesium can be removed by heating at 900° C for five hours. In addition, separation of radioactive components by direct oxide reduction, or leaching with a molten salt will be tested. Calcine reaction with halides will also be tested as an alternative separation process to calcine-salt melting. For the processing steps which appear feasible, tests will be continued to better define reaction rates and ranges of desirable processing conditions.

Glass and glass-ceramic waste form compositions have been identified with potentially low leach rates for HLW streams resulting after pyrochemical separations. Other potential waste forms for pyrochemical waste streams include metal and grout. Using data from the pyrochemical separations tests, the chemical composition of the possible waste streams arising from the pyrochemical process must be determined. Scoping tests will be run for those compositions to determine the acceptability of glass, glass-ceramic and other waste forms, followed by refinement of additive composition and detailed phase diagram evaluation. Material properties, including detailed physical and chemical microstructure and leach rates will be measured to arrive at a recommended waste form.

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