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ABSTRACT

The importance of effective waste management in the nuclear fuel cycle cannot be overestimated. At Oak Ridge National Laboratory (ORNL), development work in waste reprocessing and treatment includes the testing and use of various additives for the purpose of facilitating adherence to both process and regulatory performance criteria.

Three waste reprocessing/treatment technologies and the associated materials will be discussed in this paper: (1) suspension and transfer of sludge from waste storage tanks; (2) treatment to render a waste in compliance with regulatory requirements; and (3) fluoride-rich waste reprocessing.

INTRODUCTION

During the past 44 years, the Chemical Technology Division (CTD) of ORNL has been a major contributor to all aspects of the nuclear fuel cycle in the defense and commercial sectors. Early development emphasized fuel processing and reprocessing technology. In recent years, the emphasis has shifted to the "back end of the fuel cycle" or waste management.

This paper discusses three waste reprocessing/treatment technologies to which CTD has contributed in recent years and the materials associated with these technologies. The technologies discussed are (1) suspension and transfer of sludge from waste storage tanks; (2) treatment to render a mixed waste in compliance with regulatory requirements; and (3) fluoride-rich waste reprocessing. In each case, the addition of a specific material will result in the desired properties.

SLUDGE REPROCESSING

In 1943, the Clinton Laboratories were built at Oak Ridge, Tennessee, to serve as a pilot plant for production operations at Hanford, Washington. The work included the construction of six underground tanks for storage of the wastes generated at the laboratories. These tanks were in operational use by November 1943. Subsequently, Clinton Laboratories became Oak Ridge National Laboratory, and the waste storage tanks became an integral part of the laboratory's waste system. The waste handled by this system is routinely treated with caustic to a pH of 10 or greater; substances that are insoluble in alkaline solutions precipitate and settle, principally in the waste storage tanks. By 1980, when the waste system was revised and

these tanks were no longer being used, they had accumulated ~1.5 x 10^6 L (400,000 gal) of sludge containing the insoluble fraction of the radionuclides that had been generated at the laboratory. A program to empty the waste tanks and dispose of the accumulated radioactive sludge had already begun (in 1977). Process development, system design, and facility construction were completed by June 1982. In ~18 months of operations, all six tanks were sluiced and ~90% of the sludge was resuspended[1] and was pumped to the ORNL Hydrofracture Facility for temporary storage and, subsequently, permanent disposal.[2]

The diameter of the waste storage tanks is 15 m (50 ft) with a center depth of 5.5 m (18.25 ft) and an individual tank capacity of ~640,000 L (170,000 gal). The tanks were built by spraying a cement slurry against a lattice of reinforcing bars (the Gunite process) for a final wall thickness of 19 cm (7.5 in). A French drain at the base of the outside wall was provided with a leak detection system, but there was no provision for double containment. The interiors of the tanks are relatively uncluttered; there is a pump suction leg and a level probe, but no cooling coils.

The depth of sludge varied from ~30 cm (1 ft) found in three tanks to 3 m (10 ft) in one of the tanks. Chemical and radiochemical analyses of sludge samples showed great variability among the tanks, between different levels in the same tank, and even between supposedly duplicate samples taken from the same level in the tank. Data collecting through inventory sampling showed the major elements in the tanks to be uranium, iron, thorium, calcium, and aluminum. The primary radionuclide (representing 95% of the total activity) was ^{90}Sr. Analyses indicated ~2 x 10^6 C_i of ^{90}Sr (which was later shown to be an overestimate) and 4,500 C_i of TRU isotopes (about 10 times higher than estimates based on accountability records). Radionuclide assays subsequently done in support of disposal operations indicated ~730,000 C_i of ^{90}Sr and 2,500 C_i of TRU isotopes. These figures are about half the estimates generated by grab sampling prior to sluicing. The lower figures are considered to be more accurate because they represent measurements made on samples from the "homogenized" sludge.

Laboratory tests indicated that ~50 wt % of the sludge consisted of small particles (< 10 μm diam) which settled slowly in water. Tests on a separated fraction of the particles > 10 μm diam showed that they were quite friable. A series of laboratory and field tests with simulated sludges and hot-cell tests with actual sludges demonstrated[3] that:

1. the sludge agglomerates could be reduced to < 20-μm size with a commercially available grinder;
2. sludge particles < 20 μm diam would not settle for several days if dispersed in 2.5 wt % bentonite suspension;
3. slurries containing 2.5 wt % bentonite could be pumped at concentrations up to 25% wt %;
4. a single sluicer mounted high in each tank could be used to resuspend the sludge;
5. instrumentation was a problem because most available instruments would not work on slurries under field conditions; and

6. vision into the tank during sluicing would be essential to monitor process operations.

A diagram of the batch process used for emptying the waste tanks is shown in Fig. 1. In this process, a bentonite suspension is continuously pumped between the tank being sluiced and a near-empty waste tank located nearby. Initially, a 150,000-L (40,000-gal) batch of 2.5% bentonite suspension in water is mixed and collected in the near-empty tank that serves both as a feed tank and as the container for the resuspended waste sludge. This suspension is then pumped through a remotely controlled sluicer nozzle to impinge on the sludge in the waste tank being emptied. The impact of the jet stream breaks up the settled sludge and resuspends the individual particles while the bentonite suspension hinders settling. The resuspended sludge is pumped from the waste tank through a grinder that breaks up oversized particles and then returned to the feed tank. This operation continues until the sludge concentration in the feed tank approaches 15 wt %. At this point, the sluicing is stopped, and the slurry in the feed tank is pumped to storage. A new batch of bentonite feed suspension is then prepared, and the cycle is repeated until the waste tank is judged empty. Fig. 2 shows the arrangement of tank sluicing equipment.

Calculations indicated that the weight of the sludge solids transferred from the six waste storage tanks was ~40% more than was originally thought to be there. Radionuclide assays were as previously described. Each of these values is approximately half the value estimated from analyses of grab samples prior to the sluicing operations.

In evaluating possible suspending materials, a delicate balance between (1) having enough material to suspend the sluiced sludge and (2) creating a gelatinous mass that could not be pumped, had to be maintained. Many organic viscosity "enhancers" were evaluated that fell into the latter category. Others were rejected because of the uncertainty in the long-term effect of the waste stream on the suspender.

Laboratory experiments determined that both bentonite and attapulgite clays were effective suspending agents. Bentonite was chosen because of more reliable performance in laboratory settling tests and viscosity determinations.[3]

REPROCESSING/TREATMENT IN ORDER TO CONFORM TO REGULATORY REQUIREMENTS

In the United States three categories of radioactive waste exist: (1) high-level or that which has had direct contact with the fuel element; (2) Transuranic (TRU), if TRU isotopes equal or exceed 100 nC_i/gram; and (3) low-level. These wastes are regulated by either U.S. Department of Energy (USDOE) or Nuclear Regulatory Commission (NRC) directives.

The disposal of low-level wastes in grout (a cement mixture) requires, of course, that the leaching of radionuclides be kept within acceptable limits, as well as that the waste form meet standards of compressive

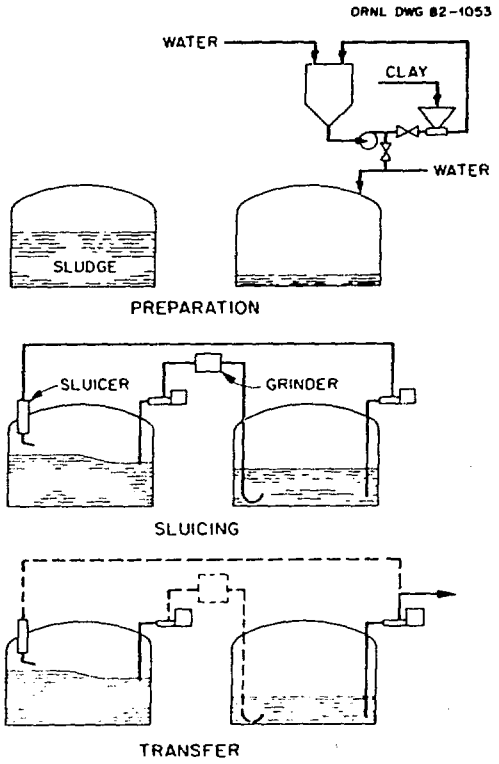

Fig. 1. Schematic of batch process used for emptying the waste tanks.

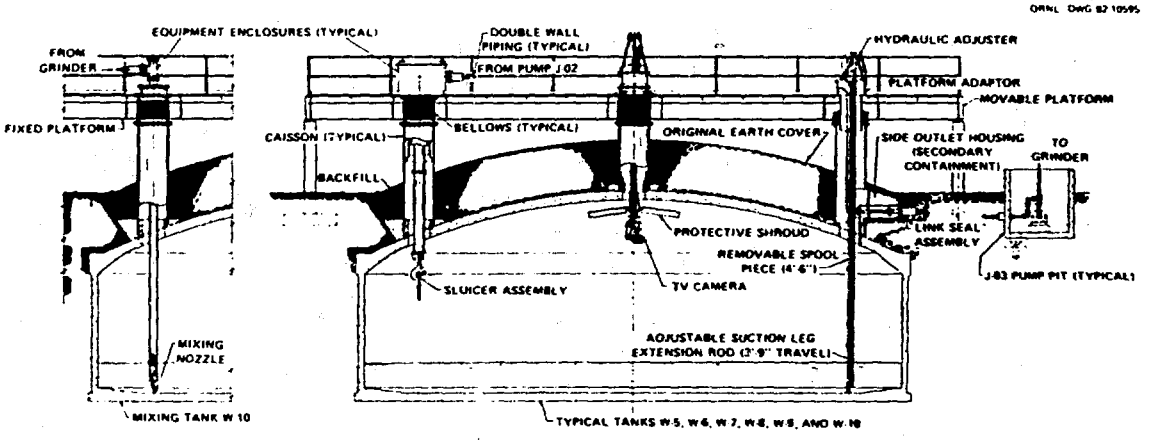

Fig. 2. Arrangement of tank sluicing equipment.

strength and phase separation. In other words, the radionuclides should be retained in the set grout and not lost either in the liquid phase, if phase separation occurs, or by leaching from the solid after the grout has set.

Non-gelling clays were evaluated for their ion-exchange capabilities in studies at ORNL. These illitic clays serve as a natural ion exchanger for cesium; their inclusion in a grout mix greatly improves ^{137}Cs retention. Retention of radioactive strontium was shown in tests at ORNL to be relatively unaffected by the mix ratio (proportion of water to cement).

The amount of calcium in the mix did have an effect, and Portland cement is composed mainly of calcium silicates, which react with water to form hydrated calcium silicates. Since strontium and calcium have similar chemical behavior, ^{90}Sr rapidly enters into these reactions in common with calcium. Reducing the amount of calcium in the waste immobilization matrix reduces the strontium leachability by increasing the availability of reaction sites for strontium.

Suspension of the solids, and thereby reduction of phase separation, is an important objective of grout formulation. If an appropriate minimization of phase separation can be achieved, the waste loading can be increased (within limits) which makes the process more economical. It was found that a gel clay additive can be used in this way to optimize waste loading.[4,5]

If the materials discussed above are blended with cements in the proper amounts and mixed with the waste, the result is a grout that can be processed in a variety of equipment and, if permitted to solidify before disposal, gives a product that will meet or exceed EP-TOX, USDOE, and NRC regulations.[6]

TREATMENT OF FLUORIDE-RICH WASTE

In fabricating nuclear fuel elements, metallurgists have found that zirconium alloys make excellent fuel claddings for selected fuel mixtures. The chop-leach method is used to reprocess the irradiated fuel assemblies whereby the fuel is removed by treating the hull with an ammonium fluoride solution. The hulls and other fuel hardware are categorized as solid waste and are disposed of in an appropriate manner which is outside the scope of discussion in this paper. The leached fuel is separated from the leachate which contains little of the fuel but significant amounts of dissolved zirconium. This fluoride-rich liquid, which by USDOE definition is high-level waste, must be further processed to render it suitable for storage and perhaps disposal. The slightly acidic liquid's pH is increased to 12 or 13 by the addition of sodium hydroxide to render it suitable for storage in carbon steel tanks. Any dissolved zirconium precipitates, along with sodium flouride, at high pH.

The resulting filtrate is little more than water and is separated and treated as waste water. The precipitate, which may be either TRU or low-level waste, is ready for disposal after a suitable cooling period. A flow diagram is shown in Fig. 3. However, the cladding removal waste precipitate presents several problems, with the major one being fluoride, which is difficult and expensive to vitrify in glass. If a cement-based host is chosen, fluoride prevents cement from setting. Further reprocessing, such as washing, serves only to dilute the fluoride. An obvious solution is a combination treatment-disposal step that renders the fluoride, chemically benign, thereby making it possible to immobilize the slurry with only sluicing and transfer to an immobilization system.

Studies at Oak Ridge National Laboratory have developed a process that overcomes the retardation problem when a cement-based matrix is used by adding $Ca(OH)_2$ to the matrix-forming materials which reacts with the fluoride to produce insoluble CaF_2. The reaction proceeds according to the following equation:

$$Ca(OH)_2 + 2NaF \rightarrow CaF_2\downarrow + 2NaOH.$$

Thus, the addition of concentrated NaOH and $Ca(OH)_2$ serves to immobilize the zirconium and fluoride in the waste. Other waste constituents are immobilized by the physical characteristics of the grout.

Preliminary experimentation confirmed that the fluoride was indeed being inactivated by the calcium hydroxide. The results of these tests led to the development of an empirical equation used to optimize the amount of calcium hydroxide added to the dry-solids blend. The following equation defines the fluoride/calcium equivalence ratio in a neutralized cladding removal waste grout:

$$Eq = \frac{(F^-)}{(Ca^{2+})} = \frac{0.2125\ D_s}{PR},$$

where

Eq = fluoride/calcium equivalence ratio;
D_s = sludge dilution factor;
P = $Ca(OH)_2$ in dry blend, wt %;
R = mix ratio, kg/L.

Based on this equation, grouts with preferred properties should be obtained when the equivalence ratio is ~1.0 which was found to be true,[7] and the requirement of $Eq < 1$ was subsequently used to determine the preliminary reference grout formula shown below:

(6)

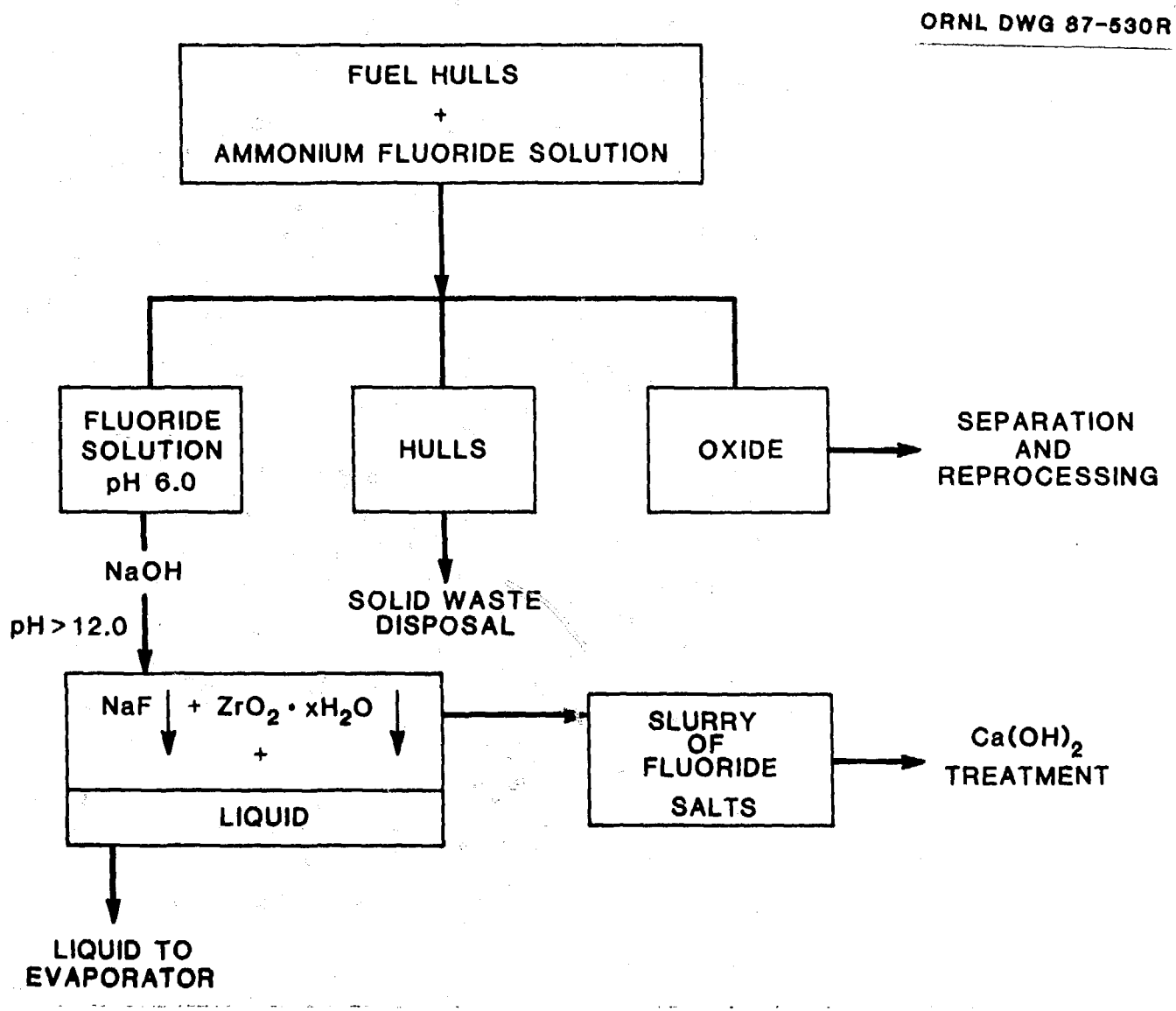

Fig. 3. Flow diagram of the chop-leach method for reprocessing fuel assemblies.

Type III Portland cement	45 wt %
Centralia, Washington, Class F fly ash	35 wt %
Hydrated lime [$Ca(OH)_2$]	12 wt %
Indian Red Pottery clay	8 wt %
Mix Ratio	0.84 kg/L

This grout formula, which is the result of many experiments, became the basis for the final formulation experimental design.

CONCLUSIONS

A variety of process technologies are available to treat and process different waste types to render them suitable for immobilization and disposal.

Oak Ridge National Laboratory has developed technology and equipment for sludge removal and transfer, treatment of mixed waste, and technology for immobilizing fluoride-rich waste.

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