RADIOACTIVE WASTE STABILIZATION PROGRAM

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ABSTRACT

In early 1983, Chem-Nuclear Systems, Inc. (CNSI) engaged in extensive research and development to certify low-level waste solidification processes to satisfy customer regulatory compliance requirements. Program objectives were: 1) exceed all 10 CFR 61 requirements; 2) maximize waste loadings; 3) remain cost-effective; 4) respond quickly to new waste forms; 5) simplify processing and meet intent of ALARA. Boric acid, sodium sulfate, Powdex filter sludges, resin beads, and diatomaceous earth waste forms were certified in 1983. CNSI subsequently extended the program to certify additional solidification formulas including numerous EDTA-based decontamination solutions, responding to an NRC mandate to demonstrate stability of each solidification formula for specific decontamination waste forms. This paper presents test data results and case histories, confirming that program objectives were met. Bench- and full-scale test results are included.

INTRODUCTION

The immobilization of low-level radioactive wastes with cement as a binder is a popular method within the international nuclear community. Cement has long been recognized as a versatile, readily available and effective binder. However, cement by itself or cement and caustic alone cannot be applied universally to radioactive wastes of varying chemical properties. An understanding of waste chemistry and cement chemistry is vital to producing a stable high-quality solidified waste product.

Pre-treatments of the waste streams as well as additives to the final product are necessary in order to ensure complete, homogeneous solidification. Each waste stream must be treated as a unique chemical process. Chem-Nuclear Systems, Inc. (CNSI) has been processing low-level radioactive wastes for the nuclear industry since 1974. It was recognized very early that standard immobilization techniques were frequently unacceptable. A research and development program was established to develop process control boundaries, identify waste pre-treatments and additives, and assist solidification operations.

The December, 1982, issue of Science '82 reported university and large R&D corporation findings which clearly showed that cement could be modified to suit needs other than construction. The authors cited studies of Roman cements poured underwater which are intact and structurally sound today. Sea water and rain water have not permeated into the structures nearly 2000 years after *formation*. These studies led our research to appropriate additives and pre-treatments which attempt to duplicate long-term integrity of this type cement. These studies represent an exciting new departure from the industry's heavy reliance upon Portland cement to stabilize radioactive wastes. As this paper will illustrate, the use of naturally-occurring cement additives has greatly enhanced CNSI's ability to process unique radioactive waste. These wastes have been previously considered incompatible with cementatious binders.

REGULATORY REQUIREMENTS

In May, 1983, the Nuclear Regulatory Commission (NRC) issued two technical position papers (Branch Technical Position papers, or BTP) on Radioactive Waste Classification and Waste Form. These documents were intended to further clarify and provide guidelines for 10 CFR 61 issued in December, 1982. The impact of this regulation and subsequent position papers upon radioactive waste management and processing has been significant. The practical impact of these position papers has been to clarify and segregate radwaste by type of nuclide, specific activity, and physical form (i.e., solid, liquid, or gas).

Most licensees took immediate steps to develop programs to classify the radioactive waste according to the BTP. In most cases, this program involved obtaining and analyzing samples of the various waste streams. Quality control in the sampling, analysis, processing and packaging of the radwaste was also an important part of their programs.

Compliance with the second technical paper, dealing with Waste Form, was more difficult for most licensees. This paper set forth a number of test criteria that a "stable waste form" was required to meet. These criteria include:

1. 90-day water immersion (followed by compression testing to 50 psi);
2. leach testing;
3. freeze testing (cycling waste between 60°F and -40°F);
4. irradiation testing (100 mega-rads total dose;
5. biodegradation testing (exposure to fungi and bacteria).

CNSI, in the interests of continuing to serve its customers, added the necessary personnel and equipment to develop a new set of solidification formulas to meet the various waste forms encountered during utility operation. In undertaking the research and testing program, our goal was to develop formulas which maximized waste loadings and yet met or exceeded the test criteria.

CHEM-NUCLEAR RESEARCH LABORATORY

CNSI maintains a fully-equipped research laboratory at the Barnwell, SC, Low-Level Waste Disposal Facility. The research installation consists of three separate laboratories (each designed for a particular area of research).

The Cement Solidification Laboratory

This laboratory is equipped with scales, oven, compression testing equipment, slump tester, Brookfield viscometer, conductivity and pH meters, a Hobart mixer, and other equipment necessary to test properties of cement and mortars. A copy of each referenced test procedure, including calibration standards and procedures, is maintained by the Product Development Chemist in the CNSI Barnwell laboratory.

Compressive strength testing is conducted in accordance with ASTM C39, entitled "Compressive Strength of Cylindrical Concrete Specimens," with the following exceptions:

1. A manually operated Carver press is used in place of a motorized press. The Carver press gives better control over the loading rate when working in ranges less than 1000 psi.

2. When performing full-scale testing, 2.8-inch diameter cylindrical specimens are substituted for 2-inch specimens. This procedural change is due to the poor sample quality obtained with core drills less than 2.8 inches in diameter (specimens tend to crack and chip as the diameter decreases). Comparative tests of 2.0- and 2.8-inch cylindrical specimens indicate similar results.

Water immersion test specimens are prepared using standard 3-gang brass 2-inch cube molds. Following curing, these specimens are covered with deionized water in large open-mouthed polypropylene bottles sealed with screw-top lids. The duration of testing is 90 days. Periodically specimens are inspected for signs of crumbling or cracking. Control specimens are compression-tested and compared with water-immersed specimens after 90 days.

Biodegradation testing to determine waste form resistance to microbial growth is conducted according to ASTM G21 and ASTM G22 which are entitled "Determining Resistance of Synthetic Polymeric Materials to Fungi," and "Determining Resistance of Plastics to Bacteria." There are two modifications to these procedures:

1. At the recommendation of the American Type Culture Collection, a substitute of ATCC 11797 is made for the ATCC 9644, due to poor sporulation of the latter culture.

2. Waste form specimens are placed in tall form beakers and covered with the inoculated and un-inoculated nutrient agar (instead of petri dishes, due to the requirement to perform subsequent compression strength tests).

All biodegradation testing has been performed by the University of South Carolina (USC). Compression strength testing (both of controls, un-inoculated, and inoculated specimens) is performed in accordance with ASTM C39 under the direction of the Engineering Department, USC. Results are summarized in reports from USC.

Irradiation testing to assess waste form radiation stability is performed for CNSI under contract by Oak Ridge National Laboratory (ORNS). Standard 2-inch cubes are prepared (with a 1/4-inch eye bolt) by Chem-Nuclear. These specimens are then shipped to ORNL, neutron-shielded, and irradiated to 10^8 rads total absorbed dose (temperature not to exceed 150°F). The source, an irradiated fuel rod, gives a wide energy spectrum of gamma. Un-irradiated control specimens and irradiated test specimens are returned to CNSI for compressive strength analysis.

Thermodegration testing for waste form durability to temperature extremes is conducted according to ASTM B553. The test apparatus used includes a thermostatically controlled oven and freezer maintaining the appropriate temperature ranges specified in the test procedure. A total of four specimens is tested for each waste form. (Two serve as controls maintained at ambient or room temperature.) Results and observations are recorded. All compression strength tests are performed in accordance with the procedures listed in the compressive strength discussion, above.

It should be noted that test results are usually averaged among several specimens. This simple arithmetic averaging gives a result which is statistically sound and more closely approaches the actual waste form properties.

Finally, all contractors are expected to maintain quality assurance programs and follow approved test procedures.

The Radioactive Leach Testing Laboratory

CNSI has been actively involved in the measurement and control of waste form leachability since 1980. At that time, simulated boric acid waste solutions were solidified with urea-formaldehyde, and then tested by Allied General Nuclear Services according to a proposed ANS 16.1 method. It was recognized from these early evaluations that soluble radionuclides, most notably cesium, diffused readily through open-cell type matrices. Even for a constant Leachability Index of 6.0, which is the minimum allowed for stable wastes under 10 CFR 61, a typical test cylinder would lose about 30 percent of the radionuclide originally present during the first 24 hours of water soaking.

Beginning in 1981, cement solidification had been adopted by CNSI as an improved waste binder that offered consistently dry products as well as more efficient waste loadings. Leach testing was now performed at Barnwell under license by the State of South Carolina, and in cooperation with the Site Environmental Laboratory. A radiological facility was dedicated for sample preparation, including a vented hood, mixing equipment, curing oven, and storage area for processing a number of samples simultaneously. Initial leach values for cement waste products showed excellent binding of Cobalt-60, satisfactory retention of Strontium-85; but only marginal control of Cesium-137.

CNSI's Waste Processing Division in 1983 assumed full responsibility for certification of 10 CFR 61 regulations. Acquisition of a sodium iodide detector and multi-channel analyzer permitted convenient leach testing without transporting radioactive samples to other facilities. Many more tests could be conducted, and selected additives were investigated for refined control of radionuclide leachability. This program has resulted in formula modifications that sharply decrease the general permeability of cement itself; and with the use of appropriate agents, cesium ion retention has been improved by two or more orders of magnitude. The improved leachability performance has led to more durable waste forms, including resin beads and concentrated sulfates, that now resist deterioration under extended periods of water immersion.

Chem-Nuclear has endeavored to share its laboratory experience concerning leachability, and has cooperated in this regard with the American Nuclear Society. This technical part of 10 CFR 61 certification is now an ongoing testing effort to upgrade the solidification of existing waste materials, and develop satisfactory formulas for new waste streams.

SPECIAL FORMULA DEVELOPMENT

Waste formula development begins with a thorough characterization of the simulated waste. Important parameters are measured in the laboratory:

1. pH
2. suspended solids
3. specific gravity
4. organic content
5. total solids
6. viscosity
7. volatile content

The Chem-Nuclear chemist seeks to identify any chemical compounds present in the generated waste which could influence the cement hydration and set. For example: boric acid and ammonia tend to retard or delay cement set. Conversely, the presence of sulfate ion or calcium tends to accelerate the set. These effects have been reported in the literature.

Once the simulated waste solution has been characterized, the next step is to prepare a reference mixture with ordinary Portland cement at a nominal waste loading (usually 50 percent). This specimen is prepared and cured according to the standard Process Control Program procedure. Observations are made during this process, including rheology of the mixture, possible gas evolution, relative time of set, and exotherm.

Subsequent waste formulations will include appropriate additives (set accelerators or retardants, chelate modifiers, leachability enhancers) to improve waste specimen properties. This stage of waste formula development may take several weeks and is often supported by cement chemistry literature research.

CASE HISTORIES

With the successful development of the waste solidification formula, full-scale waste processing can be scheduled with the customer. Two case histories involving actual waste solidification are presented in this paper. In both of these cases, the waste was shown to be incompatible with ordinary Portland cement. Thus, Chem-Nuclear researchers were called upon to develop special formulas to properly solidify this waste.

Case 1

As a result of a decontamination job, the utility had several thousand gallons of highly radioactive solution and resin beads. The mixture was found to contain about eight percent chelate and evolved ammonia when mixed with cement. A NATIONAL LABORATORY HAD DETERMINED THE WASTE COULD NOT BE SOLIDIFIED WITH ORDINARY PORTLAND CEMENT. CNSI developed a special formula, which properly stabilized the waste, reduced the ammonia evolution, and achieved a 50 percent by volume waste loading.

Case 2

This customer turned to Chem-Nuclear to solidify scores of 55-gallon drums full of waste oil. The oil was a mixture of sludge, mineral and synthetic oils which was difficult to emulsify and stabilize. Once again, Chem-Nuclear developed a special formula to solidify the oil. A minimum 40 percent by volume waste loading and excellent final product were achieved.

SUMMARY

In summary, CNSI has developed formulas necessary to properly stabilize a wide variety of wastes, renging from acids to decontamination solutions and oils. In many cases, the challenge has been met with a successful combination of equipment design and compatible chemistry.