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LOCKHEED MARTIN 

**Quarterly Progress Report for the
Chemical Development Section of the
Chemical Technology Division:
January–March 1996**

R. T. Jubin

MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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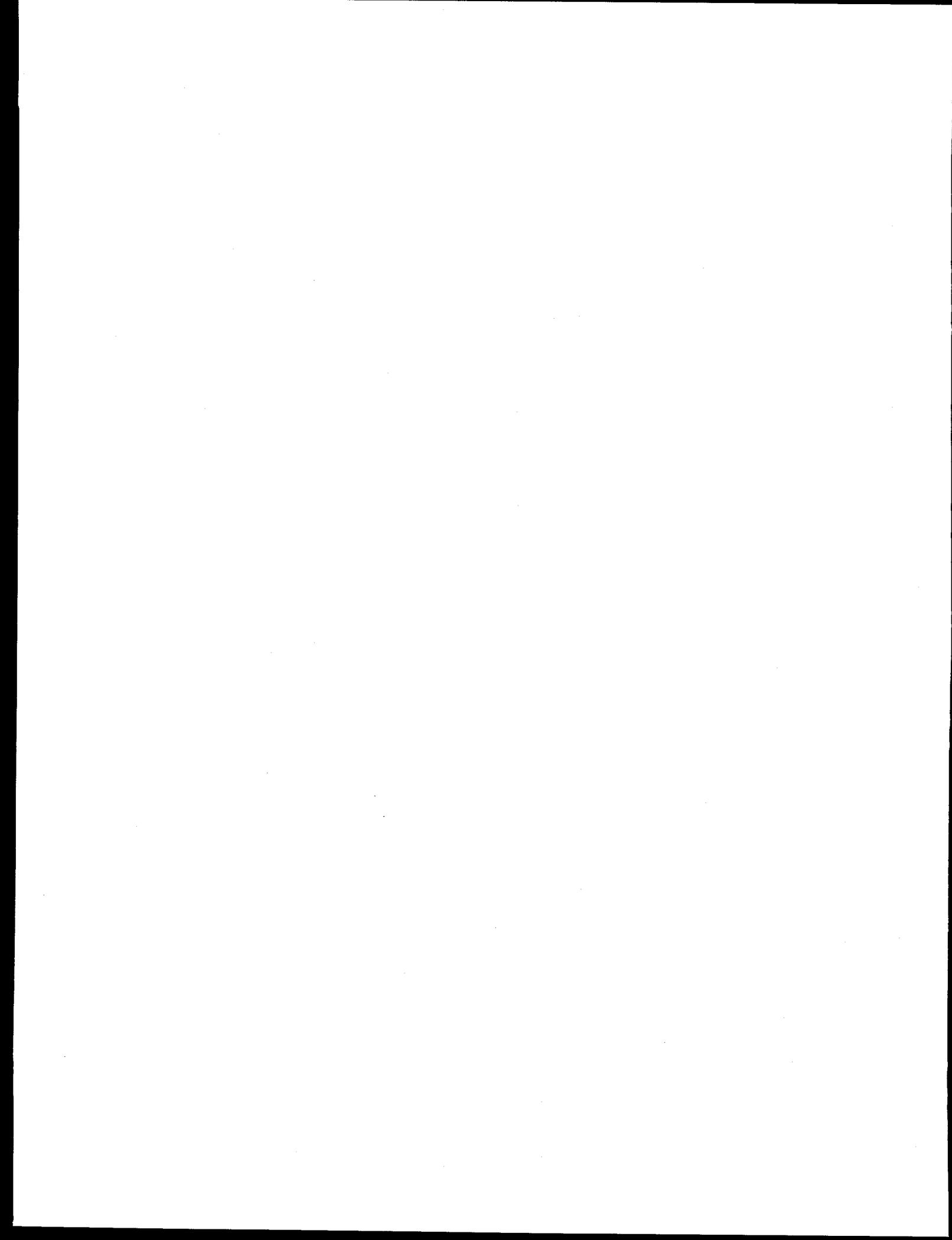
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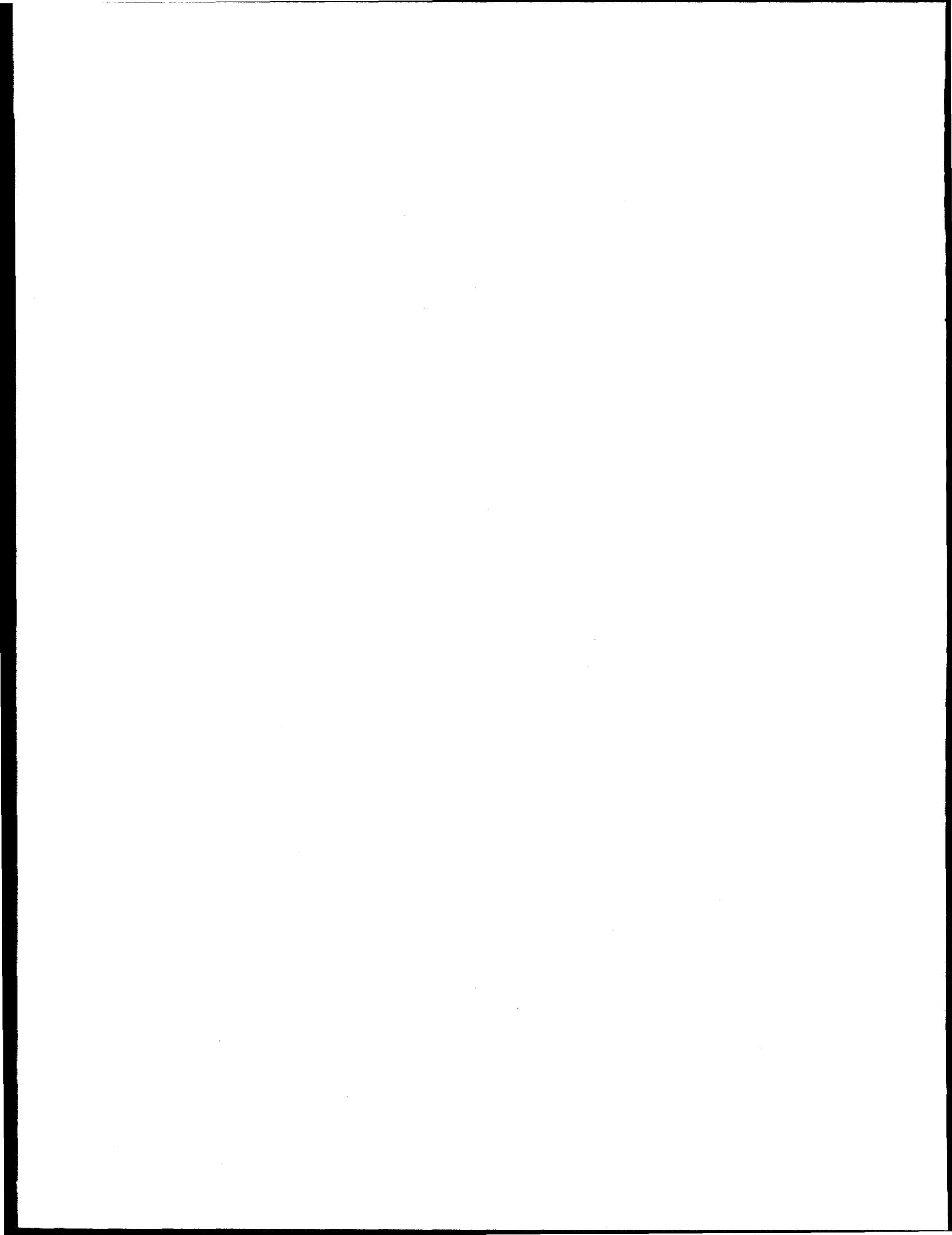
Chemical Technology Division

QUARTERLY PROGRESS REPORT FOR THE
CHEMICAL DEVELOPMENT SECTION OF THE
CHEMICAL TECHNOLOGY DIVISION:
JANUARY-MARCH 1996

R. T. Jubin

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EXECUTIVE SUMMARY

This report provides a timely summary of the major activities conducted in the Chemical Development Section of the Chemical Technology Division at the Oak Ridge National Laboratory (ORNL) during the period January–March 1996. The report summarizes ten major tasks conducted with five major areas of research and development within the section.

The first major research area—Chemical Processes for Waste Management—includes the following tasks: Comprehensive Supernate Treatment, Partitioning of Sludge Compounds by Caustic Leaching, Studies on Treatment of Dissolved MVST Sludge Using TRUEX Process, ACT*DE*CONSM Test Program, Hot Demonstration of Proposed Commercial Nuclide Removal Technology, and Sludge Washing and Dissolution of ORNL Waste: Data for Modeling Sludge Science.

As noted last quarter, the Comprehensive Supernate Treatment task has completed all originally planned batch tests to evaluate several sorbents for removing strontium, technetium, and cesium from ORNL Melton Valley Storage Tank (MVST) supernatant solutions. However, additional batch tests are to be made as new sorbents become available. As a result, several new sorbents have been evaluated in batch tests for removing strontium and technetium from ORNL MVST supernatant solutions, and the results were discussed at the Efficient Separations and Processing Technical Information Exchange Meeting in January. The focus of this task is now shifting to the process of testing promising materials in continuous-flow small-column studies. A small-column test was conducted using Reillex HPQ anion-exchange resin to measure the removal of pertechnetate from ORNL MVST W-27 supernatant. Afterward, the technetium was eluted from the column using an eluent solution containing 0.017 *M* stannous chloride, 0.1 *M* ethylenediamine, and 0.075 *M* sodium hydroxide.

As part of the Partitioning of Sludge Components task, planned caustic dissolution tests on ORNL MVST sludge have been completed and chemical analyses of the leachates and residues are continuing. Chemical analyses were completed of leachates from a test to measure the dissolution behavior of a sludge sample at 75°C. Tests were initiated to measure the caustic dissolution behavior of a Hanford sludge sample from tank S-104. Samples of leachate and residue from the first test are being analyzed. Analyses of several samples derived from the first leach test of sludge from Hanford tank S-104 were completed, and two additional caustic dissolution tests were conducted with samples of Hanford sludge from tank S-104. The sludge samples were leached with 3.8 *M* NaOH at 70°C for about 21 h using different ratios of caustic volume to sludge mass.

Analysis of data from the two transuranium extraction (TRUEX) test campaigns continued as part of the third task—Studies on Treatment of Dissolved MVST Sludge Using TRUEX Process. An analysis and comparison of the two methods used to dissolve the sludge were completed, along with an analysis of the first TRUEX run. Analysis of data from the second run will continue. Preparation of a report on this work is about one-half completed.

A majority activity of the ACT*DE*CONSM Test Program task involved preparation of an ORNL/TM report describing the results of a test to evaluate the proprietary ACT*DE*CONSM process for selectively removing actinides from Gunitite tank sludge. Final publication of this report is expected next quarter.

The fifth task—Hot Demonstration of Proposed Commercial Nuclide Removal Technology—covers work in the continuous removal and concentration of radioactive components of supernatant at the various U.S. Department of Energy sites. The primary objective is to test candidate absorbers and ion exchangers under continuous-flow conditions using actual supernatant from the MVSTs. An experimental system contained in a hot-cell facility is used to test the materials in columns or modules using the same batch of supernatant so that results can be directly compared. During this quarter, the preproduction and the production batches of crystalline silicotitanates from UOP were tested at a loading flow rate of 6 column volumes per hour at supernatant concentrations of 1 M hydroxide and 5×10^{-5} M cesium.

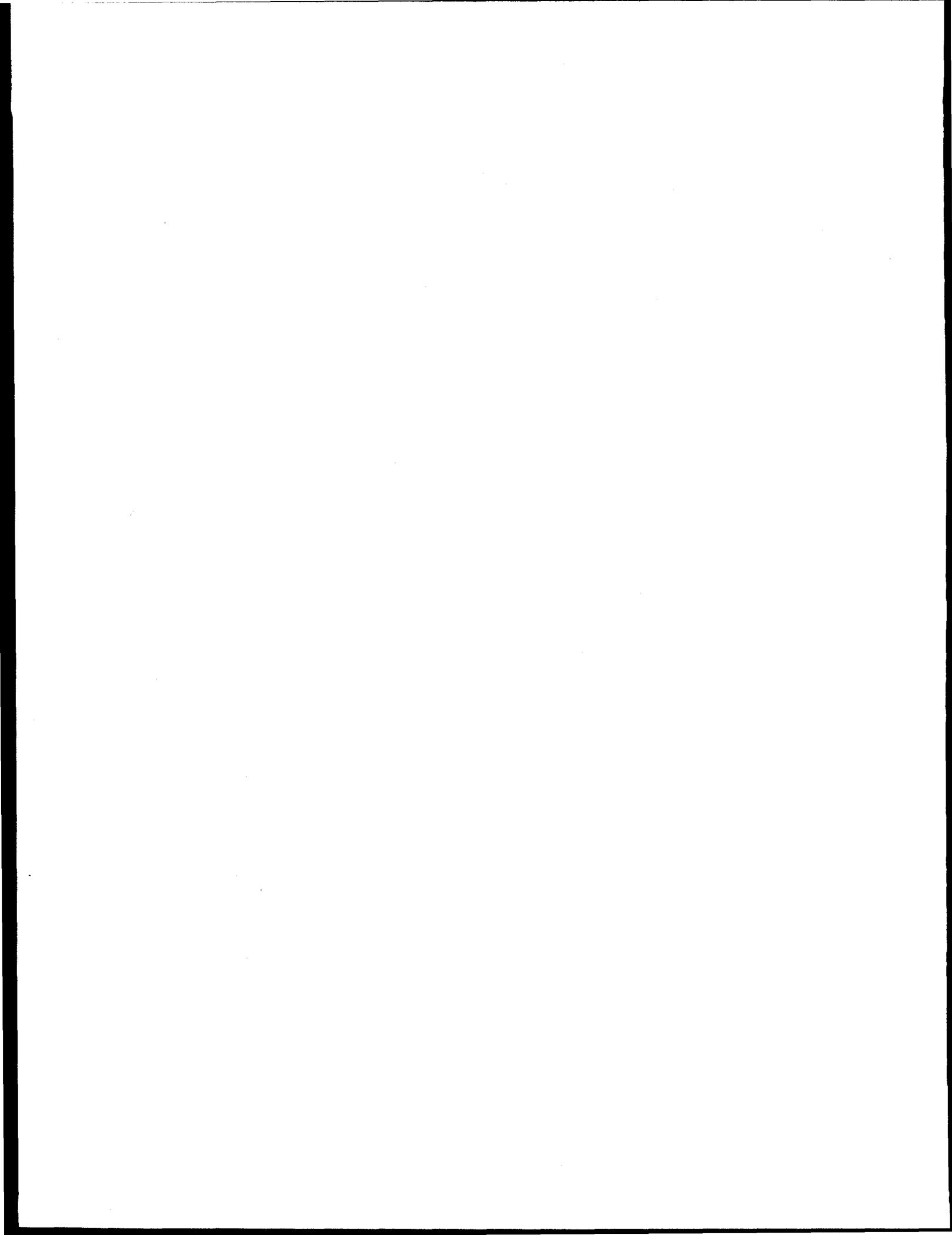
As part of the final task within the Chemical Processes for Waste Management area—Sludge Washing and Dissolution of ORNL Waste—enhanced sludge washing of Hanford Underground Storage Tank T-104 sludge produced a gel-like material in leachates that were equilibrated at 95 and 60°C. The material consisted of microcrystals ($<10 \mu\text{m}$) of natriophosphate, $\text{Na}_7(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$. This material, which is thought to be a slurry of these microcrystals, has also been found in sludge from the Gunitite tanks at ORNL. Because gels or gel-like materials prevent pumping, clog filters, hinder separations, and coat surfaces, this material must be identified so that it can be avoided in the enhanced sludge washing process.

Within the area of Reactor Fuel Chemistry, personnel associated with the Technical Assistance in Review of Advanced Reactors task made a presentation to the U.S. Nuclear Regulatory Commission staff at Rockville, Maryland. Iodine behavior in the 3 BE sequence in an AP600 reactor and acid formation due to radiolysis and pyrolysis of organic materials in reactor containments were described. A new scope of work for this task has been established to include assessments of iodine behavior and pH control in operating nuclear reactor containments as well as in advanced reactor systems.

The Thermodynamics and Kinetics of Energy-Related Materials task within the Thermodynamics area has investigated the chemical diffusion of oxygen from 350 to 975°C in large specimens of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The specimens were a 15-g melt-processed single crystal, two melt-processed large-crystal bodies, and the common polycrystalline pellets. All specimens reached equilibrium values of $7-x$ in 0.1 MPa O_2 in <10 h at temperatures $\geq 550^\circ\text{C}$, while all specimens except the single crystal closely approached equilibrium at $\geq 450^\circ\text{C}$. Diffusion coefficients for the chemical diffusion of oxygen in polycrystalline pellets decreased with decreasing temperature for the high-temperature tetragonal phase but increased with decreasing temperature in the orthorhombic phase. This suggested either high-diffusivity paths or even microcracking. The thermodynamic factor that correlates tracer and chemical diffusion of oxygen was calculated and led to close agreement of the measured and predicted diffusion coefficients.

Ion-Exchange Process for Heavy Metals Removal—a task currently ongoing within the Processes for Waste Management area—involves the demonstration of a pilot-scale ion-exchange system to remove heavy metals from multiple sites using the most effective commercially available sorbent based on laboratory screening experiments. This is an extension of the Acid Mine Drainage Treatment Project. This system will operate alongside three novel treatment systems and act as baseline technology. This project is conducted by the National Institute of Environmental Renewal (NIER), which investigated suitable replacement sites throughout this quarter. The original mine drainage site proposed by NIER was rejected by the NIER scientific advisory board because it was not sufficiently contaminated, and evaluation of sorbents has been discontinued until a new site is identified. Construction of the ion-exchange system is under way and is due to be completed in mid-May.

Finally, the Chemical Development Section continued its involvement in work-for-others activities with the U.S. Army Field Artillery Liquid Propellant (LP) Stability Program. In March of this quarter, however, the Army decided to cancel the LP Program and revert to the use of solid propellants for its artillery. In light of the potential cancellation of the LP Program, several experiments were run under very harsh conditions using 400 ppm iron and a temperature of 65°C to push the stabilizer system to higher limits. Various ratios of stabilizer to iron were employed in the experiments. At the lowest concentration of stabilizer, two of the experiments did decompose and the experimental apparatus vented the pressure after only 2 weeks; however, at higher concentrations of stabilizer, the LP was stabilized for 70 d (until the experiments were halted). Recently, it was learned that the U.S. Department of Defense is currently considering reviving the LP efforts using the XM-46 propellant or one of the other LPs at its disposal.



1. CHEMICAL PROCESSES FOR WASTE MANAGEMENT

B. Z. Egan

1.1 COMPREHENSIVE SUPERNATE TREATMENT (J. L. Collins, K. K. Anderson, and B. Z. Egan)

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Summary: As noted last quarter, all planned batch tests to evaluate several sorbents for removing strontium, technetium, and cesium from Oak Ridge National Laboratory (ORNL) Melton Valley Storage Tank (MVST) supernatant solutions have been completed. The focus of this task is now shifting to testing promising materials in continuous-flow small-column studies. However, additional batch tests are to be made as new sorbents become available. As such, several new sorbents have been evaluated in batch tests for removing strontium and technetium from ORNL MVST supernatant solutions. The results were discussed at the Efficient Separations and Processing (ESP) Technical Information Exchange Meeting in January.

A small-column test was conducted using Reillex HPQ anion-exchange resin to measure the removal of pertechnetate from ORNL MVST W-27 supernatant. Afterward, the technetium was eluted from the column using an eluent solution containing 0.017 M stannous chloride, 0.1 M ethylenediamine, and 0.075 M sodium hydroxide.

1.1.1 Purpose and Scope

This task involves testing sorbent materials for removing cesium, strontium, and technetium from the saline solutions in U.S. Department of Energy (DOE) storage tank supernatant at Oak Ridge and other sites. Batch tests are used to evaluate and select the most promising materials for supernatant treatment to reduce the amount of waste for final disposal. Small-column tests will be made on selected sorbents to verify the batch data and to obtain additional data for process design. Methods will be evaluated for recovering the radionuclides from the sorbents.

Supernatants used in the tests have been retrieved from MVST W-25, W-27, and W-29. These supernatants have many similarities to supernatants in tanks at other DOE sites. Efforts will be made to obtain samples of tank supernatants from Hanford for comparison. Many of the sorbents have been proposed for waste treatment, but most have not been tested on actual waste solutions.

1.1.2 Progress

Samples of a cation exchanger, MERSORB-S, obtained from NUCON International, Inc., were tested for removing strontium from MVST W-29 supernatant. Duplicate batch tests were conducted by mixing the supernatant and ion exchanger for 0.25, 2, 24, and 72 h. The average strontium distribution ratios were 317 mL/g (60% removal) for the 0.25-h tests, 306 mL/g (60%

removal) for the 2-h tests, 436 mL/g (68% removal) for the 24-h tests, and 520 mL/g (72% removal) for the 72-h tests. These values are near the lower end of the range of the exchangers that have been tested under similar conditions for strontium removal.

Additional batch tests were conducted with samples of an experimental anion resin, synthesized at The University of Tennessee by S. Alexandratos and provided by G. Brown of ORNL, to measure the removal of technetium from MVST W-27 supernatant. This material is also currently being evaluated by G. Brown for removing technetium from groundwater as part of another program. The supernatant that was used was effluent from a column run in which most of the cesium was removed using resorcinol/formaldehyde (R-F) resin. The supernatant effluent was further treated by mixing it for 2 h with granular potassium cobalt hexacyanoferrate to remove additional cesium. Then, technetium was added as ammonium pertechnetate to a final concentration of 5.4 mg/L. Duplicate samples were mixed for periods of 2 and 24 h at ambient temperature. In each test, the mass of exchanger equivalent to 0.050 g of dry material was mixed with 10 mL of supernatant. The average technetium distribution ratios ranged from 500 mL/g (72% removal) to 680 mL/g (78% removal). These values are comparable to values obtained with commercial resins such as Reillex HPQ and Purolite A520E. However, since the resin tended to float on the supernatant, resulting in mixing difficulties, the maximum values may be higher. The commercial resin, ABEC-5000 from Eichrom, gave higher pertechnetate distribution ratios, but also tended to float on the supernatant. Any further batch tests will be limited to new sorbents or new supernatants as they become available.

A paper entitled "Sorptions Studies on the Removal of Cesium, Strontium, and Technetium from Supernatants from Underground Storage Tanks at ORNL" was presented at the American Chemical Society Spring National Meeting, March 24-28, 1996, in New Orleans.

Reillex HPQ was selected for the first column run to measure the removal of pertechnetate from ORNL MVST W-27 supernatant. This sorbent has been tested at Los Alamos National Laboratory, and further tests are planned at Pacific Northwest Laboratory for technetium removal from Hanford tank supernatants. The Reillex HPQ tests at ORNL will serve as a "benchmark" for comparison with other tests and other sorbents that may be tested in the future. The supernatant used was column effluent in which a large portion of the cesium had been removed using a column of granular crystalline silicotitanate (CST). To improve the technetium radiochemical analysis, most of the remaining cesium in the supernatant was removed by treating it with R-F resin and granular potassium cobalt hexacyanoferrate. The supernatant was then filtered through a 0.45- μ m filter. Analyses showed that the concentrations of the primary constituents of the supernatant were

5.4 ± 0.2 M sodium, 0.30 ± 0.01 M potassium, 5.1 ± 0.03 M nitrate, and 0.1 ± 0.01 M chloride. The pH was measured at 12.86. Because of the relatively low technetium content of the supernatant (0.43 mg/L), ammonium pertechnetate was added to the feed to adjust the concentration to 3.0 mg/L.

The particle size of the sieved Reillex HPQ resin was between 249 and 595 μm . Before the resin was added to the column, 6.97 g of "as-received" resin (hydroxide form) was contacted for about 24 h with 0.16 M NaOH and transferred to the 1.45 cm (ID) \times 15 cm ion-exchange column. The resin bed was then conditioned with a solution of 5.0 M sodium nitrate and 0.16 M sodium hydroxide. The effluent was a dark amber color that faded as additional solution passed through the bed. The resin at the top of the bed tended to become and remain suspended as the saline solution was added. To provide a stable packed bed, a frit housed in a lightweight Teflon holder was placed on top of the bed. The supernatant was able to flow through the frit as well as through the annular gap of the holder. The height of the preconditioned bed was 6.3 cm, which provided a packed bed of about 10.4 cm^3 .

About 1300 mL of supernatant was passed through the column at a rate of about 6 bed volumes (BV)/h. Eluate fractions were collected in 15-mL polypropylene centrifuge tubes to better define the loading profile with time. Filtered and unfiltered samples of these solutions will be analyzed to determine the technetium concentrations.

The technetium was eluted from the column at a flow rate of about 3 BV/h using an eluent solution (0.017 M stannous chloride, 0.1 M ethylenediamine, 0.075 M sodium hydroxide) that was developed and used successfully by N. C. Schroeder of Los Alamos National Laboratory. Volumes of effluent equivalent to about one-third of a BV were collected in 15-mL polypropylene centrifuge tubes. Samples of these solutions will be analyzed to calculate the technetium concentrations and determine the elution profile.

1.2 PARTITIONING OF SLUDGE COMPONENTS BY CAUSTIC LEACHING (B. Z. Egan, J. L. Collins, D. D. Ensor,* and C. W. Chase)

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Summary: Planned caustic dissolution tests on ORNL MVST sludge have been completed and chemical analyses of the leachates and residues are continuing. Chemical analyses of leachates

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from a test to measure the dissolution behavior of a sludge sample at 75°C were completed. Tests were initiated to measure the caustic dissolution behavior of a Hanford sludge sample from tank S-104. Samples of leachate and residue from the first test are being analyzed. Analyses of several samples derived from the first leach test of sludge from Hanford tank S-104 were completed. Two additional caustic dissolution tests were conducted with samples of Hanford sludge from tank S-104. The sludge samples were leached with 3.8 *M* NaOH at 70°C for about 21 h using different ratios of caustic volume to sludge mass.

1.2.1 Purpose and Scope

Many underground storage tanks contain high concentrations of nonradioactive materials such as aluminum, chromium, and phosphates that can significantly increase the volume of the final high-level waste (HLW) waste form for disposal. There is increasing emphasis on removing these materials through "enhanced sludge washing," such as taking advantage of the solubility of these materials under very caustic conditions to partition the radioactive and nonradioactive components. The behavior of some of the components, such as chromium and phosphate, is also important to vitrification processes. A purpose of this project is to measure the caustic dissolution behavior of sludge components from ORNL MVST sludge, surrogate Hanford sludges, and selected Hanford sludge samples. If the nonradioactive components could be preferentially solubilized, then the volume of the remaining radioactive waste to be treated and/or stored would be significantly reduced.

1.2.2 Progress

The planned caustic leaching tests on ORNL MVST W-25 sludge were completed, and the chemical analyses of leachates and residues have been performed. The results are being compiled and evaluated. The effects of temperature, mixing time, and concentration of NaOH on the dissolution behavior of the sludge were determined. Sludge samples have been leached at ambient temperature and at 75 and 95°C. Concentrations of NaOH ranged from 0.16 *M* to 6 *M*. Leach times ranged from 4 to 30 h. Leachates and residues were analyzed for both radioactive and nonradioactive components. Analyses of the leachates indicated that increasing the temperature from 75 to 95°C had only a small effect on metal removal. Mixing for longer than 4 h at 95°C did not significantly increase the metal dissolution.

Tests on Hanford sludge samples were begun. The first sample tested was from tank S-104. The analyses of the sludge solids from leaching tests in which two 3-g samples of Hanford sludge from tank S-104 were each mixed with 24 mL of 3.8 *M* NaOH at 65–70°C for 4 and 24 h were completed. In these tests the leached sludge solids were also washed three times with a solution containing 0.01 *M* sodium hydroxide and 0.01 *M* sodium nitrite. Analyses of the residues showed

that both of the tests removed about 98% of the ^{137}Cs and 98–99% of the chromium. Increasing the mixing time from 4 to 24 h enhanced the removal of aluminum from 35 to 51%. Data for other components and leachate solutions are being evaluated.

Two additional caustic leaching tests with samples of Hanford sludge from tank S-104 were completed. Samples containing 1.5 and 3.0 g were mixed in 35-mL polypropylene centrifuge tubes with 16-mL volumes of 3.8 M NaOH for 21 h at 70°C. Afterward, the samples were centrifuged and the leachates were removed by decantation. The solids were washed four times with 16-mL volumes of a solution containing 0.01 M sodium hydroxide and 0.01 M sodium nitrite to remove the interstitial leachate. The leachates and cumulative washes, along with the residues, are being analyzed for both radioactive and nonradioactive components.

The principal investigator participated in the Tanks Focus Area (TFA) Midyear Review in Richland, Washington, March 19–22, 1996.

1.3 STUDIES ON TREATMENT OF DISSOLVED MVST SLUDGE USING TRUEX PROCESS (B. B. Spencer* and C. W. Chase)

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Summary: Analysis of data from the two transuranium extraction (TRUEX) test campaigns continued. An analysis and comparison of the two methods used to dissolve the sludge were completed, along with an analysis of the first TRUEX run. Analysis of data from the second run will continue. Preparation of a report on this work is about one-half completed.

1.3.1 Purpose and Scope

The focus of this experimental program was to evaluate the TRUEX solvent extraction process for partitioning actinides from actual HLW sludge dissolved in nitric acid. A large sludge sample, previously removed from MVST W-25, has been well characterized and was available for the test program. The experimental phase of the evaluation program included dissolving portions of this sludge in nitric acid, followed by batch liquid-liquid equilibrium tests of both the extraction and stripping operations. Chemical analyses of both phases are being used to evaluate the process. Evaluation is based on two metrics: the fraction of transuranic (TRU) elements removed from the

*Robotics and Process Systems Division, ORNL.

dissolved sludge and comparison of the results with predictions made with the Generic TRUEX Model.

1.3.2 Progress

Analyses of the data and preparation of the report on the two TRUEX experiments with MVST W-25 dissolved sludge are continuing. The report is planned as an ORNL/TM and is about one-half complete. An analysis and comparison of the two methods used to dissolve the sludge were completed, along with an analysis of the first TRUEX run.

In the first TRUEX run, the first-stage batch extraction removed >97% of the europium, ~96% of the curium, and ~99% of the plutonium from the dissolved sludge. Thorium and uranium were removed to the extent of ~99 and ~99+%, respectively. Cobalt, strontium, and cesium essentially did not extract. The loaded organic phase was subjected to two stripping stages. In the first stripping contact with mild nitric acid (0.01 M HNO₃) and sodium nitrate (0.5 M NaNO₃), little of the actinides or europium was recovered. The actinides were not easily stripped because the high nitrate concentration in the aqueous solution provides a salting-out effect.

In the second stripping stage, the aqueous strip solution contained oxalic acid (0.5 M H₂C₂O₄). It was visually observed that a white precipitate formed during the test. Presence of the precipitate indicated removal of substantial amounts of solute from the organic. Europium is stripped from the organic to the extent of >99%; americium, ~96%; thorium, ~98%; and uranium, only ~20%. The low stripping and recovery factors for uranium indicate that either more stripping stages or a more effective stripping agent is required. It also makes separation of uranium from the other actinides appear to be an attractive option.

A poster paper entitled "Extraction Equilibria Between Organic CMPO-*n*-Dodecane and Aqueous Nitric Acid Phases for Selected Tank Waste Components" was presented at the American Chemical Society Spring National Meeting in New Orleans in March. This paper summarized our measured extraction equilibria for nitric acid, uranyl nitrate, and bismuth nitrate in pure component systems. These data are useful in extending the TRUEX data base.

A journal article was prepared entitled "Thermodynamics of Extraction Equilibria Between OφD(iB)CMPO-*n*-Dodecane and Aqueous Nitric Acid Media. I. Nitric Acid." An internal peer review was completed, the paper was revised to reflect those comments, and the paper was edited by the Publications Services staff.

1.4 ACT*DE*CONSM PROCESS TEST PROGRAM (B. B. Spencer and C. W. Chase)

Contact: Barry B. Spencer
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Summary: An ORNL TM report describing the results of a test to evaluate the proprietary ACT*DE*CONSM process for selectively removing actinides from Gunite tank sludge was prepared. Final publication is expected next quarter.

1.4.1 Purpose and Scope

The ACT*DE*CONSM process, a proprietary process of Selective Environmental Technologies, Inc. (Selentec), is designed to remove actinides from soils or soil-like media. The process is proposed as an alternative for removal of actinides from tank-stored HLW sludges. The ACT*DE*CONSM solvent is an aqueous carbonate solution containing a chelating agent and an oxidant. This combination of chemicals is rather benign and is intended to leach specific metal species from a soil matrix without destroying the bulk of the soil. The objective of the test program is to evaluate the ACT*DE*CONSM process for pretreating Gunite and associated tanks sludge as part of the sludge-processing flow-sheet development effort.

1.4.2 Progress

A report describing the results of the ACT*DE*CONSM test has been prepared. The report (ORNL/TM-13201) has been reviewed by Selective Environmental Technologies, Inc. (Selentec); received internal peer review; and been edited by Publications Services staff. The recommended changes are being incorporated into a final version of the report to be issued next quarter.

1.5 HOT DEMONSTRATION OF PROPOSED COMMERCIAL NUCLIDE REMOVAL TECHNOLOGY (D. D. Lee and J. R. Travis)

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Summary: This task covers work in the continuous removal and concentration of radioactive components of supernatant at the various DOE sites. The primary objective is to test candidate absorbers and ion exchangers under continuous-flow conditions using actual supernatant from the MVSTs. An experimental system contained in a hot-cell facility is used to test the materials in columns or modules using the same batch of supernatant so that results can be directly compared. During the last quarter, the preproduction and the production batches of CSTs from UOP were tested

at a loading flow rate of 6 CV/h at supernatant concentrations of 1 *M* hydroxide and 5×10^{-5} *M* cesium.

1.5.1 Purpose and Scope

This task covers the operation of an experimental test unit that is located in a Building 4501 hot cell. This equipment is designed to test radionuclide removal technologies under continuous operation on actual ORNL MVST supernatant, Savannah River HLW supernatant, and Hanford supernatant. The latter two may be simulated by adding the appropriate chemicals and/or nuclides to the MVST supernatant. The technologies tested are housed in modules or placed in columns which can be attached to the experimental system inside the hot cell and continuously fed the test supernatant until the nuclide of interest exhausts the capacity of the module. Initial candidate sorbents for cesium removal are the R-F resin, CSTs, Superlig® 644 resin, and granular potassium cobalt hexacyanoferrate. Sodium and potassium are competitors for cesium removal. The results of these tests will be compared with batch results and small-column tests results obtained in the Comprehensive Supernate Treatment task (B. Z. Egan). The results will be used to supply the Cesium Removal Demonstration Project (T. E. Kent) with the information to determine the design parameters for that project. The rate of removal, resin required, and regeneration requirements are important design parameters, and the loading capacity of each sorbent will help to determine the size of the column required and help define the final volume of solid waste to be disposed of.

This task works in close cooperation with the ESP and the TFA in order to ultimately transfer the technologies being developed to the end user. As part of this work, TFA requested through ESP that we test AEA Technology's electro dialysis-ion-exchange (ED/IX) system because ORNL was the only site with sufficient available supernatant for testing the multiple-cycle ED/IX system.

1.5.2 Progress

Two ion-exchange material tests were completed in Hot Cell C during the second quarter of FY1996. The feed supernatant for the tests was obtained from MVST W-27 in April 1995. Tank W-27 contains supernatant at pH 7.2 and has the lowest potassium and ^{137}Cs levels of the available tanks. This supernatant was adjusted to pH 14.0 (1 *M* hydroxide concentration), and additional cold cesium was added to provide a total cesium concentration of 5×10^{-5} *M*.

1.5.2.1 CST Run 3

CSTs from UOP, IONSIV IE-911 #07398-38B, was run in Cell C equipment in a 1.5-cm ID column using a volume of 10 cm³, with a bed height of 6 cm. The dry tapped density of the material was 1.173 g/cm³. The supernatant was adjusted to 1 M hydroxide and 5×10^{-5} M cesium. Previous runs had used supernatant adjusted to 0.1 M hydroxide with a cesium concentration of 7×10^{-6} M. The column volumes to 1, 10, and 50% breakthrough were ~58, 127, and 283, respectively. No operational problems were seen. This compares with a 50% breakthrough of 335 CV at the lower hydroxide and cesium concentrations.

1.5.2.2 CST Run 4

The production batch of CSTs from UOP, IONSIV IE-911 Lot 999096810001, was tested under the same conditions as the previous run with the -38B material (1 M hydroxide and 5×10^{-5} M cesium). This experiment also used 10.0 mL (10.59 g dry weight) in a 1.5 × 6 cm column. The test was run at a flow rate of 6.0 CV/h with a total of 415 CV fed. Column volumes to 1, 10, and 50% breakthrough were ~64, 131, and 308. These results show that the production form performs at least as well as the developmental form (-38B) tested earlier.

1.5.2.3 Conclusions

The CSTs were recommended for the Cesium Removal Demonstration Project using MVST W-27 Supernatant (pH 12.9–13.3), based on the best CV at 50% breakthrough and the fewest operational difficulties using that feed. The new production form of CST performs at least as well as the developmental form (-38B) tested earlier at the conditions of the test.

1.6 SLUDGE WASHING AND DISSOLUTION OF ORNL MVST WASTE: DATA FOR MODELING SLUDGE SCIENCE (E. C. Beahm, S. A. Bush, C. W. Chase, J. L. Collins, and T. A. Dillow)

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Summary: Enhanced sludge washing of Hanford Underground Storage Tank T-104 sludge produced a gel-like material in leachates that were equilibrated at 95 and 60°C. The material consisted of microcrystals, <10 μm, of natriphosphate Na₇(PO₄)₂F•19H₂O. This material has also been found in sludge from the Gunit tanks at ORNL. The "gel" is thought to be a slurry of these microcrystals. Because gels or gel-like materials prevent pumping, clog filters, hinder separations,

and coat surfaces, this material must be identified so that it can be avoided in the enhanced sludge washing process.

1.6.1 Purpose and Scope

A particular objective of selected washing and leaching tests is to minimize the resulting TRU residue that would be dissolved. A series of washing steps at decreasing pH (14, 12, 10, and 8) may remove sludge components in supernatants. Equally important in these wash steps is to not dissolve the TRU components and to determine the transfer of fission products (Se, Tc, I, Cs, etc.). After the TRU sludge has been minimized in these washing steps, a selective leaching series of experiments can determine the TRU dissolution from the sludge. It may be possible to dissolve the TRU components from the washed sludge, leaving a non-TRU residue.

1.6.2 Progress

Enhanced sludge washing of Hanford Underground Storage Tank T-104 sludge produced a gel-like material in leachates that were equilibrated at 95 and 60°C. A portion of this material was dried at ambient temperature and characterized by X-ray diffraction and scanning electron microscopy. The material consisted of microcrystals, <10 μm, of natrophosphate $\text{Na}_7(\text{PO}_4)_2\text{F}\cdot 19\text{H}_2\text{O}$. This material has also been found in sludge from the Gunit tanks at ORNL. The "gel" is thought to be a slurry of these microcrystals. An additional test with "gel" material in its original leachate indicates that the microcrystals were present when the material was wet. Because gels or gel-like materials prevent pumping, clog filters, hinder separations, and coat surfaces, this material must be identified so that it can be avoided in the enhanced sludge washing process.

Similar difficulties will be encountered in enhanced sludge washing if solids precipitate from leachates or wash solutions. Some method of controlling solids formation in this process will be necessary. A series of equilibrium thermochemical calculations based on dissolution of alumina has been run for enhanced sludge washing of sludge from tank S-104. This evaluation showed that controlling the formation of solids can be done by a combination of the following: (1) addition of excess caustic during leaching or to the separated wash solutions, (2) controlled precipitation as in the Bayer process, and (3) close control of process temperatures.

The principal investigator participated in the TFA Midyear Review in Richland, Washington, March 19–22, 1996.

2. REACTOR FUEL CHEMISTRY

E. C. Beahm

TECHNICAL ASSISTANCE IN REVIEW OF ADVANCED REACTORS (E. C. Beahm, C. F. Weber, S. A. Bush, T. A. Dillow, and R. J. Weaver)

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Summary: A presentation was given to the U.S. Nuclear Regulatory Commission (NRC) staff at Rockville, Maryland. Iodine behavior in the 3 BE sequence in an AP600 reactor was described. In addition, acid formation due to radiolysis and pyrolysis of organic materials in reactor containments was presented. A new scope of work for this task has been established to include assessments of iodine behavior and pH control in operating nuclear reactor containments as well as in advanced reactor systems.

2.1 PURPOSE AND SCOPE

The objective of this project is to provide assistance to the NRC staff in reviewing the four advanced reactor designs submitted under 10 CFR Part 52. This work specifically addresses the following issues: (1) the distribution of iodine species in containment following a loss-of-coolant accident, (2) the generation of hydrochloric acid and nitric acid by irradiation and heating in containment, (3) the formation of elemental iodine in containment water that has both chloride and iodide ions, and (4) the evaluation of pH levels in containment water.

2.2 PROGRESS

A presentation was given to the NRC staff at Rockville, Maryland. Iodine behavior in the 3 BE sequence in an AP600 reactor was described. In addition, acid formation due to radiolysis and pyrolysis of organic materials in reactor containments was presented.

A new statement of work for this project has been received from the NRC, and a revised proposal is being prepared. This work will include assessments of iodine behavior and pH control in operating nuclear reactor containments as well as in advanced reactor systems.

3. THERMODYNAMICS

E. C. Beahm / T. B. Lindemer

THERMODYNAMICS AND KINETICS OF ENERGY-RELATED MATERIALS (E. C. Beahm, T. B. Lindemer, and R. D. Hunt)

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Summary: The chemical diffusion of oxygen was studied from 350 to 975°C in large specimens of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The specimens were a 15-g melt-processed single crystal, two melt-processed large-crystal bodies, and the common polycrystalline pellets. All specimens reached equilibrium values of $7-x$ in 0.1 MPa O_2 in <10 h at temperatures $\geq 550^\circ\text{C}$, while all specimens except the single crystal closely approached equilibrium at $\geq 450^\circ\text{C}$. Diffusion coefficients for the chemical diffusion of oxygen in polycrystalline pellets decreased with decreasing temperature for the high-temperature tetragonal phase but increased with decreasing temperature in the orthorhombic phase. This suggested either high-diffusivity paths or even microcracking. The thermodynamic factor that correlates tracer and chemical diffusion of oxygen was calculated and led to close agreement of the measured and predicted diffusion coefficients.

3.1 PURPOSE AND SCOPE

The objective of this program is measurement and interpretation of chemical thermodynamics in applied-technology ceramic systems. Presently, this project concerns phase equilibria and thermodynamics of the R-Ba-Ca-Cu-O system, with R representing Y, La, Pr, and Nd. Emphasis is being placed on the phase fields that include the superconducting compounds.

3.2 PROGRESS

The chemical diffusion of oxygen was studied from 350 to 975°C in large specimens of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The specimens were a 15-g melt-processed single crystal, two melt-processed large-crystal bodies, and the common polycrystalline pellets. All specimens reached equilibrium values of $7-x$ in 0.1 MPa O_2 in <10 h at temperatures $\geq 550^\circ\text{C}$, while all specimens except the single crystal closely approached equilibrium at $\geq 450^\circ\text{C}$. Diffusion coefficients for the chemical diffusion of oxygen were measured in polycrystalline pellets. They decreased with decreasing temperature for the high-temperature tetragonal phase but increased with decreasing temperature in the orthorhombic phase, which suggested either high-diffusivity paths or even microcracking. The thermodynamic factor that correlates tracer and chemical diffusion of oxygen was calculated and led to close agreement of the measured and predicted diffusion coefficients.

4. PROCESSES FOR WASTE MANAGEMENT

J. C. Rudolph

ION-EXCHANGE PROCESS FOR HEAVY METALS REMOVAL (J. C. Rudolph and M. R. Gibson)

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Summary: This project is the demonstration of a pilot-scale ion-exchange system to remove heavy metals from multiple sites using the most effective commercially available sorbent based on laboratory screening experiments. (This is an extension of the Acid Mine Drainage Treatment Project.) This system will operate alongside three novel treatment systems and act as baseline technology. This project is run by the National Institute of Environmental Renewal (NIER). Throughout the past quarter, suitable replacement sites were under investigation by the NIER. The original mine drainage site proposed by NIER was rejected by the NIER scientific advisory board (SAB) because it was not sufficiently contaminated. Evaluation of sorbents has been discontinued until a site is identified. Construction of the ion-exchange system is under way and is due to be completed in mid-May.

4.1 PURPOSE AND SCOPE

The scope of this project has been modified. The original scope was to demonstrate the ability of a pilot-scale ion-exchange system to remove heavy metals from an acid mine drainage site. An initial screening of materials was to be performed to choose the most effective sorbent. This process would then serve as a baseline to compare the abilities of three new innovative technologies to treat the same stream. The modified scope is now looking at heavy metals contamination at multiple sites, none of which are mine drainage sites. This expands the scope since each stream must be treated separately for the purpose of screening tests.

4.2 PROGRESS

This project is on hold, with the exception of system construction, pending the identification of a suitably contaminated site. The original mine drainage site proposed by NIER was rejected by the NIER SAB because it was not sufficiently contaminated. Throughout the past quarter, suitable replacement sites were under investigation by the NIER. Evaluation of sorbents has been discontinued until a site is identified. Due to the delay in site identification, extensive evaluation of materials relative to the site-specific requirements may not be possible. This has been communicated

to the NIER, and NIER personnel are aware that much of the previous effort was lost in changing sites.

Construction of the ion-exchange system is under way and is due to be completed in mid-May. The ion-exchange system under construction will consist of a filter system to remove suspended solids followed by ion-exchange columns for removing the metal ion constituents. The exiting water will be periodically sampled and analyzed for breakthrough. The system is also set up for regeneration and precipitation of the regenerant. The entire system will be controlled by a programmable logic controller, which will be operated by modem. The system is designed to allow up to 2.2 L/min of contaminated water to flow. The entire system will be located in a trailer.

5. U.S. ARMY FIELD ARTILLERY LIQUID PROPELLANT STABILITY PROGRAM: WORK FOR OTHERS

A. J. Mattus

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Summary: In March of this quarter, the U.S. Army decided to cancel the LP program and revert to the use of solid propellants for its artillery. In light of the proposed cancellation of the LP Program, several experiments were run under very harsh conditions using 400 ppm Fe in combination with a 65°C to push the stabilizer system to higher limits. Various ratios of stabilizer to iron were employed in the experiments. At the lowest concentration of stabilizer, two of the experiments did decompose, and the experimental apparatus vented the pressure after only 2 weeks; however, at higher concentrations of stabilizer, the LP was stabilized for 70 d until the experiments were halted. Recently, however, the U.S. Department of Defense is considering reviving the LP laboratory efforts using the XM-46 propellant or one of the other LPs at its disposal.

5.1 PURPOSE AND SCOPE

The primary objective of this work-for-others program is to supply the Army Research Laboratory at Aberdeen, Maryland, with potential means for increasing the storage and handling stability of its LPXM-46 liquid propellant. This 2-year program is being coordinated through the Robotics and Process Systems Division and has a multidivisional team with the following tasks: (1) determine chemical analysis needs, (2) evaluate stabilizing techniques used with relevant analog compounds, (3) evaluate prior work related to propellant stability and decomposition, (4) assess material compatibility, and (5) develop and execute a crosscutting experimental program. Task 2 is the primary task for this team member and will be limited to a paper study and experimental work to test various stabilizers.

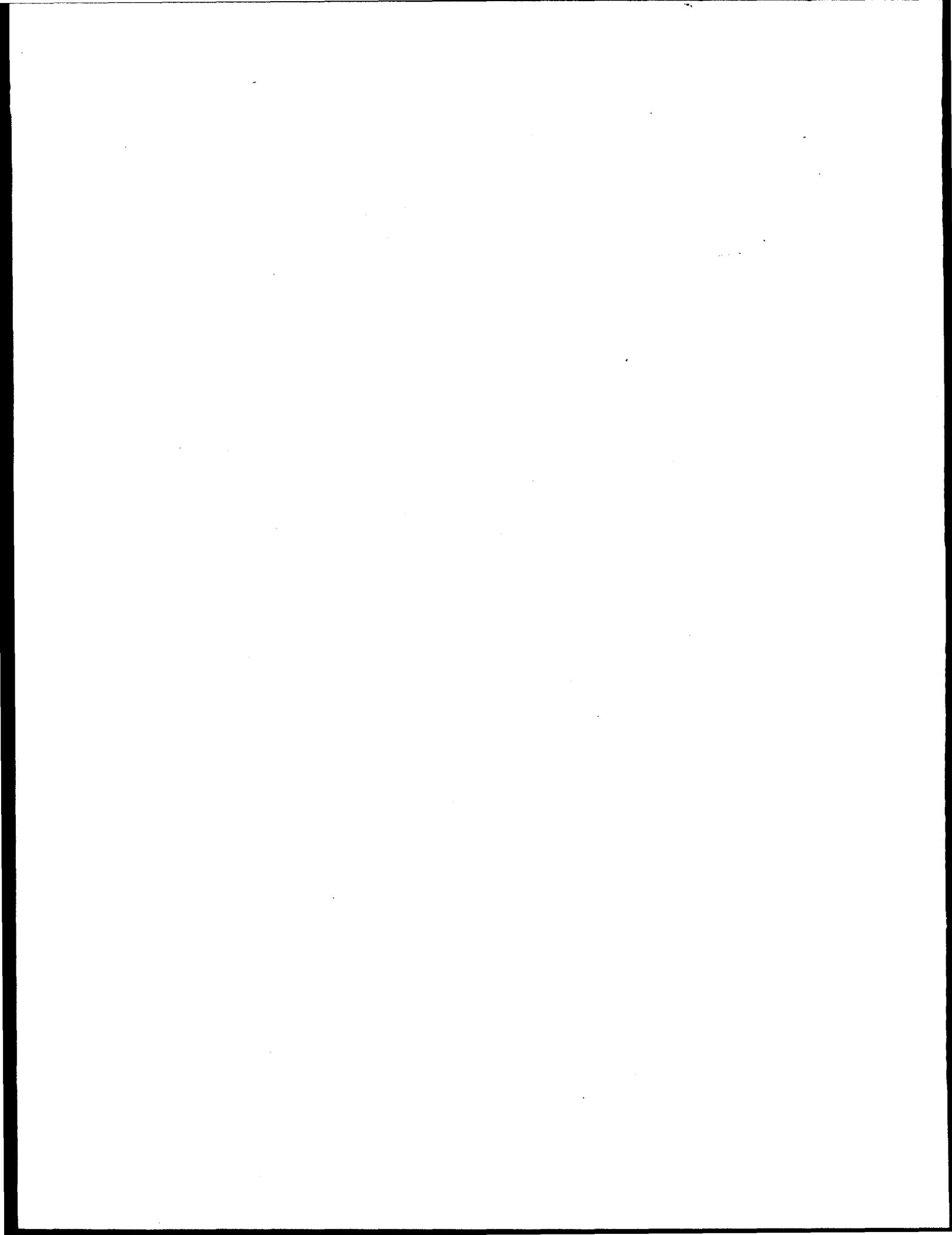
5.2 PROGRESS

In March of this quarter, the Army decided to cancel the LP Program and revert to the use of solid propellants for its artillery. Recently, however, it was learned that the Department of Defense is considering reviving the LP laboratory efforts using the XM-46 propellant or one of the other LPs at its disposal.

Earlier indications of the potential for a cancellation of the LP Program caused us to run several experiments under very harsh conditions using 400 ppm Fe in combination with a 65°C to push the stabilizer system to higher limits. This concentration of iron may be much higher than will ever be encountered in the field and was chosen arbitrarily. Various ratios of stabilizer to iron were employed in the experiments. At the lowest concentration of stabilizer, two of the experiments did decompose, and the experimental apparatus vented the pressure after only 2 weeks; however, at higher concentrations of stabilizer, the LP was stabilized for 70 d until the experiments were halted.

Samples of the LP have been removed from ongoing experiments in order to have the residual hydroxylamine nitrate (HAN) component analyzed in all samples to confirm that the LP has been prevented from decomposing. The HAN concentrations will be determined using a new high-performance liquid chromatography method of analysis developed in the Chemistry Division at ORNL specifically for this project. These data will be incorporated into a final report.

The final tests to be performed in this test program will include a series of stabilizer adsorption tests to determine the capacity of the stabilizer to remove various amounts of iron from the LP. The iron concentrations will range from 10 to 600 ppm iron while using a constant ratio of stabilizer to LP. The solutions will be gravity filtered through 0.45- μ m glass filter paper, and the filtrate will be analyzed for soluble iron.



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