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National Measurement Laboratory Office of Measurements for Nuclear Technology Annual Report 1981

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Washington, DC 20234

January 1982

Annual Report, Fiscal Year 1981
(October 1, 1980 - September 30, 1981)

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

NBSIR 81-2441

NATIONAL MEASUREMENT LABORATORY OFFICE OF MEASUREMENTS FOR NUCLEAR TECHNOLOGY ANNUAL REPORT 1981

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

Preface

This annual report is a summary of the National Bureau of Standards (NBS) Measurements for Nuclear Technology (MNT) Program for Fiscal Year 1981. The MNT activities at NBS are divided into two programs: Nuclear Safeguards and Nuclear Waste Management. The Nuclear Safeguards Program was the first to be initiated near the end of Fiscal Year 1977, while the Nuclear Waste Management Program was initiated near the end of Fiscal Year 1980. However, NBS did make significant contributions to the nuclear safeguards field in years past. For example, in the 1950's, C. J. Rodden and other NBS scientists founded a laboratory for the measurement of nuclear fuels at NBS. This laboratory was later transferred to the U.S. Atomic Energy Commission and became known as the New Brunswick Laboratory. In addition, work by W. Shields and co-workers in the 1960's established NBS as a world leader in the development of ultra-high accuracy mass spectrometry for chemical and isotopic assay of nuclear fuels. NBS Standard Reference Materials for the chemical and isotopic assay of uranium and plutonium provide the foundation for nuclear safeguards measurements throughout the world.

The Department of Energy (DOE) in late August 1979 invited the National Bureau of Standards to consider the establishment of an appropriate technical assistance program to meet the measurement standards needs of the waste disposal problem.

NBS assembled a study group consisting of 13 experts in a variety of scientific and engineering disciplines. The group was asked by NBS management to study the problem, to explore critical questions, and to define an appropriate NBS technical program in a final report to be completed and reviewed by March 31, 1980. The report was completed on March 31, 1980, and submitted to DOE. The goal of the NBS program stated in the report was to provide a measurement base (including reference methods, Standard Reference Materials, Standard Reference Data, measurement assurance procedures, and scientific laws and concepts of waste behavior) to allow other organizations to (a) measure short-term behavior, (b) predict long-term behavior (c) choose acceptable disposal systems, and (d) provide quality control of processing and assembly in nuclear waste management. The NBS Nuclear Waste Management Program was initiated in September 1980 and was completely supported by DOE funds.

Because of a number of decisions in the Federal Government, with regard to the direction of the programs and availability of financial resources, both programs were terminated at the end of this fiscal year (September 30, 1981).

In the case of the nuclear safeguards program, the termination resulted in an orderly turnover of responsibilities and the phase out of operations. For the Nuclear Waste Management Program, the decision not to fund the program was made in the fourth quarter of the first fiscal year of the program. As a result, a number of tasks did not reach a natural stopping point. Thus, this annual report for the Nuclear Waste Management Program will contain a number of fragmented technical reports.

It is hoped that if sufficient technical content becomes available during Fiscal Year 82, individual authors will publish them either in the open literature or as NBSIR's. Should the financial situation change it is entirely possible that many of the technical activities would be reinitiated.

We hope that this annual report will provide the technical community with a view of the Program's direction. We encourage members of the community to make recommendations to us concerning the needs and future direction of individual research efforts presented here.

We wish to acknowledge the help and support of Dr. B. Stephen Carpenter who managed the Nuclear Safeguards Program through the first half of Fiscal Year 1981. His planning and guidance helped make this program successful.

William P. Reed
H. Thomas Yolken
Office of Measurements for
Nuclear Technology

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I. INTRODUCTION

The Office of Measurements for Nuclear Technology (OMNT) was established to provide national measurement standards needed to safeguard nuclear materials. In addition, during the past year, a program in nuclear waste management was established. Thus, the OMNT for FY 81 consists of two separate activities, Nuclear Safeguards and Nuclear Waste.

A. Nuclear Safeguards

1. Introduction

Rapid and sensitive methods to detect the diversion of nuclear materials are an essential objective of the measurements for nuclear technology program. This objective can be achieved with the aid of accurate and precise methods of measurement of nuclear materials at all phases of manufacture, use, and transfer to maintain material accounting. Effective and universal measurement standards are required to attain the necessary accuracy of measurement.

The NBS program for nuclear safeguards serves three sets of clients: the Nuclear Regulatory Commission (NRC) and the U.S. commercial nuclear industry; the Department of Energy (DOE) (as developer of nuclear safeguards technology and as regulator of nuclear facilities operated for DOE) and U.S. Government-owned DOE nuclear facilities; and the International Atomic Energy Agency (IAEA) and countries that have nuclear facilities under the jurisdiction of the Non-Proliferation Treaty. The FY 1981 NBS Nuclear Safeguards Program was funded by DOE and the Department of State (DOS).

2. Goals and Objectives

The goals and objectives of the NBS program are derived from the perceived needs of the sponsoring agencies--to reduce the risk to the public from the illegal diversion of nuclear materials by providing a common and accurate standardization basis for measurement of nuclear fuels. This goal is to be achieved for all of the measurements that need to be made throughout the fuel cycle on a wide variety of material forms. In order to meet this goal, our objectives are to provide measurement standards and services for the four major measurement areas for nuclear safeguards accountability.

3. Tasks

To achieve these goals and objectives, three task areas are utilized that combine similar technological resources of NBS. These three task areas are:

a. Bulk and Nondestructive Measurements for Nuclear Safeguards

b. Chemical Measurements for Nuclear Safeguards

c. Systems Studies and Statistical Analysis

B. Nuclear Waste Management

1. Introduction

In August 1979, DOE invited NBS to consider establishment of a technical program that would contribute to the measurement standards foundation required for disposal of nuclear waste. A group of NBS scientists was asked by the management of NBS to examine the needs for measurement standards in nuclear waste management and, if desirable, to recommend a technical program. The NBS study (funded by DOE) was completed, approved by the NBS Executive Board, and submitted to DOE on March 31, 1980. DOE staff have reviewed the NBS proposal and have provided $350,000 to NBS to initiate a portion of the program in FY 1980 (last quarter) and $1,500,000 (later reduced to $1,175,000) to fund the program in FY 1981, with the intention to increase the funding in future years, to allow additional activities to be included in the program. NBS and DOE consummated a Memorandum of Understanding in the nuclear waste management area in February 1981.

2. Goals and Objectives

The summary of the NBS report on nuclear waste management follows ". . . The National Bureau of Standards proposes to support the national program in nuclear waste disposal by: assisting in the development of measurement techniques and standards to assess stability, providing knowledge of factors controlling stability of the waste package, determination and evaluation of data critically needed for evaluation of alternative waste forms and packages, and development of measurement standards and procedures needed for quality control. This is an appropriate role for NBS for several reasons. First, accuracy is required in difficult measurements that are essential to the solution of a national problem. Second, competence in similar measurements on other materials already exists at NBS. Third, credibility of results is extremely important; the traditional NBS measurement and standards role of third party objectivity with no promotional or regulatory interest is appropriate. Fourth, certain voluntary consensus standards are needed, as well as regulatory standards; the existing extensive work of NBS in support of the voluntary consensus standards system makes a good base for similar standards work in support of nuclear waste disposal."

The strategy of the NBS program recognizes the need to disseminate existing NBS capability, mainly in the area of short-term performance, and to concurrently develop the new scientific basis needed for long-term prediction, and to provide the additional basis needed for short-term performance capability. For example, work is needed to improve the accuracy of existing leach tests and develop consensus on standard tests to determine short-term performance. This work is critically needed, but must be supplemented by work on the mechanisms controlling release so that long-term predictions can be made. NBS will accordingly pursue parallel and interactive efforts centered respectively on reference leach tests involving chemical analysis and on the kinetics of long-term release. The NBS strategy also recognizes the importance of collaboration with work already in progress in a number of government, industry, and university laboratories. NBS will make optimum use of its existing experimental facilities in carrying out this work. NBS will concentrate on model systems using the same chemical compounds and structures, but employing isotopes with no or relatively low levels of radioactivity. Work on actual, high activity waste forms will be carried out in a cooperative manner at existing hot cells in other laboratories.

With the foregoing considerations in mind, the overall goal of the NBS program can be stated as follows: To provide a measurement base (including methods, data, traceability to basic standards, and assurance procedures) and scientific laws and concepts of waste behavior to support: (a) measurement of short-term behavior, (b) prediction of long-term behavior, (c) choice of acceptable disposal systems, and (d) quality control of processing and assembly in nuclear waste management.

The NBS program was developed in terms of work needed on each component of the multi-barrier system and the need to monitor the system. The following technical themes run through much of the work:

a. the interactions between components of the system,

b. quantitative analysis of elements and phase,

c. stability of phases over relatively short times,

d. leach and corrosion rates over relatively short times,

e. mechanisms and quantitative basis of phase changes, mechanical deterioration, leaching, corrosion, absorption, and transport,

f. predictive scientific laws and concepts to allow choice of disposal systems, and

g. test methods and procedures for quality control.

3. Tasks

To achieve these goals and objectives, the NBS program on nuclear waste has developed, for FY 1981, three tasks which combine similar technology resources of NBS. These three task areas are:

a. Leachability Mechanisms for Waste Forms

b. Nuclear Waste Form Reference Materials and Data

c. Containers, Overpack, Corrosion and Backfill

II. PERSONNEL

The Office of Measurements for Nuclear Technology (OMNT) is in the NBS National Measurement Laboratory (see organizational chart in Appendix). The OMNT consists of two major programs: Measurements for Nuclear Safeguards and Nuclear Waste Management. Each program is run by the Team Management concept, which allows members from different centers or programs within NBS to help the programs run effectively. The OMNT interacts with four centers in NML and two centers and the Continuous Process Technology Program in NEL. The Management Team concept has been demonstrated to be a fruitful approach to matrix management.

An FY 1981 organizational chart is shown in Appendix G. Tables 1 and 2 provide a summary of the NBS-OMNT personnel.

TABLE 1. Summary of NBS personnel involved in the OMNT Safeguards Program.

Technical Area		Principal Investigators
A.	Bulk Measurements	
	Flow	G. Baumgarten, A. Gaigalas, B. Robertson, T. Yeh
	Tank Vol. Cal. Algorithm	F. Jones
B.	Nondestructive Assay	
	Half-Life Measurements	L. Lucas
	Calorimetry	D. Ditmars
	NDA-gamma	S. Carpenter
	Resonance Neutron Radiography	R. Schrack, J. Behrens, R. Johnson
	Resonance Neutron Tomography	T. Cheng, D. Garrett
C.	Chemical and Isotopic Measurements	
	Low enriched U_3O_8 Isotopic	L. Machlan, J. Gramlich
	Resin Beads	J. Fassett, W. Kelly
	Davies-Gray U	J. Moody
	IDA-80 U and Pu	L. Machlan, J. Fassett, J. Gramlich
	Moisture in Pu Oxide	F. Jones
	^{244}Pu Spike SRM	J. Fassett, H. Kingston, L. Machlan
D.	Statistics	
	Measurement Assurance Programs	H. Ku, J. Lechner, W. Liggett
	Reference Materials	C. Spiegelman
	Calibrations	
	In-Plant Error Analysis	
E.	Safeguards Systems Studies	S. Bologa, M. D. K. Maltese, J. Schleter

TABLE 2. Summary of NBS personnel involved in the OMNT Waste Program.

Technical Area	Principal Investigators
A. Waste Forms	
(1) Leachability Mechanisms	
Concepts - Theory	R. Mountain, R. Munro
Radiation Effects	T. Cheng, D. Garrett
Transport, Thermochemistry, Microstructures	R. Roth, C. Chiang
Mechanical Properties	S. Wiederhorn
Microfracture	S. Freiman, G. White
(2) Research & Reference Materials, Data Measurement Methods	
Phase Diagrams of Relevant Ceramics	R. Roth, W. Brower, M. Austin, M. Koob
Leachability Research Materials (Glass)	W. Haller, D. Cronin
Leachability Reference Test Methods	H. Kingston, G. Lutz, M. Epstein
B. Containers, Overpacks, Sleeves	
Corrosion Mechanisms	J. Kruger
Data and Methods	B. Anderson
Feasibility and Long-Term Deep Test	M. Rodriguez, K. Hardman
C. Backfill	
Mechanisms	
Research Materials	F. Yokel, R. Chung
Data and Test Methods	L. Solomone
D. Mathematical Support	
Statistical Engineering	H. Ku
Submodeling	J. Fong
E. Material Review Board	H. Frederikse

III. MEASUREMENTS FOR NUCLEAR SAFEGUARDS PROGRAM - A TECHNICAL OVERVIEW

A description of the technical activities in each of the Program's areas is given in this section. In addition, accomplishments during FY 1981, the fourth year of the Program, are reviewed.

A. Nondestructive Assay

The NBS effort on standards for nondestructive assay (NDA) of nuclear materials is motivated by the need for reliable, accurate, timely and economic methods for the measurement of special nuclear materials. A wide variety of activities are being carried out in NBS laboratories to fulfill this objective. The activities may be grouped into three major categories: reference methods, standard reference materials, and data development and calibration.

1. Reference Methods

Reference methods are methods having demonstrated precision and accuracy. Due to their complexity, these techniques are generally suited only for a specially equipped laboratory. These reference measurement methods are used to characterize reference materials or as references for developing and calibrating simpler techniques that are inherently less accurate.

a. Resonance Neutron Radiography

The effort on the resonance neutron tomography project during last year was devoted to: (1) the construction of the reactor-based resonance neutron safeguards experimental system and the making of provisions for its use, and (2) the initial tomographic construction of a nuclear waste container.

The tomographic reconstruction of a point object using the filtered back projection technique has been carried out before. In an effort to further study the reconstruction technique as applied to those actual fuel pellets within a gallon-sized container, a second experiment was conducted on the BT-7 beam port of the NBSR.

The experiment consisted of three parts: (1) the production of reference calibrations, (2) the scanning of the waste container by the resonance neutron beam, and (3) the mathematical reconstruction of the container based on the results of (1) and (2). The reference calibrations were necessary to interpret the responses of the fission detectors. The responses were functions of particular neutron beam characteristics, detector system efficiencies, and the effect of neutron beam softening in the object to be studied.

U-235 and U-238 reference discs were made from SRM U-970 and U-0002 materials, respectively. The U-235/U-238 reference discs were then placed in the resonance neutron beam and the transmitted beam recorded by both U-235 and Pu-239 foils in the NBS double fission detectors.

The uranium was available as uranium oxide in a finely powdered form which had to be encapsulated to form samples of a known thickness which could then be used for the transmission measurements. The containers consisted of an outer shell which had a well to contain the sample and a plug to compress the powder. The plug was 0.002 to 0.003 inch oversize and after loading was pressed into the container using an arbor press which exerted a force of several tons. The mass of the specimen was measured with an accuracy of 0.1 milligram.

In order to get other information on the thickness of the specimen, transmission measurements were made using gamma rays from a Cobalt-60 source. A well collimated beam, 1/4 inch in diameter, was used, and measurements were made for the lower peak (1.10 to 1.25 meV), the upper peak (1.25 to 1.40 meV), and the two combined. The average of the three measurements was used as the value for the gamma ray transmission.

Radiographs were taken of the samples using a 250 kvp x-ray system. It is apparent from the radiographs that, for some of the samples, leakage of the powder from the well had occurred and that in others the distribution of the powder was not uniform. Finally, it is apparent that the density of the powder varies from sample to sample. For nine of the samples the radiographs indicate that the data should be reliable. For these samples the gamma ray transmission values were fitted by linear regression to the equation

$$I = I_o \exp(-\alpha m_s), \tag{1}$$

where m_s is the mass of a cylinder of U_3O_8 6.4 mm in diameter. Figures 1 and 2 show the data used and the fitted line. The self-indication effect is clearly demonstrated in the case of U-235 detector, while the responses of Pu-239 detector to both U-235 and U-238 materials are very similar due to the fact that Pu-239 resonant cross sections do not match the total cross sections of either materials. The equation was then used to calculate m_s for the other sample. Three methods were used to calculate the total mass of the samples used for the neutron transmission measurements. They were as follows:

Method I is the one just described--a combination of the values of m_s obtained from measurements made on the radiographs and the known masses of the reliable samples with the values of m_s for the other samples calculated from the gamma ray transmission using eq (1).

Method II smooths the data by using eq (1) to calculate all of the values of m_s from the gamma ray transmission.

Method III was suggested by the fact that when the neutron transmission is plotted against the design values of the thickness, the resulting curve appears to be as good as the one obtained from Methods I or II which are based on the gamma ray transmission. Method III, in effect, assumes that all of the sample is effective in absorbing the neutrons.

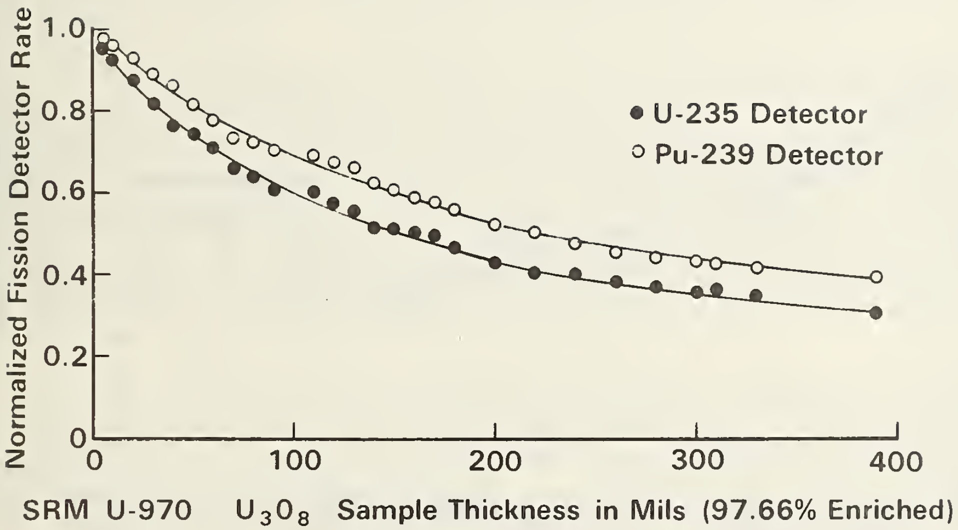

Figure 1. Normalized U-235 and Pu-239 fission detector rates as a function of SRM U-970 sample thicknesses.

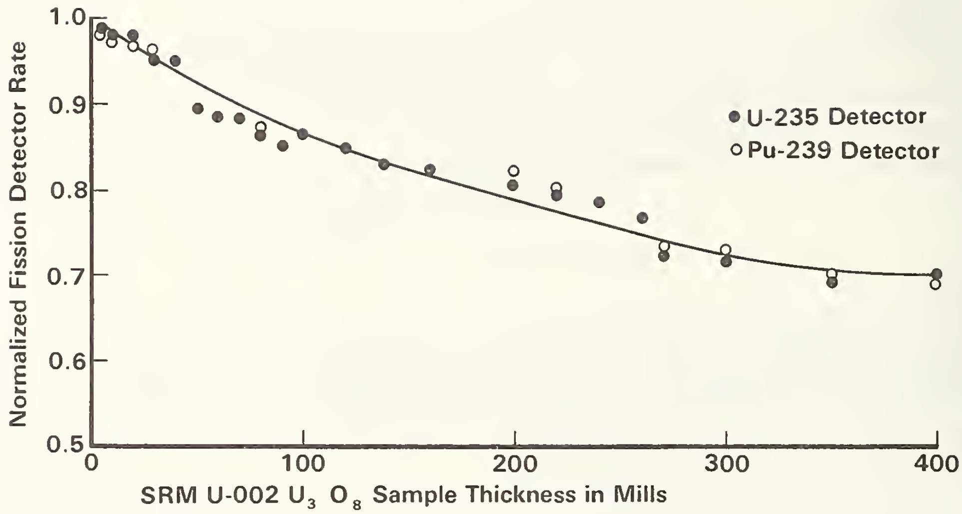

Figure 2. Normalized U-235 and Pu-239 fission detector rates as a function of SRM U-002 sample thicknesses.

As shown in previous reports, a plot of the neutron transmission versus the thickness of the absorber is expected to follow the equation:

$$I = I_o (a_o + a_1 x + a_2 x^2), \tag{2}$$

with the expected value of a_o being 1.

The neutron transmission was measured using a two compartment fission chamber with one foil being U-235 and the other Pu-239. The absorbers were 97 percent enriched U-235 (NBS SRM U-970) and fully depleted U-238 (NBS SRM U-0002).

When the data are fitted to eq (2) by a least square calculation, a_o is found to be 0.9 for U-235,/U-235 sample detector combination, about 0.95 for U-235,/Pu-239 combination, and about 0.97 for U-238 with either detector. No reasonable explanation for this is known.

It was decided to set $a_o = 1$ in eq (2) and to weight the data so that larger values of x are given more weight. The 26 data points were divided into groups of 9, 9, and 8 which were given weights of 1, 2, and 3, respectively. The results for Methods II and III agree quite well and are considered to be the best available from the present data. Table 3 gives the values of a_1 and a_2 obtained by this method for all four combinations of sample and detector, expressed in cm ^{1} and cm^2. These are the numbers that would apply if the sample is a solid metal foil.

The set up for the scanning procedure is shown in figures 3 and 4. The waste container was first moved horizontally with respect to the neutron beam at 1.6 mm intervals, the total width covered was 6.4 cm. At the end of each horizontal scan, the container was rotated 3°. Sixty such rotations were acquired for each slice of the container to be reconstructed. A total count of > 10,000 was recorded for each point scanned on both U-235 and Pu-239 detectors. Dwell times on each point varied from 15 s to 25 s.

The preliminary tomographic reconstruction of the slice of the container that passes through the centers of all three pellets is shown in figure 5. The heights of the three columns indicate the relative U-235 contents. The initial results show the isotopic U-235 enrichments in the three pellets to be 4.35 percent, 2.69 percent, and 1.03 percent as compared to the known values of 3.96 percent, 2.52 percent, and 1.19 percent, respectively. The errors are mainly introduced by the calibration process. To minimize the errors, one has to use metallic reference discs instead of the ones made from powder SRM's so the effective thickness of each disc can be measured more accurately.

Y. T. Cheng, D. Garrett, W. Parker, M. Ganoczy, M. Dorsey

TABLE 3. Calculated values of a_1 and a_2.

Absorber		U^{235}	U^{238}
U^{238}		$a_1 = 4.941\ cm^{-1}$	$a_1 = 1.518\ cm^{-1}$
		$a_2 = 9.534\ cm^{-2}$	$a_2 = 1.467\ cm^{-2}$
U^{235}		$a_1 = 3.776\ cm^{-1}$	$a_1 = 1.440\ cm^{-1}$
		$a_2 = 6.233\ cm^{-2}$	$a_2 = 1.321\ cm^{-2}$

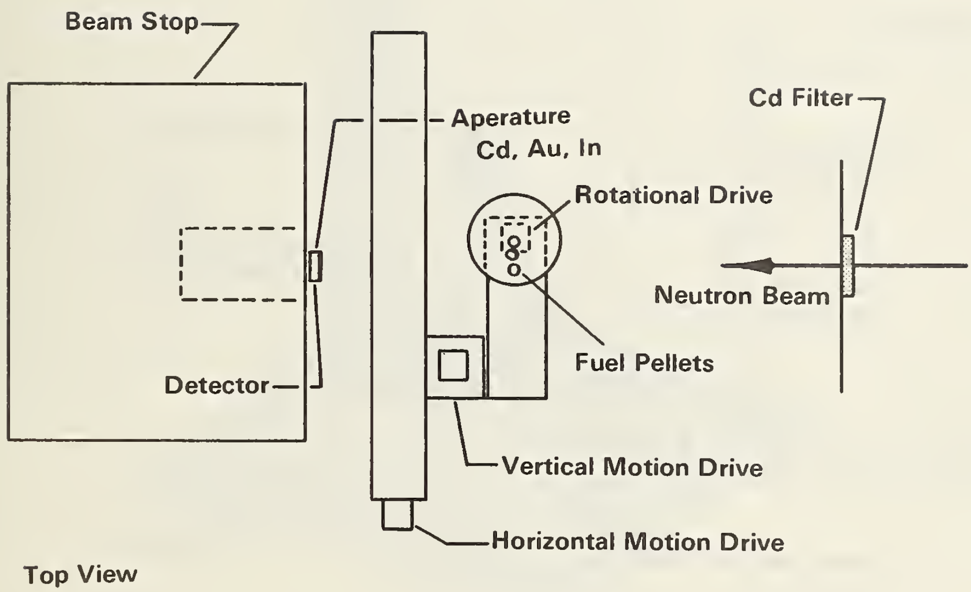

Figure 3. Top view of the tomography scanning setup.

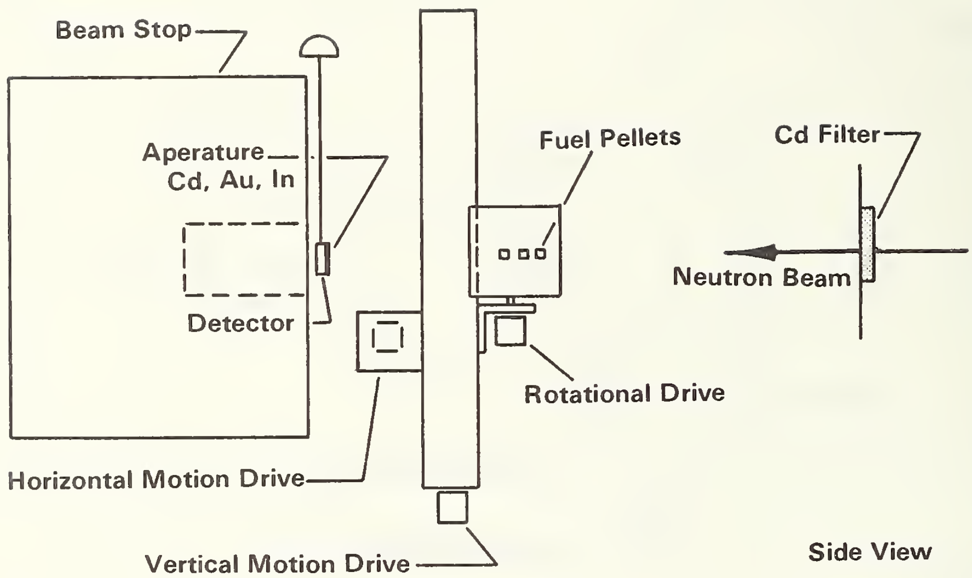

Figure 4. Side view of the tomography scanning setup.

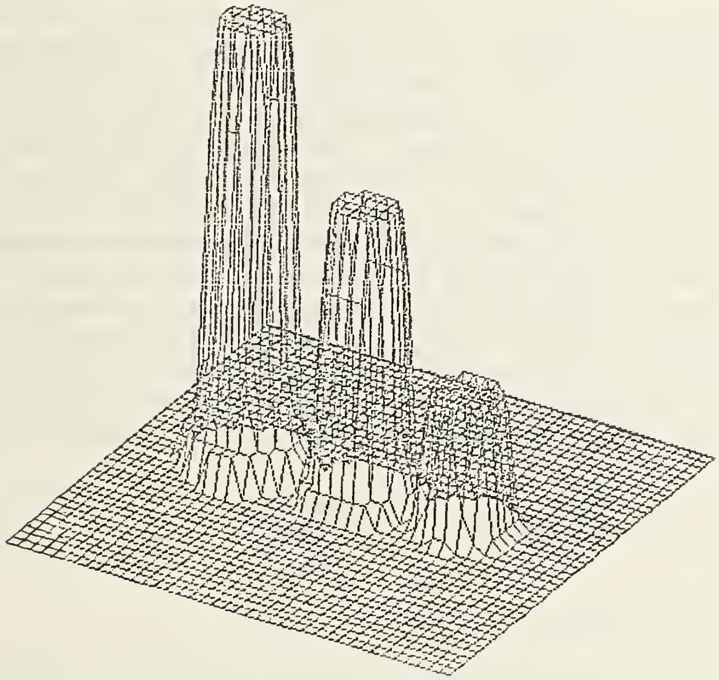

Figure 5. Tomographic construction of U-235 contents in the fuel pellets.

b. Other Neutron Measurement Techniques

The development of high resolution two-dimensional position sensitive neutron detectors has continued. This work has resulted in successful detectors based on both proportional ionization counting and scintillators. Resolution has been improved into the submillimeter range and neutron detection efficiency improved by several orders of magnitude. Accurate radiography is now possible along with a complete quantitative assay of small samples (5 cm or less in width). With the improved detector efficiency it is now possible to consider measurements away from a reactor or large accelerators usually associated with radiographic methods. The method is now ready for testing in practical situations such as nondestructive assay of standard samples prepared for nuclear material measurement.

The development of a related new method called Neutron Resonance Transmission Assay (NRTA) has been pursued. This method uses the neutron resonance structure of the actinides for isotopic identification and accurate assay and does not require position sensitive detectors. Measurements are possible with the small radiographic accelerators typically used for inspection of heavy section steel by adapting them for neutron production. The method is capable of a complete nondestructive isotopic assay of intact spent nuclear fuel assemblies. Measurements demonstrate that nine actinides and four fission products can be measured in about ten minutes. Optimization accuracies in the 1 percent range may be expected. Current precisions are shown in table 4 for commercial spent fuel. Adoption of the method would have a significant impact on safeguards measurements related to the storage of spent fuel, the front end of fuel reprocessing facilities, and national and international commerce in fresh and spent nuclear fuel.

C. D. Bowman, J. W. Behrens, R. A. Schrack

c. Calorimetry

The aim of the calorimetric NDA activity is to provide measurement assurance and traceability to National Standards for calorimetric measurements made in the industrial assay of photonium-bearing solids. This is to be achieved through the exchange of calibrated plutonium heat sources between major suppliers and the NBS. Calorimetric measurements at NBS will be made in a Bunsen ice calorimeter and in an automated twin-bridge heat-flow calorimeter under construction at NBS.

In FY 1981, construction was completed on the thermal sensing elements for the NBS heat-flow calorimeter. These were installed in the complete calorimeter body and thermal testing of the unit was begun. Construction of the automated sample-changing assembly was started.

Four encapsulated plutonium heat sources provided by the Mound Facility which had previously been measured by NBS were returned to Mound for radiographic examination. At the same time, Mound will perform new thermal power measurements and re-certify their predicted power levels for the next three-year period. The Mound results have been received, but there has been an extended delay in shipping these sources due to a requirement that they be moved by special carrier.

TABLE 4. Current analysis results for center cut 2.5 cm sample.

Isotope	E_o(eV)	Atoms/Barn	Current Precision	Relative Abundance
^{234}U	5.19	1.E-5	*	2.E-4
^{235}U	8.78	(4.36±0.15) E-4	3%	9.4E-3
^{236}U	5.45	1.E-4	*	2.E-3
^{238}U	6.6	.0465±.0004	1%	1.0
^{238}Pu	18.6	3.E-5	*	6.E-4
^{239}Pu	10.93	(2.60±.11) E-4	4%	5.6E-3
^{240}Pu	1.05	(1.11±.02) E-4	2%	2.4E-3
^{241}Pu	13.4	8.5E-5	*	1.8E-3
^{242}Pu	2.67	(1.40±.04) E-5	3%	3.0E-4
^{131}Xe	15.0	(3.26±.05) E-5	2%	7.0E-4
^{133}Cs	5.8	8.E-5	*	1.7E-3
^{241}Am	1.27	6.E-5	*	1.3E-3
^{243}Am	1.36	8.E-6	*	1.7E-4
^{152}Sm	8.1	(7.27±.14) E-6	2%	1.6E-4
^{145}Nd	4.35	2.E-5	*	4.E-4
^{99}Tc	5.6		*	4.E-4

*Visual fit only, probably good to 10%.

In consultation with members of the NBS Statistical Engineering Division, we have developed a number of guidelines for an NBS Measurement Assurance Program covering encapsulated plutonium heat sources. They include annual thermal measurement in each of four power decades (from 0.001 W to 10.0 W) of two different plutonium heat sources in a heat-flow calorimeter. In addition, one of these sources from each decade should be checked in the ice calorimeter. The guidelines have been presented to the Mound Facility for consideration.

D. Ditmars

2. Standard Reference Materials for NDA - U_3O_8 Low Enriched Gamma-Ray Standards

The isotopic analysis of four of the five low-enriched materials intended for certification as SRMs for NDA gamma-ray standards has been completed. These materials were received from the Central Bureau of Nuclear Measurements (CBNM), Geel, Belgium. The four materials consisted of U_3O_8 with ^{235}U enrichments of 0.31 percent, 0.71 percent, 1.9 percent, and 2.9 percent.

The goal of the isotopic measurement at NBS was to accurately determine the level of ^{235}U enrichment and to demonstrate the degree of isotopic homogeneity. A sampling scheme to achieve these objectives was designed by the NBS Center for Applied Mathematics and supplied to CBNM for guidance during the packaging of the NDA samples. As a result of this sampling scheme, NBS received 13 samples from each enrichment batch. Of the total, twelve 0.5 gram samples were for isotopic measurements by thermal ionization mass spectrometry, and one 20 gram sample was for determining the quantity of ^{232}U contamination via gamma-ray spectrometry. After completion of the gamma-ray measurements, the 20 gram samples were shipped to NBL for uranium assay. The gamma-ray spectrometry results indicated no detectable quantities of ^{232}U in the samples.

Mass spectrometric measurements of the isotopic composition of the sample showed that the ^{235}U homogeneity was better than 0.1 percent for the 0.7 percent, 1.9 percent, and 2.9 percent enriched material. A range of slightly greater than 0.1 percent for the 0.3 percent ^{235}U material is within the measurement uncertainty of the isotope ratio measurements and may therefore not reflect any sample inhomogeneity.

In addition to the characterization measurements of the bulk materials by gamma-ray spectrometry and mass spectrometry, aluminum cans were designed and fabricated to package the material. Very rigorous specifications were required to produce containers of reproducible dimensions. Calibration experiments to verify that all cans would meet specifications were conducted both at NBS and CBNM.

The final and most enriched standard (4.5 percent ^{235}U) has arrived at CNBM and is being packaged. Samples are ready for shipment to NBS for gamma-ray and mass spectrometric measurements.

B. S. Carpenter, J. W. Gramlich, L. A. Machlan

3. Data Development and Calibration

a. Radioactivity Program

A technical article on the results of the NBS measurements of the half-life of plutonium-240 has been completed and is in the process of editorial review. It will be published during FY 82 in the International Journal of Applied Radiation and Isotopes jointly with the results of the measurements of the other members of the DOE Half-Life Evaluation Committee. A copy of the abstract is shown in figure 6.

In anticipation that x- and gamma-ray measurements were to be made on mixtures of plutonium isotopes (plus ^{241}Am) in an SRM for nondestructive analysis calibrations, the efficiency calibrations of germanium spectrometer systems were checked in the region below 400 keV (fig. 7), and a thick (15 cm) planar detector was obtained in order to obtain a flatter response in the 50 to 110 keV energy region.

Investigations showed that most existing calibration points in the region below 122 keV were not trustworthy, so a special effort was made to establish a few accurate points, independent of past spectrometric measurements or nuclear-decay-scheme data.

NaI(Tl) well detectors of high and calculable efficiency were used to measure accurately the emission rate of gamma rays at 60 keV (from the decay of ^{241}Am) and 88 keV (from the decay of ^{109m}Ag). In the 20 and 30 keV regions, x-ray emission rates were directly measured with detectors of established geometrical and intrinsic efficiency. The accurate calibration points were then used to adjust an efficiency curve calculated from the collimator geometry, interaction probabilities, transmission of intervening materials, and x-ray escape fractions.

These calibrated detector systems can be used with thin sources of plutonium isotopes of known activity to measure gamma-ray probabilities per decay, and then with sources to be distributed as NDA standards to investigate scattering and absorption.

L. Lucas, J. R. Noyse, W. Mann

B. Destructive Analytical Chemistry

The goal of the Destructive Analytical Chemistry Task is to provide standardization for wet chemical and mass spectrometric methodology used for the assay of nuclear materials. This task has three component functions:

- Research to produce and certify Standard Reference Materials (SRMs)
- Support for Measurement Assurance Programs (MAPs)
- Chemical and isotopic measurements to support NDA

Figure 6.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET *(See instructions)*	1. PUBLICATION OR REPORT NO.	2. Performing Organ. Report No.	3. Publication Date

4. TITLE AND SUBTITLE

The Half Life of Plutonium-240

5. AUTHOR(S)

Larry L. Lucas and James R. Noyce

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

U.S. Department of Energy
Office of Safeguards and Security
Germantown, MD 20874

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

The alpha-particle-emission rates of solutions of plutonium-240 oxide were determined from defined-solid-angle-counter measurements. These results were combined with composition data obtained from other laboratories, and the half life of plutonium-240 was calculated to be 6552.2 yr. Associated with this value is a standard deviation of the mean of ± 2.0 yr and a systematic uncertainty limit of ± 13.8 yr.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

alpha-particle emission, half life, plutonium, plutonium-240, safeguards, special nuclear materials

13. AVAILABILITY

☒ Unlimited
☐ For Official Distribution. Do Not Release to NTIS
☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☐ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

15. Price

Figure 7.

FITTING RESULTS FOR THE EXPANSION OF THE NATURAL LOGARITHM OF THE EFFICIENCY FOR DETECTOR 1.

GOODNESS OF FIT = 0.979151E 0

```
A(-3) =  0.285717E  7+,-   320813.
A(-2) =  -87150.9    +,-   7949.46
A(-1) =    869.717   +,-   67.8377
A( 0) =  -10.0116    +,-  0.236949
A( 1) = -0.159864E -3+,-  0.281965E -3
```

PT #	ENERGY	OBS EFF	% RESIDUAL
1	88.037	0.000743700	-0.0025
2	122.063	0.000758000	-0.0598
3	140.479	0.000728000	0.3340
4	165.853	0.000652400	0.1367
5	171.280	0.000629800	-0.6775
6	245.390	0.000427900	0.3922
7	279.188	0.000358300	-0.6264
8	364.480	0.000253500	0.0548
9	411.795	0.000214700	-0.7811
10	433.927	0.000203460	0.4514

FITTING RESULTS FOR THE EXPANSION OF THE NATURAL LOGARITHM OF THE EFFICIENCY FOR DETECTOR 2.

GOODNESS OF FIT = 0.990432E 0

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A(-3) =  0.211960E  7+,-   330160.
A(-2) =  -66457.3    +,-   8133.78
A(-1) =    669.481   +,-   68.7024
A( 0) =  -8.84039    +,-  0.237333
A( 1) = -0.532320E -3+,-  0.281387E -3
```

PT #	ENERGY	OBS EFF	% RESIDUAL
1	88.037	0.001169400	-0.0388
2	122.063	0.001214500	0.2166
3	140.479	0.001171500	0.3023
4	165.853	0.001066400	0.0006
5	171.280	0.001038200	-0.3895
6	245.390	0.000747000	0.3542
7	279.188	0.000640800	-0.6518
8	364.480	0.000471400	-0.5708
9	411.795	0.000413100	0.3567
10	433.927	0.000389700	0.5442

When requested, and as needed, assistance is provided to other domestic laboratories in government and industry. Assistance is also provided to other countries and to international and/or multinational organizations in the accurate measurement of certified reference materials.

1. Methodology for Chemical Assay of Nuclear Materials

High-precision and high-accuracy chemical assay techniques are essential if there is to be adequate safeguarding of the nuclear materials in the fuel cycle. These techniques, in conjunction with well characterized SRMs, help provide a sound base for materials measurement and accountability. Chemical assay procedures are also essential to the preparation of high-accuracy primary reference materials of known isotopic composition for mass spectrometer calibration.

a. Uranium Assays

The goal of this project was to develop a method for the high precision assay of 10-25 mg of uranium in separated isotope solutions. The Davies-Gray titration is capable of the required precision of better than one part in 10^4 but does require larger (2-3 g) samples for high accuracy and precision. Since large quantities of separated isotopes are expensive, scarce, and in some cases, a radiation hazard, there was an acute need to develop a high precision assay utilizing less than 100 mg of sample. When this work was initiated, no method existed which was capable of yielding better than 1 part in 10^4 precision on a sample of less than 100 mg.

A manual titration procedure has been developed by a methodical study of the effects of various parameters upon the Davies-Gray titration and through the application of improved techniques to the basic method. The precision for this new method, for a 100 mg sample, is nearly as good as would be determined from 2-3 gram samples by the conventional method. Alternatively, samples of 10 mg or less might be titrated to the 0.05 percent precision level of the standard Davies-Gray titration. The usefulness of such an improvement is the fact that no significant changes in equipment or chemistry is required.

The initial aspect of this research has been accomplished within set precisions of 0.006 percent for 100 mg samples. Although there is a consistent bias of 0.09 percent, this will not interfere in the preparation of accurate calibration standards from two master solutions of uranium separated isotope since the method would only be used to certify isotope ratio standards. The results of this research will be presented in part in an invited paper at an upcoming American Nuclear Society meeting and is being prepared for submission to Analytical Chimica Acta.

J. R. Moody

2. High Sensitivity Mass Spectrometry of U and Pu

a. Resin Beads

High-Precision and High-Accuracy mass spectrometry techniques are essential to the measurement and safeguarding of nuclear materials. In addition, the high sensitivity of the resin bead technique coupled with the high precision and high accuracy of the thermal mass spectrometry technique offers unique possibility for measurement and accountability.

High sensitivity isotopic measurements of uranium and plutonium by thermal ionization mass spectrometry using an anion resin bead as the emitter has been investigated. The use of the resin bead has been studied for its promising advantages in facilitating shipping, minimizing sample size and sample handling in the isotopic analysis of uranium (U) and plutonium (Pu) for required nuclear safeguards measurements. Some of the specific advantages of the resin bead technique result from; (1) the selective absorption by the beads of U and Pu from the fission and actinide products in dissolver solutions, (2) the ability to load and analyze beads directly by mass spectrometry, and (3) the high ion yield from the bead matrix which markedly reduces the required sample size and thus, the potential radiation hazard.

The NBS effort in the U and Pu isotopic analysis program has been directed at the critical evaluation of the resin bead technique with respect to routinely achievable precision and accuracy. Efforts in the previous year have been directed at the identification of the factors which affect precision and accuracy as measured using NBS instrumentation and mass spectrometric practices. In the past year, a round robin has been organized to introduce other mass spectrometric laboratories which have the capability of making high sensitivity measurements to the resin bead technique and to receive, in turn, the critical evaluations of these laboratories and a more general indication of measurement state-of-the-art as related to high sensitivity U and Pu analysis.

A request to participate in the round robin was made to all laboratories with the known ability to make high sensitivity U and Pu measurements including military, government, industrial, and academic laboratories, both domestic and foreign. Of the fifteen labs contacted, eleven expressed interest in participating and received samples. Six of these laboratories continued in the round robin exercise and formally submitted data for all the phases of it. It must be emphasized that the round robin was a voluntary exercise and did require a significant expenditure of effort by the participants. This level of effort required was the primary reason expressed for inability to participate. The laboratories that did participate generally had extensive previous experience with either small particle handling or the resin bead technique.

The round robin was divided into four phases. The initial phase consisted of beads of two different sizes that were fully loaded, that is, the bead capacity was saturated with uranium. These samples were designed to allow baseline measurements and calibration of instrumentation with relatively unlimited uranium, 300 or 30 nanograms. The three other phases of the round robin consisted of samples containing U and Pu alone and together with beads containing about 3 ng of the element(s). In all phases of the round robin, both standards and unknowns were submitted for analysis which allowed external standardization of the results.

Table 5 summarizes the round robin design. Samples were shipped by isolating a known and limited number of beads for each sample between an optical microscope well slide and flat slide. When it was observed that there was movement of the beads occurring in the slide "sandwich" which had the potential of causing the beads to be crushed or lost, the beads were immobilized in a drop of collodion diluted 1:10 with ethanol. It was concluded that beads could be shipped confidently with their integrity maintained in this manner.

The analysis of well-characterized unknowns in replicate by the participating laboratories in the round robin has provided invaluable information concerning the precision and accuracy achievable with the resin bead technique and high sensitivity mass spectrometry. The fact that unknowns were prepared with the isotopic spikes ^{244}Pu and ^{233}U requiring the measurement of the major $^{244}Pu/^{239}Pu$ and $^{233}U/^{238}U$ ratios maximized the evidence of isotopic fractionation. This fact is especially important for plutonium since the only isotopic standards available possess ^{240}Pu and ^{239}Pu as major isotopes and thus any uncertainty in corrections for fractionation extrapolated from these standards is magnified. Measurement of the minor isotopes (< 100 ppm) has allowed estimates of interference levels, which appear negligible, as well as limits of detection. The anecdotal information about instrumentation used and measurement practices followed have indicated the generality of the technique since single, double, and triple sector mass spectrometers, both voltage and magnetic peak switching, and both electron multiplier and Daly detectors in pulse counting operation were used. Figure 8 illustrates the results for a U and a Pu unknown.

This round robin has allowed a number of generalized conclusions to be made concerning the resin bead sample loading technique. These include the following: (1) The technique is convenient for shipping, handling, and inventorying very small known amounts of uranium and plutonium, (2) a few nanograms of U and Pu can produce a signal intensity adequate to make precise measurements of major isotopes, and (3) that laboratories familiar with the handling of small samples can routinely use the technique. Questions that were not addressed or were unanswered by this round robin are, (1) the transferability of the technology to routine measurement conditions where the care necessary to handle small samples or delicate instrumentation may not exist, and (2) the ability to control fractionation which may be inherently less than both conventional and other high sensitivity methods of loading uranium and plutonium. Table 6 summarizes the accuracies and precisions achieved on the major isotopic ratios of the unknowns A, B, C, D, E, and G.

J. D. Fassett, W. R. Kelly

TABLE 5. Resin bead round robin design.

Phase	Element	Bead Size	Amount	Samples Standards	Unknowns
I	U	150 µm	300 ng	3	1
		50 µm	30 ng	1	1
II	U	150 µm	3 ng	1	2
III	Pu	150 µm	3 ng	1	2
IV*	U/Pu	150 µm	3 ng ea.	1	1

*Not completed at time of this report.

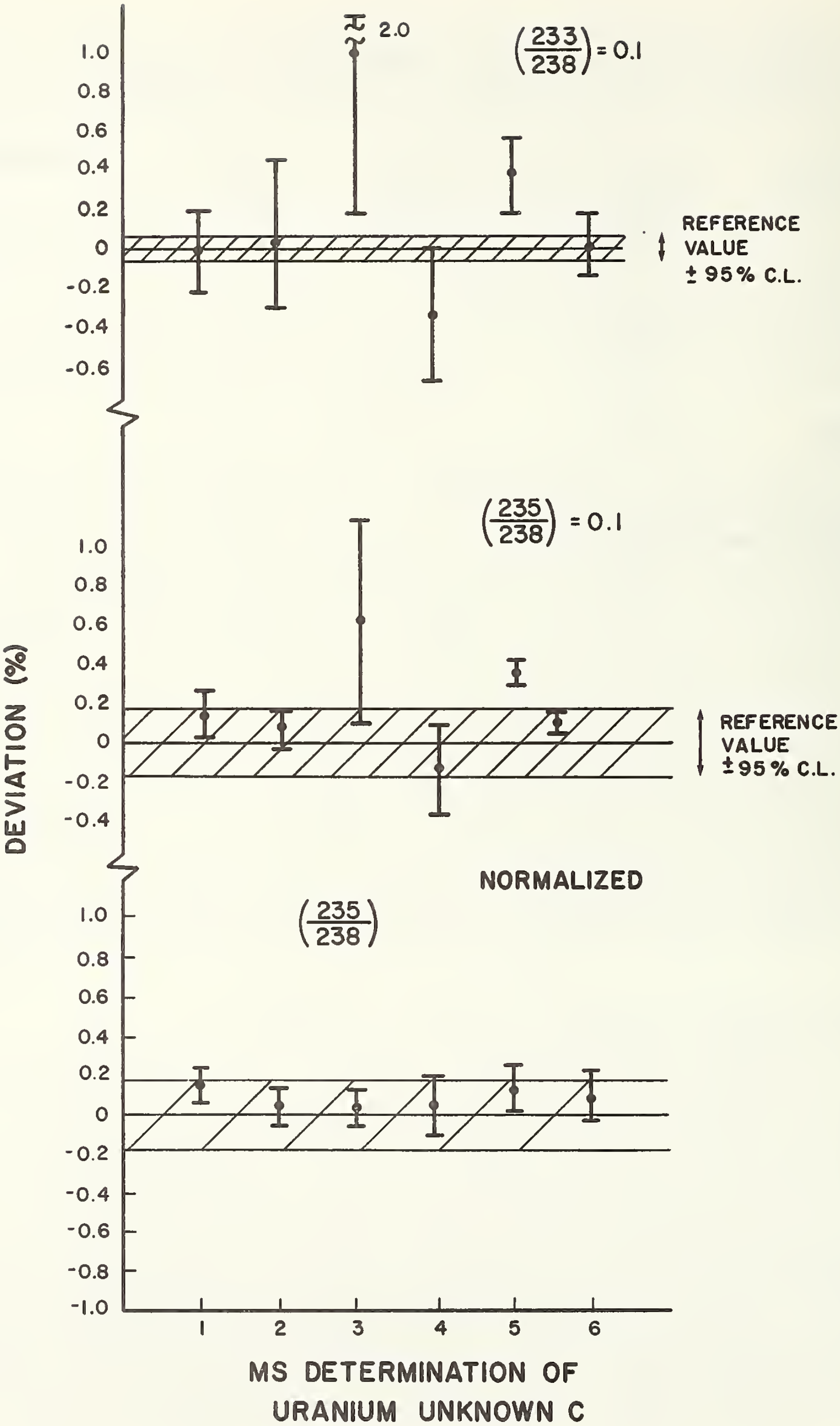

2.0
(233/238) = 0.1
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
REFERENCE
VALUE
± 95% C.L.
(235/238) = 0.1
DEVIATION (%)
NORMALIZED
(235/238)
-0.8
-1.0
1
2
3
4
5
6
MS DETERMINATION OF
URANIUM UNKNOWN C

Figure 8.

TABLE 6. Measurement, precision, and accuracy.

Unknown	Reported Results	Isotopic Ratio	Value	Precision Avg.	Precision Median	Accuracy Avg.	Accuracy Median Absolute Error
A	7	$^{235}U/^{238}U$	.12	.40%	.18%	+.33%	.30%
B	7	$^{235}U/^{238}U$	.10	.24	.25	-.05	.27
C	6	$^{235}U/^{238}U$	.10	.18	.12	+.21	.14
		$^{233}U/^{238}U$	.08	.37	.27	+.19	.20
D	6	$^{235}U/^{238}U$	.02	.41	.27	+.35	.25
E	5	$^{244}Pu/^{239}Pu$	.61	.22	.18	+.43	.46
G	5	$^{240}Pu/^{239}Pu$	.22	.10	.10	-.12	.08

b. IDA-80

NBS and the Central Bureau for Nuclear Measurements (CBNM), Geel Establishment, Belgium, are jointly providing assay and isotopic characterization for uranium and plutonium in a series of samples for IDA-80. IDA-80 is a worldwide test program to assess the state-of-the-art for interlaboratory measurement by isotope dilution mass spectrometry. This measurement program focuses on the determination of uranium and plutonium elemental concentrations as well as their isotopic composition in solutions from nuclear installations and reprocessing plants under routine operating conditions.

Thirty-nine samples were received at NBS including; input for a reprocessing plant, both spiked and unspiked samples; synthetic uranium and plutonium mixture, both spiked and unspiked samples; and a mixed uranium and plutonium spike. At NBS, the unspiked samples were spiked with aliquots of SRM 993 (^{235}U) and SRM 996 (^{244}Pu) and separate aliquots of the samples were spiked with the included spike solution. The spike and sample mixtures were equilibrated by an oxidation-reduction step and then the uranium and plutonium were separated and purified by anion exchange separations.

The plutonium samples were analyzed by high sensitivity thermal ionization mass spectrometry using ion counting detection. The size of sample required per measurement by this technique was a nanogram. This technique was utilized in order to minimize both radioactivity in the laboratory and contamination of the mass spectrometer and represents a factor of 1000 less than is required for conventional plutonium measurement procedures using Faraday cup detection. Fractionation corrections were made relative to the plutonium isotopic SRM 947 which was measured in replicate throughout the plutonium measurement program. The $^{240}Pu/^{239}Pu$ ratio of this standard was measured to 0.06 percent (1α, N=28).

The uranium samples were analyzed by thermal ionization mass spectrometry using a Faraday cage collector. Approximately two micrograms of uranium were loaded onto each sample filament of a triple filament rhenium ion source for analysis in the mass spectrometer. All analyses were corrected for mass dependent isotopic fractionation by comparison with SRM U-500, analyzed under identical conditions.

J. D. Fassett, J. W. Gramlich, L. A. Machlan

c. Mass Spectrometer Facility at New Brunswick Laboratory

The NBS mass spectrometer facility at New Brunswick Laboratory (NBL), Argonne, Illinois was visited by scientists of the Mass Spectrometry Group in order to verify instrument performance according to established specifications and to verify that the support facilities were complete and functional. Furthermore, NBL personnel responsible for this facility were instructed in all phases of sample loading and instrument operation during these visits. In return, the staff scientist at NBL responsible for this facility, visited NBS to receive more extensive training in NBS developed mass spectrometric procedures.

Two of the most recent instrument changes in the basic NBS design were incorporated in the NBL instrument. A turbomolecular pump was installed which will alleviate the difficulties associated with maintaining a liquid nitrogen supply to trap a mercury diffusion pump. This type of pump has been evaluated and is presently in routine operation at NBS. A pyrometer mount, one of the latest refinements in the making of high precision measurements, was also installed. Since these visits, NBL personnel have used the instrument extensively with demonstrated measurement precisions of a few parts in ten thousand for the NBS uranium series isotopic standards.

W. A. Bowman, J. D. Fassett, J. W. Gramlich

d. Pu Isotopic Reference Materials Working Group Meeting

The Second International Pu Isotopic Reference Materials Working Group Meeting was held in Vienna, Austria, April 8-10, 1981. Insofar as new reference materials are concerned, the top priority is an equal atom mixture ^{239}Pu and ^{242}Pu for mass spectrometry. The need for both CBNM and NBS to produce two different, rather than a common reference material, was seriously questioned. In addition to the equal atom reference material, the need for three plutonium isotopic reference materials for isotopic analysis and non-destructive analysis (NDA) was discussed. Reference materials of 90 percent, 75 percent, and 60 percent ^{239}Pu were identified as sufficient to cover all projected needs of the nuclear industry on either the national or international scale. At the present time, CBNM has acquired 1.2 Kg of 60 percent ^{239}Pu and the Department of Energy has identified and has on hold 1.5 Kg of 90 percent and 2.0 Kg of 75 percent ^{239}Pu. It was agreed that the chemical form should be medium to high fired oxide, possibly as micro-spheres. The amount of material required to provide a ten year supply of each reference material was estimated at 950 g.

The Working Group was informed that NBS would no longer coordinate activities of the Group and would pass the duties to a representative of the Department of Energy's New Brunswick Laboratory.

B. S. Carpenter

C. Bulk Measurements

The Bulk Measurements Task occupies a position of strategic importance in nuclear safeguards. The activities of the Task involve the determination of the quantity of nuclear material in specific areas and processes in a nuclear fuel cycle plant and between specific areas and processes. Measurements of mass, volume, density, flow, pressure, and temperature contribute to the determination of the quantity of nuclear material; the measurements of these physical variables interact with each other and with the activities of the other three Tasks in the NBS Nuclear Safeguards Program.

1. Laser Doppler Velocimeter

The laser Doppler velocimeter was used to study the flow field of a strut placed in a pipe flow. Figure 9 shows the geometry of the strut and defines the coordinate system. In figure 10 is shown the mean velocity across the pipe diameter at several locations downstream of the strut. The locations are defined in figure 9. At any point in the flow the velocity is characterized by a mean value as shown in figure 10 and a fluctuating part. Figure 11 shows the power spectrum of the velocity fluctuations measured at the point $x = 3$ cm, $y = 0.5$ cm. Two sharp peaks are distinguishable and correspond to velocity fluctuations caused by vortex shedding from the strut. The slowly varying component of the power spectrum in figure 11 is due to turbulence. Using the data in figure 11 it is possible to determine the energy contained in the vortex fluctuations (area in the peak), and the energy contained in the velocity fluctuations due to turbulence (area under the peak). Figure 12 shows the energy in the first vortex peak, the second vortex peak, and turbulence, all a function of position across the pipe diameter. Vortex visibility is defined as the ratio of the energy contained in the vortex peak to the energy in the background turbulence. Figure 13 shows vortex visibility as a function of the position along the pipe diameter. The data summarized in figure 13 will be of great utility in the design and use of vortex shedding flow meters.

T. T. Yeh

2. Correlation Flowmeter

Improvements to the correlation flowmeter were implemented. A new capacitive probe was designed and constructed in such a way as to separate the high voltage (10 vpp) driving signal, which is applied to the active plate of the capacitive probe, and the sensing and balancing electronics which are attached to the ground plate of the probe. It was possible to null the bridge to about 25 μV which is the rms amplitude of the noise. A circuit to automatically balance the bridge was designed, constructed, and debugged. The circuit consists of five ADC and five DAC elements interfaced to a AM Z8002 computer and to the analog inputs and outputs of the bridge circuit. Software development for the control function has started. Construction has started on a "calibrator" for the correlation flowmeter. The calibrator is an adaptation of the one used for the laser Doppler velocimeter and it will allow us to introduce known disturbances into the correlation flowmeter. This will facilitate the design of sensing electrodes and the development of algorithms for computing various moments of the correlation function.

A. Gaigulas

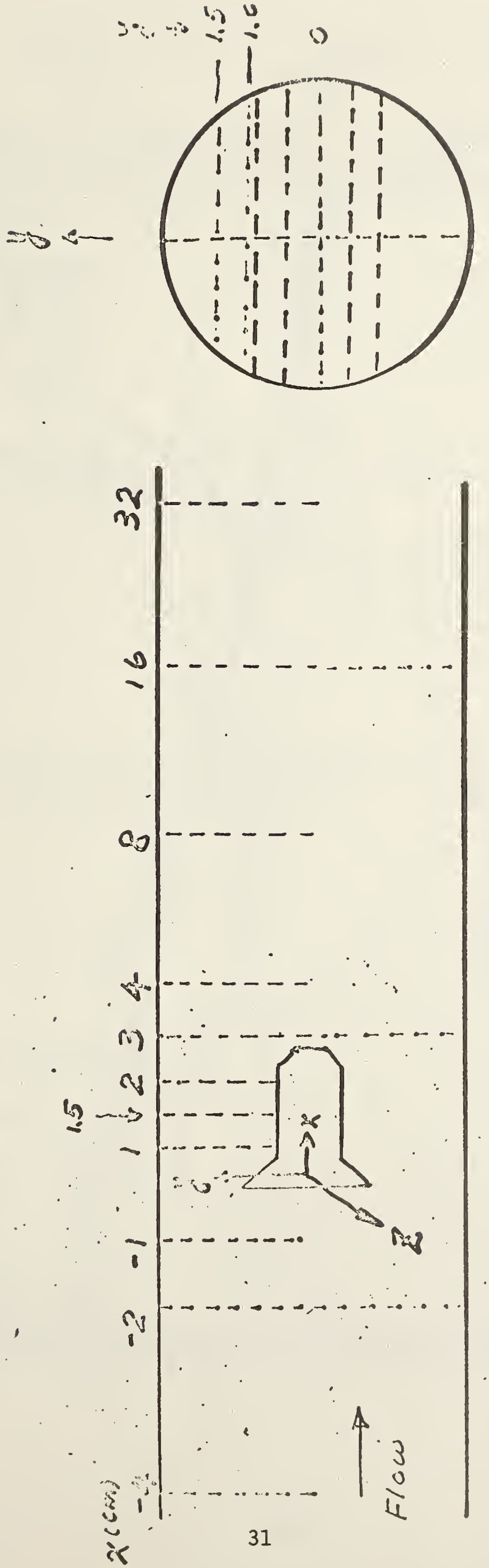
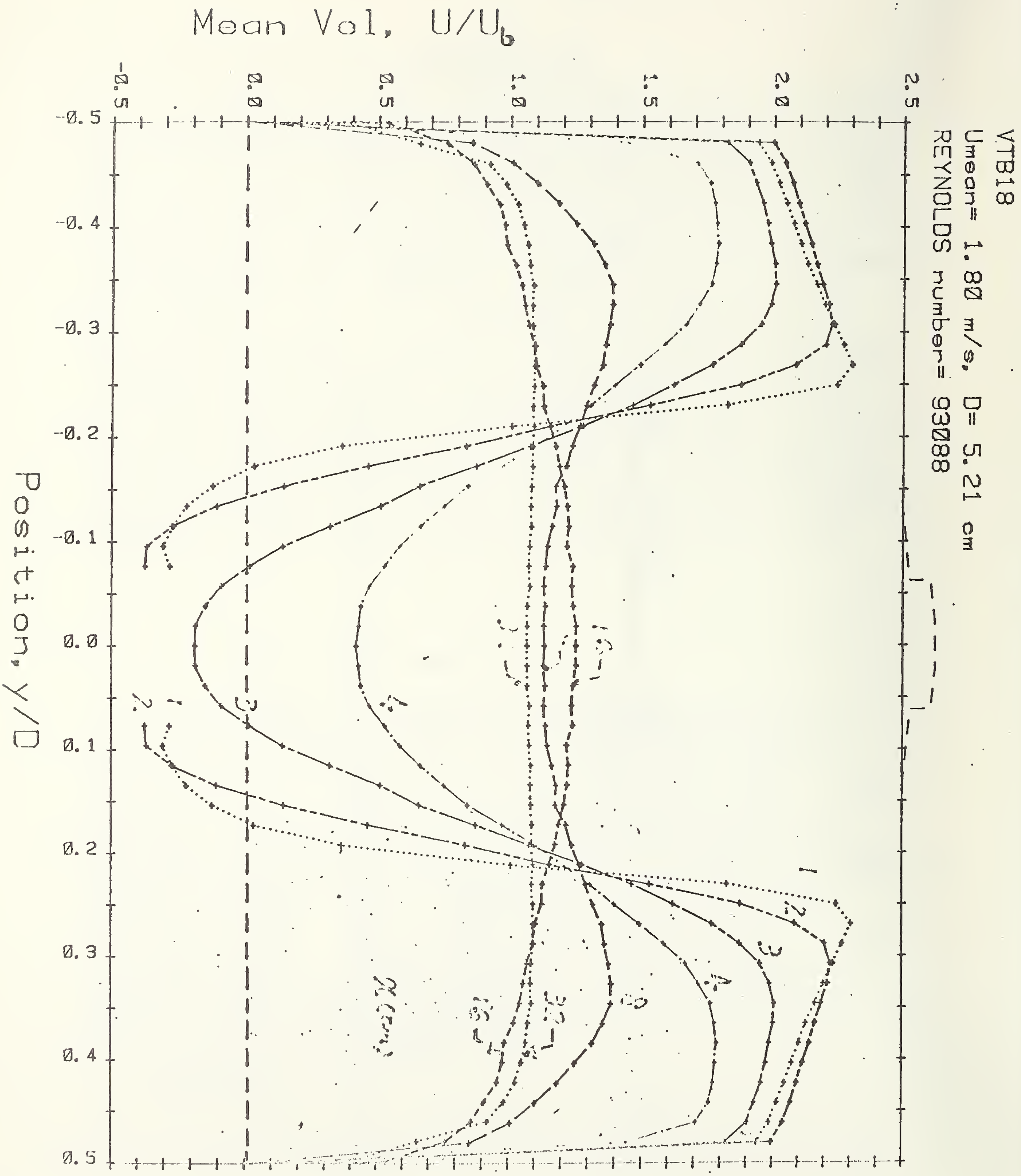


Figure 9.


Mean Vel, U/U_b
VTB18
Umean= 1.80 m/s, D= 5.21 cm
REYNOLDS number= 93088
Position, y/D
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0.5
1.0
1.5
2.0
2.5
-0.4
-0.3
-0.2
-0.1
0.1
0.2
0.3
0.4

Figure 10.

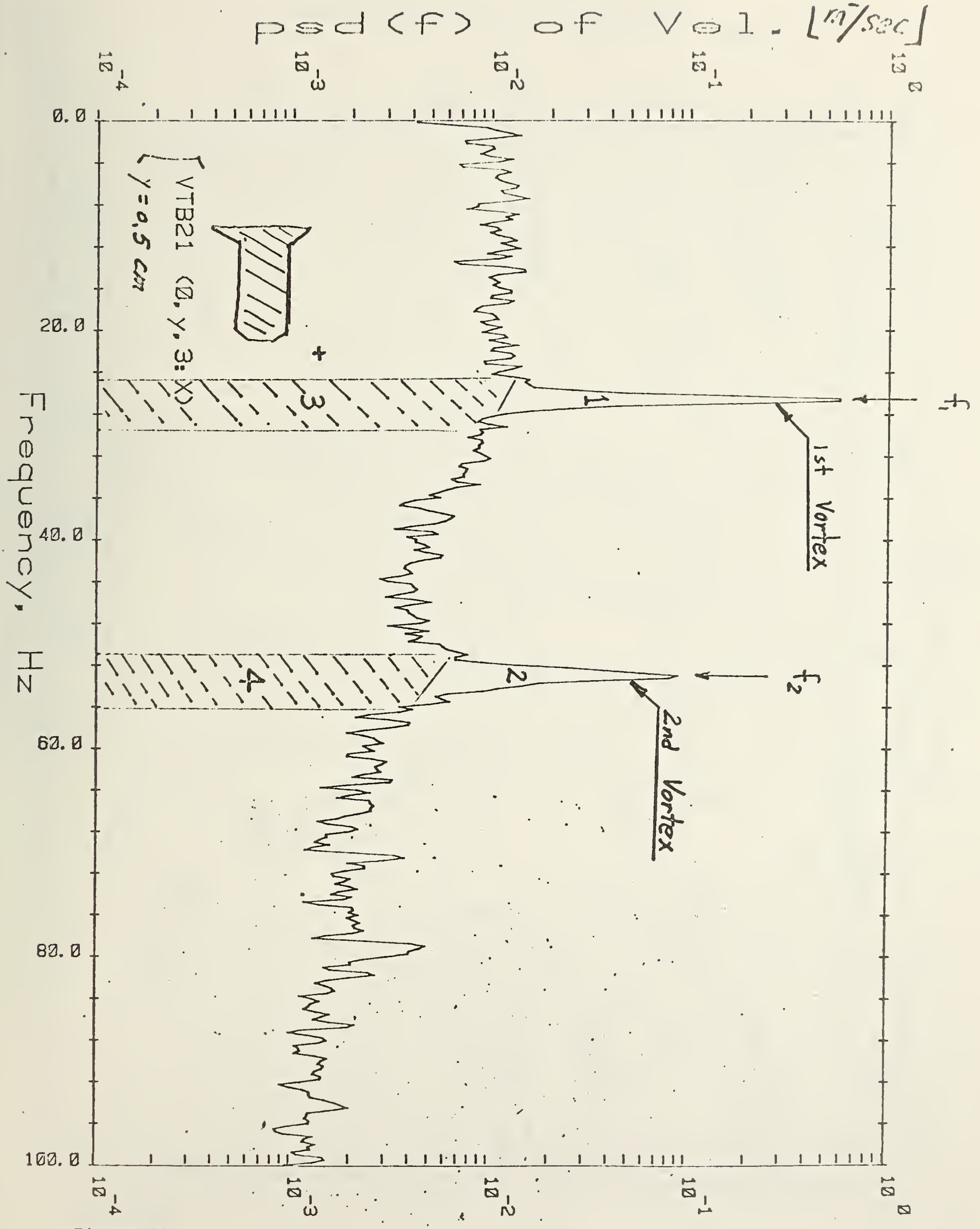

psd(f) of Vel. [m/sec]
Frequency, Hz
VTB21 (0, y, 3: X)
y = 0.5 cm
1st Vortex
2nd Vortex
f_1
f_2
1
2
3
4
0.0
20.0
40.0
60.0
80.0
100.0
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}

Figure 11.

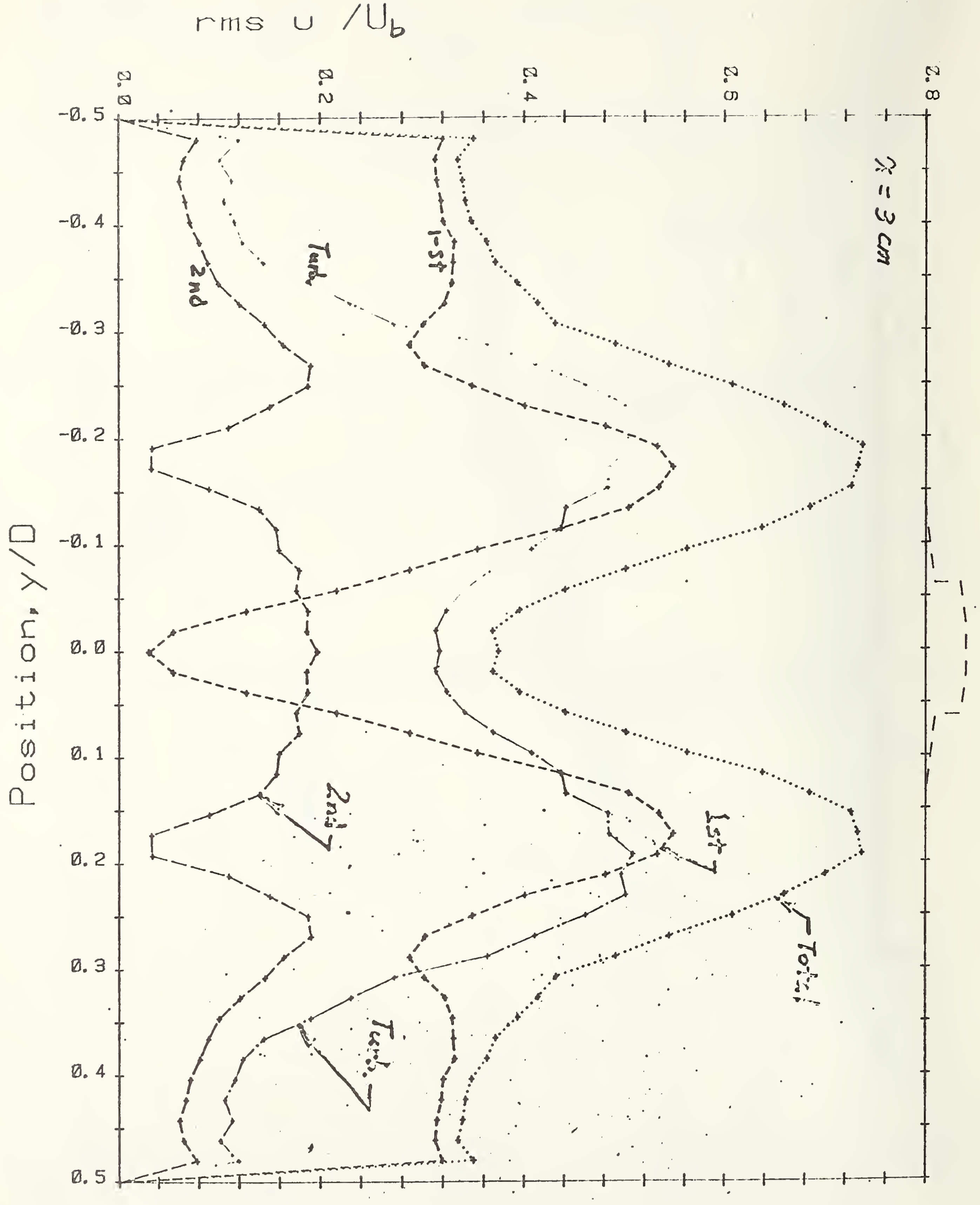


Figure 12.

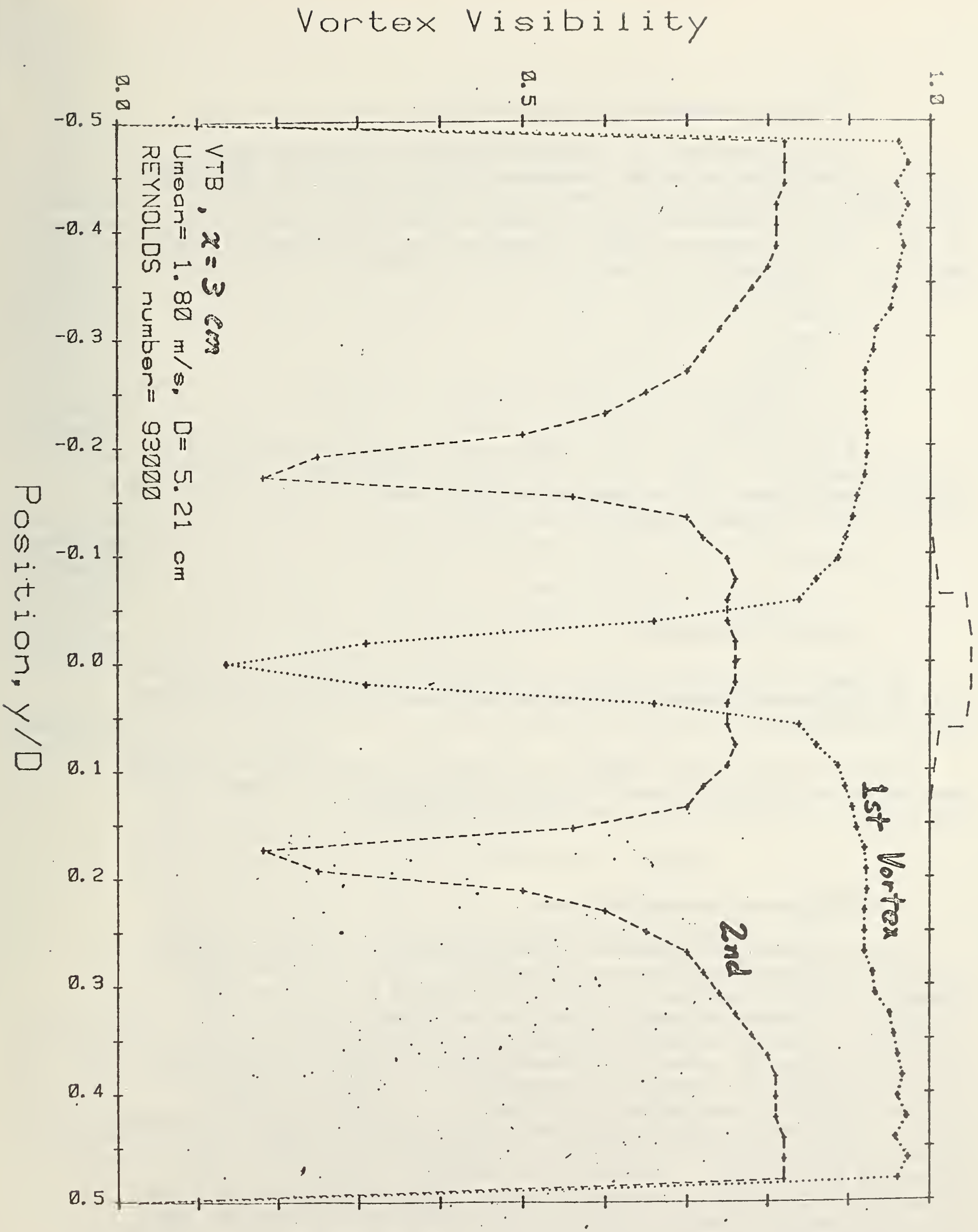

Vortex Visibility
0.0
0.5
1.0
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
VTB, x=3 cm
Umean= 1.80 m/s, D= 5.21 cm
REYNOLDS number= 9300
Position, y/D
1st Vortex
2nd

Figure 13.

3. Tank Volume Calibration Algorithm

An algorithm has been developed to relate the volume of a nuclear process solution at its temperature to the calibration performed with water at a temperature near ambient. A manuscript titled "A Tank Volume Calibration Algorithm" by F. E. Jones is undergoing editorial review. Another manuscript titled "Accountability Tank Volume Calibration Data," by F. E. Jones, J. F. Houser, and R. M. Schoonover is undergoing editorial review also.

F. E. Jones

4. Determination of Water in Plutonium Dioxide

A manuscript covering the measurements of the moisture content of plutonium dioxide, made at the Hanford Energy Development Laboratories, Richland, Washington, titled, "Determination of Water in Plutonium Dioxide," by F. E. Jones, is undergoing editorial review.

F. E. Jones

D. Applied Mathematics

The applied mathematics effort in support of safeguards consists not only of independent efforts, but also of collaborative efforts with other scientists at NBS.

During the past year a number of articles were published on statistical approaches to Safeguards Measurements and the Safeguards Problems. These are listed in the publications section of this Report.

E. Safeguards Systems Studies

The objective of Safeguards Systems Studies is to provide technical support to the safeguards program of the DOE Office of Safeguards and Security (DOE/OSS) and the U.S. Initiative Program for International Safeguards. Systems analysis studies are performed leading to a more effective utilization of data and information from all sources for achieving safeguards goals. Program efforts contribute sound technical input for design, development, and operation of DOE/OSS and domestic nuclear plant programs that will be effective in protecting against covert diversion of special nuclear materials (SNM) by persons authorized access to the material or international programs aimed at detecting diversion by the State. Task activities addressed completion of the Concepts for Safeguards Information Systems study, modification of Diversion Path Analysis Computer Program 2, and adaptation of Diversion Path Analysis concepts to evaluation of international safeguards as applied by the International Atomic Energy Agency.

1. Study of DOE Safeguards Measurement Implementation Needs

Nuclear material measurement problems, from a safeguards point of view, currently exist at the major DOE processing facilities and can be expected to magnify as future high-throughput facilities come on-line. To address these problems, measurement methods have been developed for a significant number of material classes in the DOE complex, however, substantial effort on the part of development laboratories and DOE contractors may be required to adapt many of the methods for site-specific application. Administrative problems may also hinder technology transfer, or implementation of proven methodology, to the process line. Thus, any actions taken to improve the material control and accounting subsystems of the safeguards system must address not only the technical problems but the administrative issues as well. In addition, uniform documentation suitable for cost benefit analyses and the establishment of implementation priorities throughout the DOE complex are needed.

The objectives of the DOE Safeguards Measurement Implementation Needs Study were to identify the material control and accounting subsystem measurement needs at selected DOE contractor facilities and to recommend a prioritized plan for transferring technology presently available at development laboratories to address site-specific needs at these facilities. The significance of the administrative issues in regard to technology transfer was recognized early in the study; their identification, therefore, also was included as an objective.

To achieve these objectives, interviews were held with key Operations Office and contractor staff concerned with safeguards measurements at the following sites:

- Savannah River Operations Office (SR)
  Savannah River Plant [DuPont] (SR);
- Albuquerque Operations Office (AL)*
  Rocky Flats Plant [Rockwell International] (RFP);
- Richland Operations Office (RL)
  Hanford Engineering Development Laboratory [Westinghouse] (HEDL)
  Pacific Northwest Laboratories [Battelle] (PNL)
  Rockwell Hanford Operations [Rockwell International] (RHO)

The final draft of the report discussing the findings of the study together with the conclusions drawn from them has been prepared. The technical problems and administrative issues identified at each site are listed separately even though the same class of problem or issue was identified at more than one site. When this was the case, it can be seen that the perception and/or impact of the problem or issue often varied from site to site. By maintaining the separate listings, these variations are preserved.

S. Bologa, J. Schleter, M. D. K. Maltese

IV. MEASUREMENTS AND STANDARDS FOR NUCLEAR WASTE MANAGEMENT - A TECHNICAL OVERVIEW

The Program of Measurements and Standards for Nuclear Waste Management was established late in Fiscal Year 1980, after an extensive study of the materials and measurements problems involved in nuclear waste management. Thus, this technical overview for Fiscal Year 1981 represents the first full year of operation as a program.

The technical efforts for the Nuclear Waste Program are divided into the following areas: (1) Waste Forms Leachability Mechanisms; (2) Waste Forms Research, Reference Materials Data and Measurement Methods; and (3) Containers, Backfill and Math Support.

A. Waste Forms - Leachability Mechanisms

This task reviewed existing efforts by others, as well as carried out experiments in selected areas at NBS to improve and understand the mechanisms involved in leaching of radioactive waste species from an immobilizing matrix. In order to accomplish this, the role or effect of radiation, mechanical properties, microstructure, microchemistry, thermodynamics, transport mechanisms, thermochemistry, and various other disruptive processes were investigated.

1. Leachability Concepts and Theory

A survey of the literature on the theoretical modeling of leach measurements was conducted utilizing online computer based search codes. A primary finding was that the great majority of modeling efforts have been concerned with closed-form analytic solutions to the normal diffusion equation. This has necessitated a number of approximations which limit the value of these works to short-time evaluations of leaching trends. These treatments do not give adequate considerations to the mechanistic aspects of the transport phenomena. This is unfortunate since a detailed understanding of the leaching of radioactive wastes, and hence the opportunity to make long-term predictions, requires a corresponding understanding of the transport mechanisms.

In response to the foregoing situation, it was decided to pursue a threefold approach to the problem of modeling the MCC leach test measurements. The first step was to consider the added flexibility that would be obtained by using numerical rather than analytical solutions for transport problems. The second step was to develop a model that would emphasize the role of chemical and physical mechanisms in the transport of waste material in and from a solid host substance. The third step was to apply the model to the analysis of MCC measurements.

We found that diffusion problems could be treated very powerfully by numerical methods when compared to the rather restrictive limitations of the solutions found in closed forms. Spatial and time dependent diffusion parameters could be included with equal ease, as could dependences on concentrations and chemical reactions. As an illustration of the added power of numerical methods, a problem applicable to the phenomenology of leaching mechanisms was treated. We considered a leachant A that could react with a constituent B of the solvent and thereby form a reactant C. Compound C could adhere to the solid-solvent interface causing a change in the diffusion characteristics of the system. Allowing the adhered layer to flake off periodically, we found it possible to produce either a linear ("matrix dissolution") or a parabolic ("simple diffusion") leach rate depending on how the data points were sampled. Neither of the phenomenologically suggested mechanisms was correct.

The phenomenological approach to the modeling of leach measurements is useful for the discussion of short-time trends, but as seen in the preceding example, it is only crudely related to the actual transport mechanisms. Therefore, as an important alternative, a microscopic formulation of the diffusion and leaching process was developed. Based on the use of a recurrence relation for a random walk on a lattice, this model has several attractive features. (1) When the continuum limit is taken, a nonlinear diffusion equation with appropriate boundary conditions is recovered. (2) The incorporation of specific molecular mechanisms is a straightforward task. (3) The numerical solution of the model can be easily and inexpensively achieved.

To illustrate the application of this new model to the MCC-1 leach test measurements, two applications were considered. First, to establish a reference case, simple exchange and diffusion of Na^+ and H_3O^+ ions between SiO_2 glass and a water solvent was modeled. Then, the SiO_2 matrix was allowed to dissolve due to the reaction of OH^- solvent ions with the hydrated glass surface. Figure 14 shows that leached amounts over a 28 day period can be significantly affected by surface interactions.

R. Mountain, R. Munro

2. Radiation Effects

This effort was initiated to study the effects of radiation on nuclear waste forms. The study was designated to simulate long term radiation damage to the integrity of waste forms and to characterize the structural changes in the waste forms both macroscopically and microscopically. Our purpose is two fold, i.e., to conduct the feasibility study of, (1) using NBSR as a viable irradiation source for radiation damage study, and (2) establishing neutron measurement techniques to complement the more common x-ray methods.

Li-6 and B-10 neutron activation methods were chosen to simulate alpha particle and transmutation effects. Activation methods are preferred because the MCC-6 recommended Cm-244 doping process would require long waiting time and special handling. The use of the NBSR research reactor as a neutron source gives further ability in studying neutron and γ effects.

The total radiation dosage and dose rate given to the waste form can be moderated by varying the amount of Li and B dopants and by

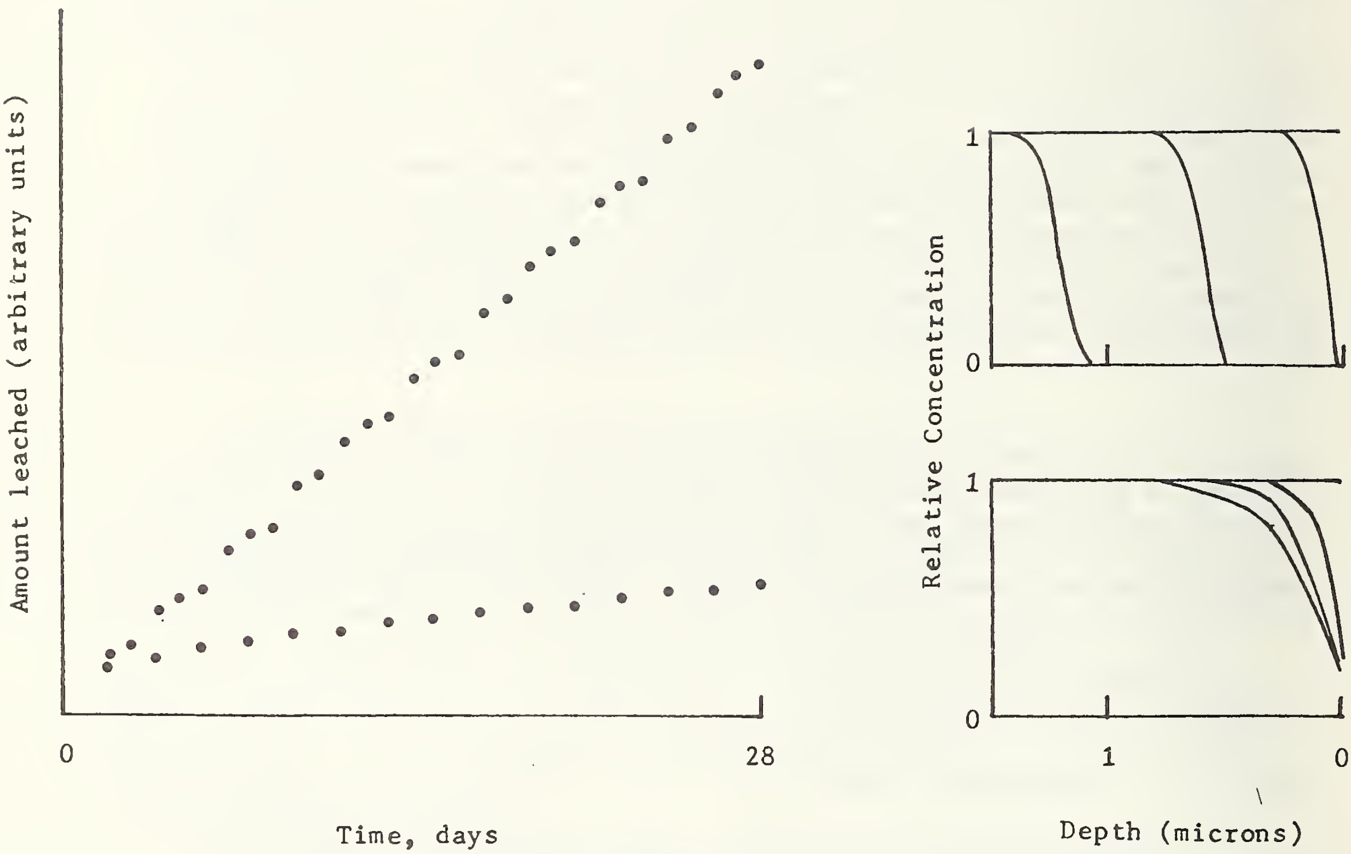


Figure 14. Leaching results with (upper curves) and without (lower curves) matrix dissolution at the surface. The concentration profiles are after 2, 14, and 28 days, moving from right to left. With surface dissolution, the amount leached grows linearly with time. Without surface dissolution, the amount leached grows approximately as time to the power 0.6 (i.e., T**0.6).

putting the sample in different positions in the reactor. This also allows one to change the n/γ or α/γ ratios to qualitatively study synergistic effects.

The waste form currently under study is magnetoplumbite ($X^{2+}M_{12}^{3+}O_{19}$). This is one of the four ceramic phases developed to contain high-level waste from the Savannah River Plant operations. Two natural Li doped magnetoplumbite samples ($Li_{0.5}La_{0.5}Al_{11}O_{17.5}$) were supplied to us by the Energy Systems Group of Rockwell International.

X-ray and neutron diffraction patterns of the sample were taken as microscopic bench marks for the pre-irradiation and small angle neutron scattering facilities are used to characterize the macroscopic properties of the sample. The sample was enclosed in sealed aluminum containers and was exposed to thermal neutron fluence of 1.2×10^{20} n/cm^2 to simulate the saturation α dosage. After irradiation, the sample was allowed to cool down for 30 days before examined again by neutron and x-ray techniques to characterize its post-irradiation conditions. These pre- and post-irradiation examinations will then be correlated with the result of leachability tests which will be conducted by the Rockwell International Group.

3. Mechanical Properties

One of the primary objectives of this work has been to determine the susceptibility of the glasses proposed for nuclear waste encapsulation, to subcritical crack growth and microcracking. Crack growth data has been obtained on a simulated waste glass composition in both moist air and H_2O. The glass was formulated by NBS based on a composition suggested by Battelle Northwest Laboratories. The glass was melted, cast, and annealed, and cut into double cantilever beam specimens. Crack velocities from 10^{-11} to 10^{-4} m/s were obtained as a function of stress intensity, K_I. As with most glasses, crack velocities were higher in water than in air. Data is now being obtained at lower velocities to determine if a stress corrosion exists for this composition.

The possible acceleration of stress corrosion by gamma irradiation is also being investigated. A fixture for obtaining crack growth data in the NBS gamma-ray source was designed and built. Baseline data on a soda-lime-silica glass has been obtained. A few preliminary data points have been taken on this same glass in a gamma-ray environment.

A fixture has also been designed and built to allow us to determine the effect of nuclear recoil on the strength and crack propagation behavior of glasses and ceramics. Baseline strength and crack propagation data have been obtained on two borosilicate glass compositions. By exposing these glasses to a thermal neutron flux, a transformation of some of the boron of lithium occurs with the production of an alpha-particle. The nuclear recoil could lead to residual tensile stresses in the glass which would produce lower strengths and possibly a lower resistance to crack growth. Experiments to evaluate these effects are planned for the near future.

S. Freiman, A. C. Gonzalez, S. M. Wiederhorn

4. Phase Stability

During the current year an effort was made to begin to understand the structural stability of crystalline materials containing large cations, such as Cs^+ in hollandite. This work was necessary as there are few, if any, data concerning the thermal and structural stability of hollandite minerals containing Ba^+ ions and/or Cs^+ ions in the channels of the Ti-hollandite network. This crystalline phase is the most important of the Cs-containing crystalline constituents of "Synrock" which is under current investigation as a possible host for nuclear waste.

As part of the general studies, the compatibility relations were re-examined for the system $BaO-Al_2O_3-TiO_2$. The subsolidus relations in this system had been previously reported by Guha [J. Solid State Chem. 34, 17 (1980]. The primary phase fields were roughly mapped so that small single crystals could be obtained of all the phases. The diagram shown as figure 15 should be considered as very tentative. It has been drawn to be consistent with all the experimental data obtained in the present study, but many more experiments would be needed to more accurately locate the phase boundaries. Single crystals of each of the phases were examined by x-ray diffraction with a precession camera and the unit cell dimensions and space group symmetry of the three ternary compounds are shown in table 3. It should be noted that the hollandite single phase was found to melt directly to a liquid of approximately the same composition at 1480 ± 2 °C.

A tetragonal hollandite had been previously reported in this system by Ringwood [Acta Cryst. B36, 2913 (1980)] and other hollandites have been reported in similar systems by Cadee [Acta Cryst. B34, 3554 (1978)]. Single crystals of hollandite grown from the primary phase field of the ternary system $BaO:Al_2O_3:TiO_2$ show much stronger diffuse scattering characteristics than do the hollandite crystals grown using a flux containing CaO and ZrO_2 (a mixture of hollandite, rutile, and zirconalite). Although the superstructure spots have stronger intensity they are still very diffuse and disk shaped rather than spherical.

Phase equilibria in the system $BaO-MgO-TiO_2$ was also examined, as a tetragonal hollandite phase has previously been reported in this system by Dryden and Wadsley [Trans. Faraday Soc. 54, 1574 (1958)]. No tetragonal hollandite was encountered in the previously reported range of compositions, $Ba_x(Mg_xTi_{8-x})O_{16}$ $(1.14 \geq x \geq 0.67)$ which had been synthesized by a Verneuil technique. However, a solid solution region of a monoclinic distorted hollandite structure was synthesized between 1:1:6 and 1:1:5 $BaO:MgO:TiO_2$ or $Ba_x(Mg_xTi_{8-x})\ O_{16}$ $(1.33_3 \geq x \geq 1.14_3)$. The difference in composition and structure is unexplained at this time. Substitution of SrO for 10 mole percent of the BaO made little or no difference in the unit cell dimensions and symmetry. Reduction of the monoclinic phase by heating in N_2 at 1400 °C caused an increase in volume of the unit cell but little change in the amount of monoclinic distortion.

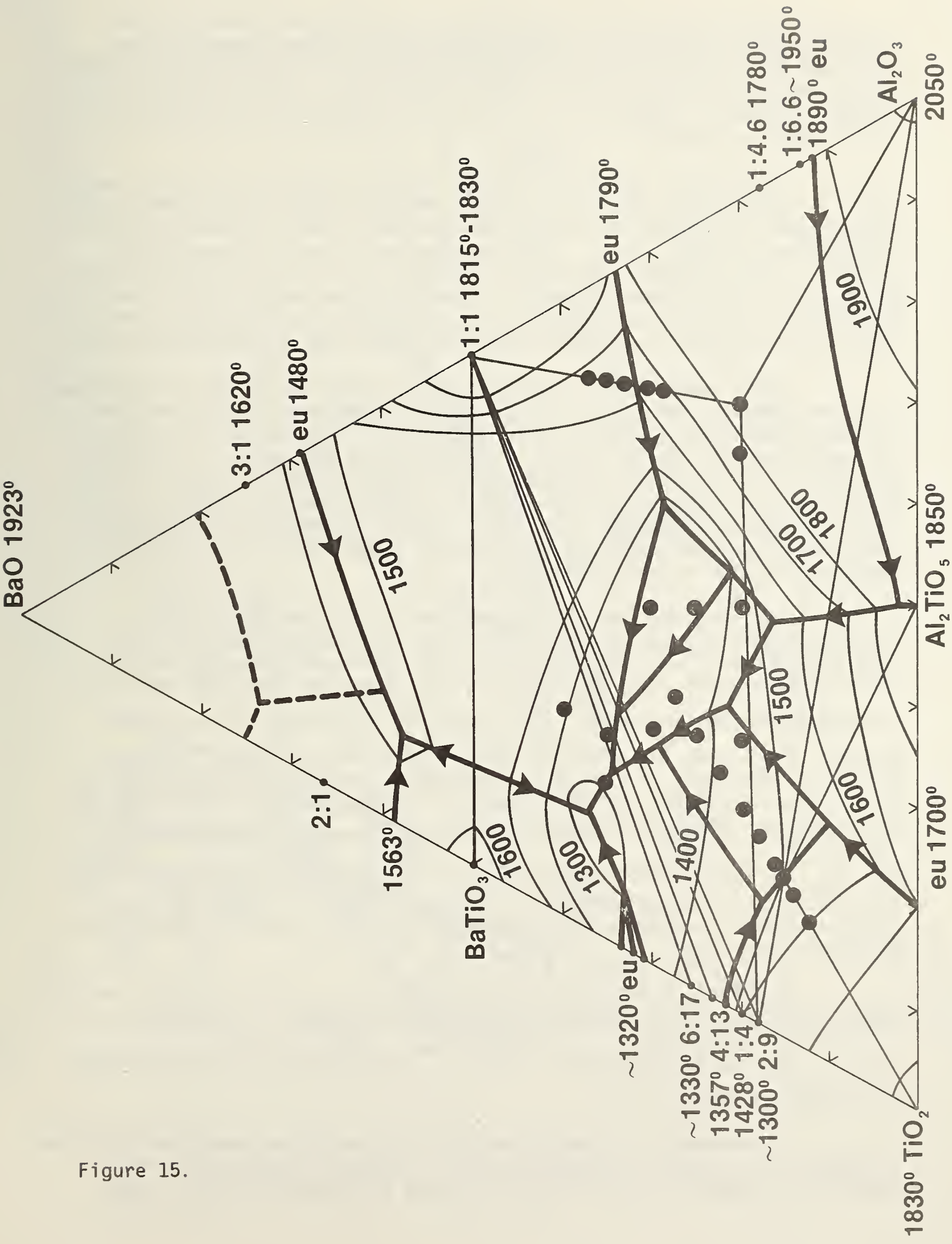

BaO 1923°
3:1 1620°
eu 1480°
1:1 1815°-1830°
eu 1790°
1:4.6 1780°
1:6.6~1950°
1890° eu
Al_2O_3
2050°
Al_2TiO_5 1850°
eu 1700°
1830° TiO_2
~1300° 2:9
1428° 1:4
1357° 4:13
~1330° 6:17
~1320° eu
$BaTiO_3$
1563°
2:1
1500
1600
1300
1400
1700
1800
1900

Figure 15.

In addition to the hollandite, two new phases, never before reported, were encountered in the $BaO:MgO:TiO_2$ ternary system at the 1:1:3 and 1:1:6 compositions. Single crystals of all three ternary phase were prepared from compositions determined to be in their primary phase fields as shown in figure 16. The unit cell dimensions and symmetry are also listed in table 7.

The single crystals of the hollandite phase were found to have unit cell dimensions similar to the end member of the solid solution with the maximum distortion and the maximum BaO:MgO content corresponding to a composition of about 1:1:5. The superstructure found in these single crystals is the sharpest and most intense of any of the hollandite phases encountered in the present study. In addition the superstructure was found to be clearly incommensurate and not of exactly the value corresponding to the trippled $\underline{c}$ axis which had previously been suggested by Cadee.

High temperature x-ray diffraction powder patterns were obtained from the compositions 1:1:5, 1:1:5.5, and 1:1:6$BaO:MgO:TiO_2$ as well as for the composition $0.9BaO:0.1SrO:1.0MgO:5TiO_2$. The monoclinic lattice of the hollandite-type was found to transform to tetragonal in all compositions. The transition temperatures in the $BaO:MgO:TiO_2$ compositions decreased with increasing TiO_2 content, ranging from about 265° ± 15 in the 1:1:5 and 1:1:5.5 specimens to 110° ± 10° in the 1:1:6 composition. The transition temperature in the $0.9BaO:0.1SrO:1.0MgO:5TiO_2$ specimen was apparently higher at about 340° ± 40.

The compound $BaMg_6Ti_6O_{19}$ is apparently isostructural with magnetoplumbite and barium hexaferrite and, by analogy, can be called barium hexageikielite. No experiments have yet been conducted in this study in the system $BaO:FeO:Fe_2O_3:TiO_2$ but it may be predicted that the corresponding compound $BaFe^{+2}_6Ti^{+4}_6O_{19}$ (barium hexailmenite) is a stable phase in the system and probably forms a solid solution with $BaFe_{12}O_{19}$, barium hexaferrite. In the four component system $BaO:MgO:Al_2O_3:TiO_2$, a solid solution between barium hexageikielite and barium hexaluminate can be predicted, as well as the hollandite solid solution, with both Mg^{+2} and Al^{+3} in the framework. Both solid solutions should be equally useful host lattices for incorporation of Rb^+, Cs^+, and Sr^{+2} in nuclear waste ceramic systems, and have been shown in this study to be in equilibrium with each other.

Crystals of a hollandite-type phase were also obtained in melted specimens prepared in the ternary system $BaO:Li_2O:TiO_2$. Apparently Li^+ can also be used to substitute in the Ti^{+4} lattice to balance the charge of the Ba^{+2} and Cs^{+1} ions.

To determine the amount of Cs^+ which could be incorporated in the hollandite structure, preliminary studies have been conducted in the systems $Cs_2O:MgO:TiO_2$, $Cs_2O:Al_2O_3:TiO_2$, and $BaO:Cs_2O:Al_2O_3:TiO_2$. The

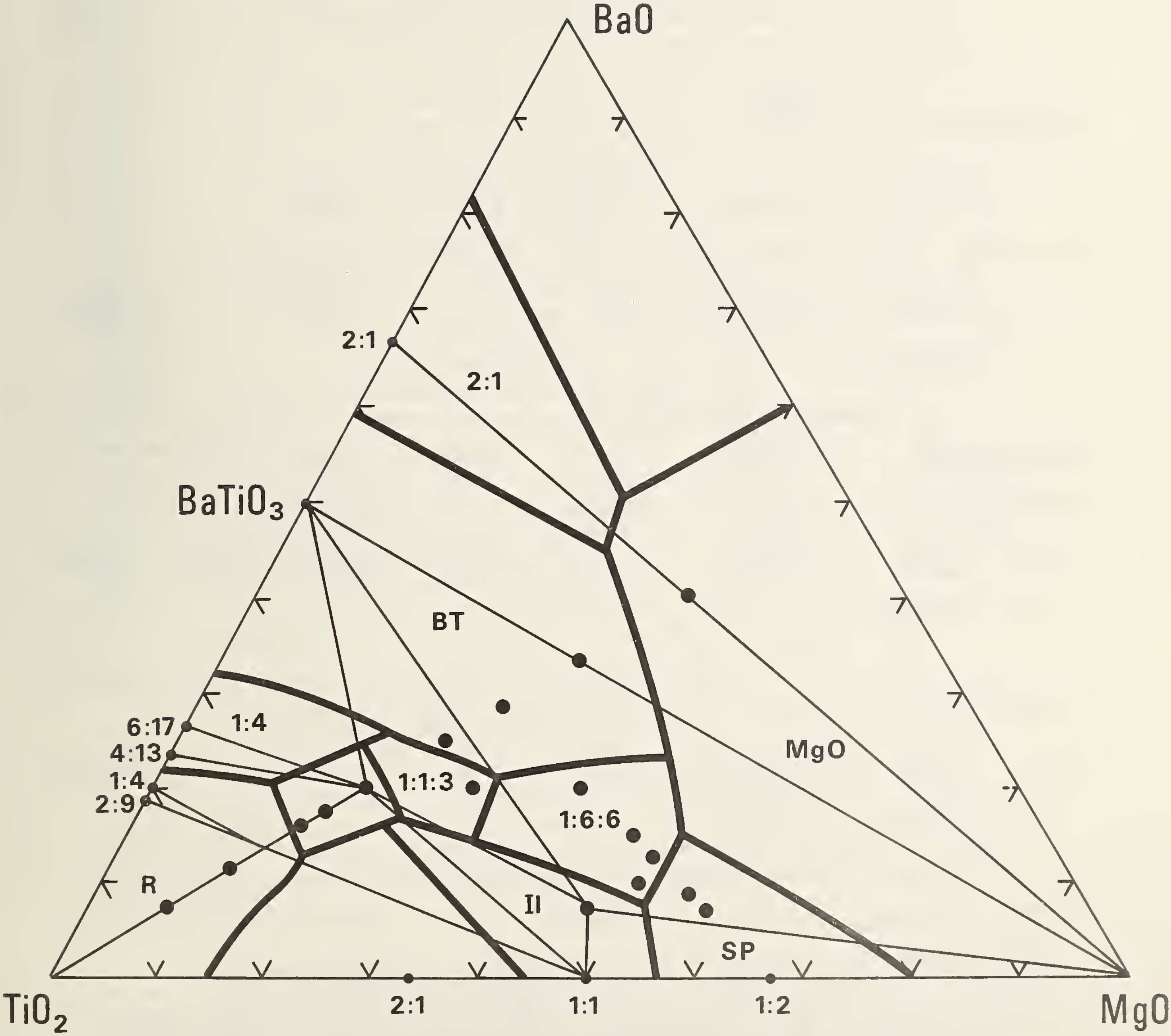

BaO
2:1
2:1
BaTiO$_3$
BT
6:17
1:4
4:13
1:4
1:1:3
2:9
1:6:6
MgO
R
II
SP
TiO$_2$
2:1
1:1
1:2
MgO

Figure 16.

TABLE 7. Unit cell data of titanate phases synthesized during phase equilibria studies of ceramics for nuclear waste encapsulation.

Composition	Space Group	a	b	c	β	y*
$BaO \cdot 3Al_2O_3 \cdot TiO_2$	Pnnm,Pnn2	7.139	4.865	13.598		
$3BaO \cdot 5Al_2O_3 \cdot TiO_2$	C2/m,Cm,C2	15.754	11.341	4.985	109.5	
$Ba_xAl_{2x}Ti_{8-2x}O_{16}$ ($x \sim 1.23-1.14$)	I4/m,$I\bar{4}$,I4	9.94		2.920		8.122
$BaO \cdot MgO \cdot 3TiO_2$	C2/m,Cm,C2	15.208	3.899	9.109	98.5	
$BaO \cdot 6MgO \cdot 6TiO_2$	$P6_3mmc$	5.935		23.37		
$Ba_xMg_xTi_{8-x}O_{16}$ ($x \sim 1.33-1.23$)	I2/m,I2	9.920	2.992	10.256	91.5	8.528
$Cs_2O \cdot Al_2O_3 \cdot 2TiO_2$	Pbnn	9.973	5.480	9.025		
$Cs_xAl_xTi_{8-x}O_{16}$ ($x \sim 1.66-1.33$)	I4/m,$I\bar{4}$,I4	10.194		2.938		9.476
$Cs_xMg_{x/2}Ti_{8-x/2}O_{16}$ ($x \sim 1.45$)	I4/m,$I\bar{4}$,I4	10.278		2.970		

*Value of the modulation vector (in real space) for the incommensurate diffraction effect observed along the unique axis in the hollandite structure type.

hollandite phase has been previously reported by Beyeler and Sobuler [Solid State Ionics 1, 77 (1980)] to occur in the system containing MgO, but not in the ternary system containing Al_2O_3. The single phase tetragonal hollandite structure was found to occur at approximately 1:1:10 in the Cs_2O:MgO:TiO_2 system or $Cs_x(Mg_{x/2}Ti_{8-x/2})O_{16}$ (x = 1.45). Another non-stoichiometric phase originally reported by Reid, Mumme, and Wadsley [Acta Cryst. B24, 1228 (1968)] was also confirmed to exist in the system Cs_2O:MgO:TiO_2 at a ratio of about 1:1:4.7. However, x-ray powder diffraction patterns of specimens in the system Cs_2O:Al_2O_3:TiO_2 are very complex and could not be directly interpreted in terms of a hollandite phase corresponding to $Cs_x(Al_xTi_{8-x})O_{16}$. Single crystals were obtained of a new phase corresponding to a compound at a composition $CsAlTiO_4$. The unit cell dimension and symmetry, given in table 1, together with the observation that this phase is pseudohexagonal, indicate that it probably has a structure very similar to $CsAlSiO_4$. There is no sign of the second phase found in the MgO system, even though this phase had originally been suggested to be present in the Cs_2O:Al_2O_3:TiO_2 system. Instead a tetragonal hollandite occurs, but in solid state preparations at one atmosphere of air, or in a sealed Pt tube, compositions between TiO_2 and $CsAlTiO_4$ are always three phases. A single phase hollandite can be synthesized by the application of a small amount of pressure at an as yet undetermined composition between about $Cs_xAl_xTi_{8-x}O_{16}$ ($1.66 \geq x \geq 1.33$). Apparently, at one atmosphere total pressure, there is a competition for the Ti^{+4} ion between 6-fold (TiO_2) and 4-fold ($CsAlTiO_4$) coordination. Under these conditions single phase hollandite cannot be synthesized and may be only metastable. It is apparently stabilized by a small amount of pressure. It may be predicted that a slight increase in the size of the impurity ion incorporated in the lattice will also stabilize the formation of the hollandite lattice and therefore solid solution with $Cs_xMg_{x/2}Ti_{8-x/2}O_{16}$ should increase the stability as would incorporation of the Ti^{+4} as the reduced ion Ti^{+3}. In the four component system, BaO:Cs^2O:Al^2O^3:TiO^2, it was found that in the hollandite lattice about 20 mole percent of the BaO could be replaced by Cs_2O with a corresponding increase of the Al_2O_3 content. An additional Cs_2O content caused the phase $CsAlTiO_4$ to occur in the specimens prepared at one atmosphere total pressure. It can be assumed that a complete series of solid solutions can be prepared between $Ba_xAl_{2-x}Ti_{8-2x}O_{16}$ and $Cs_xAl_xTi_{8-x}O_{16}$ by the application of a small amount of total pressure.

Ceramic samples were prepared for AC impedance measurements from the following compositions: BaO:Al_2O_3:4.5TiO_2, 0.5BaO:0.5SrO:Al_2O_3:4.5TiO_2, 0.9BaO:0.1SrO:Al_2O_3:4.5TIO_2, 0.9BaO:0.1Cs_2O:Al_2O_3:4.5TiO_2, 0.9BaO:0.1K_2O:Al_2O_3: 4.5TiO_2, and BaO:Al_2O_3:5TiO_2. The ceramic pellets were generally all about 86 percent theoretical density. In addition the oxidation of partially reduced BaO:Al_2O_3:5TiO_2 hollandite was examined as a function of different temperatures in air and pure oxygen.

The phase equilibria results were utilized to synthesize single crystals of the various phases encountered in ternary and quaternary combinations within the Cs_2O-BaO-SrO-MgO-Al_2O_3-TiO_2 system. All crystals of incongruently melted phases were grown by very slow cooling of compositions within the primary phase field of the desired compound. Only for the Cs-Al-Ti hollandite phase was it necessary to use an additional flux. In this case a small amount of CsF was sufficient to enable small single crystals to be grown in sealed Pt tubes.

Dr. Arne Olsen, a foreign guestworker at the National Bureau of Standards, examined some of the specimens prepared for this study by high resolution electron microscopy and electron diffraction. He used the two STEM units at NBS, the Philips EM 400 Microscope in the Center for Materials Science and the JEOL 200 CX in the Center for Analytical Chemistry. A summary of his conclusions are included below.

No commensurate superstructures were found in this study. There seems to be a correlation between the diffusiveness of the superstructure reflections, the intensity of the diffuse planes normal to c* (or b* in the monoclinic case) and the period of the superstructure. For $Ba_xAl_{2x}Ti_{8-2x}O_{16}$ hollandites the superstructure reflections are sharp, but become more diffuse at larger deviations from the commensurate value x/c=2. There are no (or only weak) diffuse planes for all the $Ba_xAl_{2x}Ti_{8-2x}O_{16}$ hollandites. The $Ba_xMg_xTi_{8-x}O_{16}$ hollandites have superstructures close to 3c. The superstructure reflections are still very sharp, but the diffuse planes have higher intensity than for $Ba_xAl_{2x}Ti_{8-2x}O_{16}$. In the $Cs_xAl_xTi_{8-x}O_{16}$ case the superstructure reflections are in general diffuse and there are diffuse planes through all the superstructure reflections.

It is important to notice that there are large variations in the intensity within the diffuse planes. The intensity is maximum along the (110) directions and is very low in (100) directions. This indicates that they reflect the correlation between the structures in neighboring tunnels. Only tunnels of one size have been found for Ba^{+2} and Cs^+ in all the investigated compounds. The incommensurate superstructures appear to be due to the distribution of Ba^{+2} and Cs^+ ions and vacancies within the tunnels.

The heat treatment of the Ba-Mg and Cs-Al hollandites does not seem to affect the period of the superstructure. For the Ba-Al hollandites the heat treatment seems to affect the period of the superstructure, but more experimental data are necessary in order to make a firm conclusion.

5. Mass Transport in Crystalline Materials

Materials having a hollandite type structure and containing alkali metals have been studied extensively in recent years. This class of compounds was considered as a model quasi-one dimensional fast ion conductor. For example, K-hollandite, $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ $(0.77 < x < 1.0)$ is one of such materials. The reported intrinsic conductivity of a single crystal $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ at room temperature is as high as 0.46 S/cm; however, this high ionic conductivity is likely to be reduced by the presence of those grain boundaries in a ceramic. Here we use the term "grain boundaries" generally to describe all those structure imperfections which are able to block the conduction of the mobile ions. In the case of Cs in the hollandite structure, the Cs ions are expected to be mobile. Since the Cs ion is much larger in size, the change in coordination is expected to effect the ion conduction in Cs-hollandite.

During this study period we have examined several ceramic samples of pure hollandites and hollandites containing a K and Cs ions. Those pure hollandites were studied to serve as a guide for material preparation. K-hollandites were selected as reference for its wider literature base. Pure hollandite ceramics, $Ba_xAl_{2x}Ti_{8-2x}O_{16}$ and $Ba_xMg_xTi_{8-x}O_{16}$ were pressed at 10,000 psi and sintered at 1400-1450 °C for 4-6 hours in air. Ten percent of BaO was replaced by Cs_2O or K_2O to form Cs-hollandites or K-hollandites. These samples were sintered at 1275-1350 °C for 6 hours and annealed at 950 °C for 24 hours. $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ ceramics were also prepared at the same conditions as above. The density of these ceramics was about 85-90 percent of theoretical value. To avoid possible reduction of TiO_2 due to high temperature sintering all samples were carefully annealed and show milk white color. Platinum paste was used to make electrical contacts. AC impedance spectra from 100 Hz to 10 MHz were measured to determine the electrical conductivity of the sample. Temperature dependence of the conductivity was made from 100 °C to 800 °C in air.

Figures 17 and 18 show the impedance spectra of $(Cs,Ba)_x(Al,Ti)_{8-x}O_{16}$ at 400 °C and 600 °C. Total conductivity can be obtained by fitting high frequency data to a Cole-Cole distribution function. Since the conductivity of the hollandite is distributed, the computer fitting results in a large uncertainty. More detailed analysis of the impedance spectra requires a suitable detailed model which is not available at the present stage. The fact that the impedance spectra of all hollandites behave in a similar manner suggested the ion transport in the hollandites may be governed by a similar mechanism. These spectra are reproducible. The thermal cycle was repeated from 100 °C to 800 °C for over 15 times. No changes were seen. This is shown in figure 19 where the AC conductivities at 1 MHz from different runs were plotted against temperature. In figure 20 we compare the conductivity of high conducting $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ with $Cs_xAl_xTi_{8-x}O_{16}$. We found that the conductivity of Cs hollandite is about three to four orders smaller than that of K-hollandite. The activation energy of the K compound was 0.9 eV and that of the Cs compound was 1.5 eV. The large difference in the conductivity and activation energy are probably due to the size of the ion. The effect of interionic potential due to K and Cs ions should be considered.

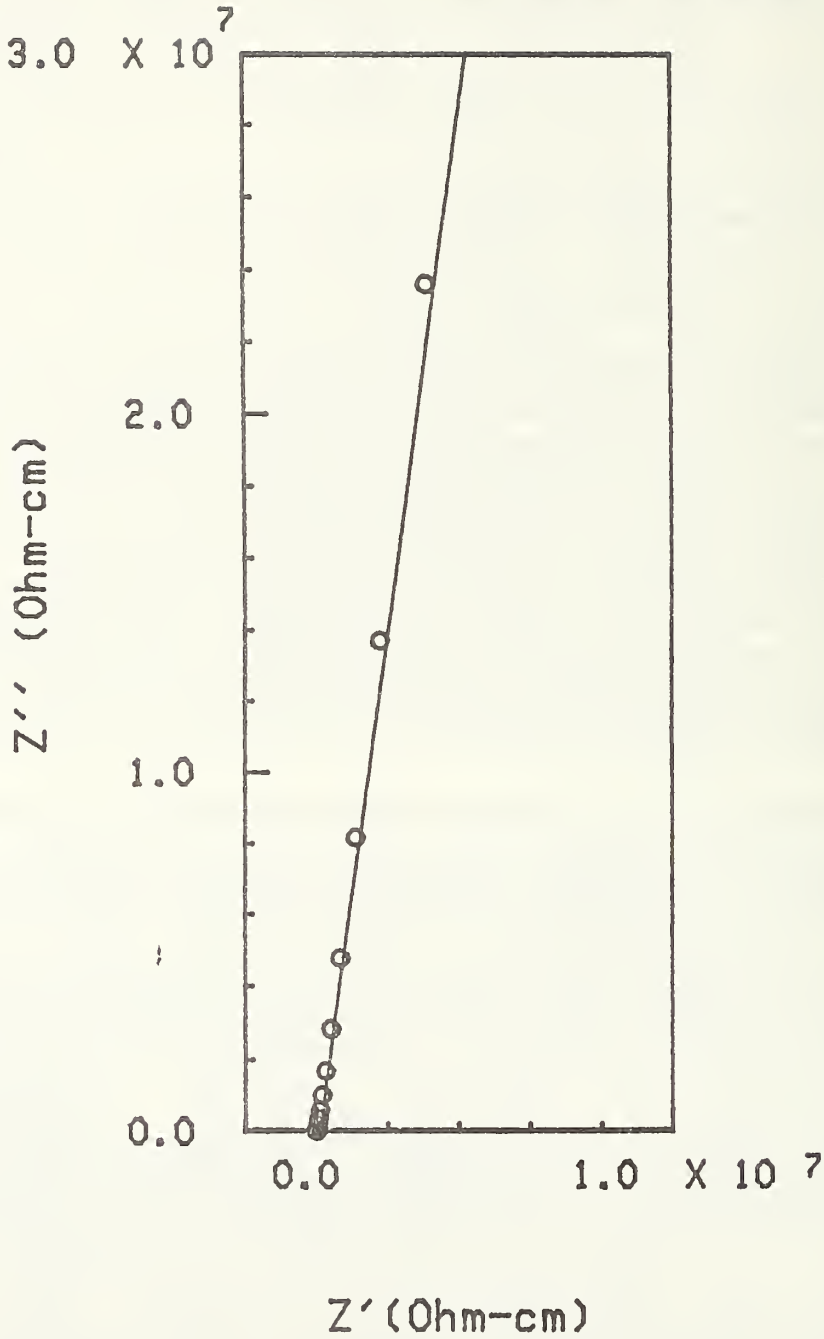
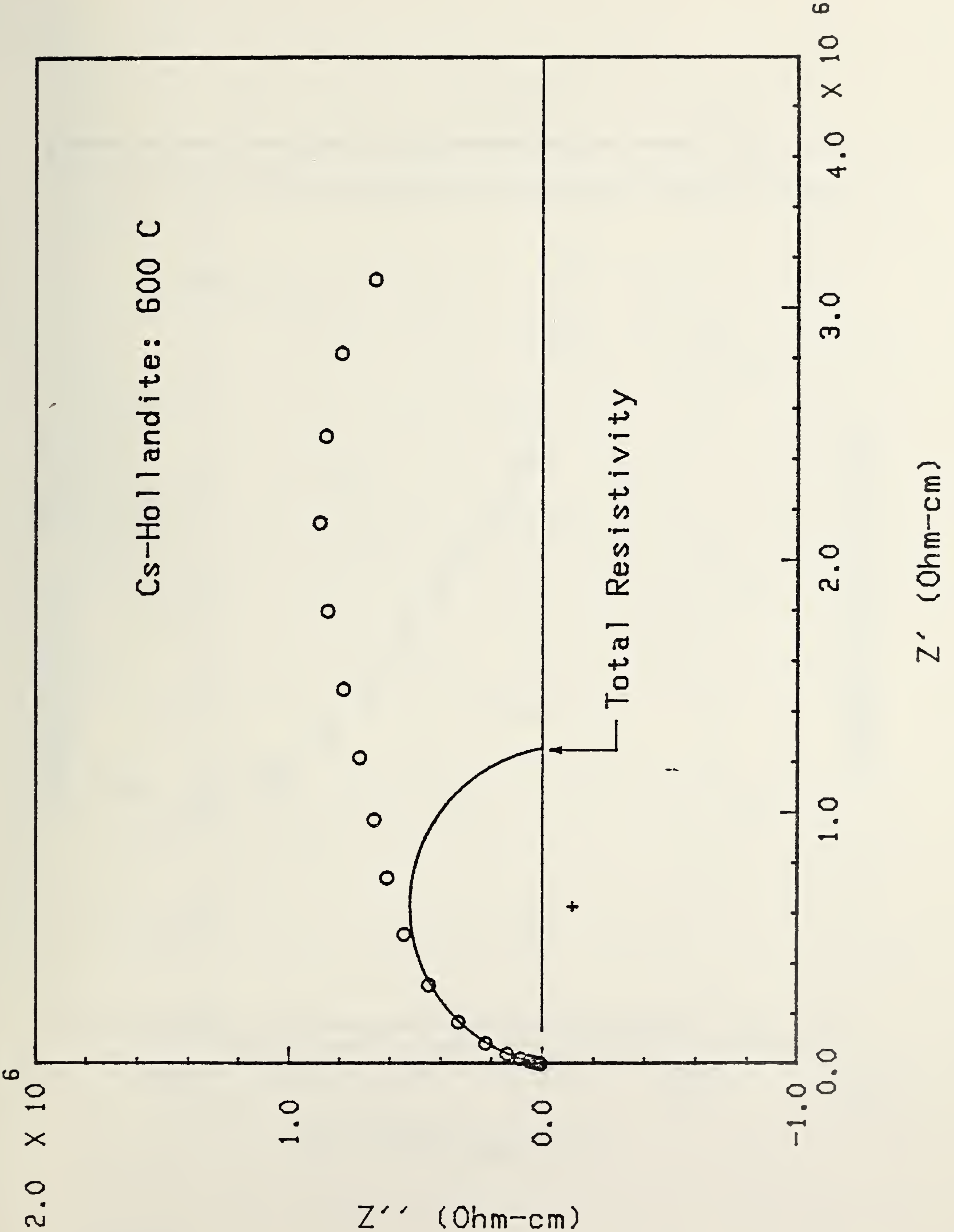
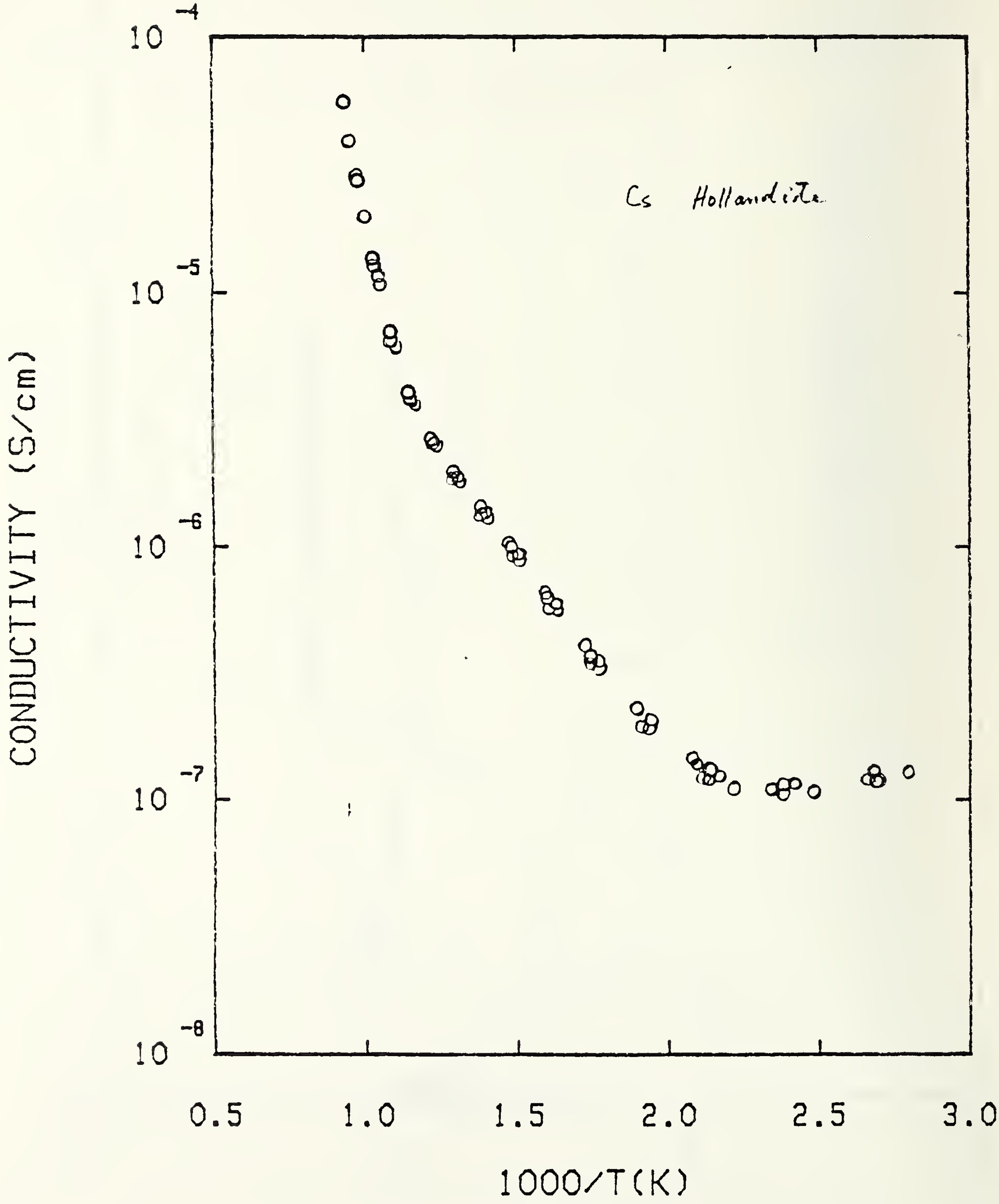


Figure 17.



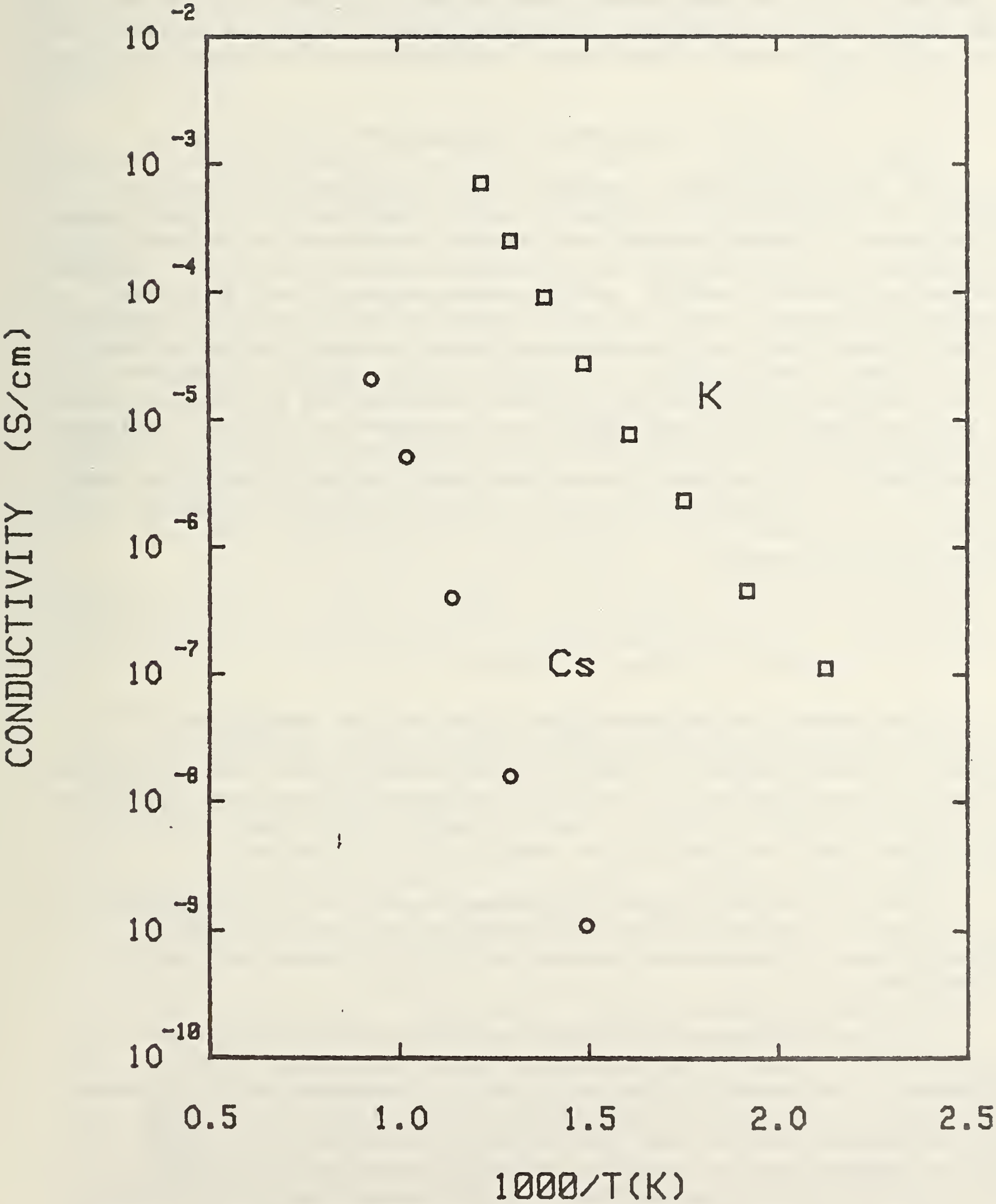
Cs-Hollandite: 600 C
Total Resistivity
Z′ (Ohm-cm)
Z′′ (Ohm-cm)
2.0 X 10^6
1.0
0.0
-1.0
0.0
1.0
2.0
3.0
4.0 X 10^6

Figure 18.



10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
CONDUCTIVITY (S/cm)
Cs Hollandite
0.5
1.0
1.5
2.0
2.5
3.0
1000/T(K)

Figure 19.



CONDUCTIVITY (S/cm)
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
K
Cs
0.5
1.0
1.5
2.0
2.5
1000/T(K)

Figure 20.

B. Waste Forms - Research, Reference Materials Data and Measurement Methods

This task includes the development and dissemination of generic research materials with well-characterized elemental composition to aid in the development and promulgation of leach tests. Materials (glass) with varying leach rates containing non-radioactive cesium, strontium, etc., were planned.

1. Phase Equilibria Data for Nuclear Waste Form Materials

A survey was made of pertinent phase equilibria diagrams to determine if enough data was available in the literature for a compilation to be prepared of "Phase Diagrams for Ceramists Pertinent to Nuclear Waste Management." In addition to searching Volumes I-V of "Phase Diagrams for Ceramists" several computer searches were undertaken using Chemical Abstracts, DOE reports, etc. The total number of published phase diagrams specifically applicable to the glass and ceramic compositions suggested for nuclear waste encapsulation are limited to only about 5-6 diagrams, mostly of simple binary or ternary systems. Most of the pertinent diagrams have not been studied in enough detail to have appeared in the literature. It may, therefore, be concluded that the study of phase diagrams of the type reported in this section is very important in order to determine the phases which may be expected to occur in ceramic systems in which the "tailoring" of compositions is in exact due to knowledge of the real composition of the waste.

R. Roth

2. Leachability Research Materials

The overall objective of the subtask was to develop two glasses for use as research materials in leach testing. These materials are needed for standardization of leach testing, assuring that all laboratories are testing the same material. If all laboratories obtain comparable results for the leach rate of the research material then data produced using the procedure involved can be compared with confidence.

In addition to the glass development work, NBS also supplied, at the request of the MCC, a borosilicate glass for use in the MCC-1 round robin test. The material was an available standard glass which is very homogeneous.

In conjunction with the MCC-1 and other interested parties, it was decided that the first research material to be produced, RM8400, should have a leach rate similar to that of an average borosilicate waste glass. Further discussion with the MCC and representatives of other organizations involved in leach testing resulted in the choice of PNL 7668 glass composition as a starting point for development of RM8400. This composition was chosen because there has been a great deal of experience with this glass. It has been well characterized and would appear to be suitable for production in the quantity required, 1000 lb. However, 7668 as such has several drawbacks as a standard material. In addition to the leach rate specification the homogeneity of the research material is of prime importance. One of the drawbacks of the 7668 formulation is the fact that the high iron content along with lesser amounts of Cr_2O_3 and NiO result in a nearly opaque glass. This prevents use of optical techniques for determining homogeneity and requires the use of instrumental techniques that are time consuming, expensive and less precise than the optical methods.

To facilitate homogeneity determination, a glass based on PNL 7668 was produced containing no iron, nickel, or chromium, NBS K1620. This results in a transparent glass, though slightly colored by the rare earths present, which allows the use of optical techniques for determining homogeneity. The composition for PNL 7668 and NBS K1620 are shown in table 8. The K1620 glass was then characterized to determine if it would be suitable for use as a research material. This included determinations of physical properties needed by the glass manufacturers, investigation into the presence of phase separation and determination of leach rate. Also a series of glasses were produced to investigate the effect of various oxides and different raw materials on the final homogeneity of the glass. The physical properties of K1620 are shown in table 9, the leach rate, along with 7668 data, is shown in table 10. Investigation of phase separation indicated that under normal manufacturing conditions phase separation should not be a problem with this glass.

The characterization of K1620 showed that this composition would be suitable for use as RM8400. In light of this decision purchase specifications were written to obtain 1000 pounds of this glass. A solicitation for bids was made by the NBS Contract Office. Bids were due to be opened October 5, 1981.

Development of the second research material, RM8401, was initiated after work on RM8400 was underway. It was desired to produce a glass having a release rate approximately two orders of magnitude lower than RM8400 and contain other elements/oxides of interest that were not in RM8400, i.e., ReO_2 and I. As part of this portion of the subtask a series of compositions was designed, in conjunction with the Center for Applied Mathematics and Center for Analytical Chemistry, using K1620 as a base glass that would allow determination of the effect of individual oxides on leach rate, using the MCC-1 test. These leach tests are currently in progress. In addition to these glasses, several other glass compositions were produced with the objective of arriving at a composition with the appropriate release rate. Since MCC-1 is time consuming a preliminary test was developed for use in screening candidate glasses, promising materials would then be subjected to the full MCC-1 test. The screening test used was continuous flow extraction by distilled water at constant temperature (100 °C) rather than the frequently used Soxhlet extractor with its alternating syphoning cycles. The test chamber was continuously flushed with N_2 to assure the same atmosphere at all times. This was used since tests had shown that the leach rate was sensitive to the atmosphere in the chamber. The samples used were rods with a nearly square cross-section, approximately 3 mm on a side, with a length of approximately 75 mm. A saw cut finish on the glass was used in all

TABLE 8. Glass composition.

	PNL 7668	NBS K1620
SiO_2	41.21	46.10
B_2O_3	9.80	10.96
Na_2O	13.01	15.32
ZnO	5.14	5.75
TiO_2	5.07	3.43
CaO	2.07	2.31
Fe_2O_3	10.34	0.00
SrO	0.40	0.45
ZrO_2	1.88	2.10
MoO_3	1.97	1.96
TeO_2	0.28	0.31
Cs_2O	1.22	1.36
BaO_2	0.59	0.66
CeO_2	1.26	1.41
Cr_2O_3	0.44	0.00
NiO	0.21	0.00
P_2O_5	0.51	0.57
La_2O_3	0.56	0.63
CdO	0.04	0.00
Nd_2O_3	5.17	5.78
Pr_6O_{11}	0.56	0.63
Y_2O_3	0.23	0.25

TABLE 9. Physical properties of NBS K1620.

Density: 2828 gm/cm^3

Thermal Expansion Coefficient: 98.9 x 10^{-7}/°C (25-300 °C)

Annealing Point (ASTM C336): 539 °C

Refractive Index, N_c: 1.582

Viscosity:

Temperature, °C	Log n
1305	1.099
1250	1.268
1200	1.422
1151	1.619
1101	1.816
1050	2.072
998	2.382
946	2.775
898	3.219

TABLE 10. Leach rate measurements*. MCC-1 test.

Deionized water, 90 °C, 14 days.

Normalized Elemental Mass Loss g/m^2

Element	NBS R.M. 8400	PNL 7668
B	16.0	19.8
Si	13.9	15.4
Mo	15.4	19.5
Na	17.1	23.6
Cs	15.6	13.5
Sr	11.1	2.4
Ca	9.5	2.4
Ba	3.9	0.4
Zn	0.4	0.2

*Measurements courtesy of Material Characterization Center.

tests. Tests with Pyrex rods showed that differences in surface finish can result in up to a factor of 4 difference in leach rate when using this test. Weight loss was used as a measure of durability or leach rate. Figure 21 shows representative data for experimental and commercial glasses. The compositions of these glasses are given in table 11. No MCC-1 data is available on these materials and no decisions have been made as to the composition of RM8401.

D. Cronin, W. K. Haller

3. Leachability Measurements and Methods

a. Leachability Parameters, Importance and Control

The leachability of the nuclear waste form used to immobilize high level waste is one of the most important characteristics of the waste form. The reason for that is that leaching of the waste form by ground water is thought to be the most probable way for radioactive waste to re-enter the bisophere after immobilization. Thus designers of waste forms develop waste types (i.e., ceramics, glasses, etc.) as well as specific formulations using leachability as a major performance criteria. With this emphasis on the leachability of the nuclear waste forms, the measurement of this property is of particular importance. The difficulty of developing reliable tests and obtaining credible data is compounded by the complexity of the leaching process. Leachability as it is currently measured is totally dependent on the conditions and individual parameters of the measurement system and has no intrinsic or absolute value. The significance of each parameter of static leach tests has been under investigation as part of the NBS Nuclear Waste Program. One of the objects was to identify and evaluate the importance of each significant parameter and then to understand its influence in the measurement of leach rates. A summary of the significant parameters is listed in table 12. This list only includes the parameters specifically identified as affecting a static leach test, such as the first Materials Characterization Center leach test (MCC-1). The number of parameters listed indicate the difficulty of control of a speciation test such as aqueous leaching. The dependence of the leach rates on each of the test conditions makes precise control of each of the parameters essential in obtaining consistent results. Further, while parameter control produces more precise results, no means of judging accuracy is presently available.

The list of significant parameters controlling the leaching characteristics can be greatly expanded when other types of leach tests are considered. Some additional parameters are ground water composition, host rock interactions and flow rate (in dynamic flowing leach tests). Each new complexity investigated by the leach test introduces significantly more sophisticated parameter interactions and test control difficulties. Some leach tests produce leachates which cannot be analyzed by routine compositional analysis. Examples of these are the MCC 4 and 5 leach tests where high flow rates on durable waste forms produce volumes of distilled water, brine, and silicate water leachates so diluted that direct instrumental analysis is not feasible.

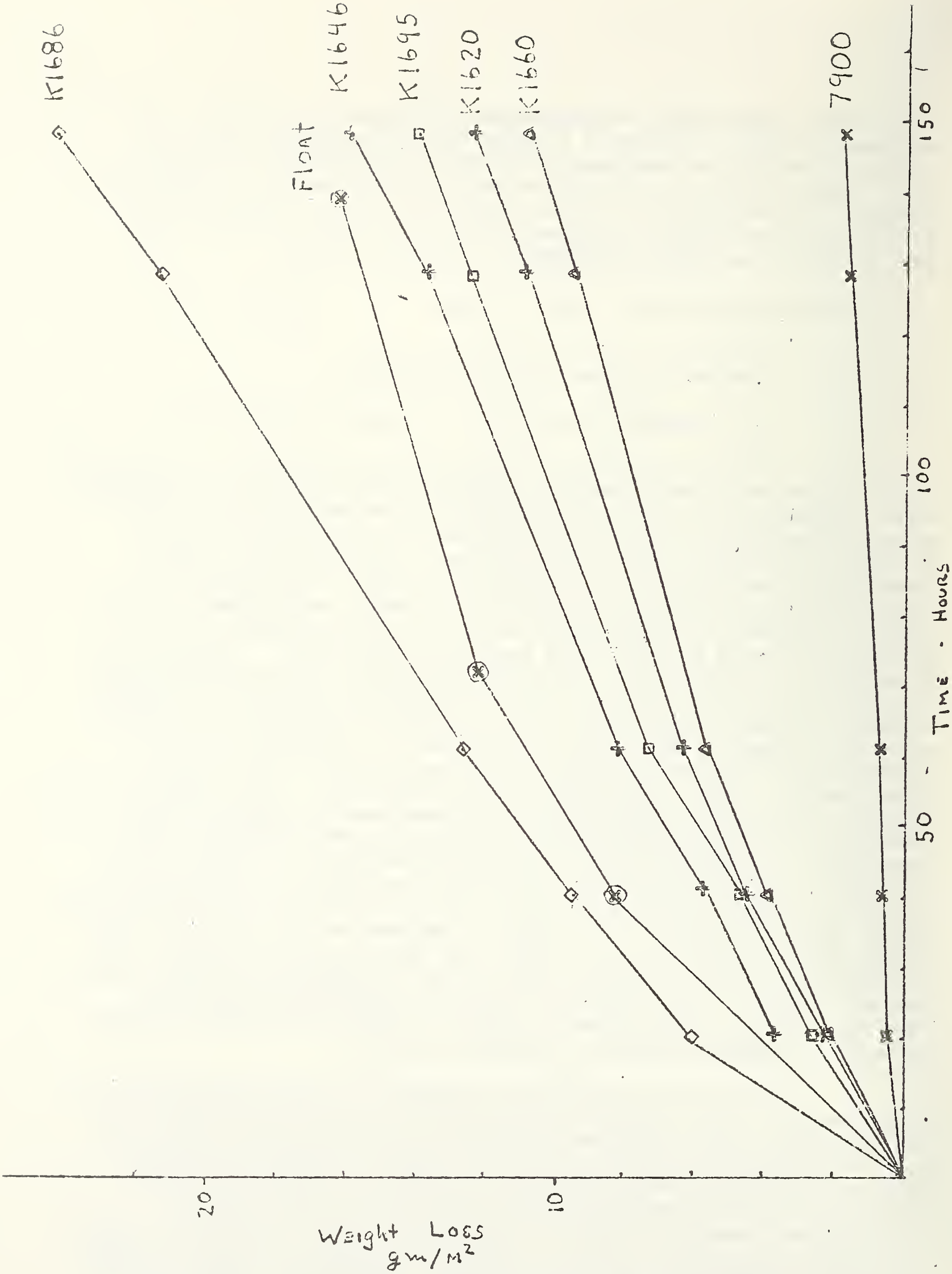


Figure 21. Weight loss vs time using modified Soxhlet test.

TABLE 11. Glass compositions.

	K1620	K1646	K1660	K1686	K1695	Float	Corning 7900
SiO_2	46.10	41.21	46.10	50.32	48.0	73.0	96.0
B_2O_3	10.96	9.80	10.96	-	-	-	3.0
Na_2O	15.32	13.01	10.32	-	1.0	13.8	-
ZnO	5.75	5.14	5.75	-	-	-	-
TiO_2	3.43	5.07	3.43	-	3.5	-	-
CaO	2.31	2.07	2.31	23.49	8.0	8.9	-
SrO	0.49	0.40	2.49	-	0.5	-	-
ZrO_2	2.10	1.88	2.10	-	-	-	-
TeO_2	0.31	0.28	0.31	-	-	-	-
Cs_2O	1.36	1.22	1.36	-	1.0	-	-
BaO	0.66	0.59	0.66	-	5.0	-	-
CeO_2	1.41	1.26	1.41	-	0.5	-	-
P_2O_5	0.57	0.51	0.57	-	-	-	-
Ca_2O_3	0.63	0.56	0.63	-	-	-	-
Nd_2O_3	5.78	5.17	5.78	-	2.5	-	-
Pr_6O_{11}	0.63	0.56	0.63	-	-	-	-
Y_2O_3	0.25	0.23	0.25	-	-	-	-
MoO_3	1.96	1.97	1.96	-	-	-	-
Al_2O_3	-	-	5.00	15.39	20.0	0.1	0.3
Fe_2O_3	-	10.34	-	-	-	0.1	-
Cr_2O_3	-	0.44	-	-	-	-	-
NiO	-	0.21	-	-	-	-	-
MgO	-	-	-	10.79	5.0	3.9	-
CaF_2	-	-	-	-	5.0	-	-
SO_3	-	-	-	-	-	0.2	-

TABLE 12. Parameters effecting leach test measurements.

Parameter	Significance
Temperature	1 °C produces 5% to 15% variation in leach rate and can control the leach mechanisms
pH	Can totally control the leach mechanisms
CO_2 (dissolved from air)	
HNO_3 (residual from cleaning)	
HF (residual from the teflon containers)	
Time	Is quantifiable but not necessarily representative
Eh	For distilled water Eh is controlled by dissolved O_2 content. Other leachate systems are more complex.
O_2 (dissolved from air)	
Surface area to volume ratio	Can cause X 2 to X 10 difference in leach rate and 1-2 pH units
Surface measurement	
Surface preparation	Can introduce additional leach mechanisms
Surface cleaning	
Surface roughness	
Composition	Determines leach rate if all other parameters are constant.
Homogeneity	Causes; congruent, incongruent, or can provide additional mechanism
Interference	Chemically perturb the test to produce results as function of their chemical effects
CO_2	
HNO_3	
F^-	
O_2	

TABLE 12. (continued)

Parameter	Significance
Leachate Composition	Must be a defined and consistently available material.
Leach Vessel	Surface activity, chemical inertness
Stability of Leachate	Directly influence results of analysis of the leachant
during leaching	
post leaching	
Mechanisms of Leaching	Many are hypothesized at present. Both removal and redeposition must be considered.
Analytical Instrumental Analysis	Leach rates are a function of the concentration determinations

The control of each of the most significant parameters as indicated presents specific problems. In addition to the control of these individual parameters is the need to understand the complex synergistic effect the parameters have with one another. It is entirely possible that rigorous control of the individual parameters without an understanding of the synergistic effects could produce precise results that are not indicative of the long term performance of the nuclear waste form in a repository.

In summary, these leach tests are in their developmental stage and require significantly more effort to achieve the desired goal of being representative of the behavior of a waste form in a geologic-repository. Obtaining precise measurement data from leach tests is the first step toward understanding the mechanisms by which nuclear waste is leached from a waste form. From this understanding, an accurate prediction can be made of the long term behavior of the waste form in the repository.

H. Kingston

b. Leachate Test Evaluation

Evaluation of the repeatability and achievable precision of the MCC-1 static leach test procedure was started using a series of homogeneous glasses. The MCC-1 protocol was refined to eliminate two potentially variable parameters consisting of dissolved CO_2 and O_2 contained in the leachate solution. The influence of these gases which dissolve in the leach solution was eliminated by preparing the leach solution and running the test under ascarite filtered Argon. The variability of the surface finish of the glass was reduced by using 600 grit Silicon Carbide to polish it after sawing. The temperature system was upgraded to maintain control at $90.00° \pm 0.04$ °C. Temperature control is achieved by using a very well insulated and sealed water bath with a dedicated controller. The instrument is monitored at five positions every three seconds and a tape and printed digital recording is updated every hour. The monitoring system is power interrupt protected to detect power failures and thus prevent unknown failures from influencing the leach results. Thirteen different glass formulations were prepared for a statistically designed experiment to determine independent relationships for the 9 priority elements of interest. The variations in the compositions of the 13 glasses are listed in table 13. The basic composition of the glass was that of the NBS K1620 glass. The dimensioning of the cut and polished glass ingots was done using a series of measurements to reduce surface area calculation errors. Using these measurements, the area was then calculated using a series of equations to reduce the area estimation error to below the specified limits of the MCC procedure. This study is designed to provide an estimate of leach rate variations expected from a standard homogeneous glass. The study would also estimate leachability rate changes due to an inhomogeneous glass. In addition, it would provide information relating process compositional changes and their affect on the leach rate. This study has a duration of several months, consequently, completion is tentative pending availability of funds during FY 82.

H. Kingston, M. S. Epstein, W. Koch, D. Cronin

TABLE 13. Glass compositions (presented as variations from NBS K1620 glass) for the evaluation of the influence of heterogeneity and composition on leaching.

Glass/Component No.	Si	B	Na	Ti	Sr	Mo	Cs	Ce	Nd
1.	0	0	0	0	0	0	0	0	0
2.	10	-5	-5	0	0	0	0	0	0
3.	0	-5	5	0	0	0	0	0	0
4.	- 5	5	0	0	0	0	0	0	0
5.	0	5	-5	0	0	0	0	0	0
6.	-10	5	5	0	0	0	0	0	0
7.	- 5	0	5	0	0	0	0	0	0
8.	- 5	0	0	1	1	1	0	1	1
9.	- 5	0	0	1	1	1	1	0	1
10.	- 5	0	0	1	1	1	1	1	0
11.	- 4	0	0	1	0	0	1	1	1
12.	- 4	0	0	0	1	0	1	1	1
13.	- 4	0	0	0	0	1	1	1	1

1 = increase from base glass of 1 wt percent

0 = no change

-1 = decrease from base glass of 1 wt percent

c. Leachate Stability Study

The stability of the final leachate solution is essential to obtaining credible analytical composition analysis results upon which to calculate the leach rates. The MCC-1 procedure dictates that a volume of concentrated nitric acid be added to the leachate solution equal to 1 percent of the leachate volume after 28 days of leaching at a neutral or higher pH. This is done to stabilize the anionic and cationic species and to redesolve any adsorbed ions from the container walls. The adsopriton of ions onto plastic or glass container walls, thus changing the solution concentration, is a well-documented phenomenon. The addition of acid to prevent this process is also well-documented; however, the addition of small quantities of acid to resolubilize previously adsorbed material has not been thoroughly studied. In this investigation, NBS prepared glass (K1620) which was irradiated in the NBS reactor facility was then subjected to leaching following the MCC-1 guidelines. After leaching, gamma counting of containers and leachate solutions revealed that Cs and Sb did not detectably adsorb onto the PFA Teflon containers over the 28 day test periods. Zinc, however, was 27 percent adsorbed onto the container walls. Subsequent addition of 1 percent nitric acid as specified in the MCC-1 procedure totally removed the adsorbed Zn and resolubilized it producing leachate containing 100 percent of the Zn removed from the glass during the leaching period.

Other elements of importance which are likely to be adsorbed during the leaching were unable to be detected due to the high gamma field produced by the Cesium. Therefore, a special glass was prepared by the NBS Glass Group having the same formulation minus the Cesium. This glass will hopefully allow the observation of other important elements and their adsorption and degree of resolubilization. This work remains uncompleted at this time. The results thus far have verified both the necessity and the effectiveness of the MCC-1 procedure for the elements cesium, antimony and zinc. However, further tests of other elements including the rare earth elements are necessary before complete conformation of the effectiveness of this portion of the test procedure is assured.

G. Lutz and H. Kingston

d. Analytical Leachate Analysis

The D.C. plasma emission spectrometer has been modified for the simultaneous determination of up to ten elements in the simulated nuclear waste leachates. Detection limits in the multielement mode are as follows (μg/ml):

B, .01	Si, .03
Ba, .001	Sr, .0005
Ca, .0004	Ti, .01
Mo, .003	Zn, .02
Nd, .01	Ce, N.D.

The system has been designed to determine the above specialized set of elements which have been designated as priority elements of interest in nuclear waste leachate analysis.

M. S. Epstein, C. G. Blundell

C. Containers, Backfill, and Mathematical Support

This task is focused on the container and backfill material and includes also the statistical and quality control effort for the whole program.

In the area of containers, existing efforts to understand corrosion mechanism were reviewed, and specific research was carried out in selected areas to improve the understanding of degradation mechanisms of candidate materials, particularly as they apply to long-term prediction and accelerated testing.

Work on the backfill effort for the Nuclear Waste Program includes a review of existing efforts elsewhere, as well as developing specific plans to perform selected research at NBS to improve the understanding of the basic functional mechanisms (excluding sorption coefficient) related to emplacement of backfill materials.

Extensive use of statistical services available at NBS was planned for the effective use of the interlaboratory testing required in the performance of these tasks.

1. Canister Corrosion

The technical activities related to canister corrosion were divided into four parts. The accomplishments during the past year in each of these four parts were as follows:

a. Corrosion Mechanisms

This activity required a review of existing efforts and research in selected areas as needed to improve the understanding of degradation mechanisms of candidate materials, particularly as it applied to long-term prediction and accelerated testing.

The second portion of this task required the setting up of a research program aimed at improving the understanding of degradation mechanisms and developing test methods. The following accomplishments can be reported:

- o An experimental approach was developed consisting of three elements:

  (1) Characterization of the environment that develops in pits, cracks, and crevices under simulated repository conditions.

(2) The carrying out of studies of electrochemical corrosion mechanisms in the environments characterized in element "a" above.

(3) The use of mechanistic studies as a basis for developing test methods to assess susceptibility of alloys to localized corrosion.

- A laboratory was set up to carry out electrochemical polarization studies and microanalytical characterization of the localized environments. An autoclave is on order to carry out high temperature corrosion measurements.

- Work was started on the characterization of localized environments, and the following results were obtained:

(1) Good results for Cl^- at the 5 to 10 μg level using potentiometric titration and an Ag/Ag_2O - Ag/Hg electrode pair.

(2) Techniques developed for removing 0.5 - 2 μℓ aliquots of localized environments.

(3) Work in progress on microanalysis of other ions such as Na^+, etc.

(4) Spectrophotometric experiments involving Cl, Fe, Cr, and Ti ions in the UV-VIS-NIR range started.

- Work on the electrochemistry of localized corrosion has been started involving the following:

(1) Potentiodynamic polarization plots to determine crevice and pitting susceptibilities and rates at different temperatures.

(2) Cyclic polarization studies to determine critical potential for pitting.

(3) Repassivation rate studies to assess susceptibility.

(4) Crevice and pit chemistry study approach developed.

(5) Theoretical study on corrosion thermodynamics of $Ti-H_2OCl$ systems started.

b. Research and Reference Materials and Definitive Test Methods

This part of the task involves the development of a stock of two or three different characterized research alloys for use in NBS tests and as research materials for use by others.

Based on discussions with Sandia, a decision to stock Ti, Tl CODE-12, and an austenitic stainless steel was made.

c. Key Data Generation and Evaluation

This effort requires cooperation with MCC in surveying and evaluating existing data on underground corrosion of potential canister materials. Our accomplishments have been the following:

(1) Collection data and literature from MCC, Sandia, Bureau of Mines (Geothermal) and Oak Ridge.

(2) Bibliography on corrosion of metals in repository environments completed.

(3) Completion of long-term (eight years) study of stainless steels in underground environment (sponsored by AISI)--available for distribution.

d. Long-Term Field Tests

This task requires the assessment of the feasibility of long-term tests of container materials under geologic conditions. While work on this task was not scheduled for this year, work on _in situ_ polarization measurement techniques developed in other areas may prove applicable to canister corrosion problems. This needs to be explored further.

J. Kruger, K. Hardman, B. T. Sanderson, J. Mullen, M. J. Rodriquez

2. Backfill

In the proposed underground scheme of nuclear waste management, a multi-barrier isolation system is considered to contain the radionuclides and thus to isolate them from reaching the biosphere over a long period of time. As a simplified example, the multi-barrier system consists of a glass waste form, a metal container containing the waste form lowered into a borehole drilled from the floor of tunnels in the repository, backfill placed between the canister and borehole wall, and the repository rock. The Geotechnical Engineering Group of CBT/NEL focused its efforts on the study of the backfill component of the multi-barrier isolation system.

The major item of our work is a state-of-the-art study on the existing data, capabilities, and knowledge in selected areas as needed to improve the understanding of the functional mechanisms such as hydraulic conductivity, chemical physical, and mechanical stability, swelling potential on wetting, and thermal conductivity of the backfill materials when they are emplaced in a repository. To accomplish this task, the following activities have been carried out: literature and data search, communication with experts, and a two-day international workshop on backfill.

The NBS Library computer data bases were utilized to locate current publications pertinent to the backfill investigation. RECON, which is the energy-related data base, appears to provide the best source in locating publications specifically for the study of backfill functions for nuclear waste management problems. Literature searches have also included the areas of: (1) soil sciences, (2) highway and airfield engineering, and (3) cable industry. The first area, which includes journals of clays and clay minerals, Soil Science Society of America, soil science, irrigation and power, and water resources, provides information on hydraulic conductivity under both saturated and unsaturated soil conditions. The second area concerns the characteristics of soil swelling in pavement design, how to identify the swelling potential, and the test method and equipment to quantatively determine the magnitude of swelling and swelling pressure. The cable industry provides many experimental results on the soil thermal properties in conjunction with the heat generated from buried transmission lines. Additionally, the damage to houses caused by swelling of soils in many parts of the world challenged geotechnical engineers for many years. Much work was done in trying to understand the mechanisms of swelling and to develop construction methods which minimize the magnitude of swelling.

A two-day workshop entitled, "Research and Development Needs in Backfill for Nuclear Waste Storage in Deep Geologic Repositories," was held on April 13 and 14, 1981, at the NBS Campus. On the first day, ten lectures were given by experts from national laboratories and private industry in the States and from Canada and Sweden. Thirty-eight people attended the first day presentation. On the second day, many of the participants stayed on for an informal in-depth discussion on the subject. Areas such as test materials, test methods, and test procedures used in various laboratories for the evaluation of the backfill properties were discussed. Summaries and conclusions of the Workshop will be included in the Workshop report. The report is in preparation and is planned to be published late in 1981. Workshop proceedings which include all the papers presented to the Workshop are also in preparation.

Many material properties are desirable for the candidate materials to be considered as backfill. These include sufficiently high swelling potential and plasticity, low hydraulic conductivity, adequate thermal conductivity, high sorption capability, adequate shear strength, and chemical stability over a wide range of temperatures and pressures. Candidate backfill materials include mixtures of bentonite, montmorillonite, zeolite, sand, crushed host rock, and additives for sorption of selected radionuclides.

Our studies have been focused on three of the many cited pertinent properties of the backfill. Those properties are swelling, hydraulic conductivity, and thermal conductivity. Relative high magnitude of swelling and plasticity of the backfill material is desirable to provide a self-sealing ability for material cracks within the backfill and localized cracks and flaws in the surrounding rocks in order to minimize the potential of groundwater intrusion. Backfill with low hydraulic conductivity, when placed around the waste package, may shield the waste canister from the intrusion of groundwater for a long time period and subsequently inhibit mass movement of molecules and thereby minimize the corrosion potential of the canister and delay leakage of radionuclides to the groundwater.

The backfill will also be expected to conduct thermal energy from the canisters to the host rock, thereby preventing excessive heating. Consequently, assessment of the thermal conductivity of the backfill surrounding the canisters is critical. Soils with high thermal resistance will not dissipate as rapidly away from the canister as soils with a low thermal resistance.

It is the present consensus among the researchers in the field that at least 10 percent of bentonite, or other types of clay minerals should be included in the backfill. For backfill placed around the canister, the clay content should be substantially higher. Thus, the backfill will behave like a fine-grained soil.

The volume of a backfill will change with variations in external pressure, temperature, and chemical environment. Changes in volume lead to changes in material strength, subsequent deformation behavior, and hydraulic conductivity. The swelling, and likewise compressibility of the backfill, is a measure of its volume change characteristics and is governed by the following factors: temperature, degree of saturation, chemical cementation and organic bonding, particle shape, geometric arrangement of particles, mechanical interactions, and physico-chemical interactions. Since the hydraulic conductivity of the backfill changes with the soil structure, the controlling factors for swelling should be equally applicable in explaining the mechanisms of this property.

It is logical to assume that the smaller the particle size, the smaller will be the void sizes of a soil. Since voids serve as flow channels, smaller void sizes will yield a lower hydraulic conductivity for a soil--all other variables remaining constant. In fact, a theoretical model developed by Taylor using Poiseiulle's law showed that the hydraulic conductivity varies in direct proportion to the square of a characteristic particle diameter.

In the physico-chemical interaction, long range forces, such as the repulsive forces of the double layer and the van der Waal attractive forces, are considered. Many research efforts have been directed toward developing an understanding of the effect of physico-chemical interactions on the swelling potential and hydraulic conductivity of clays. In summary, the variables that control these interactions are particle shape, geometric arrangement of particles, and clay chemistry.

Particles with large diameter-to-thickness ratios, such as those of bentonite, are subject to most favorable geometric conditions for double layer interaction, and thus the physico-chemical effects are predominant. Chemical variables include surface charge density and distribution, valency of the adsorbed cations, dielectric constant and dipole moment of the pore fluid, and concentration of electrolyte in the free pore fluid. It is understood that the existence of a net negative charge on the surface of clay particles leads to the adsorption of cations. A higher surface charge results in a stronger double layer effect. The distribution of charges is also important; for instance, a kaolinite clay with negative surface charge and positive edge charge will lead to flocculation rather than to dispersion under a low pH environment. A monovalent cation can produce a thicker double layer than a divalent cation, thus increasing the physico-chemical effect and resulting in a higher swelling potential. Thicker double layers result in lower hydraulic conductivity by reducing the effective opening of pores. Test results on Ca bentonite indicated approximately 2 to 5 times higher hydraulic conductivity than those on Na bentonite. The dielectric constant of the pore fluid is important because only for fluids with high dielectric constants, such as water, is the degree to which adsorbed layers developed on the clay particle surface significantly influenced. When the pore fluid is water, its possession of dipole moment and high dielectric constant yield the lowest value of hydraulic conductivity. The hydraulic conductivity is higher for a polar fluid with a low dielectric constant, such as carbon tetrachloride. The reason is that when fluids of low dielectric constant are used as a permeant, the cations are held tightly against the clay particle surface and thus the tendency of the double layer to block the flow channels is minimized. Finally, when a nonpolar fluid is used, the flow channels are almost completely open because of the inability of cations or particle surfaces to adsorb fluid molecules. The thickness of the double layer is influenced by the concentration of an electrolyte; the lower the concentration, the thicker the double layer. The hydraulic conductivity is also affected by the concentration of electrolyte; a reduction in concentration leads to a reduction in the value of the hydraulic conductivity.

Examination of the literature reveals that information on the factors affecting the thermal resistivity of soils can be found in a variety of technical fields. For example, references can be found in the areas of agronomy, soil mechanics, highway research, electric power research and nuclear waste management. Each technical area has a list of references that are often cited, but no list is comprehensive covering all the information available in those fields in which the thermal properties of soils are important.

The thermal resistivity of a soil is influenced primarily by the following parameters:

- Soil composition
- Density
- Moisture content and degree of saturation

The relative importance of these factors is illustrated in figure 22. Of particular interest is the importance of soil moisture. As moisture is added to the soil as a thin film around the soil particles, a path for the flow of heat which bridges the air gaps between the solid particles is provided. By increasing the effective contact areas between

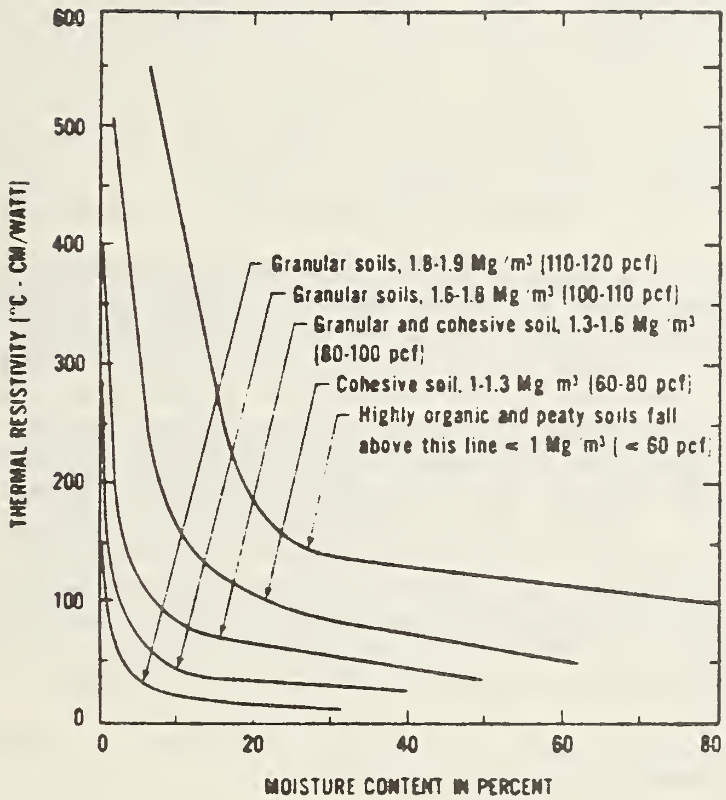


Figure 22. The effect of moisture content and dry density on the thermal resistivity of soils (from Salomone and others, 1979).

particles, these films greatly reduce the thermal resistivity of the soil. When the moisture condition in the soil approaches a wet condition, the effective contact area no longer increases with increasing moisture content. Consequently, the significant decrease in thermal resistivity with increasing moisture content as the films around the solid particles are forming is not evident when additional moisture is added to fill the pore space. This trend is observed in figure 22.

Moisture migration is also an important consideration. The moisture regime within the backfill barrier will be a function of two driving forces: the porewater pressure gradients from the outer boundary towards the canister and the thermal gradient from the inner boundary toward the outer boundary. The thermal gradients existing in the backfill can cause a redistribution of moisture in the soil, thereby changing the thermal resistivity of the soil. Because moisture migration under a thermal gradient involves capillary moisture, i.e., moisture in excess of adsorbed (hygroscopic) water and which is held against the force of gravity, the existing moisture content in the soil is an important consideration in deciding whether moisture migration is a problem.

We have identified problems with existing measurement techniques related to the material properties, including hydraulic conductivity and swelling. One important problem needs to be conveyed to DOE as soon as possible: The test variables of the compaction method, compaction effort, and the amount of moisture content within the specimen at the time of compaction were found by us to have a profound effect on the determination of the values of both swelling potential and hydraulic conductivity. For example, some references in the published literature indicate that the values of hydraulic conductivity are so sensitive to these test variables that they may change by as much as three orders of magnitude. The planned NBS laboratory program was to determine these effects, so that reliable measurements of anticipated performance can be made. With the NBS program cancelled, somebody will have to do this work, so that no unpleasant surprises are encountered when the backfill is installed.

An understanding of the factors affecting the thermal conductivity of soils leads us to conclude that:

- the thermal conductivity of the backfill material needs to be evaluated for the design conditions,

- the available steady state and transient methods for determining the thermal conductivity of soils should be compared and the optimum approach determined, and

- concepts from the fields of agronomy and geotechnical engineering and information on the heat transfer mechanisms in soils should be combined to determine those index properties of soils which correlate well with the thermal properties of soils. Knowledge of these index properties can be used to screen the backfill materials being considered and to develop a classification system for purposes of having a common language for researchers to document their thermal conductivity test data.

Two papers have been prepared and submitted to conferences for disseminating the information. One is an invited paper on the thermal properties of soil materials which has been presented to a symposium sponsored by EPRI and Ontario Hydro in September, 1981. The second one is on reference laboratory testing for the determination of swelling and hydraulic conductivity and has been accepted for presentation to the Material Research Society's Annual Meeting in Boston, MA, November, 1981.

A state-of-the-art report is also in preparation. Much of the information in the two papers mentioned above was generated from the preparation work. However, with the sudden termination of this project, we do not think we can incorporate the collected information into a comprehensive report since our efforts will have to reflect our funding starting on October 1, 1981.

R. Chung, L. Salomone, F. Yokel

3. Development of Mathematical Methods

During FY 81, work was done on two mathematical techniques which were intended for application not only in nuclear waste modeling, but also in two additional areas of interest to NBS. The two techniques are:

- A diagnostic tool for screening a rectangular array of data such that a structure index can be computed to suggest the presence or the absence of a random component in a mechanism model.

- A modeling tool involving the concept of a nested element and the existence of a single-integral entropic functional.

J. Fong

Appendix A

Major Consulting and Advisory Services

J. W. Behrens advised the Oak Ridge National Laboratory on the preparation of large fission deposits for the Clinch River Breeder Reactor Program.

C. D. Bowman consulted with the Hanford Engineering Development Laboratory on the nondestructive analysis of spent fuel from the FFTF.

C. D. Bowman advised the Electric Power Research Institute on the nondestructive assay of spent power reactor fuel.

A. D. Carlson organized the national Department of Energy effort for evaluation of measurements on neutron cross section standards.

J. Fong, et al., advised DOE and NRC staffs on Modeling and Statistical Design for Assessment of Waste Packages.

H. M. Kingston consultation on leachability measurements and quality control at Battelle. Battelle Richland, Washington, January 19-30, 1981.

W. F. Koch, G. Marinenko, D. Cronin, H. M. Kingston, Vitreous State Labs of Catholic University on leachability testing, June 16, 1981.

G. J. Lutz, consultation with Dr. L. Jardine at Argonne National Laboratory on activation of nuclear waste glasses, November 13, 1980.

R. S. Roth advised Savannah River Laboratory on the chemical problems associated with the development of a possible crystalline alternative to glass, August 1981.

R. A. Schrack advised the Brookhaven National Laboratory Safeguards staff on the nondestructive assay of spent commercial reactor fuel.

Appendix B

Committee/Workshop Participation

James W. Behrens - Member, DOE Cross Section Evaluation Working Group (CSEWG), Standards Subcommittee; Member, Safeguards Committee, Institute for Nuclear Materials Management.

Charles D. Bowman - Member, Department of Energy (DOE) Nuclear Data Committee.

Allen D. Carlson - Member, DOE Cross Section Evaluation Working Group (CSEWG), Standards Subcommittee.

B. Stephen Carpenter - Board of Directors, American Nuclear Society; Member, Isotope and Radiations Division, Technical Committee for Nuclear Safeguards; Member, Institute of Nuclear Materials Management Subcommittee INMM-9.3 on Nondestructive Assay of Standards Committee N15 on Methods of Nuclear Material Control; Member, Department of Energy, Office of Safeguards and Security, Ad Hoc Task Group on Measurements and Standards.

Randall S. Caswell - Member, International Society of Radiology, International Commission on Radiation Units and Measurements.

David A. Ditmars - Member, INMM 8.4, "Calibration Techniques in the Calorimetric Assay of Pu-Bearing Solids"; Member, NBS Pu Steering Committee; Member, ISPO Laboratory Coordinators Group.

John W. Gramlich - Member, Institute of Nuclear Materials Management Committee N15,9.3, Nondestructive Assay - Physical Methods.

James A. Grundle - Member, ASTM E10.05, Committee on Neutron Dosimetry.

J. M. Robin Hutchinson - Chairman, International Committee of Radionuclide Metrology (ICRM), Subcommittee on Low-Level Techniques Group; Member, American National Standards Institute (ANSI) Committee on Nuclear Instruments and Detectors; Secretary, ANSI Subcommittee N42.2 on Procedural Standards for Calibration of Detectors for Radioactive Measurements.

Harry H. Ku - serves on the Steering Committee of the Safeguards Analytical Laboratory Evaluation Program.

J. Kruger - IWG of ONWI on Materials Degradation Mechanisms, participated in Materials Characterization Center Workshop on Test Procedures for Corrosion of Engineered Barriers for Nuclear Waste Repositories.

James A. Lechner - Member of American Society for Testing and Materials (ASTM) Committee C26 on Nuclear Fuel Cycle, Chairman of Subcommittee (26.06 on Statistical Methods; Member of ASTM Committee N15; advising the Institute for Nuclear Materials Management Committee 9.4 on revised standard for measurement control of NDA processes.

Walter Liggett - IAEA Advisory Group on Evaluation of Quality of Safeguards NDA Measurement Data.

Lawrence A. Machlan - Member, Plutonium Steering Committee at NBS; Member, ASTM C26 (Nuclear Fuel Cycle).

William P. Reed - Member of American Society for Testing and Materials (ASTM) Committee C26 on the Nuclear Fuel Cycle. Member, ANSI N15 Nuclear Standards, Member, INMM N15.9.3, USDOE Materials Characterization Organization Steering Committee.

R. S. Roth - participated in Materials Characterization Center Workshop on the Compositional and Microstructural Analysis of Nuclear Waste Materials.

S. J. Schneider - MCC Workshop on Test Procedures for Corrosion of Engineered Barrier for Nuclear Waste Repositories; IWG of ONWI on Materials Degradation Mechanisms.

G. White - participated in Materials Characterization Center Workshop on Radiation Effects.

Appendix C

Publications

Behrens, J. W., Schrack, R. A., and Bowman, C. D., Nondestructive Examination of a Defective Silver Braze Using Resonance-Neutron Radiography, Nuclear Technology, Vol. 51, No. 1, pp. 78-82, Nov. 1980.

Behrens, J. W., Preparation of Accelerator Targets by Painting, invited paper for 9th World Conf. of International Nuclear Target Development Society held at Gatlinburg, TN, October 12-16, 1980 (proceedings to be published in Nuclear Instrum. Methods).

Bowman, C. D., Efficient Neutron Production Using 12 MeV Electrons, Proceedings of 1980 Conference on the Application of Accelerators in Research and Industry held at North Texas State University, Denton, Texas, Nov. 3-5, 1980, IEEE Transactions on Nuclear Science, pp. 1485-1487, Vol. NS-28, #2, April 1981.

Bowman, C. D. and Johnson, R. G., Measurements of Inelastic Scattering of eV Neutrons (accepted for publication in proceedings of IPNS Symposium on Neutron Scattering held at Argonne National Lab., Argonne, IL, August 12-14, 1981).

Fassett, J. D. and Kelly, W. R., "Mass Spectrometric Analysis on Uranium and Plutonium Loaded Anion Exchange Resin Beads: An Interlaboratory Round Robin," Analytical Chemistry in Nuclear Technology, W. S. Lyon, ed., (Proceedings of 25th Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, 1981), in preparation.

Johnson, R. G. and Bowman, C. D., High Resolution Powder Diffraction by White Source Transmission Measurements, (accepted for publication in proceedings of IPNS Symposium on Neutron Scattering held at Argonne National Lab., Argonne, IL, August 12-14, 1981).

Johnson, R. G., Behrens, J. W., and Bowman, C. D., Source Imaging Using Neutron Pinhole Cameras Based on Position-Sensitive Proportional Counters (accepted for publication in Nuclear Technology).

Jones, F. E., Determination of Water in Solids by Automatic Karl Fischer Titration, Analytical Chemistry 53, 1955-1956 (1981).

Jones, F. E. and Brickenkamp, C. S., Calculation of Solvent-Water Mixture Volumes, Analytical Chemistry 53, 362-363 (1981).

Jones, F. E., Schoonover, R. M., and Houser, J. F., In-Tank Measurement of Solution Density, J. of Res., Natl. Bur. Stand. 85, 219-221 (1980).

Kopp, M. K., Behrens, J. W., Meacham, M. A., and Williams, J. A., Development of Proportional Counter Cameras for Neutron Imaging with 1 mm Resolution (to be published in Rev. Sci. Instrum.).

Kruger, J. and Hardman, V. K., Current Understanding of Pitting and Crevice Corrosion and Its Application to Test Methods for Determining that Susceptibility to Such Corrosion of Nuclear Waste Containers (in press).

Lechner, J., Inventory Difference Calculations: Problems and Possibilities, NBSIR 81-2219.

Liggett, W., Robust Inference for Items Measured a Few Times (draft form).

Sanderson, B. T. and Kruger, J., Bibliography on Corrosion of Metals in Underground Repository Environments (in press).

Schleter, J. C. and Baloga, S. M., Study of DOE Safeguards Measurement Implementation Needs (draft form).

Schoonover, R. M. and Jones, F. E., Air Buoyancy Correction in High-Accuracy Weighing on Analytical Balances, Analytical Chemistry 53, 900-902 (1981).

Schrack, R. A., Behrens, J. W., Johnson, R. G., and Bowman, C. D., Resonance Neutron Radiography Using an Electron Linac, Proceedings of the Sixth Conference on the Application of Accelerators in Research and Industry, held at North Texas State University, Denton, Texas, November 3-5, 1980. IEEE Transactions on Nuclear Science, Vol. NS-28, No. 2, April 1981, pp. 1640-1643.

Spiegelman, C., Some Conservative Statistical Approaches for Presenting Interlaboratory NDA Enrichment Measurements, NBSIR 81-222.

Spiegelman, C., Lechner, J., and Reeve, C., A New Method of Assigning Uncertainty in Volume Calibration, NBSIR 80-2151.

Spiegelman, C., Sacks, J., and Ylvisaker, D., Nonparametric Calibration (submitted to a technical journal).

Wasson, O. A. and Meier, M. M., Measurement of the ^{235}U Mass in a Large Volume Multiplated Fission Ionization Chamber (accepted for publication in Nuclear Instrum. Methods).

Appendix D

Talks

Bowman, C. D., "Efficient Neutron Production Using 12 MeV Electrons," 6th Conference on the Application of Accelerators in Research and Industry, North Texas State University, Denton, TX, November 4, 1980.

Chung, R. C., "Thermal Properties of Soil Materials," sponsored by EPRI and Ontario Hydro, September 1981.

Chung, R. C., "Reference Laboratory Testing for the Determination of Swelling and Hydraulic Conductivity," Material Research Society, Boston, MA, November 1981.

Epstein, M. S., "Review of Analytical Methods for Liquids and Solutions at NBS," Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials, Battelle Research Center, Seattle, WA, November 11, 1980.

Epstein, M. S., "Analysis of Nuclear Waste Leachates for Trace Elements by Atomic Spectroscopy: Problems and Solutions," 8th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 23, 1981.

Fassett, J. D., Kelly, W. R., and Machlan, L. A., "Mass Spectrometric Analysis of Nanogram Levels of Plutonium," 24th Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 7, 1980.

Fassett, J. D. and Kelly, W. R., "The Mass Spectrometric Analysis on Uranium and Plutonium Loaded Anion Exchange Resin Beads: An Interlaboratory Round Robin," 25th Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 7, 1981.

Fong, J. T. "Mathematical Modeling Support for NBS Nuclear Waste Project," NBS Technical Staff Meeting, February 24, 1981.

Fong, J. T., "Some Applications of Mathematics in Materials Science: Before and After," Johns Hopkins University, Baltimore, MD, March 4, 1981.

Fong, J. T., "On Upgrading the Mathematics Requirements of Mechanics and Materials Science Majors," Lehigh University, Bethlehem, PA, September 11, 1981.

Kelly, W. R. and Fassett, J. D., "The Determination of Subnanogram Quantities of Uranium by Isotope Dilution Mass Spectrometry," 29th Annual Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN, May 27, 1981.

Kingston, H. M., "State-of-the-Art Analytical Measurements of Trace Elements in Aqueous and Other Matrices with an Emphasis on Chemical Manipulation," Rockwell International Labs, Richland, WA, January 27, 1981.

Kingston, H. M., "Trace Metal Analysis: The Effects of Chemical Manipulation on the Results," Battelle Pacific Northwest Labs, Richland, WA, January 28, 1981.

Kingston, H. M., "The Analytical Constraints that Influence Leach Measurements and Reference Materials," 8th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, PA, September 23, 1981.

Lutz, G. J., "The Analysis of Solids," Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials," Battelle Research Center, Seattle, WA, November 11, 1980.

Moody, J. R., "Some Considerations of Analytical Methodology Relevant to Radioactive Solid Leachate Testing," ORNL Conference on the Leachability of Radioactive Solids, Gatlinburg, TN, December 10, 1980.

Reed, W. P., "Measurements and Standards for Nuclear Waste Management" Eighth Annual FACSS Meeting, Philadelphia, PA, September 23, 1981.

Roth, R. S., "Phase and Microstructure Analysis" at MCC Workshop on Compositional and Micro Structural Analysis of Nuclear Waste Materials.

Roth, R. S., "Crystallography Concerning Some of the BaO-Containing Phases in Our Current Nuclear Waste Studies," 12th Congress of the International Union of Crystallography.

Roth, R. S., "Crystallography Concerning Some of the BaO-Containing Phases in Our Current Nuclear Waste Studies," Grenoble, France.

Roth, R. S., "Crystallography Concerning Some of the BaO-Containing Phases in Our Current Nuclear Waste Studies," Ljubljana, Yugoslavia.

Schrack, R. A., "Resonance Neutron Radiography Using an Electron Linac," 6th Conference on the Application of Accelerators in Research and Industry, North Texas State University, Denton, TX, November 4, 1980.

Appendix E

Organized Symposia and Workshops

Chung, R. C., "Research and Development Needs in Backfill for Nuclear Waste Storage in Deep Geologic Repositories," two-day conference held at NBS on April 13-14, 1981.

Magnani, N., Sandia Laboratory, "Sandiás Canister Corrosion Activities, at NBS, February 9, 1981.

Nelson, R., Pacific Northwest Laboratory and Steindler, M., Argonne National Laboratory, "The Role of the Material Characterization Organization in High Level Nuclear Waste Management," at NBS, May 14, 1981.

Pearlman, H., Energy Systems Group, Rockwell International, Canoga Park, CA, "Effects of Radiation on Tailored Ceramic High Level Waste Forms," at NBS, June 15, 1981.

Reed, W. P. and Kingston, H. S., "The Analytical Chemistry of the Nuclear Waste Form." Held at the 8th Annual FACSS Meeting in Philadelphia, PA, September 23, 1981.

Yolken, H. T., "Methods Used to Measure Leachability and Present Data." Held at ORNL Conference on the Leachability of Radioactive Solid, Gatlinburg, TN, December 10, 1980.

Appendix F

Functional Statements

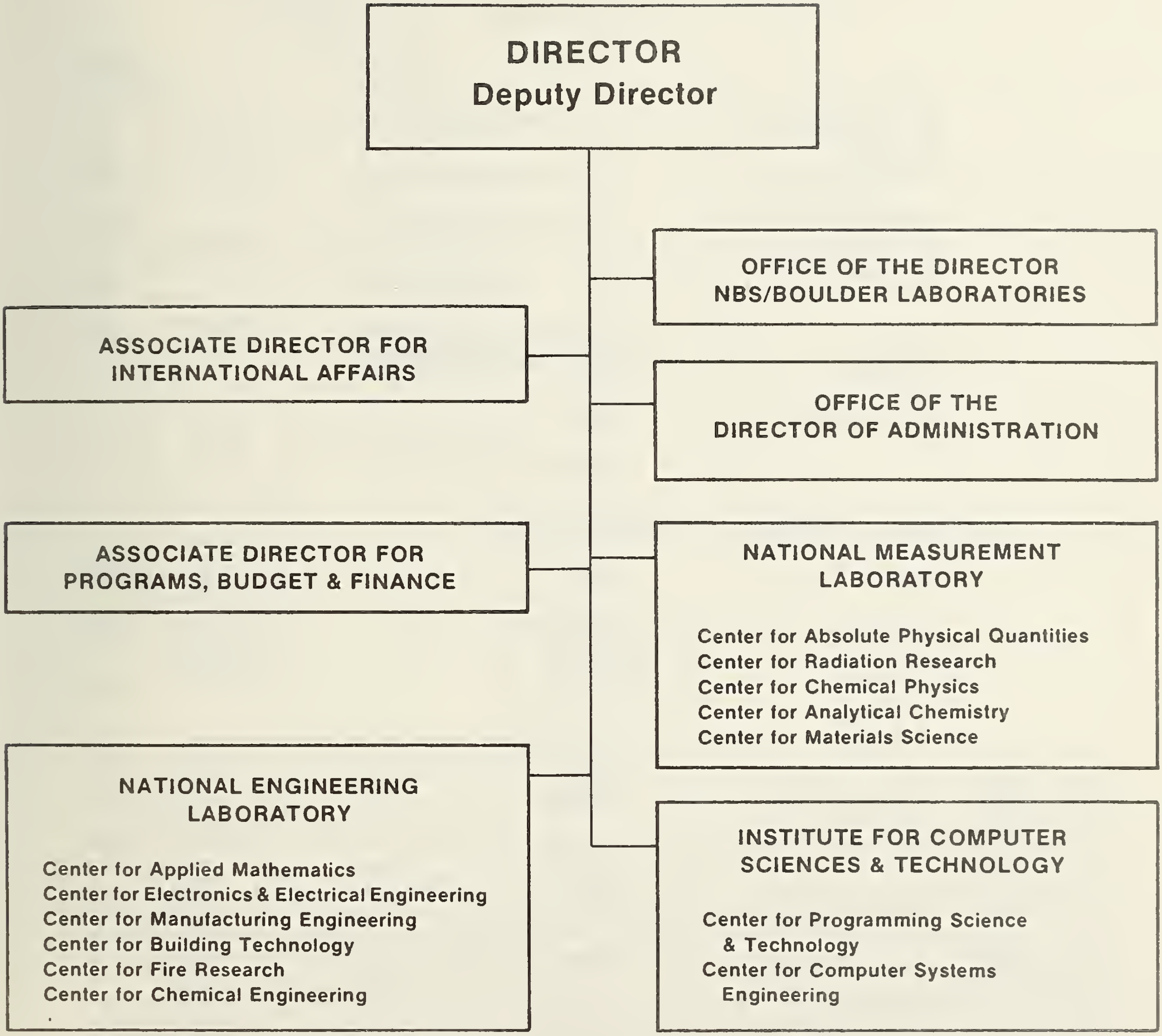
NATIONAL MEASUREMENT LABORATORY

Provides the national system of physical and chemical and materials measurement; coordinates the system with measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical and chemical measurement throughout the Nation's scientific community, industry, and commerce; conducts materials research leading to improved methods of measurement, standards, and data on the properties of materials needed by industry, commerce, educational institutions, and government; provides advisory and research services to other government agencies; conducts physical and chemical research; develops, produces, and distributes standard reference materials; provides standard reference data; provides calibration services; and collaborates with the Bureau's major organizational units in carrying out its responsibilities.

OFFICE OF MEASUREMENTS FOR NUCLEAR TECHNOLOGY

Provides the Nation with needed measurement standards and services for nuclear technology in the areas of nuclear waste management and safeguarding nuclear materials; plans, directs, and coordinates the Program's laboratory work that is carried out within NBS units; and disseminates these standards and services domestically and to other nations and to international organzations.

Appendix G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NBS/BOULDER LABORATORIES
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INTERNATIONAL AFFAIRS
OFFICE OF THE
DIRECTOR OF ADMINISTRATION
ASSOCIATE DIRECTOR FOR
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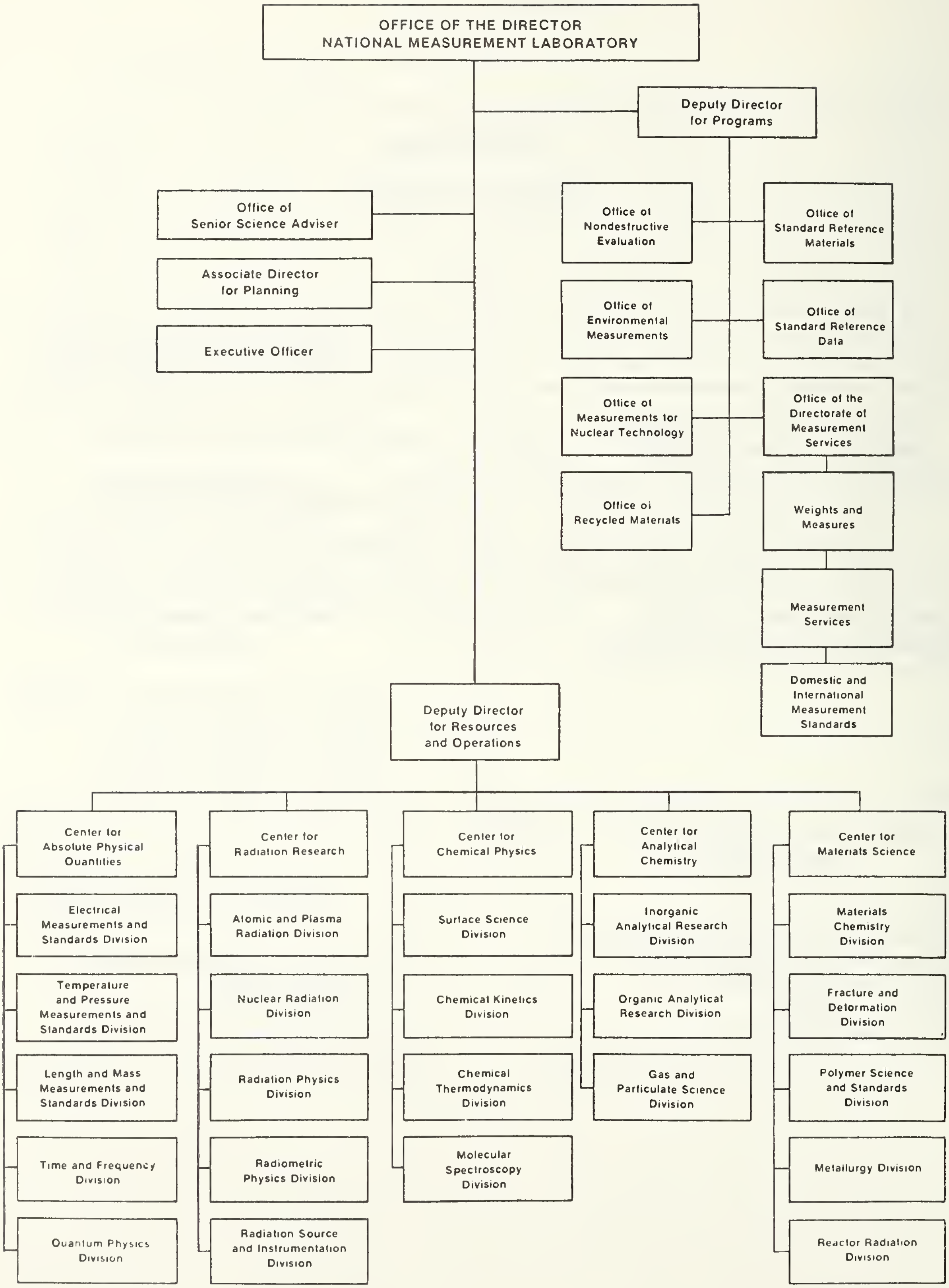
Center for Absolute Physical Quantities
Center for Radiation Research
Center for Chemical Physics
Center for Analytical Chemistry
Center for Materials Science
NATIONAL ENGINEERING
LABORATORY
Center for Applied Mathematics
Center for Electronics & Electrical Engineering
Center for Manufacturing Engineering
Center for Building Technology
Center for Fire Research
Center for Chemical Engineering
INSTITUTE FOR COMPUTER
SCIENCES & TECHNOLOGY
Center for Programming Science
& Technology
Center for Computer Systems
Engineering

Appendix H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Domestic and International Measurement Standards
Deputy Director for Resources and Operations
Center for Absolute Physical Quantities
Electrical Measurements and Standards Division
Temperature and Pressure Measurements and Standards Division
Length and Mass Measurements and Standards Division
Time and Frequency Division
Quantum Physics Division
Center for Radiation Research
Atomic and Plasma Radiation Division
Nuclear Radiation Division
Radiation Physics Division
Radiometric Physics Division
Radiation Source and Instrumentation Division
Center for Chemical Physics
Surface Science Division
Chemical Kinetics Division
Chemical Thermodynamics Division
Molecular Spectroscopy Division
Center for Analytical Chemistry
Inorganic Analytical Research Division
Organic Analytical Research Division
Gas and Particulate Science Division
Center for Materials Science
Materials Chemistry Division
Fracture and Deformation Division
Polymer Science and Standards Division
Metallurgy Division
Reactor Radiation Division

Appendix I

BUDGET

Office of Measurements for Nuclear Technology

Sponsor	Program	
NRC	Nuclear Safeguards	$ 13,000
DOE	Nuclear Safeguards	933,600
ISPO	Nuclear Safeguards	127,700
DOE	Nuclear Waste	1,105,000
DOE	Nuclear Waste Equipment Including Carry-Over	125,000
	TOTAL	$2,304,300

BY CENTER

	Nuclear Waste	Nuclear Safeguards
Reactor Services	$ 9,000	$ 5,000
OMNT	92,800	99,100
CRR	--	320,200
CCP	53,000	65,000
CAC	199,500	343,300
CMS	676,000	20,000
CAM	50,300	75,000
CBT	149,400	--
CCE	--	144,700
TOTAL	$1,230,000	$1,074,300

NBS-114A (REV. 2-80)

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	NBSIR 81-2441		January 1982

4. TITLE AND SUBTITLE

Office of Measurements for Nuclear Technology

5. AUTHOR(S)

W. P. Reed and H. T. Yolken

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

Office Annual Report
Fiscal Year 1981

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

National Bureau of Standards

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

This annual report is a summary of the National Bureau of Standards (NBS) Measurements for Nuclear Technology (MNT) Program for Fiscal Year 1981. The MNT activities at NBS are divided into two programs: Nuclear Safeguards and Nuclear Waste Management.

The MNT Program is one of several matrix managed efforts at NBS. The programs provide a focus for the activity, both inside and outside NBS. The programs provide funds and directions for needed technical work that is done within NBS Centers. People remain attached to Centers but are funded for specific activities in a matrix management approach. A program provides central organization for outside inquiries and for distribution of results. Often programmatic focus can provide improved assistance to outside agencies with measurement problems. The MNT Program is operating in this manner.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

accountability guide; bulk measurements; isotopic assay; leachability studies; nondestructive assay; nuclear safeguards; nuclear waste management; Standard Reference Materials; statistical evaluation

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